The distribution, fate and application as tracers of quaternary ammonium compounds (QACs) in sewage impacted estuaries.

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Abstract of the Dissertation

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Dedication Page

To my grandparents Cornelia and Ted Ellefson, Sr. and John P. Southerland, Sr., who didn’t live long enough to see me reach this point, but their love and support ensured that I got here.

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List of Abbreviations

ATMAC	alkyltrimethyl ammonium compound
BAC	benzylammonium compound
BPO	Bay Park sewage treatment plant outfall
CSO	combined sewer overflow
DEHP	diethylhexyl phthalate
DP	dodecylpyridinium
DTDMAC	ditallowdimethyl ammonium compound
ERL	effects range low
ERM	effects range medium
HB	Hempstead Bay
HOCs	hydrophobic organic contaminants
QACs	quaternary ammonium compounds
JB	Jamaica Bay
LAS	linear alkylbenzene sulfonate
LIS	Long Island Sound
MGD	millions of gallons per day
PCB	polychlorinated biphenyl
PBDE	polybrominated diphenyl ether
STP	sewage treatment plant
TAMs	trialkylamines
TAMAC	trialkylmethyl ammonium compounds
USEPA	United States Environmental Protection Agency
USITC	United States International Trade Commission
WLIS	Western Long Island Sound

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I now know that getting a PhD is far more than an individual pursuit. I know without a doubt that I would not have gotten here without the unconditional love and support of my family and friends who helped me make it through the emotional roller coaster that is graduate school.

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CHAPTER ONE: INTRODUCTION

Quaternary ammonium compounds (QACs) are a class of cationic surfactants that have been measured at very high concentrations in sewage-impacted environments (Fernández et al., 1996; Ferrer and Furlong, 2002; Lara-Martín et al., 2010; Li and Brownawell, 2010; Martinez-Carballo et al., 2007). While QACs are of concern due to high environmental concentrations, they are also of interest due to recent suggestions for using QACs as particle reactive tracers of sewage (Li and Brownawell, 2010). In this dissertation, the distribution and persistence of QACs in sewage impacted environments are assessed for the purpose of informing their use as sewage tracers, and are further explored through measurements of QACs with distance from a source, and geochronologies from sediment cores in muddy, depositional environments, and oxic and anoxic sediment incubations. QACs have also been applied as sewage tracers in this dissertation to better understand the source and geochemical fate of other contaminants from these systems as well as illustrate the uses of QACs as particle reactive tracers of sewage.

Municipal sewage waste is a known source of both chemical and biological contaminants to aquatic systems, as sewage outfalls serve as a pathway from land activities to the environment. Components of sewage such as excess nutrients can have large effects on local ecosystems, including eutrophication and hypoxia (Savage et al., 2002). In addition, the chemical contaminants discharged into aquatic systems can vary widely in concentration, environmental fate, and aquatic toxicity. The number of chemical contaminants found in sewage is vast, and only a small portion of these compounds have been studied, and of these contaminants, few have sufficient research to understand the fate and risk of these contaminants in the aquatic environment.

1.1 Sewage Tracers

One tool that can be used better understand not only the distribution of sewage within an aquatic system but also the fate and persistence of sewage derived contaminants is sewage tracers. Sewage tracers are often specific contaminants or qualities of sewage that can be used to better understand the extent and distribution of sewage in an aquatic environment. There are a large number of sewage tracers that have been used in this role in the past. One example is the use of stable isotope ratios (e.g. carbon and nitrogen) of organic matter in sediments to trace sewage derived organic matter, as these ratios vary based on the extent of sewage/terrestrial and marine input (Peters et al., 1978; Vivian, 1986), although problems with this approach can occur when studying eutrophied regions due to seasonal differences in nitrogen use as a result of changes in the types of phytoplankton present (Peters et al., 1978).

In addition to carbon and nitrogen isotopes, a large number of contaminants have also been used as sewage tracers. Contaminants used as sewage tracers, and in particular particle reactive sewage tracers, must possess several qualities, including:

a) *Sewage as a unique source to the aquatic environment*
b) *High concentrations in sewage affected environments to allow for dilution of the signal and low environmental background levels (can be a problem for some metals, metalloids, fecal sterols)*
c) *Sensitive analytical methods*
d) *Strong sorption to particles*
e) *Persistence in the environment being studied*

Silver has been applied in a number of studies to trace the distribution of sewage (Lamoureux et al., 1996; Sanudo-Wilhelmy and Flegal, 1992), yet the future use of silver as a tracer is in doubt due to decreasing anthropogenic inputs of this metal in the environment as a result of regulations on inputs from dentistry as well as a continuing decrease in silver-based photo-processing. Trialkylamines (TAMs), which are similar in structure to the ditallowdimethylammonium QACs studied here (minus one methyl group), have also been used as sewage tracers and are particularly of interest to this dissertation as they are impurities in QAC formulations (Valls et al., 1989). These tertiary amine compounds, which are similar in structure to QACs, have been suggested as persistent tracers of sewage affected particles because of their high particle reactivity and persistence in sediments (Chalaux et al., 1995; Fernandez et al., 1991; Maldonado et al., 1999, 2000; Valls et al., 1989), and have been used to trace sewage up to 20km from a source in 300m of water in Tokyo Bay (Chalaux et al., 1995). Coprostanol, a fecal steroid, has also been used as a sewage tracer, although more recent studies have indicated that this compound is preferentially degraded relative to TAMs during long range transport in the Mediterranean and the Black Sea (Maldonado et al., 1999) as well as the San Pedro Shelf in southern California (Maldonado et al., 2000). Other very commonly used sewage tracers are the surfactants linear alkyl benzenes, however these compounds have been shown to be preferentially degraded in sediments from a deep water dump site located 106 miles off the New Jersey coast (Lamoureux et al., 1996) .

More recently, Li and Brownawell (2010) have suggested the use of QACs as a new class of sewage tracers. Sewage is the dominant source of these compounds to the aquatic environment due to their residential uses as well as high particle reactivity that would preclude them from being in road run-off or in leachate from landfills. While there are other land based uses that could serve as additional sources of QACs to the environment, the particle reactive nature of QACs indicates that they will not be easily moved into surrounding water bodies. QACs are also non-volatile, so atmospheric deposition does not represent an additional source for these compounds. In comparison to TAMs, QACs are more hydrophobic and have been found at higher concentrations than these impurities and may therefore represent even better sewage tracers than TAMs, compounds that have received far more attention for their sewage tracing abilities.

1.2 QACs

The QACs studied in this thesis are a class of surfactants with a positively charged nitrogen atom surrounded by four substituents. QACs are generally divided into three classes: dialkyldimethyl ammonium compounds (DADMACs), benzylalkyl dimethyl ammonium compounds (BACs) and alkyltrimethyl ammonium compounds (ATMACs) (Figure 1.1). DADMACs are often subdivided into two groups, those with shorter side chains, referred to here as DADMACs, and longer side chain compounds termed ditallowdimethyl ammonium compounds (DTDMACs), and this practice is retained in this dissertation. QACs are classified as high production volume chemicals by the United States Environmental Protection Agency (USEPA) and constitute the dominant fraction of cationic surfactants produced worldwide (Li, 2009). As described by Li (2009) and Lara-Martin et al. (2010), data on the production of QACs in the United States is difficult to obtain due to differences in nomenclature as well as changes in industry reporting requirements, but using available data from the United States International Trade Commission (USITC) and a small number of geochronologies from Li (2009) and Lara-Martin et al. (2010), some information on the historical input of QACs to sewage-impacted environments has been established.

Many applications of QACs lead to the potential of direct inputs into municipal wastewaters. Of particular interest is the use of QACs in fabric softeners, hair care, and other personal care products, and in sanitation applications. DTDMACs, which for many years were the primary ingredient in fabric softeners, are the largest and most hydrophobic of all QACs targeted in this work, with two n-alkyl side chains that range from 12 to 18 carbons long. DTDMACs also have the highest production of all QACs (USITC) and have primarily been used as fabric softeners (Cross and Singer, 1994; Fernández et al., 1996; Schaeufele, 1984) since their introduction in the 1950's (Levinson, 1999). Production and use of DTDMACs increased from the 1950's until the late 1980's, at which point extremely high (2.57-5.87 mg/g, Fernández et al., 1996) levels of DTDMACs were measured in Austrian sewage sludges. This, as well as concerns over the potential for these compounds to break down in the environment, resulted in a voluntary phase-out of these compounds in Europe, after which much lower levels of DTDMACs were measured within two years of the phase-out, with concentrations at 6% of pre-phase out values (Fernández et al., 1996). While this phase-out did not occur in the United States, decreases of DTDMACs have also been noted in US sediments over the same time frame, although levels in the US only decreased to 20% of pre-phase out values (Li, 2009). DTDMAC appears to have leveled off since that time in both Europe and the United States (Levinson, 1999; Li, 2009). Alkyl side chains used in DTDMACs are generally hydrogenated and animal fat sources of DADMACs that result in mixtures dominated by 16 carbon and especially 18 carbon side chains. However, vegetable oils have also been used to make DTDMACs in the 12-18 range. Surfactant manufacturers have increased production of products based on more environmentally friendly vegetable oils. Some data presented in this thesis suggests that there may be a recent increase in 12 and 14 DTDMACs that are known to be more prevalent in vegetable oils, particularly coconut oil (Cross and Singer, 1994) More recently, producers appear to have moved from using animal oils in favor of plant oils for DTDMAC production, resulting in an increase in shorter side chained DTDMACs (Li, 2009).

DADMACs have two side chains that are 8 or 10 carbons long and are dramatically less hydrophobic than their DTDMAC counterparts, as it is known that hydrophobicity increases with every carbon in an alkyl side chain (Boethling, 1984; Brownawell et al., 1990). These compounds are generally used in biocides and disinfectants (Cross and Singer, 1994; Fernández et al., 1996; Schaeufele, 1984). DADMACs were first introduced in 1965, and their use is thought to have increased in recent years (Li, 2009).

BACs, discovered in the 1930's, are known to be the oldest of all QACs, and their utilization began in the 1940's (Schaeufele, 1984). These compounds have only one n-alkyl side chain that ranges from 12 to 18 carbons long, with a benzyl group replacing the second alkyl side chain seen in DADMACs and DTDMACs. BACs are most commonly used as biocides, sanitizers and disinfectants (Boethling, 1984). Recent USITC data indicates that production of BACs increased from the 1970's through the end of the records in the early 1990's, although this trend was not observed in geochronologies from Li's study (2009). ATMACs possess only one side chain and a methyl group replacing the benzyl group observed for BACs. These compounds are used as antimicrobials and fabric softeners as well as in personal care products and industrial applications (Lara-Martín et al., 2010; Li, 2009; Madsen et al., 2001). Interestingly, ATMACs with 16 and 18 carbons are used as additive in asphalts, so along with their use as disinfectants, there is the potential for non-sewage sources of some QACs. First production of ATMAC 12-18 as cetrimonium precedes that of DTDMAC, with literature reports of the first uses around 1950 for wound treatments (Cruickshank and Squire, 1949; Hodges, 1951). Another significant input of ATMACs may be through introduction as impurities (up to 1%) in DTDMAC which has been used in higher volumes than any other class of QACs. The production of ATMACs 20-22 (behentrimonium) has increased exponentially over the last three decades due to their use in personal care products (Lara-Martín et al., 2010; Scientific Communication on Consumer Products, 2007), with corresponding increases observed in the environment (Lara-Martín et al., 2010; Li, 2009).

1.3 QAC Environmental Toxicity

Relatively little work has been done on the environmental toxicity of QACs (Lewis and Wee, 1983), with the predominance of the available studies focusing on the toxicity of dissolved QACs, and in particular BACs due to their known biocidal activity. The literature on QAC toxicity has been reviewed by Lewis and Wee (1983), Boethling (1984), Ying (2006), and Kreuzinger (2007). In general, studies indicate that cationic surfactants are more toxic than their nonionic or anionic counterparts (García et al., 2001; Singh et al., 2002; Ying, 2006). A review by Boethling (1984) indicates that QACs are toxic in the mg/L range and lower, with these effects extending to a wide variety of non-targeted organisms. Many studies have shown that the toxicity of QACs is diminished through adsorption onto particles (Cross and Singer, 1994; Lewis and Wee, 1983; Van de Voorde et al., 2012) as well as complexation with anionic surfactants, and linear alkylbenzene sulfonate (LAS) in particular (Boethling, 1984; Lewis and Wee, 1983; Sütterlin et al., 2008a).

Studies in sewage treatment plants indicate that at sufficiently high levels (>10 mg/L of DADMACs and BACs), inhibition of nitrification can occur (Boethling, 1984; Kreuzinger et al., 2007), although concentrations of QACs in most STPs are thought to be below these levels (Kreuzinger et al., 2007). Garcia et al. (1999) found that the inhibitory effect of both ATMACs and BACs decreased with increasing chain length, an effect that has been observed by others and is often attributed to decreased bioavailability related to sorption (Boethling, 1984; van Ginkel and Kolvenbach, 1991; Natecz-Jawecki et al., 2003).

Studies on the toxicity of QACs to aquatic organisms are fragmented and often conflicting. In general, most studies have found that ATMACs and BACs are the most toxic QACs, with DTDMACs being the least toxic (García et al., 2001; Pantani et al., 1995; Singh et al., 2002; Utsunomiya et al., 1997). However, more limited data for DADMACs suggest effective concentration levels that are on par with BACs (Kreuzinger et al., 2007). Pantani et al. (1995) found that ATMACs had LC50 values from 7.7 to 118 mg/L for the amphipod *E. tibaldii,* while small DTDMAC values ranged from 1.1 – 1.2 mg/L. The USEPA determined EC50 values for the acute toxicity of BACs of 280 μg/L for fish and as low as 5.9 μg/L for invertebrates (USEPA, 2006), but these values are much lower than values determined from other studies (Lewis and Wee, 1983; Utsunomiya et al., 1997). Chronic effects were observed in fish at lower concentrations of 32.2 μg/L, with a no observable adverse concentration of 4.15 μg/L established for aquatic invertebrates (USEPA, 2006). EC50 values have been found to be much higher for bacteria, with values ranging from 500 to 6000 μg/L (Sütterlin et al., 2008b). These levels of concern put forth by the USEPA are in the range of BACs measured in river water by Ferrer and Furlong (2001), indicating that QACs may pose a concern in sewage-impacted systems in the United States (Kreuzinger et al., 2007). Kreuzinger et al. (2007) have also found phytoplankton to be the most sensitive organisms to QACs.

Long-term studies on the toxicity of QACs are lacking (Kreuzinger et al., 2007) and chronic exposures may represent a significant concern. In addition, few studies exist on the toxicity of QACs when sorbed to sediment and these types of studies are warranted considering the large concentrations of QACs measured in sediments in the environment. Historically concern for the toxicity of QACs has been limited, as acute or sublethal toxicity values are generally much higher than those expected for treated wastewater concentrations. However, there are very few measurements of QACs in wastewater effluents, let alone receiving waters, and there is not much difference, or “margin of safety”, between lower estimates of toxicity (low µg/L) and levels that have been measured in sewage effluents (Kreuzinger et al., 2007). There is also a great deal of concern about the role that smaller QACs may be playing in increased bacterial resistance as a result of environmental exposures, as the ability of QACs to select for QAC resistant genes has been noted (Gaze et al., 2005; Natecz-Jawecki et al., 2003; Tezel et al., 2012).

1.4 Environmental Occurrence and Fate of QACs

QACs have been measured at extremely high concentrations in sewage impacted aquatic environments (Fernández et al., 1996; Gerike et al., 1994; Kreuzinger et al., 2007; Lara-Martín et al., 2010; Li, 2009; Li and Brownawell, 2010; Martinez-Carballo et al., 2007), with concentrations of DTDMACs as high as 1140 µg/g in highly polluted sediments from Barcelona, Spain. While there are very few studies of QACs in the United States, research by Li and Brownawell (2010) conducted in the New York/New Jersey Harbor complex has found levels of total QACs in sediments that range from 1 to 114 µg/g, with QACs representing the highest measured organic contaminant in those samples. DTDMACs were found at the highest concentrations of all QACs in this study, followed by BACs, ATMACs, and then DADMACs. Lara-Martin et al. (2010) have also measured ATMACs in sediments from Jamaica Bay at concentrations from 0.421-6.750 µg/g, with large increases noted in behentrimonium in recent years. Ferrer and Furlong have conducted the only other studies of QACs in the United States and found levels at BACs that ranged from 22-260 ng/g in sewage impacted river sediments (2002) and from 1.22 to 2.38 µg/L in sewage impacted riverine waters (2001). Despite such high measurements of compounds that can have biocidal properties, there is a paucity of data on the behavior of QACs in the aquatic environment.

Adsorption of QACs

There is very limited research available on the adsorption of QACs onto soils or sediments, especially for the structures studied here. Sorption energies are especially high for organic cations due to very large hydrophobic effects of these compounds containing long alkyl chains, as well as favorable electrostatic interactions with negatively charged particles. Cationic exchange is thought to be the dominant mechanism of adsorption of organic cations based in part on the effects of Na, much greater effects of Ca, lack of pH dependence (Brownawell, 1990, 1991), and effects of cation exchange capacity of sorbents on both the energy and capacity of sorption of dodecylpyridinium (DP), a cationic surfactant most similar to ATMAC 12 or ATMAC 14 (Brownawell and Westall, 1991; Brownawell et al., 1990).

Adsorption isotherms are considered to be extremely non-linear (Freundlich n much less than 1) as compared to other hydrophobic organic compounds, with nonlinearity extending many orders of magnitude down to environmentally relevant concentrations, as determined for DP, as seen in Figure 1.2 (Brownawell and Westall, 1991). These adsorption isotherm was fit using multi-site Langmuir isotherms. This nonlinearity has been attributed to heterogeneity in adsorption sites, with stronger sites associated with clays (Brownawell et al., 1990). In other experiments, the sorption coefficient, Kd, for DP was found to be more than two orders of magnitude stronger at low nM concentrations than at near 100 μM concentrations, which are levels often used to screen chemical sorption in OECD testing (Wagner et al., 1994). While similar information is not available for the QACs in this study, it is expected that sorption will be higher both because these QACs are much more hydrophobic and will be present at lower concentrations in the environment than those tested by Brownawell and Westall (1991). Cation exchange sites can include organic matter as well as fixed charged sites on clays, with the potential for intercalation into smectites, such as montmorillonite. Unfortunately, many laboratory sorption, toxicity and biodegradation studies are often conducted at extremely high concentrations not reflective of true environmental conditions where equilibrium sorption is much greater. In a study of the elution with clean water of DP uniformly sorbed to a sandy soil column, the concentrations decreased markedly with time, with 16% of the original loading remaining on the column after 1000 pore volumes, reinforcing the importance of non-linear adsorption on increased persistence at lower sorbed concentrations (Wagner et al., 1994).

Little is known about the kinetics of QAC adsorption and desorption, but initial adsorption is thought to be quite rapid. Within each class of QACs, adsorption is thought to change drastically, with approximately a factor of 3 increase in sorption energy (concentration dependent partition coefficient) for every 2 carbons added to alkyl chains within a homologous series of small organic cations (Brownawell et al., 1990; Droge and Goss, 2012, 2013), although this has not been extensively studied for the high chain length QACs in this study. If biodegradation is controlled by the sorbed fraction or rate of desorption from sorbed phases, then large changes in the relative composition of even structurally similar QACS with different alkyl chain lengths should be apparent after release into the environment. As pointed out above, this is the case for the relative importance of biodegradation versus loss to sludge in STPs. One major reason that there has been such little work on QAC sorption is that for more hydrophobic homologs, the sorption is so great that it becomes too difficult to measure dissolved concentrations at low surface coverages in the laboratory. If aqueous phase detection can be made in such cases, it is likely that operationally defined aqueous phases are dominated by sorption with colloidal clays or organic matter.

Biodegradation of QACs

One important factor in determining the fate of QACs in the environment is assessing the likelihood that these compounds will degrade once released from sewage outfalls. There have been multiple studies conducted on the potential for biodegradation of QACs, but the literature is conflicted, with wide ranges of biodegradability often reported for the same compound. These inconsistencies may be due to several issues associated with QACs, including strong, non-linear sediment adsorption isotherms such that large spikes are not representative of smaller concentrations in the environment (Brownawell et al., 1990; Lara-Martín et al., 2010; Li and Brownawell, 2010), as well as toxicity associated with high spiking levels, particularly for ATMACs and BACs (Boethling, 1984; van Ginkel and Kolvenbach, 1991; Madsen et al., 2001). In addition, there is a wide range of procedures used to investigate biodegradation that may also result in such inconsistencies (Boethling, 1984; Cross and Singer, 1994).

The susceptibility for biodegradation of QACs is suggested to be greatest for ATMACs, followed by BACs, with DADMACs and DTDMACs showing the least degradation (Boethling, 1984; Cross and Singer, 1994), and degradation has been found to be inversely proportional to chain length (Boethling, 1984; Garcia et al., 1999; van Ginkel and Kolvenbach, 1991). Numerous studies have also documented the importance of acclimation in the biodegradation of these compounds (Cross and Singer, 1994; Federle and Pastwa, 1988; Games et al., 1982). The major degradation pathway for QACs is thought to be through n-dealkylation at the C-N bond (García et al., 2000; Tezel et al., 2012; Ying, 2006), and most studies have found this degradation to be first order (Games et al., 1982). Studies indicate that intermediates in the degradation of QACs are not persistent (Games et al., 1982; Nishiyama et al., 1995), suggesting that once primary biodegradation occurs, ultimate biodegradation should be fairly rapid, however this has not been well tested under conditions that might be reflective of receiving waters or sediments.

Many of the studies on the biodegradation of QACs have focused on degradation in sewage treatment plants, but, as noted, results vary. Sullivan (1983) found DTDMACs to be readily degradable when spiking radiolabeled QACs and using activated sludge as a medium in semi-batch reactors. In contrast, a STP mass balance study by Clara et al. (2007) indicates that the removal of DTDMACs during sewage treatment is mostly attributed to sorption onto particles, with little evidence for biodegradation. This conclusion is similar to earlier studies conducted with less specific analytical methods (Denijs and Degreef, 1992; van Leeuwen et al., 1992). For ATMACs, many spiked incubation studies conducted with sewage sludge suggest biodegradation is possible, especially with acclimation (Garcia et al., 2001; Gerike, 1978; van Ginkel and Kolvenbach, 1991; Nishiyama et al., 1995), though larger ATMACs show slower degradation than the smallest ATMACs (van Ginkel and Kolvenbach, 1991). Several STP studies also indicate that even during adsorption to particles during sewage treatment, degradation of ATMACs is possible (Clara et al., 2007; Games et al., 1982). Complete primary degradation of BACs has been observed in these and similar experiments (Garcia et al., 2001; Gerike, 1978), as well as in an STP mass balance study (Clara et al., 2007), although there is much less data in the literature on the degradation of BACs (Tezel et al., 2012).

There are very few anoxic experiments that have been conducted to understand the potential for anoxic biodegradation of QACs, but Garcia et al. (1999) determined that both ATMACs and BACs saw very little primary and no ultimate degradation in a 200-day anoxic experiment conducted with acclimated sewage sludge. A later study by Garcia (2000) confirmed this finding and also saw no biodegradation of DTDMACs, findings confirmed in a review by

Ying (2006). Brownawell et al. (2013) have also found that none of the QACs studied in this work were significantly degraded during anaerobic digestion of sewage sludges.

Experiments to understand the biodegradation of QACs under environmental conditions are scarce and once again conflicting. Shimp and Young (1988) found that biodegradability of the smallest QAC, ATMAC 12, in a settled sediment column was a function of the amount of ATMAC 12 found in pore waters and not a function of the total ATMACs in the system, indicating that for at least some QACs, biodegradation is not possible when adsorbed onto sediments. In contrast, others have found that in experiments with river water, the amount of sediment in the experiment had no affect on the extent of biodegradation of larger ATMACs and DTDMACs and that bound QACs are readily available for biodegradation (Larson and Vashon, 1983), with half lives around 5 days; however, these studies were conducted at spiked aqueous concentrations much greater than those observed even in sewage influent. A review of data available for ATMACs by Cross and Singer (1994) states that ATMACs should be readily biodegradable in sediments and should not accumulate, yet measurements of these compounds in this thesis and elsewhere (Lara-Martín et al., 2010; Li, 2009; Li and Brownawell, 2010) indicate that this is not the case. A study by Federle and Pastwa (1988) suggests that larger QACs such as ATMAC 18 and DTDMAC 18:18 can be mineralized (16-30%) in acclimated sediments from a pond that had been exposed to QACs, but un-acclimated control sediments showed no such biodegradation, highlighting the importance of acclimation in the biodegradation of QACs. While there are several studies on the biodegradation of QACs, it is apparent that the data is conflicting and may not accurately represent environmental conditions. More research is needed to better understand the biodegradation of QACs in aquatic environments, particularly at environmentally relevant concentrations.

Environmental fate of QACs based on field studies

Studies of QACs in the environment as well as attempts to better understand their geochemical fate are scarce, and controls on the environmental distribution of QACs have not been extensively studied. A study by Li and Brownawell (2010) examined the composition of QACs throughout the sewage-impacted Jamaica Bay and other areas of the NY/NJ Harbor complex. While the relatively constant composition of the largest QACs within Jamaica Bay has been taken to indicate persistence of these compounds, the composition of smaller and more biodegradable QACs did vary throughout the region, with higher relative compositions of smaller QACs closest to combined sewage overflow (CSO) inputs of untreated sewage (Li and Brownawell, 2010). This suggests that while the largest QACs are most likely persistent in these environments, smaller QACs have the potential to be influenced by the level of sewage treatment before discharge into the environment. Multiple inputs of sewage to Jamaica Bay as well as the influence of CSOs prevents Li and Brownawell's study from providing a clear picture on the fate of QACs, and further research is needed to better understand the distribution of QACs with distance from a source in sewage-impacted environments.

Li (2009) has also measured QACs at sediments from a deep-water dump-site located 160 miles off the New Jersey coast in 2600 meters of water. In this study, the ratio of ATMAC 22 to ATMAC 18 in this deep-water sample was in line with similarly aged sediments in the New York/New Jersey Harbor complex. This similarity, in spite of the vast volumes of water available as a sink for desorption and reworking of sediments by opportunistic deposit feeders prevalent at the organically enriched deep water dump site (DWD-106, e.g. sea urchins and sea cucumbers), provides additional evidence for the persistence of QACs once deposited in fine-grain sediments.

Geochronologies of QACs

A very limited number of geochronologies have also been used to assess the persistence of QACs in sewage-impacted environments. In his 2009 thesis study, Li investigated sediment cores from Jamaica Bay and the Hackensack River as well as a time-series collection of sediment grab samples from Newtown Creek to better understand the persistence as well as historical inputs of QACs to the New York/New Jersey Harbor Complex. When date-matched portions of two extensively studied (Bopp et al., 1993; Ferguson and Brownawell, 2003; Miller et al., 2008) cores taken from Jamaica Bay in the same location eight years apart were compared, no *in situ* degradation was indicated for any of the major classes of QACs (Li, 2009) following burial in very suboxic sediments in seasonally hypoxic Grassy Bay. However, comparisons were only made in three sections of the cores and could not rule out *in situ* degradation occurring in the upper portions of the core. Interestingly, Ferguson et al. (2003) also found no difference in nonylphenol ethoxylates and their metabolites in the same sediment core comparisons, but did find good evidence for de-ethoxylation of nonylphenolmonoethoxylate converting to nonylphenol in the upper few cm of the 1996 collected core.

The sediment cores analyzed by Li (2009), and later by Lara-Martin et al. (2010), also provided important information on the historical input of QACs to the aquatic environment. Dates of first appearances as well as changes in input were consistent between the Jamaica Bay and Hackensack cores, and this data have been used to aide in the interpretation of core data from this thesis. A subsurface maximum of DTDMACs was observed in the late 1980's that coincided with the known peak in DTDMAC production that occurred before the European phase out. After this subsurface maximum, concentrations of DTDMACs appear to have leveled out (Li, 2009). First appearances of BACs and DTDMACs around the mid to late 1950's as well as first appearances of DADMACs in the mid 1960's was also observed, and these dates are in line with estimates of the first uses of these compounds from the literature and USITC data as described above (Li, 2009). While an increase in BACs from the 1970's into the 1990's might be expected based on USITC data, such increases were not observed in Li's core from Jamaica Bay. An increase in DADMAC was observed in the upper portions of this same core and is consistent with increases in the use of these compounds as later generation QAC (or Quat) disinfectants (Li, 2009). Profiles of ATMACs 16-18 mostly mirrored DTDMAC profiles, while dramatic increases in behentrimonium were observed beginning in the 1980's (Lara-Martín et al., 2010; Li, 2009), consistent with increases in the use of these compounds in hair care products. Doubling times of approximately 3-4 years for behentrimonium over this time period were reported. It is not clear whether there have been further increases in behentrimonium use since the mid-to-late 2000's. While great progress has been made with these analyses, these cores were all obtained from environments with changing sewage inputs due to increases in sewage flow and STP upgrades as well as CSO inputs that periodically release untreated sewage to the region. As such, there is much left to be learned about the geochronologies of these compounds as well as the environmental fate of QACs once deposited in muddy, depositional regions.

1.5 Use of QACs as Sewage Tracers

There have been few applications of QACs as sewage tracers to date, as their use in this capacity was not suggested until 2010 (Li and Brownawell), and all of these applications can be found in Xiaolin Li's thesis (2009). QACs have been used by Li (2009) to aid in the source allocation of the brominated flame-retardants polybrominated diphenyl ethers (PBDEs). Previous studies (Benedict, 2007) hypothesized that the congener composition of PBDEs could be used to determine the source of these contaminants (sewage, industrial, or both). QACs were used to confirm this hypothesis, finding that samples with the highest percentage of $\Sigma_{\text{tri-hexa}}$BDE congeners hypothesized to come from sewage were strongly correlated with QACs, while samples with the lowest percentage of $\Sigma_{\text{tri-hexa}}$BDE congeners hypothesized to come from industrial sources fell above this line (Li, 2009). QACs have also been used to better understand the source of polychlorinated biphenyls (PCBs) in the Hudson River, the site of intense industrial PCB inputs that have since ceased, with sewage representing an increasingly important source of these compounds, particularly to the lower regions of the Hudson River (Li, 2009). The results of this study indicated that with the exception of the lowest chlorinated congeners, a large portion of the PCBs in New York Harbor are sewage derived and not due to upstream industrial sources (Li, 2009), something that had been argued earlier based on PCB compositional analysis. QACs have also been shown to strongly correlate with total organic carbon (Li and Brownawell, 2010), and this has been hypothesized to be due to sewage derived organic matter input in some areas of the lower Hudson Basin where inputs of organic matter from phytoplankton are limited to a degree by light limitation resulting from resuspended sediments.

In addition to source allocation, QACs have also been used to determine the geochemical fate of organic contaminants, including the nonionic surfactants nonylphenol ethoxylates (NPEOs; Li, 2009). NPEO’s correlated extremely well with QACs in anoxic, highly depositional muds, which is in line with previous determinations of sewage as a dominant source of NPEOs to the aquatic environment (Ferguson et al., 2001). In contrast, sediments from non-depositional environments were below the previously determined linear correlation, indicating that NPEOs may be depleted and potentially degraded in certain environments. This application of QACs showcases the ability of these compounds to not only aid in the source allocation of contaminants, but to also provide valuable information on the geochemical fate and persistence of these compounds. Significant uncertainty remains on the environmental fate and persistence of QACs due to the limited number of environmental studies conducted to date. More research is needed to understand the controls on the environmental distribution of QACs, including the behavior of QACs with distance from a point source of sewage as well as research on the persistence of QACs both throughout a sewage-impacted environment as well as once deposited.

In this dissertation, QACs have been used to better understand the source of metals in Long Island Sound and Hempstead Bay as well as the sources and geochemical fate of di-ethylhexyl phthalate (DEHP) in Hempstead Bay.

Metals

Metals suspected of having anthropogenic sources as well as those that may serve as indicators of sediment redox conditions were selected for analysis in this thesis. These metals include silver (Ag), aluminum (Al), cadmium (Cd), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), lead (Pb), titanium (Ti), vanadium (V), and zinc (Zn). In particular, Ag, Cd, Cu, Pb and Zn are metals of toxicological concern in the environment and are known to be anthropogenically enriched in coastal and estuarine sediments. Potential sources of these metals to the aquatic environment include point (e.g. sewage, industry, marinas) (Buck et al., 2005; Mecray and ten Brink, 2000; Rozan and Benoit, 2001; Sanudo-Wilhelmy and Flegal, 1992) and non-point sources (e.g. run-off, atmospheric deposition) (Cochran et al., 1998; Mecray and ten Brink, 2000; Rozan and Benoit, 2001; Wolfe et al., 1991). A study by Cochran et al. (1998) in Long Island Sound found atmospheric deposition to be an important source of metals to LIS, particularly to the central and eastern portions of the Sound, while the East River and western LIS (WLIS) is thought to be the source of these metals to the more western regions of the Sound (Buck et al., 2005; Cochran et al., 1998; Mecray and ten Brink, 2000; Mitch and Anisfeld, 2010; Sweeney and Sañudo-Wilhelmy, 2004; Turgeon and O'Connor, 1991; Varekamp et al., 2000; Wolfe et al., 1991).

Additionally, metals including Cd, Mn and Mo may be affected by redox conditions within sediments. Cd and Mo are relatively soluble in seawater and have been found to be enriched in highly sedimentary environments with low bottom water oxygen or highly sulfidic sediments (Adelson et al., 2001; Brownawell, et al., 2009; Lyons et al., 2009; Morford et al., 2005; Nameroff et al., 2002). Similarly, Mn has been found to be mobilized from sediments under reduced sedimentary conditions (Morford et al., 2005). While Fe is subject to sediment redox processes and possible remobilization, it, along with Al, is viewed as being a good indicator of fine grained sediment (Feng et al., 1998).

Many of these metals have been previously studied in LIS (Balcom et al., 2004; Buck et al., 2005; Clark and Benoit, 2009; Cochran et al., 1998; Mecray and ten Brink, 2000; Mitch and

Anisfeld, 2010; Rozan and Benoit, 2001) as well as in a limited number of sandier samples from Hempstead Bay through EPA's coastal assessment program. In addition, a number of studies have looked at metals in nearby regions including Jamaica Bay (Ramondetta and Harris, 1978; Seidemann, 1991), the New York/New Jersey Harbor Complex (Adams and Benyi, 2003; Feng et al., 1998) and the Forge River (Brownawell et al., 2009). Studies from LIS as well as Hempstead Bay have found that Ag, Cu, Pb and Zn are enriched relative to background levels, and these levels have been found to exceed sediment quality criteria values (Fairey et al., 1998; Hyland et al., 1999; Long et al., 2002; McGee et al., 1999; Mecray and ten Brink, 2000). High levels of Cd and Mo have also been observed in the highly eutrophied Forge River, NY (Brownawell et al., 2009), and are thought to be a result of these redox sensitive metals being scavenged from the dissolved phase from highly reducing and sulfidic sediments (Brownawell et al., 2009). While sewage may represent a source of metals, it is unclear to what extent, and other sources such as atmospheric deposition and localized inputs may constitute a significant portion of the source of some metals in these environments.

Diethylhexyl phthalate

Diethylhexyl phthalate (DEHP) is a plasticizer used throughout the United States and globally (Blount et al., 2000; Staples et al., 1997; USEPA, 1979), with annual production estimated at 100-500 million pounds in 2006 (USITC). DEHP has been of concern in both the human and aquatic environment due to the potential for DEHP to cause acute toxicity and endocrine disruption for aquatic organisms (Call et al., 2001; Patyna et al., 2006; Rhodes et al., 1995; Shimada and Yamauchi, 2004; Staples et al., 1997). These concerns have resulted in an estimate of a threshold effect level (118 ng/g) as well as a probable effects level (2,647 ng/g) by MacDonald et al. (1996). DEHP has been previously measured in urbanized marine environments at concentrations beyond these levels (180-290,000 ng/g) (Bartolome et al., 2005; Fromme et al., 2002; Lin et al., 2003; McDowell and Metcalfe, 2001; Peterson and Freeman, 1982), but has remained understudied because it have proven so difficult to measure (Blount et al., 2000; Giam et al., 1975; Lin et al., 2003; Schwarzenbach et al., 2003). While estimates of the octanol-water partition coefficient (K_{ow}) of DEHP vary widely, log K_{ow} values between 4.20 and 8.90 have been reported (Staples et al., 1997), with a calculated value based on physical-chemical properties of 7.73 (Staples, 2003), and these numbers indicate that sediments are most likely the main repository for DEHP.

Estimates on the half-life of DEHP in oxidized sediments are rare, but Staples et al. (1997) suggested a half-life of greater than 100 days, while another review suggests a conservative estimate of 229 days for modeling purposes (Staples, 2003). Anaerobic degradation rates are expected to be significantly slower than aerobic degradation rates (Staples, 2003). In contrast to these estimates, Fauser et al. (2009) used a half life of just 0.4 days in aerobic sediments and 1 day in anaerobic sediments when modeling the fate of DEHP in a Danish fjord.

Possible sources of DEHP to urbanized environments include point (sewage, landfills) (Dargnat et al., 2009, 2009; Swartz et al., 1986; Vitali and Macilenti, 1997) and non-point sources (atmospheric deposition, runoff) (Bjorklund et al., 2009; Ebinghaus and Xie, 2006; Giam et al., 1978; Staples et al., 1997). A small number of studies have assumed that decreasing levels of DEHP with distance from a STP plant implies that sewage is a dominant source to urbanized environments (Fauser et al., 2009; Vitali and Macilenti, 1997), this issue has not been explicitly addressed. More research is needed to better understand the major sources as well as persistence of DEHP to urbanized marine environments.

1.6 Study Areas

Hempstead Bay

Hempstead Bay (HB) is the main study area of this thesis in part because of its unique point source of sewage in the western region of the Bay. This coastal lagoon is located along the southwestern shore of Long Island, New York between Jamaica Bay to the west and Great South Bay to the east, and together with South Oyster Bay make up an area known as the Western Bays. HB is protected from the Atlantic Ocean by barrier islands, including Long Beach and Jones Beach, which restrict the flushing of the Bay. While most of the region is shallow, Reynolds Channel and Jones Inlet (Figure 1.3) have been dredged (Swanson, 2011) to maintain navigation within the Bay. In particular, Hewlett Bay in the northern area of West Bay (Figure 1.3) has been extensively dredged, and severe hypoxia has been observed in this region of the Bay, in part, due to poor flushing as a result of the dredging (Swanson, 2013).

Hempstead Bay is divided into three major sections: West Bay, Middle Bay and East Bay (Figure 1.3). West Bay contains most of the industry found in Hempstead Bay, including a large landfill, most of which is located along the northern portions of the Bay. West Bay is also the site of almost all of the sewage outfalls in the region. In contrast, Middle Bay and East Bay have received almost no sewage inputs over the past couple of decades and are mostly devoid of industry. However, East Bay is bordered by a closed landfill along the Meadowbrook Parkway that is now a park, and there are a number of small marinas and areas of concentrated boat moorings that line the north shores of Middle and East Bays.

West Bay has been sewered since 1952 (Swanson, 2011), and as such, there is little input to the Bay from septic tanks; the exception is the hamlet of Lookout Point (Swanson et al., 2013). Hempstead Bay receives the effluent from 5 sewage treatment plants, with four of the five outfalls located in West Bay. The sewage effluent discharge into West Bay is dominated by the outfall from the Bay Park STP (50 MGD), with the Long Beach STP outfall contributing an additional 5 MGD (Interstate Environmental Commission, 2010). These two outfalls are located very close (1 km) to each other in a relatively well-flushed area in a Reynolds Channel that is located almost mid-way between East Rockaway and Jones Inlet (Figure 1.3). There are additional small STPs that discharge into the area, including the small West Long Beach plant outfall (0.6 MGD) that discharges into the highly flushed East Rockaway Inlet and is therefore considered to have a negligible impact on the Bay (Figure 1.3). Lawrence STP outfall (1.3 MGD) discharges into a poorly flushed embayment, Barrister Basin, that is hydrodynamically separated from the rest of HB and appears to have little exchange with the main portion of West Bay (Figure 1.3) so is also not considered to have significant impacts on the rest of Hempstead Bay. While there is one very small (50,000 gallons per day), seasonal outfall near the Jones Beach amphitheater in East Bay (Figure 1.3), the effects of this outfall are most likely limited to a very small area due to the small, periodic nature of the sewage input. Additional freshwater inputs include small streams (Pines Brook, East Meadow Brook) and groundwater (Swanson, R. Lawrence et al., 2013), although groundwater is not expected to be a significant source of QACs to Hempstead Bay due to the strong sorption of QACs to sediments. While 91 and 1.6 tons/year of nitrogen is estimated to enter West Bay from shallow and deep ground water, respectively, 96% of the total nitrogen loading is thought to come from STPs (Swanson, 2013). Multiple lines of evidence, including data from this thesis, indicates long retention times and poor flushing within West Bay (Swanson et al., 2013).

There have been concerns stemming from these sewage outfalls in West Bay, and recent studies (Gobler, 2012; Swanson, 2011) have documented evidence that high nutrient loads from these STPs are the likely cause of high levels of phytoplankton and macroalgal growth in parts of the Bay, and may also be contributing to localized hypoxic conditions in deeper and less flushed waters of the northern West Bay. There have also been shellfish closures due to high fecal coliform levels as well as other factors in the Western Bays, with closures occurring from 1967 until 1993 before some regions were reopened beginning in 2010 (Swanson, 2011). In addition, large losses in wetlands have been noted, particularly since the turn of the twentieth century when modification of the barrier islands began (Swanson, 2011). Bay Park STP alone has received over 50 violation notices of its State Pollutant Discharge Elimination System permits (Swanson, 2013). Hempstead Bay represents a unique environment where a point source of sewage discharges into a semi-enclosed bay, and provides an ideal location to study not only the circulation of sewage affected particles within a system, but the environmental fate and persistence of QACs upon discharge into an estuarine environment.

Jamaica Bay

Jamaica Bay (JB) is another coastal lagoon located along the south shore of Long Island. Sediments cores from JB are included in this thesis for comparison to cores from Hempstead Bay as well as to update previously analyzed matched cores to provide additional information on the *in situ* behavior of QACs once deposited. Jamaica Bay is heavily sewage impacted, with four sewage treatment plants that discharge about MGD of sewage effluent into the Bay (Swanson et al., 2013), in addition to inputs from CSOs which discharge untreated sewage during large rain events.

Tidal exchange of water in Jamaica Bay is restricted by the single opening to the greater New York Bight, resulting in extremely high concentrations of sewage contaminants (Benotti and Brownawell, 2007; Ferguson et al., 2001; Li and Brownawell, 2010; Reddy and Brownawell, 2005). Freshwater inputs to JB are limited and are dominated by STP and CSO inputs (Bopp et al., 1993; Swanson et al., 1992). Additional information on Jamaica Bay can be found in studies by Swanson et al. (1992), Li and Brownawell (2010), Reddy and Brownawell (2005), Benotti and Brownawell (2007), Ferguson et al. (2001, 2003) and Renfro et al. (2010).

Long Island Sound

Long Island Sound (LIS) is an urban estuary located between Long Island, NY and Connecticut, with the east end of the Sound opening into the Atlantic Ocean and the western edge of LIS ending in New York City. LIS has over 44 sewage treatment plants (STPs) located along its shores discharging over 1 billion gallons per 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 (Sweeney and Sañudo-Wilhelmy, 2004; Wolfe et al., 1991). Wolfe et al. (1991) noted that 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.

There are 4 sewage treatment plants (STPs) located in the northern East River adjacent to WLIS. These STPs (Tallman Island STP, Hunts Point STP, Bowery Bay STP, and Wards Island STP) discharge a combined 460 MGD and represent the strongest input of sewage into the LIS watershed (68%,Interstate Environmental Commission, 2010; Wolfe et al., 1991), with the Tallman Island STP located closest to LIS, about 1km from the Whitestone Bridge. 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 (Interstate Environmental Commission, 2010). CSOs are also a source of less treated sewage in the New York City area, extending into Eastchester Bay in the Bronx as well as Little Neck Bay just to the east of the Throgs Neck Bridge. More extensive information on Long Island Sound can be found in the *Journal of Coastal Research*'s 16th volume, 3rd issue from 2000, the 14th volume, 3rd issue from 1991 in *Estuaries*, as well as by Wolfe et al. (1991).

1.7 Dissertation Objectives

The main objective of this dissertation is to increase the knowledge about the occurrence, distributions and fate of QACs in sewage-impacted environments. This includes better understanding the geochemical behavior of QACs with distance from a point source as well as their potential to degrade in both sediment cores as well as in lab experiments intended to mimic environmental conditions. This knowledge is critical not only because of very high concentrations of QACs that have been measured in these environments, but also to better understand the applicability of these compounds as sewage tracers. The valuable knowledge that can be gained about other contaminants through the use of QACs as sewage tracers is also presented in this thesis.

The objectives of this dissertation are addressed in the following chapters:

- Chapter 1 introduces the significant concepts of this thesis and provides information about the state of the literature on QACs.
- Chapter 2 presents data for QACs from a semi-point source of sewage in Long Island Sound to provide insight into the fate of QACs with great distance from a source. Data for metals in this same transect is also provided and QACs are used to elucidate the source of metals in this environment.
- Chapter 3 presents data for the distribution of QACs in Hempstead Bay and provides detailed insight into the fate of QACs with distance from a point source in a constrained environment.
- Chapter 4 provides four new geochronologies of QACs taken from Hempstead Bay and Jamaica Bay that provide additional information concerning the fate of QACs once buried in highly depositional environments as well as indications of source changes that may be occurring for individual QACs. Data on the nature of DTDMAC inputs over the last twenty years are also presented to provide further support for the use of these compounds as sewage tracers.
- Chapter 5 details the application of QACs as sewage tracers for source allocation of metals and DEHP as well as to better understand the geochemical fate of DEHP in Hempstead Bay
- Chapter 6 presents data from lab experiments used to better understand the possibility of degradation of both aged as well as spiked QACs in oxic and anoxic sediments sampled from the major sewage outfall in Hempstead Bay.
- Chapter 7 is a summary of the most important findings from this dissertation as well as suggestions for future research.

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Figure 1.1 The structure of the major classes of QACs: dialkyldimethyl ammonium compounds (DADMACs), benzylalkyl dimethyl ammonium compounds (BACs), and alkyltrimethyl ammonium compounds (ATMACs). DADMACs are typically split into two groups, DADMACs with carbon chains 8-10, and DTDMACs with carbon chains 12 and longer.

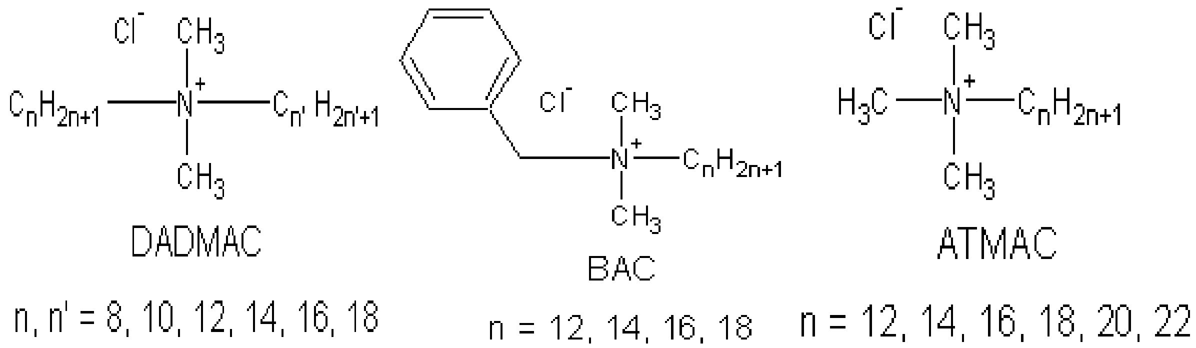


Figure 1.2. An example of Freundlich adsorption isotherms on various EPA sediments for dodecylpyridinium (Brownawell and Westall,1991).

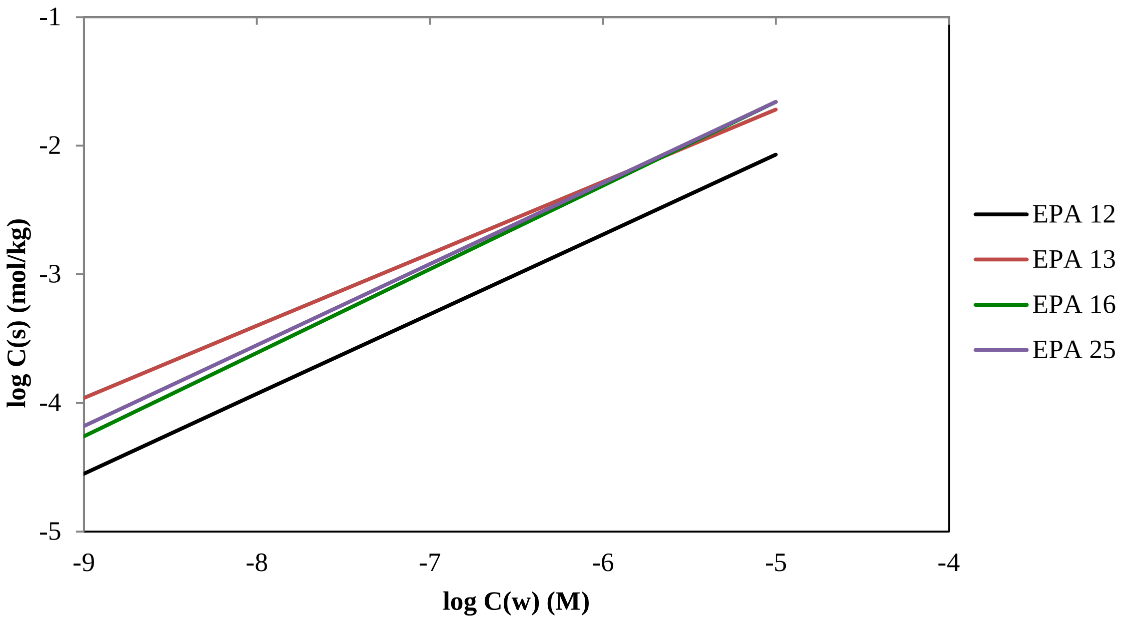
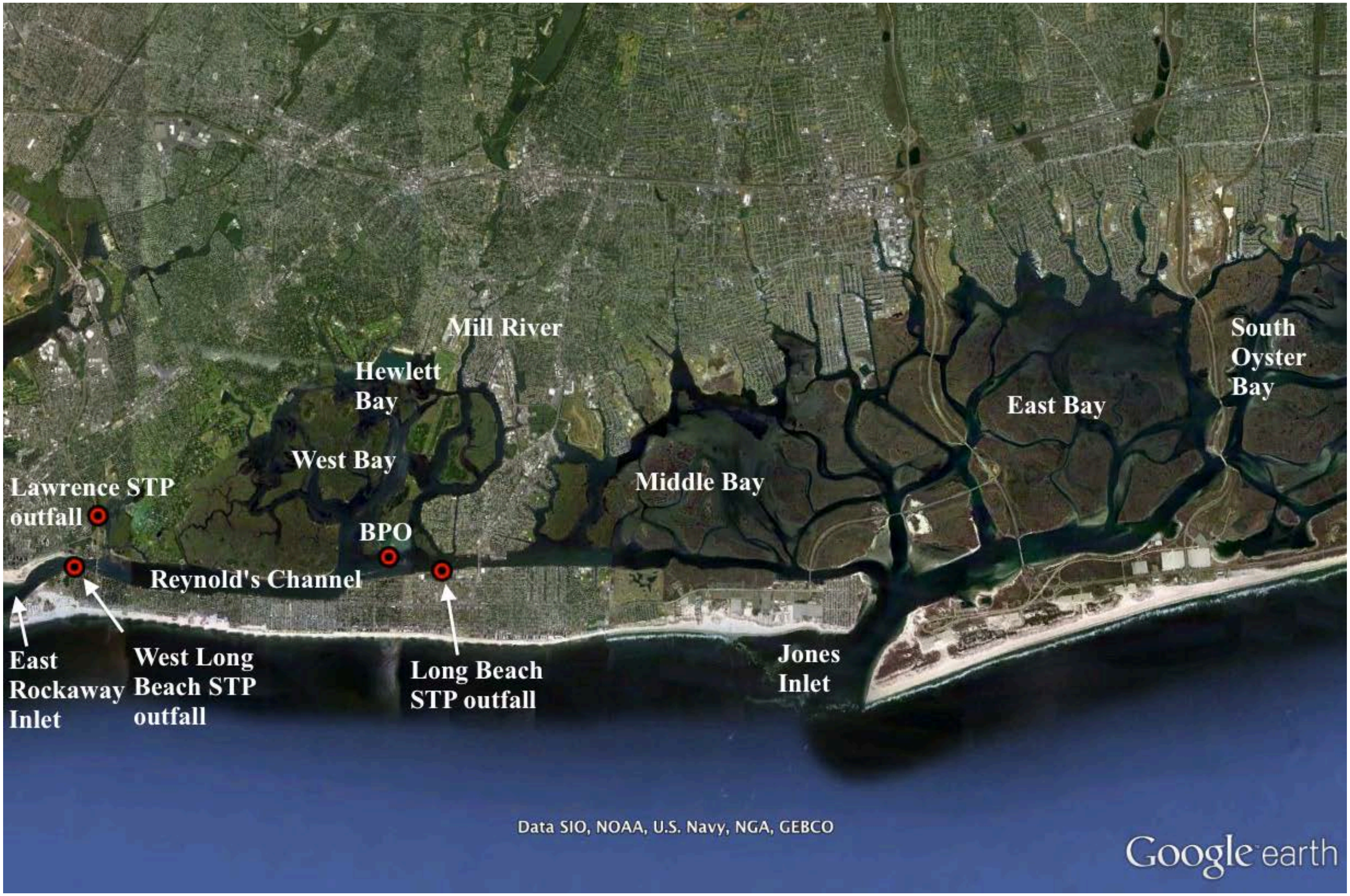


Figure 1.3. The major regions within Hempstead Bay as well as STP outfalls, denoted by red dots.



CHAPTER 2. Distribution of QACs in Long Island Sound sediments and application as sewage tracers to elucidate sources of trace metals.

2.1 Introduction

Quaternary ammonium compounds (QACs) are cationic surfactants that have been measured at very high levels in sewage impacted marine environments (Gerike et al., 1994; Fernández et al., 1996; Kreuzinger et al., 2007; Martinez-Carballo et al., 2007; Li, 2009; Li and Brownawell, 2009, 2010), yet there is little information on the fate of QACs once they enter the environment. Previous studies have highlighted the utility of QACs as a sewage tracer (Li, 2009; Li and Brownawell, 2010), although more research is needed. In this study, QACs were investigated along a transect away from the highly sewage impacted western portion of Long Island Sound (LIS) to gain insight into the differential fate of QACs during transport from a sewage source and compare their distributions to selected trace metals.

QACs are comprised of three classes, each containing an ammonium compound with at least one n-alkyl side chain between 8 and 22 carbons. Benzylalkyl dimethyl ammonium compounds (BACs) have side groups consisting of two methyl groups, one benzyl group, and one alkyl side chain that varies from 12 to 18 carbons long. BACs 12-16 have mainly been used as biocides, sanitizers and disinfectants (Boethling, 1984), and BAC 18 is used in other applications including personal care products. Alkyltrimethyl ammonium compounds (ATMACs) have three methyl groups and one alkyl side chain that can range from 12 to 22 carbons long. ATMACs have traditionally been used for their antimicrobial properties (e.g. cetrimonium) as well as in personal care products and a variety of industrial applications (Lara-Martín et al., 2010; Li, 2009; Madsen et al., 2001). There has been a large increase in use of ATMAC 20 and ATMAC 22 (behentrimonium) in hair care products in recent decades (Lara-Martín et al., 2010; Scientific Communication on Consumer Products, 2007). QACs with two long alkyl side chains, dialkyldimethyl ammonium compounds (DADMACs), are often subdivided into two groups to distinguish between smaller DADMACs (8:8 – 10:10) and larger compounds (12:12 – 18:18), referred to as ditallowdimethyl ammonium compounds (DTDMACs), and this practice is continued in this study (Cross and Singer, 1994; Fernández et al., 1996; Schaeufele, 1984). DADMACs are used as biocides and disinfectants, while larger DTDMACs are found in products such as fabric softeners (Boethling, 1984; Cross and Singer, 1994). DTDMACs are the largest and most hydrophobic of all QACs that have been targeted in this analysis.

There have been relatively few studies on the occurrence or fate of QACs in the environment (Li and Brownawell, 2010). Available studies indicate that QACs can be found in sediments at high concentrations, particularly in sewage-impacted environments (Fernández et al., 1996; Gerike et al., 1994; Kreuzinger et al., 2007; Lara-Martín et al., 2010; Li and Brownawell, 2009, 2010; Martinez-Carballo et al., 2007) with concentrations of total QACs (ΣQACs) ranging from 1 to 114 μg/g in sediments from the New York/New Jersey Harbor Complex (Lara-Martín et al., 2010; Li and Brownawell, 2009, 2010). Sewage is expected to be the dominant source of QACs in urban estuaries, especially those QACs used extensively in personal care products or fabric softeners. QACs are not volatile, so atmospheric deposition is not considered an important source to coastal environments.

QACs have been suggested as suitable tracers of sewage affected particles (Li and Brownawell, 2009, 2010) due to their high environmental concentrations, source specificity, very high particle reactivity, especially for the largest and most hydrophobic DTDMAC, and persistence in the environment (Brownawell et al., 1990; Ferrer and Furlong, 2002; Li and Brownawell, 2009, 2010; Suter et al., 1997). Several studies have shown that major DTDMAC homologs are very stable, even in sewage treatment plants with highly acclimated microbial communities (Clara et al., 2007; Denijs and Degreef, 1992; van Leeuwen et al., 1992). Li and Brownawell (2010) have argued that relatively constant compositions of QACs, and especially the more highly alkylated DTDMAC homologs, in sediments from the New York/New Jersey Harbor complex are consistent with very high persistence in estuarine environments. Studies indicate that biodegradability and solubility of QACs decreases with increasing chain length in both laboratory studies and sewage treatment plants (Boethling, 1984; Garcia et al., 1999; Van Ginkel and Kolvenbach, 1991), although non-linear adsorption isotherms may result in stronger sorption of QACs at lower concentrations (Brownawell et al., 1990; Lara-Martín et al., 2010; Li and Brownawell, 2010) that may also impact the geochemical fate of QACs once deposited in sediments. A better understanding of changes in the relative composition of individual QACs with distance from a source may give an indication of the persistence of these compounds in sewage-impacted environments.

The use of DTDMACs as sewage tracers is supported by earlier work with trialkylamines (TAMs), which are dialkylmethyl tertiary amine homologs found as impurities in DTDMAC and have received more attention than QACs for their own sewage tracing properties (Chalaux et al., 1995; Fernandez et al., 1991; Maldonado et al., 1999, 2000; Valls et al., 1989). The lack of compositional change and the relative increase in abundance of TAMs compared to other organic sewage tracers with distance have provided good evidence for especially high persistence of particle sorbed TAMs in offshore marine environments away from urban sources (Chalaux et al., 1995; Maldonado et al., 1999, 2000). QACs are suitable sewage tracers for the same reasons put forth for TAMS (sewage as a dominant source, low background levels, persistent in sewage impacted environments), but provide even more flexibility as QACs are found at much higher levels in the environment than TAMs, providing a greater sensitivity and potential for using QACs as sewage tracers. While it was previously argued that the near constant composition of larger DTDMAC homologs in sediments from the New York/New Jersey harbor complex area was also good evidence for their persistence in urban estuaries, distributions of QACs as a function of distance from a single source were not possible in these environments (Li and Brownawell, 2010).

In this work, the distribution of QACs is compared to a number of metals to both better understand the distribution of QACs as well as assess whether QAC sewage tracers may provide information about the relative importance of sewage as a source of selected trace metals to LIS. Metals investigated in this work (Ag, Al, Cd, Cu, Fe, Mn, Mo, Pb, Ti, V, and Zn) have been previously studied in LIS (Balcom et al., 2004; Buck et al., 2005; Clark and Benoit, 2009; Cochran et al., 1998; Mecray and ten Brink, 2000; Mitch and Anisfeld, 2010; Rozan and Benoit, 2001; Sweeney and Sañudo-Wilhelmy, 2004; Turekian et al., 2007; Turgeon and O’Connor, 1991; Wolfe et al., 1991) and potential sources of these metals include point (e.g sewage, industry) (Sanudo-Wilhelmy and Flegal, 1992; Mecray and ten Brink, 2000; Rozan and Benoit, 2001; Buck et al., 2005) and non point (eg. run-off, atmospheric deposition) (Cochran et al., 1998; Mecray and ten Brink, 2000; Rozan and Benoit, 2001; Wolfe et al., 1991) sources. Several studies have noted a gradient decreasing west to east in contaminant levels in western LIS

(WLIS) and, although this decrease is most often attributed to the large concentration of the region's sewage outfalls at the western end of LIS (Buck et al., 2005; Cochran et al., 1998; Mecray and ten Brink, 2000; Mitch and Anisfeld, 2010; Sweeney and Sañudo-Wilhelmy, 2004; Turgeon and O'Connor, 1991; Varekamp et al., 2000; Wolfe et al., 1991), this east to west gradient has also been attributed to a greater proportion of areas with fine grained sediments in WLIS (Aller et al., 1980, Mecray and ten Brink, 2000) as well as greater atmospheric deposition near urban sources (Cochran et al., 1998). Additional sources of these metals also exist outside of WLIS, including additional STPs, industry, runoff and the Thames, Quinnipiac and Housatonic Rivers of Connecticut (Clark and Benoit, 2009). Importantly, direct atmospheric inputs have been suggested as an important source to LIS and have been able to account for much of the sediment inventories of selected metals in areas closer to the urban airshed in WLIS (Cochran et al., 1998).

In this work, a study has been conducted in LIS to better understand the distributions of QACs over a range of 70km from New York City sewage inputs, including possible compositional changes of individual QACs that may indicate degradation/desorption of these compounds during transport. In addition, by comparing QACs with spatial distributions of metals, we aim to further illuminate the relative importance of various sources of metals to LIS.

2.2 Experimental

Study Area

Long Island Sound is an urban estuary located between Long Island, NY and Connecticut. The region has a very high population density, particularly in the western region of LIS, leading to large degree of human impact and sewage discharge to the region. LIS has over 44 sewage treatment plants (STPs) discharging over 1 billion gallons per day, and a large portion of this sewage is focused in a small area of the East River and the WLIS region of the Sound (Sweeney and Sañudo-Wilhelmy, 2004; Wolfe et al., 1991). Studies have found that sewage outfalls from the Bronx and Queens In the East River (excluding the very large Newtown Creek STP, whose discharge affects both LIS and NY Harbor via transport from the East River) supply 70% of the sewage-derived nitrogen (Wolfe et al., 1991) and comprise 68% of the total volume of sewage discharged into LIS daily (Interstate Environmental Commission, 2010). 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 (Interstate Environmental Commission, 2010).

There are 4 sewage treatment plants (STPs) just west of the westernmost station (1) sampled specifically for this work in 2008 (Tallman Island STP, Hunts Point STP, Bowery Bay STP, and Wards Island STP, noted in red in Figure 2.1b), with the Tallman Island STP located closest to Station 1 (approximately 5.6km to the west) and the main body of LIS (Figure 2.1b). Combined sewer overflows (CSOs) are also sources of less treated sewage in the New York City area, and there are extensive CSO inputs to the western portion of the study area that extend throughout NY City to the shores of LIS. The CSO discharges located closest to WLIS are in Eastchester Bay in the Bronx and Little Neck Bay just to the east of the Throgs Neck Bridge, with 3 CSO's located within 3km of Station 1 (NYSDEC, 2013).

Sample Collection

Samples were collected in LIS at stations marked in Figure 2.1a in September of 2008. Sample locations were selected based on previous work by Cochran et al. (1991) (including previous analysis of stations 1,3,5,6,9,10 and 15), and data from other LIS studies suggesting thicker deposits of post glacial sedimentation (Kim and Bokuniewicz, 1991; Lewis and DiGiacomo-Cohen, 2000) as well as sediment core analyses showing deep penetration (greater than 25cm) and high concentrations of metals or radionuclides (Mecray and ten Brink, 2000; Turgeon and O'Connor, 1991; Varekamp et al., 2000). The stations generally follow deeper depths and areas of known long-term accumulation of muddier sediments. Sampling began just east of the Throgs Neck Bridge and extended 75km eastward from the Tallman Island STP (Figure 2.1a); coordinates are provided in Table 2.1. Samples of the top five cm were placed in glass jars and frozen immediately upon return to the lab.

Data for QACs from four additional samples (FB1, FB2, UH008 and UH011) located within the region of high CSO and STP discharge were taken from Li (2009) to compare to results obtained in this study. UH008 and UH011 samples were collected in 1998 as part of the Environmental Protection Agency's REMAP program (Adams and Benyi, 2003), while FB1 and FB2 were collected in 2004 in Flushing Bay, NY (Li, 2009) (Figure 2.1b, orange dots). The three samples from the East River located west of the Tallman Island STP are represented as negative distances from the Tallman Island STP outfall, with zero equaling the outfall (Table 2.1).

QAC Extraction and Analysis

QACs were extracted based on the procedure described previously (Lara-Martín et al., 2010; Li and Brownawell, 2009, 2010). In short, 100 mg of freeze-dried sediment was extracted using acidic methanol in a heated sonication bath. Extracts were cleaned up using a chloroform/water liquid-liquid extraction as well as a final resin clean up. Analysis was performed with an HPLC-ToF-MS using electrospray ionization in positive ionization mode. As reported elsewhere (Lara-Martín et al., 2010; Li and Brownawell, 2009, 2010), QAC analytes were determined with two separate HPLC gradients, one to determine more hydrophobic DTDMAC homologues, and a second to determine all other DADMAC, BAC and ATMAC homologues which were typically found in lower abundance. Sample recovery was based on spiked DTDMAC 12:12 and averaged 72% ± 10%. The analysis showed good reproducibility, with an average relative standard deviation of 3.3% ± 2.1% relative standard deviation for two duplicates across all QACs.

Metal Analysis

Dried sediment (0.5g) was weighed into a clean beaker and 10 mL each of trace metal grade hydrochloric acid and nitric acid was added. Beakers were placed on a hotplate while covered with a watch glass until bubbling ceased. Watch glasses were then removed and the temperature increased so that the samples remained at just below a boil to allow the acid to evaporate. Samples were removed from the hotplate when most of the liquid had evaporated and 10 mL of 8M hydrochloric acid was then added to each beaker. Samples were placed back on the hotplate and evaporated to almost dryness once again. Samples were then diluted in 10% hydrochloric acid and centrifuged before final analysis.

Metal concentrations in sediment digests were measured by high resolution inductively coupled plasma mass spectrometry (ICPMS; ThermoFisher Element2) using indium as an internal standard. Digests were diluted 11-fold and injected directly into the ICPMS. Concentrations were externally calibrated using NIST-traceable multi-element standard solutions

(Inorganic Ventures). Accuracy was confirmed using standard reference material NIST 1643e, which gave recoveries within 10% of the certified value.

CHNS Analysis

For analysis of organic carbon, hydrogen, nitrogen and sulfur, about 0.5 grams of sediment was placed into a small beaker to which 20 mL of 0.1M HCl was added. This was agitated and then allowed to settle before pouring off the HCl solution. Samples were then rinsed with two aliquots of deionized water to rinse away most of the HCl and placed in a drying oven at 65°C until dried. Samples were then analyzed on a Carlo-Erba 1108 CHNS Analyzer. The instrument was calibrated with sulphanilamide. Samples were instrument blank corrected. Precision of analysis was determined on a reference LIS sample with relative standard deviation for organic carbon, nitrogen and sulfur were 1.6%, 2.1% and 5.5% respectively.

Statistical Analysis

Statistical analyses were used to determine if there was a significant relationship between each metal and DTDMAC 18:18. A Type II regression was performed for each metal, and an F-statistic and corresponding p-value was calculated based on an F-distribution. Spearman Rank Correlation test was also performed for each metal and a correlation coefficient (Rho) and corresponding p-value were determined. The correlation between each metal and DTDMAC 18:18 was considered significant if both the F-test statistic and Spearman's rho were significant (p value 0.05 or less).

2.3 Results and Discussion

2.3.1 2008 QAC results

QACs were detected in all samples, with measured concentrations of total QACs (ΣQACs) ranging from 166 – 12,500 ng/g (Table 2.2). Levels decreased sharply from Stations 1 to Station 10 (2 km-31 km) before leveling out about 30 km away at values 10% of those measured in the first three stations (Figure 2.2). Fe data (as well as Al, Ti and total organic carbon (TOC) data) indicate that samples were fine grain and of similar properties (ranging from 3.14% to 4.54% Fe) excluding Station 16, which had Fe levels of only 1.05% (Table 2.3). As expected based on sediment texture and, consequently, TOC levels (.35%), low Fe at Station 16 indicates that this station is much sandier than other samples collected in this study and is therefore excluded from some of the comparisons in this study. Excluding this low Fe sample, ΣQACs ranged from 844 ng/g to 12500 ng/g (Table 2.2). A lack of sudden changes in concentrations and compositions (see below) of QACs with distance are consistent with urban WLIS acting as the dominant source of QACs throughout the study area. If this is so, easy detection of QACs 75km away from Tallman Island STP outfall indicates that QACs can serve as sewage tracers even at great distances from sewage sources.

Total QACs in Station 1 were somewhat lower than other nearby stations, as seen in Figure 2.2. Fe levels were slightly lower at this station (3.39% Fe) compared to other nearby stations (3.89-4.54%), indicating that this sample might have been less fine grain than others in the area. This is consistent with somewhat lower TOC concentrations in Station 1 as well. To account for these potential variations in sediment types, ΣQACs concentrations (excluding Station 16) were normalized with Fe, as has been previously done to describe spatial variability in metals in the lower Hudson Basin by Feng et al. (1998), and with TOC, and are shown in Figure 2.2. The agreement between Station 1 and the rest of the data is improved when values are normalized to either Fe or TOC (Figure 2.2).

The mean ΣQACs measured in these samples (4,840 ng/g) is lower than ΣQACs measured in nearby systems, including the NY/NJ harbor complex (29,000 ng/g) (Li and Brownawell 2010) and Jamaica Bay (48,000 ng/g) (Li and Brownawell, 2010), although the average ΣQACs in the first three stations (11,200 ng/g) closest to the area of sewage discharge is much closer to these other systems. LIS has a total volume of 18 trillion gallons and is a much larger system than the NY/NJ harbor complex and Jamaica Bay, with greater flushing and dilution of sewage that would account for lower average levels. In addition, most of the samples analyzed in LIS were >15km from the major sewage discharges to LIS.

2.3.2 Compositional Changes of QACs

The changes in the ratio of individual QACs to DTDMAC 18:18 with distance from the major sewage sources in the East River and WLIS were investigated to investigate the persistence of these compounds in LIS. As Station 1 in this transect is located almost 6 km from the closest outfall (Tallman Island STP, Figure 2.1b), data from four additional samples from Li

(2009) were included in these analyses to gain additional insight into compositional changes that may be occurring closer to the source. These four points (UH 008, UH 011, FB1, FB2, Figure 2.1b, Table 2.1) are located in the East River to the west of Station 1. All of these stations, aside from UH 008, are located to the west of Tallman Island STP in the East River, and all are impacted by local sewage inputs from multiple STPs and CSOs. These samples are thus representative of CSO and STP impacted sediments and will provide additional information about compositional changes and preferential degradation or desorption that may be occurring close to the sewage source.

Total DTDMACs comprised on average 94 ± 2.5 percent of the ΣQACs measured. The percent composition of the largest DTDMACs (16:16-18:18) quickly increased from the East River to Station 3 11km away from the Tallman Island STP outfall, beyond which a much more gradual increase was observed (Figure 2.3), suggesting that smaller, more degradable and desorbable QACs are being preferentially lost in the first 10 km away from Tallman Island STP, beyond which remains a fairly resistant pool, as discussed below.

Individual QACs were normalized by DTDMAC 18:18 to illustrate compositional changes that may be occurring in LIS. DTDMAC 18:18 was the most abundant of all QACs, comprising on average 46.4 ± 2.4% of the ΣQACs measured samples from this study. In addition, DTDMAC 18:18 is the largest, most particle reactive of all QACs and is expected to be least subject to desorption or degradation during transport. Station 16, as discussed above, has been removed from this analysis to ensure that samples with similar sediment properties are compared.

BACs

All BACs (12 – 18) were enriched in the four East River samples and Station 1 when normalized to DTDMAC 18:18, as compared to the rest of LIS (Figure 2.4). This is most likely due to the close proximity to STP outfalls and CSOs inputs that result in samples being enriched in smaller, more degradable QACs, a result also seen by Li and Brownawell (2010). BAC 12 and BAC 14 reached a constant composition after Station 1 (Figure 2.4), indicating that labile or more desorbable pools of these compounds are very quickly desorbed/degraded from sediment during transport before reaching a relatively stable composition. As BAC hydrophobicity increases, the distances over which compositions continue to change also increases. BAC 16 did not reach a constant composition until 15km from Tallman Island STP outfall, while BAC 18 appears to have continued to degrade/desorb as contaminated sediment particles are transported even further eastward (Figure 2.4). This is interpreted below.

These observations are somewhat surprising, as traditionally, more soluble BACs would be expected to partition more favorably into the dissolved phase during transport, while BAC 18 would be expected to have the least changes in composition due to its increased hydrophobicity. As no changes in the source of BAC 18 to the environment over the past few decades has been indicated (Chapter 4), the trends observed are most likely related to the desorption/degradation of BACs during transport. We hypothesize that the smallest BACs desorb and degrade very quickly after leaving the region of STP and CSO impact, beyond which a recalcitrant pool of strongly sorbed compounds remains. BAC 16 appears to take longer than more soluble QACs to reach this recalcitrant state (15km), while BAC 18 appears to continue to degrade/desorb throughout all samples measured. This is interpreted as being the result of slower desorption of more hydrophobic QACs, such that "labile" sorbed pools take more time in the water column to desorb. These explanations are consistent with the known effects of hydrophobicity on loss of QACs in sewage treatment plants (Clara et al., 2007). The tendency of a homologous series of hydrophobic compounds to follow such patterns has also been previously noted, as Lamoureux and Brownawell (1999) observed greater, continued desorption of more hydrophobic polychlorinated biphenyls from field aged sediments as compared to their less hydrophobic counterparts, where they may be a greater amount of resistant fraction present in what is preserved in sediments, as well as Ten Helscher et al. (1999) who suggested the occurrence of a resistant phase for hydrophobic organic contaminants.

ATMACs

Changes in the relative compositions of ATMAC 16 and ATMAC 18 in LIS are similar to those observed by BAC 12 and BAC 14, wherein enrichment is observed in the four East River samples and Station 1, but a stable composition is reached quickly and no compositional changes are observed for stations 2 through 17 (Figure 2.4). The solubility and tendency to be degraded for ATMAC 16 and 18 are similar to that of BAC 14 and 16 based on critical micelle concentrations and retention times. The observations for these smaller ATMACs are in stark contrast to those observed for ATMAC 20 and ATMAC 22, for which there are sharp declines in concentration with increasing distance from WLIS sewage sources (Figure 2.4). While this could be due to two different reasons (changes in source or preferential loss during transport), we suspect that a change in the source of these compounds is the main reason for the trends observed. ATMAC 20 and 22, termed behentrimonium, are hair care products (Liu and Ding, 2004; Scientific Communication on Consumer Products, 2007) exhibiting rapidly increasing values in the environment since the 1980's (Lara-Martín et al., 2010; Li and Brownawell, 2010) with a doubling time of 3-4 years (Lara-Martín et al., 2010). This increase in the source of behentrimonium would result in the trends observed assuming a sediment transport model for LIS in which sediments closest to the source represent the most recent sewage signal, while sediments further way represent an older sewage signal. The conceptual model is that the distribution of QAC contaminated sediments is controlled by many resuspension and desorption events and that, on average, the sewage contaminated sediments found further from the source have undergone more resuspension events with longer timescales involved in their transport to the sites where they are accumulating. With this assumption, the higher relative abundance of behentrimonium approaching the source is related to their recent increases in use. However, while ATMAC 20 and 22 are only somewhat more hydrophobic than BAC 18, it is also possible that some of the decrease relative to DTDMAC 18:18 is related to desorption and likely degradation during transport to more distal sites.

ATMAC 20 and ATMAC 22 data for UH008, UH011, FB1 and FB2 provide an interesting comparison to the newer transect. The relative composition of ATMAC 22 at stations UH008 and UH011 (collected in 1998) is significantly lower than at Station 1 (Figure 2.4) even though it is closer to sewage sources, most likely due to the samples being taken 10 years prior to Station 1. Therefore, UH008 and UH011 reflect an older ATMAC 22/DTDMAC 18:18 signal, much lower than the signal seen in at Station 1 in 2008. The relative composition of ATMAC 22 at FB1 and FB2 are a bit more varied (Figure 2.4), with FB1 exhibiting a much lower relative composition of ATMAC 22 compared to Station 1 (yet higher than 1998 samples) while FB2 has a relative composition more in line with Station 1. These samples were taken in 2004 and might be expected to have compositions more in line with Station 1. While data for ATMAC 20 was not determined for UH008 and UH011 (Li, 2009), the relative composition of ATMAC 20 at FB1 and FB2 exhibit a pattern similar to ATMAC 22.

DADMACs and DTDMACs

Unlike BACs and ATMACs, the composition of DTDMACs (12:14 to 16:18) were relatively constant when normalized to DTDMAC 18:18, including the four East River stations from Li (2009) (Figure 2.5). These findings are in agreement with Li and Brownawell (2010) who measured relatively constant compositions of DTDMACs within the New York/New Jersey Harbor complex. As QAC solubility and biodegradation is thought to decrease with increasing side chain length (Boethling, 1984), the constant compositions of DTDMACs observed in LIS, even for smaller DTDMACs, indicates that these large QACs are not degraded and/or desorbed in this environment regardless of proximity to sewage sources. It is of interest to note that the hydrophobicity (based on HPLC retention times and estimates of CMC) of DTDMAC 12:14 are similar to that of ATMAC 22, and there is no evidence of a drop in DTDMAC 12:14/DTDMAC 18:18 with distance. If it is assumed that the sorption kinetics of structurally different DTDMAC 12:14 and ATMAC 20 and ATMAC 22 are similar, this would support the argument that much of the relative decrease of behentrimonium with distance is in fact due to long timescales for transport of sediments eastward in LIS and differences across the Sound in the average dates that sediments were contaminated with QACs.

In contrast to DTDMACs, there is a compositional change of the more soluble DADMAC 10:10 within the first 15 km from Tallman Island STP outfall. While the compositional changes observed are most likely due to degradation and/or desorption of DADMAC 10:10 with transport from sewage sources, an increase in DADMAC production may also contribute to increased DADMAC/DTDMAC 18:18 ratios closer to the source (Li, 2009). Degradation and/or desorption with transport is to be expected, as DADMAC 10:10 has shorter side chains than DTDMACs and thus an increased likelihood of degradation and desorption in the environment. DADMAC 10:10 has also been found to be greatly degraded in Austrian sewage treatment plants while longer chain length DTDMACs are not (Clara et al., 2007). Beyond 15km, a fairly stable composition of DADMAC 10:10 is observed.

Compositional changes summary

The absence of compositional changes beyond 15 km from the Tallman Island STP for most QACs is an interesting result and indicates that even smaller QACs can be very persistent in the environment. This persistence may also be a result of more soluble QACs at these sites further from WLIS being increasingly associated with stronger sorption sites that are protected from further desorption.

Relatively constant compositions also point to WLIS serving as the dominant sewage source of QACs to LIS. If the smaller outfalls along the Connecticut or northern Long Island coast became more important sources, greater variations in QAC concentrations and compositions might be expected along this transect. Lacking such observations, we hypothesize that sewage outfalls in WLIS are the dominant source of QACs, and thus most likely sewage, in LIS. This observation is supported by data indicating that a majority of the daily sewage effluent and nitrogen entering LIS originates in WLIS (Interstate Environmental Commission, 2010; Wolfe et al., 1991).

While the phase associations of less alkylated BACs and ATMACs may become dominated by very resistant pools by Station 2, DADMAC 10:10, BAC 16 and BAC 18 take longer to degrade/desorb, with BAC 18 relative abundances continuing to decline throughout the entire transect (Figure 2.4). While this will be discussed in depth in Chapter 3, briefly, these compounds represent a deviation from the way that adsorption and degradation are sometimes thought of in relation to chain length, where it is known that recently sorbed organic contaminants with longer chain lengths and greater hydrophobicity are more associated with sorbed phases which increases their tendency to end up in sewage sludges and sediments, and results in greater protection from biodegradation (Clara et al., 2007; Martinez-Carballo et al., 2007; Shimp and Young, 1988). Smaller more soluble QACs (ex. small BACs, ATMAC 16 and 18) are hypothesized to be so quickly desorbed or degraded upon entering the environment that any fraction of these compounds remaining on particles beyond the East River/WLIS are extremely tightly bound and represents a resistant pool, thus no compositional changes are observed beyond the region of STP and CSO influence. Larger compounds (ex. larger DTDMACs), as expected, are extremely slow to degrade or desorb from particles, if at all, and so no compositional changes are observed, consistent with this theory. QACs that are in between these two extremes, such as DADMAC 10:10, BAC 16 and BAC 18, appear to have slower rates of desorption/degradation that lead to continued desorption as particles are transported farther from the source of contamination. The observed compositional change in behentrimonium (Figure 2.4) combined with a lack of compositional changes in DTDMAC 12:14, a QAC with a similar retention time and CMC, supports the conceptual model for sediment transport provided above.

2.3.3 Metals and DTDMAC 18:18

Metal concentrations and distributions

Thirteen metals in total were measured in this study to represent anthropogenically mobilized metals as well as those that may serve as indicators of sediment redox conditions. Concentrations were much lower for all metals in the sandier Station 16 sample (Table 2.3). For other stations, concentrations ranged from .53-1.94 μg/g for Ag, 20900-28900 μg/g for Al, .43-1.36 μg/g for Cd, 43.6 – 102 μg/g for Cu, 3.39 – 4.54% Fe, 759 – 1540 μg/g Mn, 1.09 – 2.28 μg/g for Mo, 31.1 – 80.6 μg/g for Pb, .0118 - .0194 μg/g for Re, 625-891 μg/g for Ti, 1.35 – 1.93 μg/g for U, 47.1 – 63.0 μg/g for V, and 102 – 164 μg/g for Zn (Table 2.3). Fe, Al and Ti levels were extremely consistent aside from Station 16, indicating that all other stations sampled were comprised of sediments with similar properties.

The focus of this paper will be on those particle reactive metals that have significant relationships (as defined above) with DTDMAC 18:18 (Table 2.6), including silver (Ag), cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn), all metals with suspected anthropogenic sources. While a significant relationship between Mo and DTDMAC 18:18 was also observed, Mo is not known to have anthropogenic sources but instead to be an indicator of reducing conditions, similar to redox sensitive Cd, which is much less particle reactive in seawater than other anthropogenically mobilized metals (Adelson et al., 2001; Morford et al., 2005; Nameroff et al., 2002). We expect that the relationships observed between Mo and DTDMAC 18:18, as well a portion of the relationship observed between Cd and DTDMAC 18:18, is due to an increase in remineralization of labile organic carbon associated with an increase in sewage derived organic matter in WLIS that correlates with increasing DTDMAC (Li and Brownawell, 2009, 2010) as well as greater amounts of phytoplankton derived organic matter fueled by sewage inputs of nutrients. Increases in remineralization would lead to decreases in bottom water oxygen levels, as have been observed in WLIS (Welsh and Eller, 1991), and increasingly sulfidic sedimentary conditions that could enrich Mo and Cd in these sediments, consistent with other reports of increased concentrations of these metals under reducing conditions (Adelson et al., 2001; Brownawell et al., 1990; Lyons et al., 2009; Morford et al., 2005; Nameroff et al., 2002)

Levels of Ag, Cd, Cu, Pb and Zn observed in stations 1-15 and 17 are in line with previous measurements of these metals measured in fine grain depositional environments in LIS by Mecray and Bulchholtz ten Brink (2000), Cochran et al. (1991, 1998) and summarized by Mitch and Anisfield (2010) (Table 2.4), with the exception of low aluminum and titanium. These differences, particularly in Al concentrations, are most likely a result of the extraction procedure employed in this study, as an acid leach does not completely dissolve aluminum rich clays. Six of the sites measured in this study (1,3,5,6,9,10 and 15) are the same sites as those analyzed by Cochran et al. (1991, 1998) in samples collected in 1988-1989. While this study was not designed to study temporal changes in metals, some observations about differences between the two studies can be made (Table 2.5). It is clear that metals not thought to be influenced by anthropogenic sources (Fe, Mn) remain very similar over the two decades between samplings, as the average ratio between Cochran's study (1991) and this study is 1.0 ± 0.06 and 0.9 ± .17 for Fe and Mn respectively (Table 2.5). In contrast, Cu, Pb and Zn, metals with known anthropogenic sources, had ratios that averaged 1.4 ± .4, 2.1 ± .32 and 1.7 ± .4 times higher, respectively, in 1988/89 than in this study (Table 2.5). The lower enrichments of Cu, Pb, and Zn in samples collected in 2008, while Mn and Fe were relatively similar, may indicate that the loading of these metals to LIS may have decreased in the twenty-year span between samplings, though further study would be needed for more definitive conclusions.

Comparison of metals to DTDMAC 18:18

Ag, Cd, Cu, Pb and Zn were compared with the sewage tracer DTDMAC 18:18 to better understand the sources of these metals in LIS (Station 16 was removed for this analysis). When plotted against DTDMAC 18:18, these metals showed a statistically significant positive correlation with DTDMAC 18:18 (Figure 2.5, Table 2.6). Values measured are all above regional background values (Mecray and ten Brink, 2000), indicated by the red lines in Figure 2.6. Background values were calculated by Mecray and Buchholtz ten Brink (2000) from metal concentrations at the bottom of gravity cores taken in the area. These background values are very similar to those obtained by Cochran et al. (1991, 1998).

High correlations of Ag, Cu, Pb and Zn with DTDMAC 18:18 in LIS support the hypothesis of a shared source. This source is most likely sewage originating in WLIS and the East River, but this cannot be delineated from other potential sources of these metals that might also originate in WLIS. When metals are plotted against QACs, y-intercepts above the background level of these compounds suggest additional sources that contribute to metal enrichment in the region. As noted, Cd correlations with DTDMAC 18:18 are most likely due to the sensitivity of Cd to redox conditions. Metal distributions may also be affected by seasonal influences related to mobilization of metals from sediment pore waters that have been documented to affect certain metals (Riedel et al., 1997).

To further investigate the importance of sewage within WLIS, a simple conceptual model was employed to give a rough estimate of the percent of excess metals explained by a correlation with QACs based on the Type II regression line fitted for each metal versus DTDMAC 18:18 (Figure 2.6). The range of DTDMAC 18:18 values measured in the westernmost stations (Stations 1-6) was then used to calculate the proportion of excess metals attributed to a shared WLIS source as well as the proportion coming from other sources, including runoff and atmospheric deposition (Figure 2.7). Background levels were subtracted for these calculations. There are several assumptions made in this calculation to simplify the model. It is known that the atmospheric deposition of contaminants (ex. Pb) is spatially variable, decreasing away from urban airsheds. In LIS, this is manifested by a decrease in metal inventories in high salt marsh cores at more eastern sites (Cochran et al., 1998). This means that the atmospheric input of most metals is most likely higher in WLIS as opposed to CLIS, although the model does not take this into account. Other potential sources such as rivers are also not constant throughout the region, but are assumed to be so within this model. There is also an implicit assumption that DTDMAC, which is extremely particle reactive, is transported on particles to a similar extent as these trace metals, some of which are likely not as particle reactive (especially Cd and possibly Zn). In addition, this simplified model assumes a steady state. While there are many assumptions made to simplify the calculations, this model gives an estimate of the relative importance of sewage as a source of these metals to WLIS.

The amount of excess metals observed in LIS that could be contributing to relationships observed with DTDMAC 18:18, and thus most likely sewage, can be seen in Table 2.7. The remaining excess metal levels are thought to come from other sources, as suggested above.

These values were compared to values for the relative importance of atmospheric deposition as a source, estimated by Cochran et al. (1998) for Cu, Pb and Zn (Table 2.7). The percent of excess metal concentrations in sediments that can be attributable to sewage in Stations 1-6 in WLIS ranges from 51-73% for Ag, 56-77% for Cd, 34-58% for Cu, 62-82% for Pb and 37-61% for Zn. The range of excess metal contribution expected from sources other than those attributable to DTDMAC 18:18, such as atmospheric deposition, ranged from 27-49% for Ag, 23-44% for Cd, 42-66% for Cu, 18-38% for Pb, and 39-63% for Zn. For comparison, Cochran and coworkers (1998) estimated the contribution of direct atmospheric input (not including indirect sources from terrestrial runoff) to be 32, 72 and 46% of total cumulative fluxes for Cu, Pb, and Zn, respectively (Table 2.7). Thus the estimates from comparison with DTDMAC are very consistent with Cochran's estimates for Cu and Zn, but are slightly lower than the Cochran et al. estimate of the atmospheric contribution to Pb enrichment in WLIS. This may be due to a phase out of Pb in gasoline (beginning in 1973) which has dominated atmospheric lead inputs in the past (Benninger, 1978). Atmospheric concentrations of Pb peaked in the 1970's but have decreased rapidly since that time. Therefore, the estimates made by Cochran et al. in the 1988 collected sediments would have reflected a history of Pb inputs that may be more dominated by atmospheric deposition in LIS than is reflected more recently in the upper 0-5cm of these WLIS sediments. It should also be noted that estimates of atmospheric inputs made by Cochran et al. (1998) were obtained through inventory assessments using marsh cores, while these estimates were only determined using surface sediments and would represent a much more short term input.

High correlations of Ag, Cu, Pb and Zn with QACs in LIS suggest a shared source from the metropolitan sewage influenced region of far WLIS. While sewage inputs that control distributions of DTDMC are implicated, such sources cannot be delineated from other potential sources of these metals that might also originate in WLIS. When metals are plotted against QACs, y-intercepts above the background level of these compounds indicate additional sources, which is in agreement with suggestions of atmospheric inputs of these compounds reported by Cochran et al. (1998). Two of the bigger uncertainties associated with this simple model involve an incomplete understanding of differences in source histories of QACs and different metals that affect sediment distributions, and whether the processes that control redistribution of metals throughout WLIS are similar to that of super hydrophobic QACs. It has been argued above that the enrichment of more soluble Mo and even Cd may be more controlled by differences in scavenging or retention of these elements in sediments with either higher sediment sulfide content or low bottom water oxygen contents. Whether Ag, Cu, Pb and Zn are particle reactive enough to be transported similarly to DTDMACs on particles being transported from WLIS point sources is an open question.

2.4 Conclusion

This study provides important new information about the variation in concentrations and compositions of sediment associated QACs with distance away from sewage impacted source areas. These data support the use of QACs, and in particular DTDMAC 18:18, as effective tracers of sewage affected particles and associated contaminants. The ratio of DTDMACs 12:14 to 16:18 to DTDMAC 18:18 do not vary appreciably with distance, despite great differences in their hydrophobicities. Our results suggest that the particle reactivity of all DTDMAC homologs is so high, at this range of concentrations, that there is not appreciable desorption during transport into LIS. The spatial trends in composition of smaller and less hydrophobic QACs are variable and are explained with a conceptual model that these QACs enter the system having been more degraded either during sewage treatment or in local receiving waters. The remaining sorbed QACs are associated with both very resistant phases that are not subject to much desorption as a particle is transported through oxygenated overlying waters, as well as “labile” sorbed pools, where the rate and extent of desorption then increases with greater solubility and shorter alkyl side chain lengths. What is interesting is that for some homologous series (best illustrated for BACs), there is evidence for a larger labile pool of desorbable QACs for more hydrophobic homologs. Differences between the amounts of more soluble QACs in surficial sediments in resistant phases in WLIS and Hempstead Bay (Chapter 3) may be due to differences in the nature of sewage discharged to the region, as discussed in Chapter 3.

Compositional changes in behentrimonium (ATMAC 20 and 22) relative to DTDMAC with distance from sewage sources were pronounced and may also be affected in part by differential desorption during transport, however it seems more likely that the spatial distributions of these compounds is largely affected by large increases in loadings that occurred for these compounds prior to the 2008 sampling (Lara Martin et al., 2010). It may be that comparing the distributions of sediment contaminants with greatly different time histories of release could provide useful tools for studying the timescales of lateral sediment transport and incorporation into surface sediment beds in estuarine environments.

The use of QACs for source allocation of metals within LIS is an indication of the wide range of potential uses of QACs to study either source allocation or differential transport of metal or organic contaminants in estuarine waters. While the distribution of metals has been interpreted here in the context of estimating the contribution of metals coming from more sewage affected sediment sources, additional research should be conducted to determine if the distributions of metals in sediments in areas like WLIS are more controlled by transport of contaminated sediments or through processes that may include recycling and scavenging of metals mediated through transport in dissolved phases.

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Table 2.1 Sample coordinates and distance (km) from the Tallman Island STP outfall for samples in this study. Negative distances represent stations west of the outfall. Samples FB1, FB2, UH008 and UH011 are described elsewhere (Li, 2009).

Station	**Latitude**	**Longitude**	**Distance (km)**
1	40.80603	-73.77452	5.84
3	40.84958	-73.75213	14.34
2	40.84835	-73.75635	11.01
5	40.89165	-73.74695	14.38
6	40.8766	-73.72457	15.04
4	40.87418	-73.73140	14.94
7	40.87618	-73.72360	15.04
8	40.91585	-73.68000	20.74
9	40.94467	-73.63050	26.04
10	40.96575	-73.57862	31.04
11	40.97088	-73.36135	49.24
12	40.93847	-73.23985	57.24
13	40.97020	-73.24435	57.84
14	41.00947	-73.27967	57.24
15	41.00623	-73.22365	61.99
16	40.99237	-73.07792	74.29
17	41.01268	-73.03092	76.14
FB1	40.7847	-73.8635	-2.66
FB2	40.7819	-73.8647	-2.97
UH008	40.8018	-73.8132	2.31
UH011	40.7855	-73.8741	-3.23

Table 2.2. Individual QACs measured in this study as well as sample data for QACs from Li (2009).

Station	DADMAC			BAC				ATMAC					DTDMAC					
	8:8	8:10	10:10	12	14	16	18	12	16	18	20	22	12:14	14:14	14:16	16:16	16:18	18:18
	ng/g																	
1	9	34	148	45	150	88	172	13	30	55	22	221	100	76	169	741	2290	3290
2	6	22	143	24	79	60	218	9	19	68	32	338	143	121	307	1340	4320	6090
3	5	22	135	24	73	60	209	6	16	60	30	321	148	121	296	1250	4040	5700
4	<RL[a]	7	47	9	32	24	87	<RL	11	33	11	139	80	68	155	693	2090	2910
5	0	5	36	12	32	21	77	4	10	25	12	134	70	55	120	497	1640	2290
6	<RL	13	93	17	55	43	153	5	13	51	26	296	120	103	237	1020	3250	4730
7	3	12	78	17	57	43	138	6	15	44	25	265	115	97	217	899	2810	4040
8	<RL	2.9	15	5	13	7	45	<RL	4	18	4	55	39	33	75.6	318	938	1320
9	0	<RL	10	4	12	6	35	1	3	14	4	57	34	26	62	256	780	1070
10	<RL	<RL	7	4	8	4	21	1	3	11	3	41	23	17	39	154	462	698
11	<RL	<RL	8	4	9	4	17	1	3	10	1	22	23	17	38	146	473	636
12	0	<RL	3	2	4	2	9	0	2	9	<RL	8	13	10	24	98	330	520
13	0	<RL	5	2	7	2	14	0	3	13	<RL	11	17	13	29	121	387	624
14	0	<RL	7	3	6	3	13	<RL	2	8	0	9	18	13	28	120	378	598
15	0	<RL	6	2	6	3	12	0	2	6	0	8	16	11	23	91	288	454
16	0	0	<RL	0	<RL	0	1	0	<RL	2	0	0	3	<RL	2	10	40	107
17	0	<RL	6	1	4	1	7	0	2	4	0	3	12	9	20	79	263	432
FB1	NM[b]	NM	450	330	1290	630	1810	NM	250	630	78	504	NM	390	790	4020	11100	16600
FB2	NM	NM	680	210	960	560	1350	NM	180	350	103	910	NM	380	550	2640	7310	10200
UH008	NM	NM	210	70	510	270	410	NM	70	200	NR	48	NM	0	230	840	3910	4920
UH011	NM	NM	120	20	220	150	170	NM	70	130	NR	37.7	NM	0	120	270	2620	2820

a. Levels measured were not above reporting limits. b. individual QAC was not measured for this sample

Table 2.3. Metal and nitrogen, total organic nitrogen (TON), total organic carbon (TOC) and sulfur levels in all stations.

Station	Ag	Al	Cd	Cu	Fe	Mn	Mo	Pb	Re	Ti	U	V	Zn	TON	TOC	S
							µg/g								%	
1	1.48	20900	1.04	81.2	33900	897	1.71	66.8	0.0194	625	1.35	47.1	138	0.150	2.40	0.200
2	1.94	29200	1.36	102	45400	1170	2.27	80.6	0.0179	876	1.77	60.7	164	0.398	3.59	0.683
3	1.86	25400	1.22	97.7	38800	1100	2.28	71.2	0.0177	761	1.68	58.7	162	0.418	3.68	0.815
4	1.49	24100	1.19	93.8	39800	892	1.55	62.2	0.0160	842	1.67	54.9	159	0.368	3.36	0.489
5	1.12	19400	1.13	78.1	31400	709	1.77	65.5	0.0146	761	1.51	45.5	131	0.340	3.82	0.215
6	1.36	23300	1.16	83.4	36800	970	2.07	58.1	0.0122	752	1.68	55.3	141	0.406	3.58	0.537
8	0.98	27200	0.78	66.3	40400	923	1.68	43.8	0.0151	850	1.84	58.0	126	0.294	2.62	0.491
9	0.89	23700	0.65	67.6	37300	973	1.51	44.8	0.0122	708	1.57	52.8	122	0.296	3.11	0.432
10	0.81	22900	0.67	64.2	41000	984	1.57	42.7	0.0137	758	1.75	54.4	121	0.303	2.85	0.315
11	0.55	23600	0.56	46.4	37900	1540	1.75	31.1	0.0146	810	1.53	53.4	106	0.269	2.61	0.496
12	0.83	25400	0.71	65.7	40700	1120	1.40	40.9	0.0177	763	1.86	57.0	126	0.232	2.38	0.261
13	0.92	25600	0.54	73.7	35500	759	1.83	45.9	0.0161	889	1.77	56.8	146	0.291	2.68	0.350
14	0.65	28900	0.45	52.4	42100	1460	1.13	37.3	0.0136	816	1.53	57.9	115	0.271	2.54	0.250
15	0.53	26500	0.43	43.6	38300	1030	1.09	34.6	0.0183	745	1.47	54.7	102	0.289	2.55	0.803
16	0.22	5340	0.20	16.2	10500	425	0.68	11.6	0.0079	212	0.51	13.7	47.9	0.038	0.35	0.076
17	0.54	24200	0.46	43.6	40500	974	1.66	31.4	0.0118	891	1.93	63.0	104	0.238	2.26	0.174
FB1															3.90	
FB2															4.60	
UH008															6.21	
UH011															5.98	

Table 2.4. A comparison of metals analyzed in this study to those from Mitch and Anisfield (2010), Mecray and Bulchholtz ten Brink (2000) and Cochran et al. (1991).

		Ag	Al	Cd	Cu	Fe	Mn	Mo	Pb	Ti	V	Zn
							μg/g					
This Study[a]	**Mean**	*1.06*	*24700*	*0.824*	*70.6*	*38600*	*1030*	*1.69*	*50.5*	*790*	*55.3*	*131*
	Std Dev	*0.463*	*2680*	*0.324*	*19.1*	*3430*	*226*	*0.347*	*15.7*	*73.6*	*4.59*	*20.5*
	Median	*0.924*	*24200*	*0.712*	*67.6*	*38800*	*974*	*1.68*	*44.8*	*763*	*55.3*	*126*
Mitch and Anisfield WLIS	**Mean**	0.54	56900	0.630	89.0	27000	803	NR	57.0	NR	NR	164
	Std Dev	NR[b]	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
	Median	0.970	52900	1.180	116	26200	883	NR	87.0	NR	NR	183
Mitch and Anisfield CLIS	**Mean**	0.31	49300	0.210	51.7	25800	722	NR	37.0	NR	NR	113
	Std Dev	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
	Median	0.710	46700	0.920	83.8	24400	691	NR	45.6	NR	NR	137
Mecray and Bulchholtz ten Brink	**Mean**	0.44	61000	0.250	59.5	33100	1010	NR	47.7	3900	88.5	146
	Std Dev	0.321	11600	0.177	27.3	8550	433	NR	18.1	1250	15.6	46.1
	Median	0.420	62600	0.170	56.9	32900	903	NR	42.0	3900	91.9	144
Cochran et al.	**Mean**	NR	NR	NR	107.1	37000	803	NR	108.6	NR	NR	216
	Std Dev	NR	NR	NR	27.8	3850	165	NR	34.7	NR	NR	31.3
	Median	NR	NR	NR	115.0	38500	800	NR	112.0	NR	NR	215

a. excludes Station 16 as previously noted b. value not reported

Table 2.5. A comparison of metals concentrations measured in this study to the results from the same sites measured by Cochran et al. (1991) in 1988-1989.

Station	**Collection Date**	**Cu**	**Fe**	**Mn**	**Pb**	**Zn**
			µg/g			
1	**1988-1989**	120	32000	570	150	220
	2008	81	34000	897	67	140
	ratio	**1.5**	**0.9**	**0.6**	**2.2**	**1.6**
3	**1988-1989**	140	38000	1100	150	260
	2008	98	39000	1100	71	160
	ratio	**1.4**	**1.0**	**1.0**	**2.1**	**1.6**
5	**1988-1989**	60	39000	850	70	160
	2008	98	36000	760	46	150
	ratio	**0.6**	**1.1**	**1.1**	**1.5**	**1.1**
6	**1988-1989**	130	39000	750	130	210
	2008	83	37000	970	58	140
	ratio	**1.6**	**1.1**	**0.8**	**2.2**	**1.5**
9	**1988-1989**	110	41000	830	110	240
	2008	70	37000	970	45	120
	ratio	**1.6**	**1.1**	**0.9**	**2.5**	**2.0**
15	**1988-1989**	70	39000	800	70	220
	2008	40	38000	1000	35	100
	ratio	**1.8**	**1.0**	**0.8**	**2.0**	**2.2**
	average of ratio	**1.4**	**1.0**	**0.9**	**2.1**	**1.7**
	std dev of ratio	**0.40**	**0.06**	**0.17**	**0.32**	**0.40**

Table 2.6. The p-value for the F-test statistic as well as Spearman's Rho and associated p-value ($p \leq 0.05$) for the relationship between individual metals and the concentration of DTDMAC 18:18. A relationship was considered significant if values from both the F-test and Spearman's Rank Correlation were significant; these metals are highlighted in grey. Station 16 was removed from the analysis.

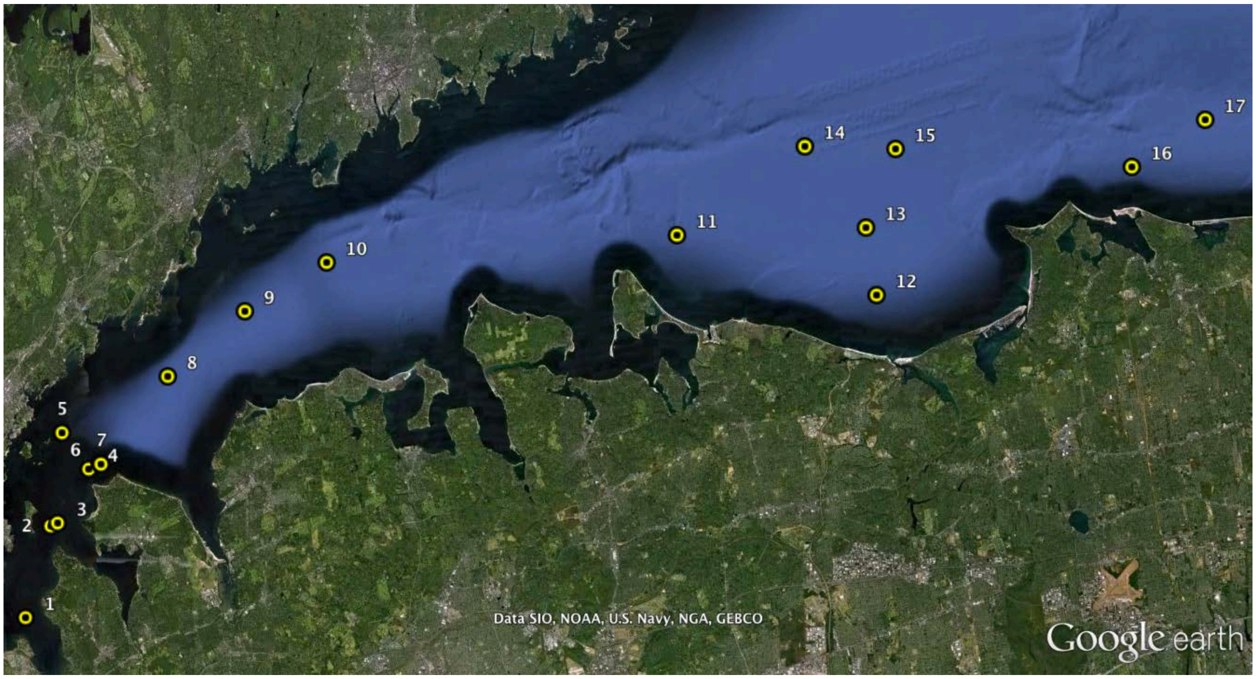
Metal	F-Test p-value	Spearman Rank Correlation	
		Rho	P-value
Ag	3.11E-08	0.925	8.0E-07
Cd	1.02E-06	0.911	2.4E-06
Cu	8.98E-06	0.911	2.4E-06
Mo	7.68E-05	0.693	0.004
Pb	1.14E-06	0.882	1.4E-05
Zn	4.17E-05	0.804	3.1E-04
Al	0.021	-0.164	0.558
Fe	0.021	-0.175	0.533
Mn	0.020	-0.207	0.459
Re	0.009	0.279	0.315
Ti	0.030	-0.112	0.703
U	0.021	-0.164	0.558
V	0.022	-0.057	0.840

Table 2.7 Estimated values of the range of excess metals that can be attributed to DTDMAC 18:18 as well as other sources based on the simple model outlined in the text. Estimates of atmospheric input from Cochran et al. (1998) are included for comparison.

Metal	Excess Attributed to DTDMAC 18:18	Excess from other sources	Cochran et al. (1998) estimates of Atmospheric Input
		%	
Ag	51-73	27-49	n/a
Cd	56-77	23-44	n/a
Cu	34-58	42-66	32
Pb	62-82	18-38	72
Zn	37-61	39-63	46

Figure 2.1. a) Locations of sediment grab samples taken in 2008 in Long Island Sound, NY and b) sample locations from the East River and WLIS. Yellow dots represent stations from the 2008 transect, orange dots represent samples from Li, 2009, and red dots represent sewage outfalls.

a)



b)

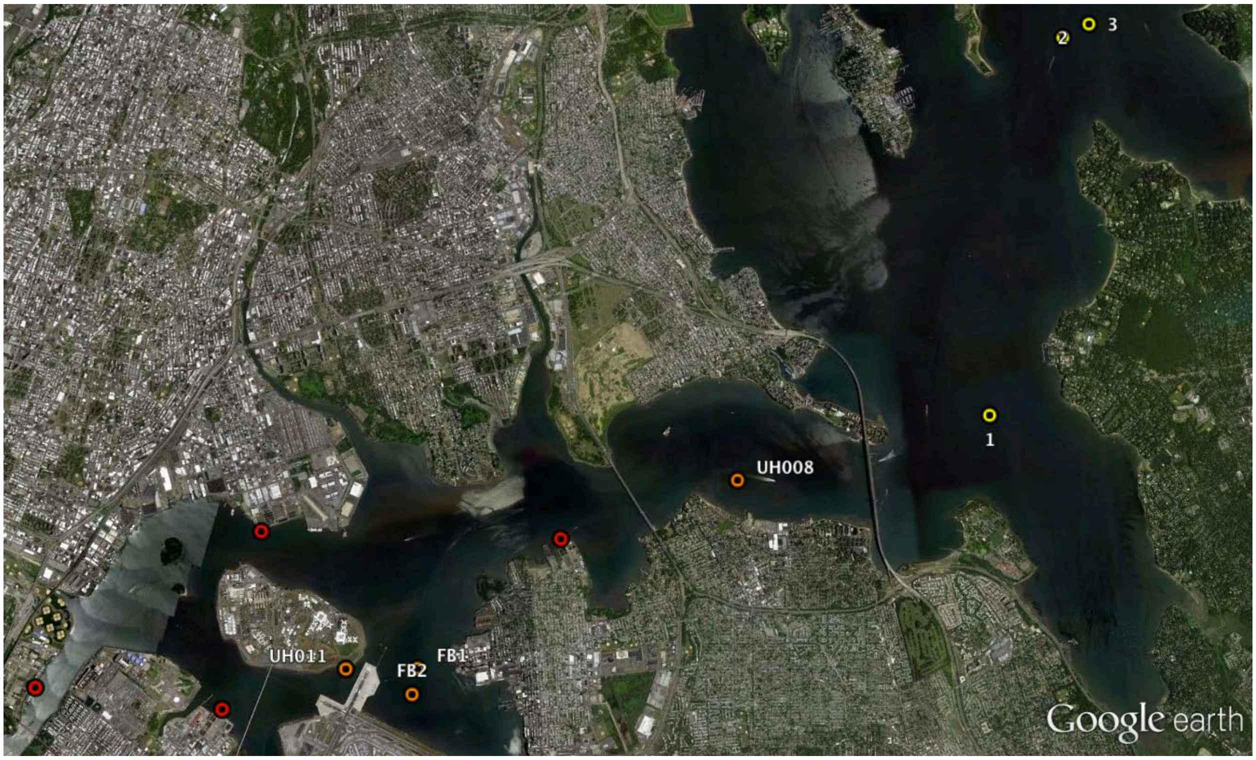


Figure 2.2. a) ΣQACs (µg/g) in LIS versus kilometers from the Tallman Island outfall. Station 16, thought to be a sandier sample, is indicated in grey. b) ΣQACs normalized to percent Fe (black dots) and organic carbon (%TOC, grey dots) in sediment samples from LIS versus kilometers from the Tallman Island Outfall.

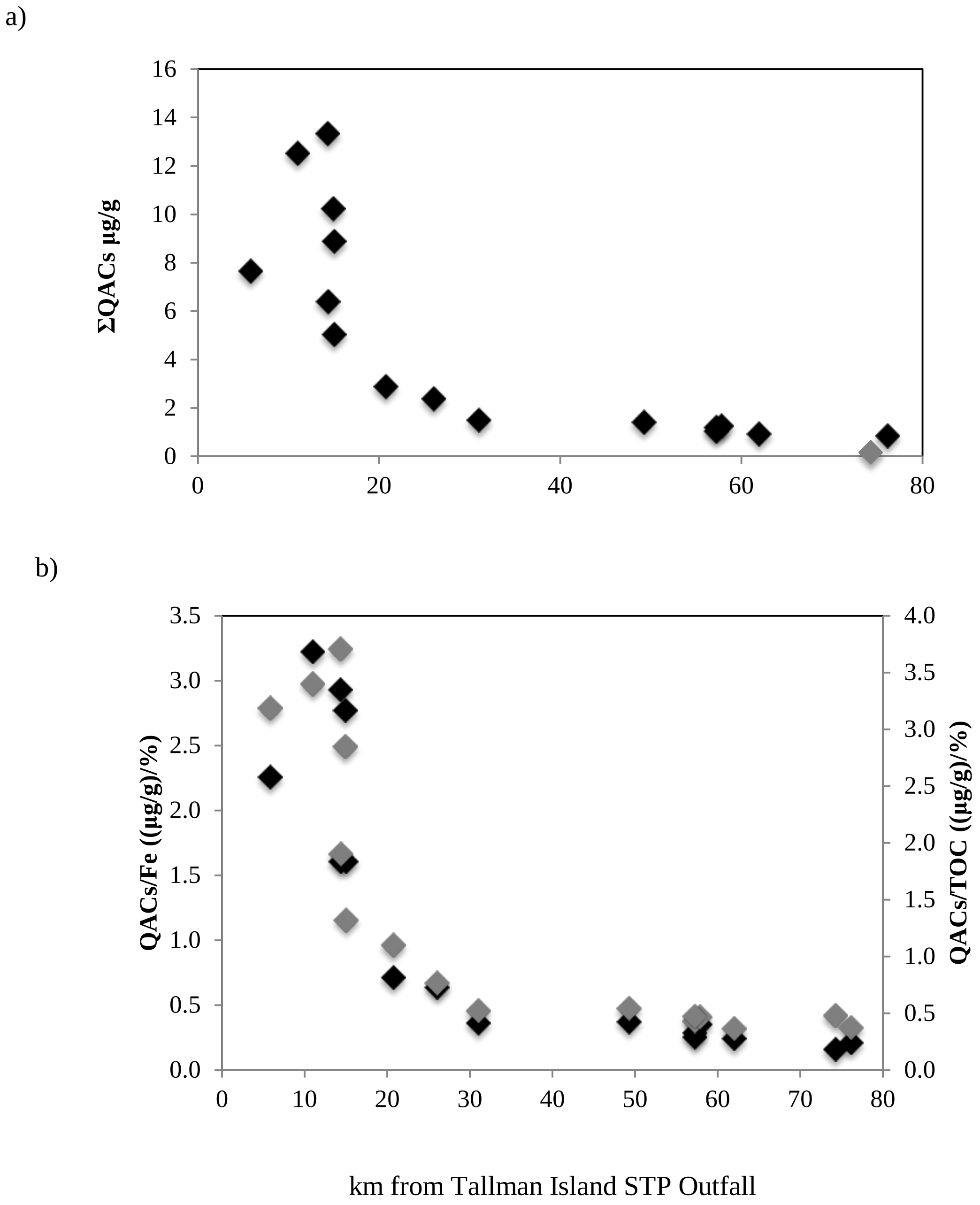


Figure 2.3 Σ(DTDMAC 16:16 – DTDMAC 18:18) as a fraction of ΣQACs with distance from the Tallman Island STP outfall. Station 16 has been removed.

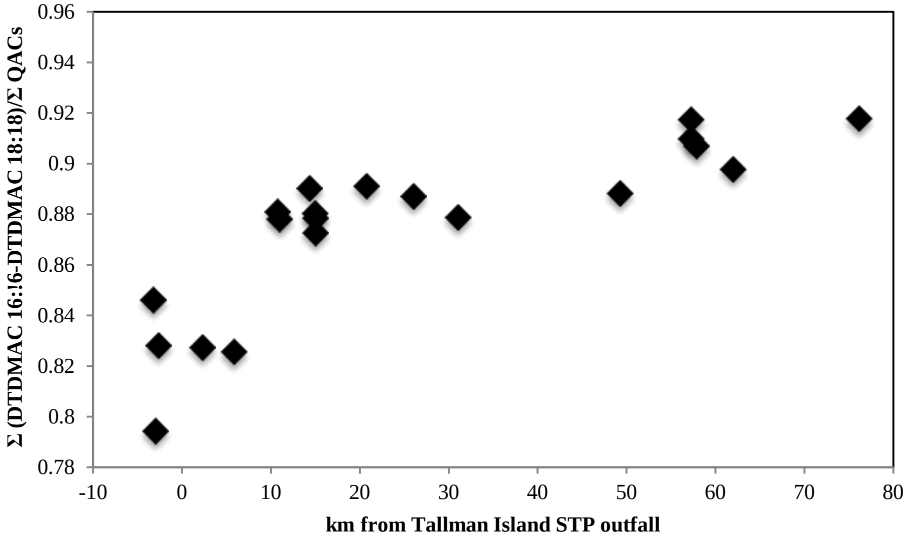


Figure 2.4. Individual BACs and ATMACs normalized to DTDMAC 18:18 with distance from the Tallman Island STP outfall. Points in red are taken from Li (2009). For ATMAC 20 and 22, UH008 and UH011 samples are in red, FB1 and FB2 sample are in blue.

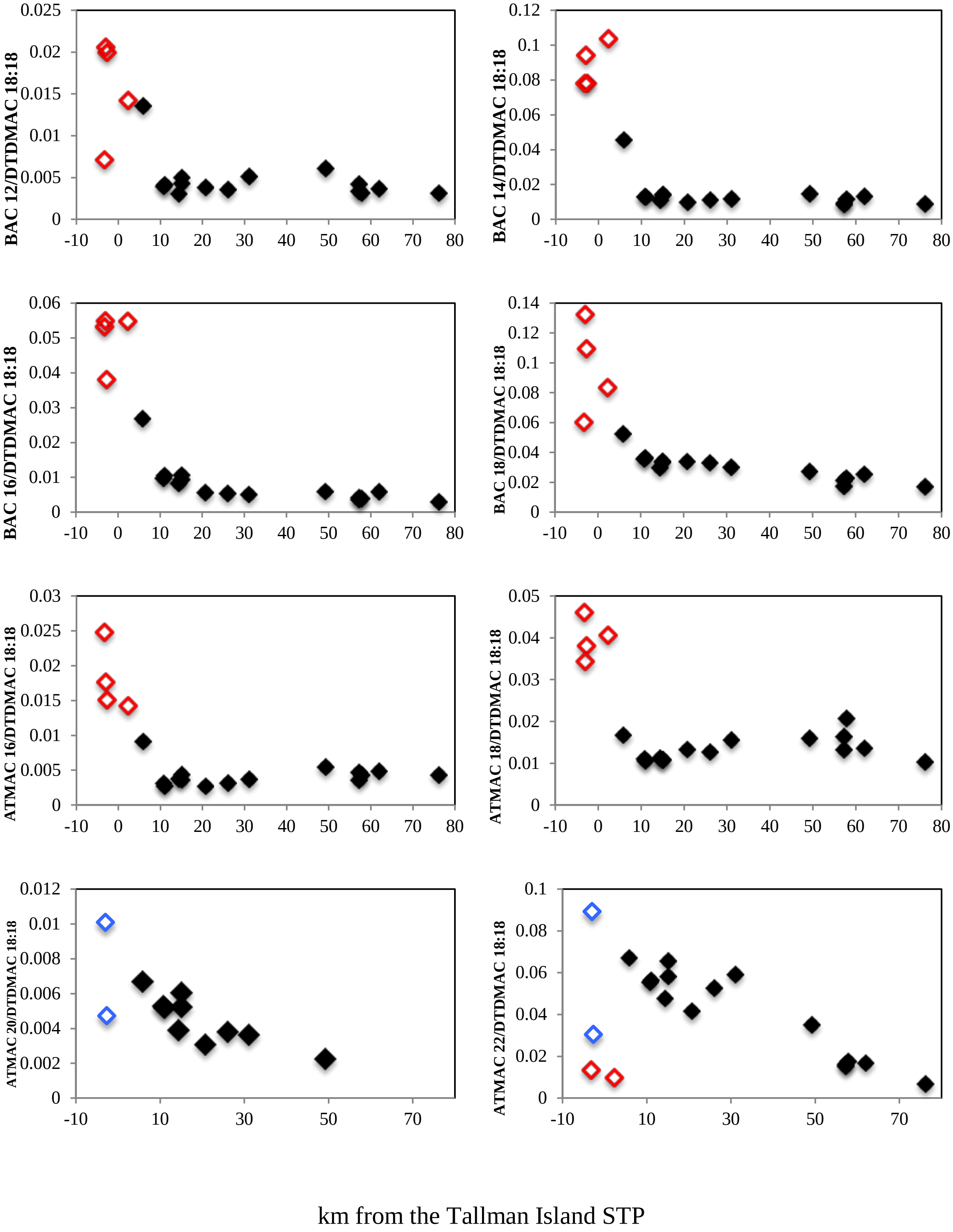


Figure 2.5. Individual DADMACs and DTDMACs normalized to DTDMAC 18:18 with distance from the Tallman Island STP outfall. Points in red are taken from Li (2009).

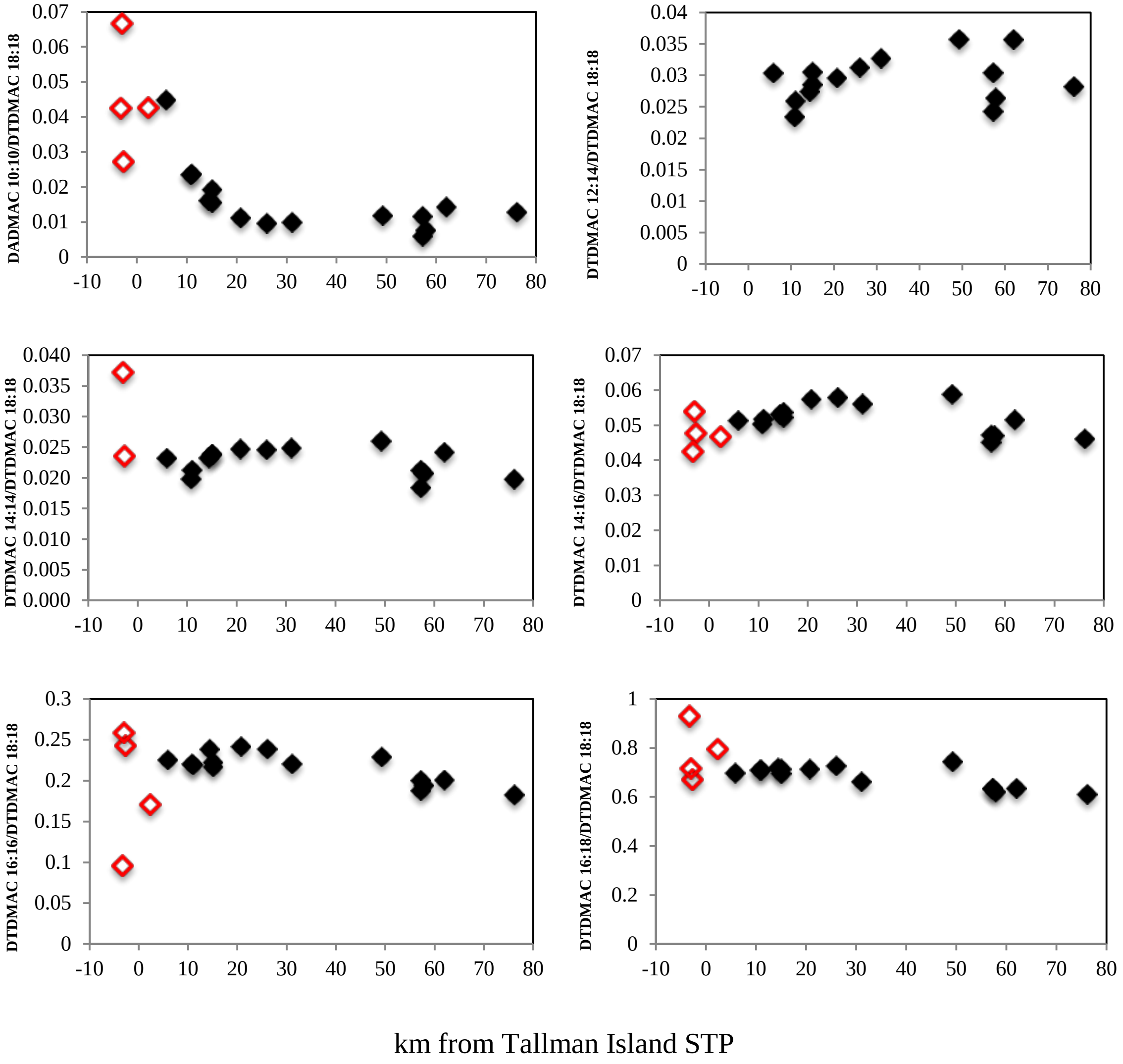


Figure 2.6 Metals measured in LIS versus DTDMAC 18:18 (µg/g). Background values (obtained from Mecray and Bulchholtz ten Brink (2000)) are indicated by the red line.

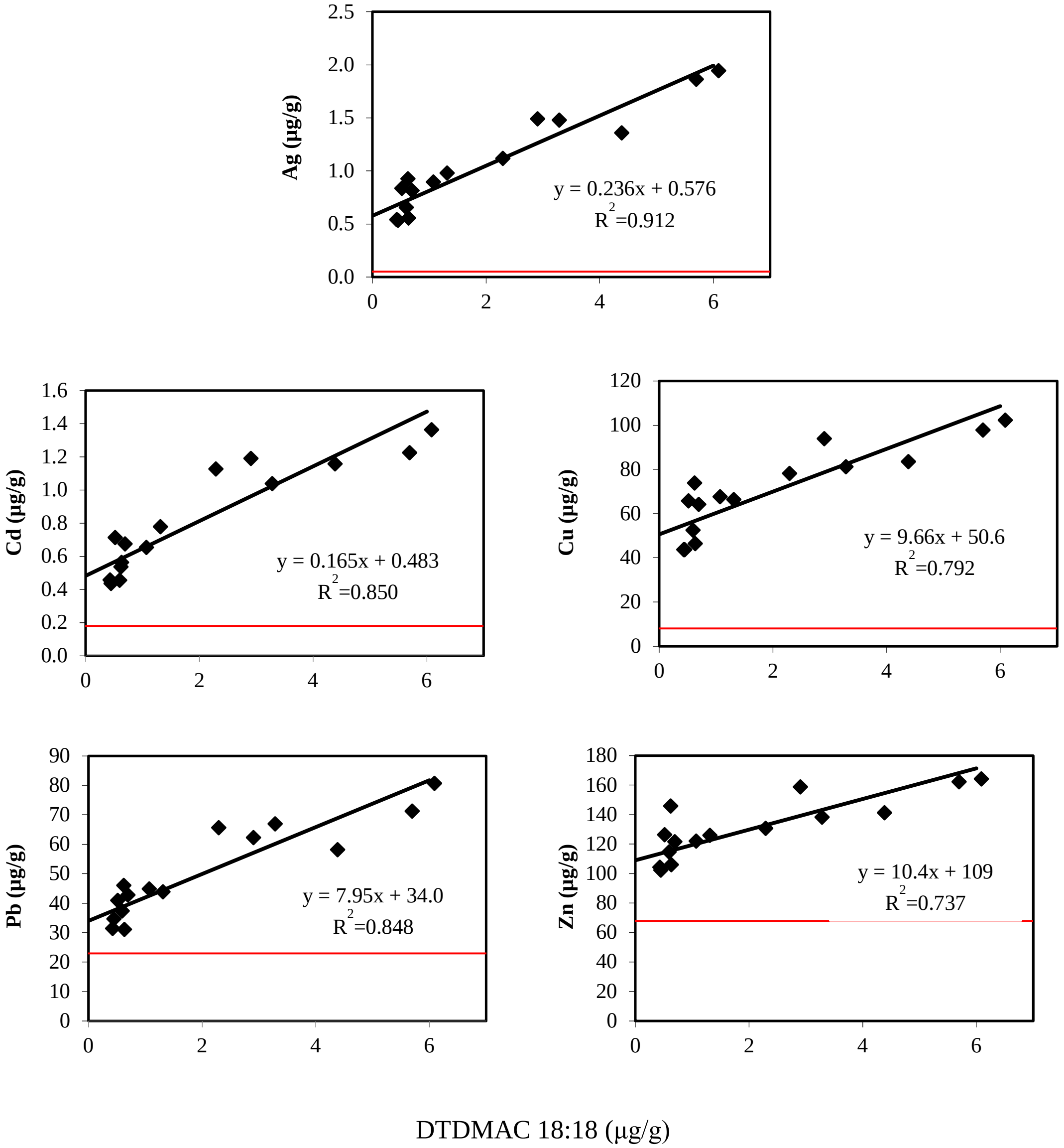
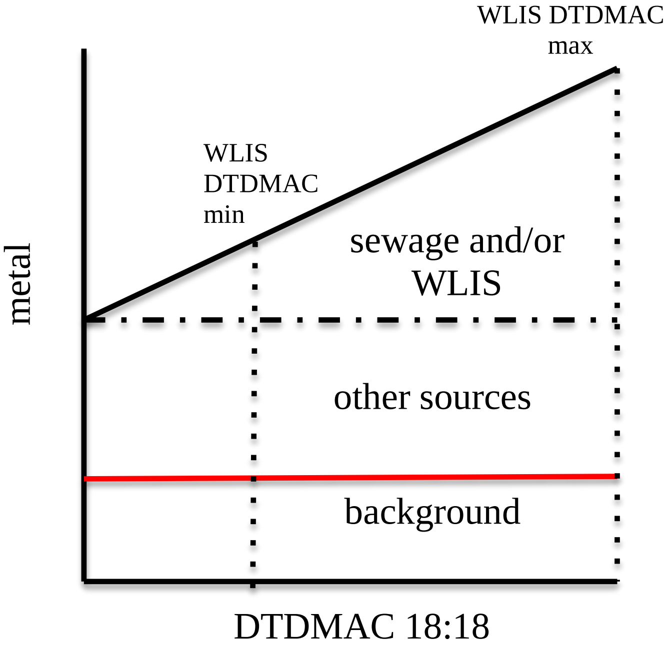


Figure 2.7 A visual representation of the simplified model for the source of metals in LIS as described in the text. The range of DTDMAC 18:18 concentrations used in this model are only representative of WLIS (Stations 1-6), and lower DTDMAC 18:18 concentrations from stations located further east were not considered.



CHAPTER 3: Quaternary ammonium compounds (QACs) in a sewage affected coastal lagoon: differential transport of QAC homologues away from a sewage point source.

3.1 Introduction

Quaternary ammonium compounds (QACs) are cationic surfactants used in a variety of applications that have resulted in these compounds being measured at high levels in the marine environment, (Chapter 2, Fernández et al., 1996; Gerike et al., 1994; Kreuzinger et al., 2007; Li, 2009; Li and Brownawell, 2010; Martinez-Carballo et al., 2007). Due to the source specificity of several QACs used in personal care products, high concentrations in the environment, particle reactivity, and apparent persistence in sediments, QACs have been suggested as excellent candidates for tracers of sewage affected particles in estuarine systems (Li, 2009; Li and Brownawell, 2010, Chapter 2). More information on the behavior of QACs in the environment is needed to better understand the behavior of these compounds and their potential to be used as an extremely persistent, particle reactive sewage tracer. In this study, the distribution and fate of QACs away from a major source has been investigated in Hempstead Bay, NY, a sewage-impacted coastal lagoon on the south shore of Long Island, where the primary source of sewage enters in a small zone, representing a likely point source input to the region. Changes in composition are also investigated that may indicate degradation/desorption of individual QACs in this environment as well as possible changes in the production and source of some QACs to the environment

The QACs of primary interest here are comprised of a positively charged nitrogen with four substituents, including two or more methyl groups and one or more long alkyl side chains. Benzylalkyl dimethyl ammonium compounds (BACs) have only one long alkyl side chain (C12 to C18) as well as a benzyl group and are primarily used as biocides, sanitizers and disinfectants (Boethling, 1984). Alkyltrimethyl ammonium compounds (ATMACs) have three methyl groups and one long alkyl side chain that can range from 12 to 22 carbons long. ATMACs are used as antimicrobials and in personal care products as well as in industrial applications (Lara-Martín et al., 2010; Li, 2009; Madsen et al., 2001). The two largest ATMACs, ATMAC 20 and ATMAC 22, are often referred to as behentrimonium and have been measured at dramatically increasing levels in recent decades due to an increase in their use in hair care products (Lara-Martín et al., 2010). Dialkyldimethyl ammonium compounds (DADMACs) have two long side chains and the class is often divided into two groups: DADMACs which have side chains between 8 and 10 carbons long, and ditallowdimethyl ammonium compounds (DTDMACs) with side chains 12 carbons and longer. DADMACs are generally used in biocides and disinfectants, while DTDMACs are primarily found in products such as fabric softeners (Cross and Singer, 1994; Fernández et al., 1996; Schaeufele, 1984). DTDMACs are the largest and most hydrophobic of the QACs that have been targeted in this study. Their use peaked in the late 1980's before declining due to a voluntary phase out of the largest DTDMACs in Europe (Fernández et al., 1996). Geochronologies from the region (Chapter 4, Li, 2009) indicate a fairly steady input of DTDMACs since the early to mid-1990's to both Hempstead Bay and the greater metropolitan NY/NJ Harbor Complex environments in recent years. There has also been an indication of a shift away from animal fat based sources for the two n-alkyl chains and towards vegetable oil based sources that supply shorter alkyl side chains, possibly resulting in an increase in the use of shorter side-chained DTDMACs (Li, 2009). Increases in these smaller DTDMACs have been observed in geochronologies from Hempstead Bay and Jamaica Bay (Chapter 4).

QACs are an understudied class of environmental contaminants, with the few studies of sewage-impacted environments indicating ΣQACs concentrations that can be as high as 1,140 μg/g (Fernández et al., 1996) in highly polluted sediments. Studies from Li (2009) and Li and Brownawell (2010) found ΣQAC concentrations ranging from 1-114 μg/g in the nearby Jamaica Bay and New York/New Jersey Harbor complex. In addition, several studies indicate that QACs are very persistent in the environment. Li and Brownawell (2010) found fairly stable relative abundances of the largest QACs in Jamaica Bay, NY, and suggested this implied persistence in this system. Li (2009) also looked at matched cores in Jamaica Bay and did not find significant *in situ* down-core degradation for the major groups of QACs discussed below. TAMS, structurally similar impurities in QACs (Fernandez et al., 1991; Valls et al., 1989), have also been previously suggested as good sewage tracers due to their persistence in the environment (Chalaux et al., 1995; Fernandez et al., 1991; Maldonado et al., 1999, 2000; Valls et al., 1989) and are seen to be transported on particles longer distances than other hydrophobic organic sewage contaminants such as coprostanol and linear alkylbenezenes (Maldonado 1999, Maldonado 2000, Valls 1990). In Chapter 2, it was seen that the composition of more soluble QACs in sediments may vary greatly with distance from direct sewage inputs into western Long Island Sound (WLIS) with apparent loss of more soluble and biodegradable homologs, but that the distribution of more hydrophobic DTDMACs was consistent with conservative transport on particles as they are transported over tens of km of distance from urban NY City sources. Unfortunately, there are other potential sewage sources in Long Island Sound, and there was a paucity of sampling sites in areas closest to the area of primary sewage input.

Although the field studies mentioned above indicate a high measure of persistence once associated with sediments, especially for the largest QACs, some lab studies do indicate a high potential for QACs to degrade under oxic conditions (Games et al., 1982; Garcia et al., 2001; Martinez-Carballo et al., 2007; Ying, 2006), with the tendency to biodegrade inversely proportional to hydrophobicity or alkyl chain length (Boethling, 1984). This trend has also been observed in Austrian sewage treatment plants, where approximately 99% of the most soluble QAC studied (ATMAC 12) was lost to biodegradation, as well as 80-94% for BACs and 90% for DADMAC 10:10s, with the percent biodegraded decreasing systematically with alkyl chain length. In the same study, there was no evidence for biodegradation of the most hydrophobic DTDMACs, which primarily ended up in sewage sludge (Clara et al., 2007).

This chapter describes the results of relatively high-resolution spatial sampling of surficial sediments in Hempstead Bay and adjacent South Oyster Bay. Hempstead Bay represents a unique environment where a point source of sewage discharges into a semi-enclosed bay, and provides an ideal location to study not only the circulation of sewage affected particles within a system, but the environmental fate and persistence of QACs upon discharge into an estuarine environment. There are marked changes observed in the concentration and compositions of QACs and sediment organic matter as a function of distance from the primary source of sewage inputs into this lagoonal estuarine system. The likely controls of transport are interpreted within the context of differences in structure and solubility of individual QACs as well as sometimes marked differences in the time history of their source functions.

3.2 Experimental Section

Study Area and Sample Collection

The study area encompasses Hempstead Bay and adjoining South Oyster Bay located on the south shore of Long Island, NY to the east of Jamaica Bay and to the west of Great South Bay. Hempstead Bay is broken up into West Bay, Middle Bay and East Bay (Figure 3.1a), with West Bay containing most of the industry found in Hempstead Bay, mostly located along the northern part of the Bay, as well as receiving over 55 million gallons per day (MGD) of sewage effluent (Interstate Environmental Commission, 2010). There have been concerns about eutrophication stemming from these wastes, and recent studies (Gobler, 2012; Swanson, 2011) have documented evidence that high nutrient loads from these sewage treatment plants (STPs) are the likely cause of high levels of phytoplankton and macroalgal growth in parts of the Bay and may also be contributing to localized hypoxic conditions in deeper and less flushed areas in northern West Bay.

The watershed of Hempstead Bay has been sewered since 1952 (Swanson, R Lawrence, 2011), with almost all of the outfalls residing in West Bay. The sewage effluent discharge in West Bay is dominated by the outfall from the Bay Park STP (50 MGD), with the Long Beach STP outfall contributing an additional 5 MGD (Interstate Environmental Commission, 2010) (Figure 3.1b). These two outfalls are located very close to each other along the relatively well-flushed Reynolds Channel, with the Long Beach STP being just under 1km to the west of the Bay Park STP outfall (BPO, Figure 3.1b). There are additional small STPs that discharge into the area, including the small West Long Beach plant outfall (0.6 MGD) that discharges into the highly flushed East Rockaway Inlet and is therefore considered to have a negligible impact on the Bay. Lawrence STP outfall (1.3 MGD) discharges into a poorly flushed embayment, Bannister Basin, which is also near the East Rockaway Inlet and is separated from the rest of HB. Bannister Basin appears to have little exchange with the main portion of West Bay so the Lawrence STP outfall impacts are thought to be local and not considered to have significant impacts on the reset of Hempstead Bay. While there is one very small (50,000 gallons per day), seasonal outfall near the Jones Beach amphitheater in East Bay, the effects of this outfall are most likely limited to a very small area due to the small, periodic nature of the sewage input.

Sample site selection was based on identifying the most likely areas of muddy, depositional sites using bathymetric and surface reflectivity data from a multi beam side scan sonar. As seen in many other regions of the South Shores Estuary Reserve, large areas in the southern portions of Hempstead Bay are covered in sandy sediments as a result of strong tidal and wind driven currents. Within the study area, muddy depositional sites are located in areas where tidal currents are less intense, primarily around the north shore of the system, with additional muddy areas found in deeper dredged areas and middle reaches of Reynolds Channel, especially in the shoaled area near the BPO. While muddy samples were targeted, some sandier sediments were also sampled to provide greater spatial coverage of the region (Table 3.1, Figure 3.1a). Special attention was given to sample sediments near potential contaminant sources, including former industrial areas, marinas, golf courses, and two landfills that border the Bay. During sampling, extensive amphipod tubes were noted in West Bay as well as other regions of Hempstead Bay, extending into western South Oyster Bay. This is notable because amphipods are opportunistic early successional species that thrive in disturbed environments. In addition, a transect of samples was obtained in Pines Creek (Figure 3.1b, also referred to as Mill River), which receives concentrated storm water run-off and has many boats and small boating service companies. Hewlett Bay, located in northern West Bay (Figure 3.1b), was not sampled, so surface sections (0-2cm and 2-4cm, results were averaged) of Core 4 (Chapter 4) located in Hewlett Bay are included here. Samples were collected with a modified Van Veen or a similarly constructed Petite Ponar grab and the top 5 cm collected and stored in solvent cleaned glass jars before being immediately frozen upon return to the lab. Station coordinates can be found in Table 3.1. Distance from the BPO to each sample site was calculated with Google Earth using the shortest route along major channels.

Suspended solids were collected from locations in West Bay (BPO, Oil City and West Bay, and Hewlett Bay) to better understand the behavior of QACs upon immediate release to the environment (Table 3.2, Figure 3.1b). A total of 6 samples (3 sets of replicates) were taken from the BPO on September 16 and October 12 of 2011 as well as June 6, 2012. The October 12, 2011 sampling included one sample in a region known as Oil City in the northern part of West Bay. A sample was also taken in Hewlett Bay during the June 6, 2012 sampling. Samples were collected in a solvent rinsed 4L amber bottle and preserved with 10 mL of formalin for every 1L of sample collected. Samples for determination of total suspended solids (TSS) analysis were collected at the same time (but without formalin) for some samples, although TSS was not determined at all collections.

Organic carbon and nitrogen analysis

For the analysis of organic carbon and nitrogen, about 0.5 grams of sediment was placed into a small beaker to which 20 mL of 0.1M HCl was added. This was agitated and then allowed to settle before pouring off the HCl solution. Samples were then rinsed with two aliquots of deionized water to rinse away most of the HCl and placed in a drying oven at 65°C until dried. Samples were analyzed on a Carlo_Erba 1108 CHNS Analyzer. The instrument was calibrated with sulphanilamide and samples were instrument-blank corrected. Precision of analysis was determined on a reference LIS sample with relative standard deviation for organic carbon and nitrogen were 2% and 5% for carbon and nitrogen, respectively.

Metal analysis

Silver (Ag), cadmium (Cd), copper (Cu), iron (Fe), molybdenum (Mo), manganese (Mn), lead (Pb) and zinc (Zn) were analyzed in sediments in this study (metals other than Fe discussed in Chapter 5). Metals were extracted using a slightly modified US EPA method 3050B acid leach by Vince Breslin at Southern Connecticut State University (Church, 2009). Ten milliliters of trace metal grade nitric acid and deionized water at a one to one ratio was added to approximately one gram of sediment in an acid washed beaker. A watch glass was placed on top of the beaker and the sample was heated at 70°C for 30 minutes without boiling, after which samples were removed from the hotplate and cooled. Concentrated nitric acid (5 mL) was then added and the sample heated again for 30 minutes. After cooling, 1 mL of 30% hydrogen peroxide was added and the mixture was once again heated until the effervescence subsided. This step was repeated two additional times, cooling the sample between each addition. The final solution was cooled, vacuum filtered through a 0.4 micron filter membrane, and then diluted to 50 mL using deionized water. Samples were refrigerated until analysis.

Metals were analyzed using a combination of atomic absorption spectroscopy (AAS) (Cu, Cd, Fe, Mn, Pb and Zn) and inductively coupled plasma mass spectrometry (ICP-MS) (Mo and Ag). The AAS used for Cu, Fe, Mn, Pb and Zn analysis was a Perkin Elmer Model 8100 and samples were quantified based on a calibration curve that was used to create a linear regression analysis. Cd and Pb were analyzed using a Graphite Furnace/Flame Perkin Elmer AAnalyst 800 atomic absorption spectrometer. The ICP-MS was an Agilent 7700x equipped with an octopole reaction system. All samples were run in triplicate with an average precision of 1.27% for Mo and 1.14% for Ag. Blank extractions produced negligible concentrations of all metals analyzed.

To determine the accuracy of the extraction, portions of National Institute of Science and Technology standard reference material (SRM) 2702 were extracted with each of four batches and extracted in triplicate in one batch (n=6). SRM 2702 recoveries were 129 ± 4.10% for Ag, 119 ± 4.00% for Cd, 90.6 ± 3.24% for Cu, 84.9 ± 3.12% for Fe, 88.3 ± 2.03% for Mn, 67.5 ± 3.49 for Mo, 90.5 ± 2.90% for Pb, and 91.4 ± 0.92% for Zn. Larger deviations from expected values of Ag and Mo were deemed sufficient for the purposes of this study, as NIST reports reference values for Ag, Cu and Mo that are less certain than the certified concentrations given for the other 5 metals.

Sediment grain size analysis

For sediment grain size analysis, samples were wet sieved through a 1mm filter to determine the fraction greater than 1mm, if any. Samples were briefly dried at 50°C and then soaked overnight in a sodium hexametaphosphate solution before sonication and analysis on a Malvern Mastersizer Particle Size Analyzer which estimates grain size distribution using laser diffraction (Sperazza et al., 2004).

QAC extraction and analysis

QACs were extracted based on the method presented by Li and Brownawell (2010) and Lara-Martin et al. (2010), with two exceptions. The first was that a deuterated surrogate standard (d25-DTDMAC 12:12) was used in place of DTDMAC 12:12; this allows for determination of native DTDMAC 12:12, which is a very minor constituent of total DTDMAC. The second major change was the combining of the HPLC method for the analysis into one run (HPLC method 2, Li, 2009) that was used to analyze all compounds. A full description of the method can be found in Appendix X, but in short, 100 mg of freeze-dried sediment was extracted using acidic methanol in a heated sonication bath. Clean up of extracts was done through a chloroform water extraction as well as a weak ion exchange resin cleanup. Analysis was performed on an HPLC-ToF-MS using electrospray ionization in positive ionization mode. Sample recovery was based on spiked deuterated DTDMAC 12:12 and recoveries averaged 100% ± 19%. Precision for total QACs was based on extractions run in triplicate for a subset of samples and averaged 9.8% ± 6.37%. This method has been validated for all targeted QACs with the exception of the most soluble analyte, ATMAC 12. It was determined during the course of this study that this homolog is not completely recovered during liquid-liquid extraction of many extracts and that ATMAC 12 could be efficiently recovered by addition of an ion pair reagent during liquid-liquid extraction (Chapter 6). The results for analysis of ATMAC 12 have been included in this chapter, but it is noted that the concentrations are lower limits and should be viewed with caution.

Analysis of suspended solids

For suspended solid analysis, approximately 1L of preserved sample was filtered through a muffled Whatman glass microfiber GF/C filter (Sigma Aldrich, St. Louis, MO) immediately upon returning to the lab. After filtration, filters were rinsed with deionized water and then frozen until analysis. Total suspended solids (TSS) were determined by filtering approximately 1L of sample through a pre-weighed muffled GF/C filter that had been washed with 100 mL of deionized water. Exact volume was determined by weight. Filters were washed with deionized water after filtration and placed in a drying oven at 60°C overnight and weighed once completely dry to determine the total mass of solids collected on the filter.

Statistical Analysis

Statistical analysis was used to determine if there was a significant relationship between the composition of QACs and distance from the BPO. An ANOVA was performed for each QAC, and the F-statistic was determined based on an F-distribution, which was then used to obtain a p-value. The relationship between each QAC and distance was considered significant if the F-test statistic was significant (p value 0.05 or less). These analyses were performed only on data with the most muddy sediments as indicated by iron values greater than 2.25% and excluded samples from Mill River. For further analysis, the data were also divided into two groups based on location relative to Jones Inlet (9km from the BPO), West of Jones Inlet and East of Jones Inlet, and the ANOVA was then performed for each group.

3.3 Results and Discussion

3.3.1 Sediment Properties

Results of the analysis of sediment properties measured suggest that this study was successful in targeting muddy, depositional sediments. TOC values measured ranged from 0.14 to 8.97% and TON from 0.01 to 1.12% (Table 3.3), with all but 10 samples having TOC values greater than 2% (Table 3.3). Higher values of TOC suggest that sediments in Hempstead Bay are organically enriched, as an extensive study of TOC in sediments around the world by Mayer (1994) indicates that sediments above 2% TOC should be considered organically enriched. TOC and volume weighted mean particle diameter both correlate well with Fe measurements (Figure 3.2), consistent with previous studies (Feng et al., 1998), although there are two outliers related to low Fe values (Fe values of 1750 μg/g and 4894 μg/g) that can be observed in both plots. These outliers are discussed in greater detail below.

A majority (38 of 60) of samples from this study have Fe values greater than 2.25%, consistent with successful targeting of fine-grained, muddy sediments. Fe will be used in this study to account for variations in sediments between samples as has been done previously (Feng et al., 1998), where an extremely strong correlation was observed between Fe and aluminum, an element commonly used to account for such variations, in samples taken from the nearby New York Harbor and Hudson River. The use of a value of 2.25% Fe to denote fine-grained, muddy, depositional sediments is supported by an analysis of the relationship between sediment type classification and grain size distribution (Figure 3.3, Brownawell et al. 2013) where these classifications were able to be related to reflectivity of the sea bed determined by multi-beam sonar surveys. Sediments were divided into four different classes based on characteristic patterns of grain size; Class 1: muds, Class 2: mud with some sand, Class 3: sand-mud mix (sandy mud), and Class 4: sand with some mud. Sediments from Class 1 have very strong modes in the 15-50 um range (ϕ between 4 and 6 in the silt size fraction) and had an average Fe concentration of 2.89 ± 0.37%, with only one sample with Fe<2.25%. This supports the use of 2.25% as a cut-off point to ensure analysis of only muddy, depositional sediments.

Enrichment of TOC close to the BPO is observed when TOC is normalized to Fe to account for variations in sediment types (Feng et al., 1998) (Figure 3.4). The two outliers noted above are once again apparent (Figure 3.4a), one occurring in Reynold's Channel and one in Oil City (Figure 3.1). These outliers have grain size distributions, TOC, TON and QAC levels consistent with other high Fe, muddy samples at nearby stations, suggesting that there may have been problems in the Fe analysis for these two samples. To better interpret the data set, the y-axis was truncated to remove these two outliers (Figure 3.4b), and when truncated, enrichment of TOC relative to Fe within 5-7km of the BPO is evident. This enrichment is most likely due to the abundance of organic matter being discharged into the Bay from the sewage outfalls as well as known eutrophication in Hempstead Bay, and in particular, West Bay (Gobler, 2012; Swanson, 2011). Levels of TOC observed in Hempstead Bay are also enriched relative to those measured in the nearby New York/New Jersey Harbor, where values ranged from around 2% to 6% TOC (Li and Brownawell, 2010) with an average of 3.63%, as well as in Long Island Sound (Chapter 2), where values ranged from .35 to 3.82%, with an average of 2.72%. In comparison, the average TOC measured in Hempstead Bay samples was 4.1%.

The impact of sewage on sediment properties within Hempstead Bay can also be seen in TON measurements in Hempstead Bay, as the ratio of TOC to TON in Hempstead Bay increases with distance from the BPO for samples with Fe levels greater than 2.25%, excluding samples from Mill River (Figure 3.5) (p value of 3.34×10^{-4}). This trend could be due to a large number of bacteria near the outfall that are known to have lower TOC:TON ratios than phytoplankton (Fukuda et al., 1998; Prahl et al., 1980). Data from Mill River (open black diamonds) indicates a large increase in the TOC:TON ratio with distance up the stream. This sharp increase is most likely a result of the introduction of terrestrial organic matter into the stream through runoff, as TOC:TON ratios are known to be higher for terrestrial organic matter than marine organic matter (Meyers, 1994; Prahl et al., 1980).

3.3.2 QACs

Sediment grab samples

QACs were measured in all samples analyzed in Hempstead Bay (Table 3.4, Figure 3.6), with ΣQAC concentrations ranging from 0.3 μg/g to 104 μg/g. ΣQAC concentrations were dominated by the most hydrophobic DTDMACs, with the sum of DTDMAC 16:16, 16:18, and 18:18 making up between 60 and 94 percent of total QACs, a result similar to that seen in LIS

(Chapter 2) and in other areas of the NY/NJ Harbor where treated sewage is the primary source (Li and Brownawell, 2010). The relative proportions of different DADMAC, ATMAC and BAC homologs vary greatly with distance from the Bay Park treatment plant and these changes are discussed in detail below.

The highest concentrations of ΣQACs were found in West Bay and in selected stations in Middle Bay closest to the Bay Park outfall (Figure 3.6). Figure 3.6 illustrates that when normalized to %TOC, the average ΣQAC concentrations (average ΣQACs 33.0 μg/g, average ΣQACs/TOC = 6.71 μg/g/%, n=26) in West Bay are appreciably higher than those seen in western and central LIS (Chapter 2) and are comparable to those that have been measured in local, sewage-impacted systems, including Jamaica Bay which receives nearly 300 MGD of municipal wastewater and the greater NY/NH Harbor complex system (2,300 MGD) (Li and Brownawell, 2010; Swanson et al., 2010). The STP outfalls in Reynolds Channel were placed in a high current environment between two ocean inlets. While strict comparisons of concentration may be misleading, the high concentrations and spatial distributions of QACs indicate that sewage associated particles and contaminants are retained in Hempstead Bay and widely dispersed. This is consistent with the results of hydrodynamic particle tracking models showing transport of water into the areas where QACs are found to be enriched and long retention times of water that is transported into northern reaches of Hempstead Bay (Swanson et al., 2013). Data obtained by Gobler (2013) also indicates a sewage source for nutrients as well as phytoplankton and benthic macroalgae (Ulva sp.), which were highly enriched with 5km of the BPO.

Total QAC concentrations decrease with distance from the outfall (Figure 3.6). Concentrations of ΣQACs east of Jones Inlet for samples with Fe > 2.25% ranged from 1.85 to 6.05 μg/g, and the average concentrations of ΣQACs east of Jones Inlet (3.65 μg/g) is similar to average levels in LIS at sites between 15km and 50km from the Tallman Island STP outfall in the East River (Chapter 2). Thus, it is clear from this data that sewage affected particles are significantly retained within Hempstead Bay but are also dispersed over long distances into areas to the east.

It is likely that some of the variability in QAC concentrations at different distances from the BPO (Figure 3.6a) is related to differences in sediment type or depositional environment. This variability is reduced when data are normalized to Fe, as is seen in Figure 3.6b. While there is some variability in ΣQAC/Fe in samples closest to the outfall, there is a clear drop in concentrations between the BPO and Jones Inlet. While some of the variability observed near the outfall in Figure 3.6b is largely reduced when total QAC concentrations are instead normalized to %TOC (Figure 3.6c), this improvement is not observed beyond the outfall, with variability increasing between 3.5 and 4.5km from the BPO when normalized to %TOC. Additional improvement in the plot of total QACs normalized to Fe is seen if only the data from sediments with the highest Fe are considered (Fe> 2.25%, Figure 3.6d). There are three samples in West Bay around 6 km from the BP outfall that have somewhat higher QAC/Fe values (Figure 3.6d), and this is explained by their location in Bannister Bay that is locally influenced by the small Lawrence STP outfall. In addition, it is interesting to note that QAC levels in samples taken from Mill River are similar to other samples at similar distances from the BPO (Figure 3.5d). Concentrations of QACs normalized to iron decrease more gradually moving farther east beyond Jones Inlet (approximately 10km from the BPO). As seen in Figure 3.8, a significant ($p=0.047$) drop in concentration of ΣQACs (normalized to Fe) is observed from East Bay and into South Oyster Bay. The continuous changes in concentrations and compositions (see below) of QACs with distance from the BPO support the assumption that the dominant source of the QACs to Hempstead Bay come from sewage discharges in Reynolds Channel. Additional analysis of samples further east may shed light on whether there may be current or historic sources of sewage into the Long Island south shore estuaries that affects background levels measured in East Hempstead and South Oyster Bays.

To better understand the persistence of DTDMAC 18:18 in Hempstead Bay, levels of trialkyl methyl ammonium compounds (TAMACs), impurities in QACs (van Leeuwen and Jaworska, 2010), were estimated based on reconstructed ion chromatograms of known masses and assuming response factors equal to DTDMAC 18:18. TAMACs are similar to QACs but have three long alkyl chains instead of just two, and as such, are larger and more particle reactive than QAC. As they are impurities in QACs, the two classes of compounds are expected to have similar time histories, particularly TAMACs and larger DTDMACs; this hypothesis is supported by results from dated sediment cores (Chapter 4). Characteristic homologous series of TAMACs (dominated by those with 16 and 18 carbon chain lengths) were observed, with maximum peak areas observed for TAMAC 16:18:18. Levels of DTDMAC 18:18 in Hempstead Bay normalized to TAMAC 16:18:18 did not indicate any consistent trend with distance from the BPO (Figure 3.9). This provides additional support for the hypothesis that there is no appreciable degradation/desorption of DTDMAC 18:18 occurring in Hempstead Bay, which is supported by previous work on the persistence of DTDMAC 18:18 in sewage impacted environments (Li 2009, Li and Brownawell 2010, Chapter 2).

QAC Sediment Compositions

To better understand changes in the relative composition of QACs in this study, individual QAC concentrations were normalized by DTDMAC 18:18. DTDMAC 18:18 is not only the dominant QAC in all samples from studies in both Hempstead Bay (this study) and LIS (Chapter 2), but is also the most hydrophobic, particle reactive, and persistent QAC studied. In addition, geochronologies indicate that the input of DTDMAC 18:18 to Hempstead Bay has been at near steady state over the last twenty years (Chapter 4). Observed changes in composition relative to DTDMAC 18:18 could therefore reflect degradation and or desorption during transport and incorporation into the sediment or a change at the source of individual QACs, as neither of these processes are expected to impact DTDMAC 18:18. For suspended solid samples, relative enrichments of other QAC homologs relative to underlying sediment is calculated using these DTDMAC 18:18 normalized values.

Large changes in the relative composition of individual QACs were observed within Hempstead Bay. Decreases in the composition of DADMACs 8:10 and 10:10, larger BACs, behentrimonium, and DTDMACs 12:12 -14:16 relative to DTDMAC 18:18 were observed with distance from the BPO (Figure 3.10), although these trends only continued east of Jones Inlet for DTDMAC 12:12 and DTDMAC 12:14. In contrast, increases in the relative composition of small BACs were observed in the far eastern portions of Hempstead Bay and into South Oyster Bay. Increases were also observed in the relative abundance of ATMAC 12 with distance from the BPO (Figure 3.10), but this trend is complicated by known issues discovered during this work (Chapter 6) that often lead to less than complete recovery of this more soluble QAC during the purification method use in this study as well as a large number of no detects at greater distance.

DTDMACs

The relative composition of the largest DTDMACs, and in particular DTDMAC 16:18, remained constant in sediment grab samples throughout Hempstead Bay, but a decrease in smaller DTDMACs (12:12 – 16:16) relative to DTDMAC 18:18 was observed with distance from the BPO (Figure 3.10). The relatively constant composition of the largest DTDMACs is consistent with observations made in Chapter 2 as well as by Li (2009) and Li and Brownawell (2010), suggesting extreme persistence of these most hydrophobic DTDMAC homologs. The decreasing trend in relative composition with distance from the source observed for DTDMACs 12:12-16:16 was significant when data from throughout the Bay were considered, but when individual portions of the Bay were studied, the relationship was restricted to only the region west of Jones Inlet for all except DTDMAC 12:12 and DTDMAC 12:14 (Table 3.7, Figure 3.10). The magnitude of the decrease relative to DTDMAC 18:18 is largest for DTDMAC 12:12 and decreases with increasing chain length (Figure 3.10), as the composition of samples near the BPO are almost 4 times as enriched in DTDMAC 12:12 as those samples near Jones Inlet, with DTDMAC 12:14, DTDMAC 14:14 and DTDMAC 14:16 being enriched 3.0, 2.7 and 2.0 times, respectively, at the BPO compared to samples near Jones Inlet. The degree of change in composition observed for DTDMAC 16:16 is much smaller than for other DTDMACs, with BPO sediment compositions only 1.43 times more enriched in DTDMAC 16:16 than sediments the Jones Beach Inlet.

While these trends observed for DTDMACs in sediments within Hempstead Bay follow trends in chain length and may be associated with desorption/degradation during transport, they may also be the result of a trend towards plant based oils, favoring the use of smaller DTDMACs over the largest, animal fat based DTDMACs. An increase in the use of smaller DTDMACs might also contribute to the trends observed here. This hypothesis is based on an assumption that sediments closest to the source of sewage reflect the most recent sewage signal, while sediments furthest from the outfall reflect the oldest sewage signal, similar to the model proposed for LIS in Chapter 2. Therefore, if use of the smallest DTDMACs were increasing, the sediments closest to the BPO would reflect these changes while sediments further away would reflect older signals when the relative composition of smaller DTDMACs was less.

While no changes in composition relative to DTDMAC 18:18 are observed for any DTDMACs in the LIS study (Chapter 2, Figure 2.5), DTDMAC 12:12 was not measured in the study and neither DTDMAC 12:12 or DTDMAC 12:14 were measured in samples within 5km of the major outfalls of western LIS. This is important, as the largest changes in composition for DTDMACs in Hempstead Bay were observed in the first 5km away from the BPO.

DADMACs

A decrease in all DADMACs relative to DTDMAC 18:18 was observed in sediment grab samples with distance from the Bay Park STP outfall, with most of the decrease focused west of Jones Inlet (Figure 3.10). DADMAC 8:10 and 10:10 normalized to DTDMAC 18:18 showed a significant relationship with distance (Table 3.7) from the BPO. While DADMAC 8:8 did not have a significant relationship, when the single high data point in S. Oyster Bay is removed, there is a significant (p=0.0163) relationship. DADMAC 10:10 was the only DADMAC with enough data for an analysis of points east of Jones Inlet, and for this compound, this relationship with distance does not continue east of Jones Inlet (Table 3.7)

An increase in the use of DADMACs over time has been previously suggested, and may explain the trends observed for these compounds, as Li (2009) also noted increases in DADMACs relative to DTDMAC 18:18 in geochronologies from Jamaica Bay and attributed these changes to an increase in the use of DADMACs. Similar observations have also been made in this thesis (Chapter 4) in more recent geochronologies from both Hempstead Bay and Jamaica Bay. These findings are also in agreement with what was observed in LIS, where DADMAC concentrations decreased relative to DTDMAC 18:18 with distance from the source, both within the region of sewage input as well as up to 15km from the source.

BACs

Changes in the composition of individual BACs were observed in sediment grab samples from Hempstead Bay. No changes in composition close to the outfall were observed for either BAC 12 or BAC 14, but slight increases relative to DTDMAC 18:18 were noted in samples farthest from the BPO. Decreasing relative compositions of both BAC 16 and BAC 18 were observed with distance from the BPO west of Jones Beach Inlet (Figure 3.10). The relative increase of BAC 12 and BAC 14 into East Bay and South Oyster Bay is significant (Table 3.7) and may suggest a source of these smaller BACs east of samples from this study, although no such sources are known at this time. The increase in smaller BACs at points furthest from the BPO may also be a function of individual QACs associating with different types of particles that are differentially transported throughout Hempstead Bay. For example, hypothetically, it may be that at higher concentrations, the most hydrophobic DTDMAC is associated with both clay and organic matter cation exchange sorption domains, but more resistantly sorbed QACs might be all associated with stronger clay sorption sites (e.g. intercalated in smectites). Additional research is needed to better understand these processes.

There is considerable noise in BAC 14 data in sediment samples from Hempstead Bay that makes a trend near the BPO hard to determine, although the relative composition of BAC 14 at BPO is enriched 1.4 times the relative composition near Jones Inlet, indicating there might be loss of BAC 14 relative to DTDMAC 18:18 not reflected in the statistics (Figure 3.10, Table 3.7). In contrast to the smallest BACs, changes in the relative composition of BAC 16 and BAC 18 in sediment grab samples have significant, non-zero relationships with distance west of Jones Inlet for both compounds, although no relationship is observed for points east of Jones Inlet (Table 3.7). A decrease in the relative composition of BACs with distance from major sewage sources was also observed in the study from LIS (Chapter 2).

ATMACs

In contrast to most QACs in this study, a significant increase in the relative composition of ATMAC 12 relative to DTDMAC 18:18 is observed with distance from the BPO (Table 3.7, Figure 3.10). The interpretation of this trend is complicated by incomplete and variable extraction of this most soluble QAC, as well as a large number of samples below detection limits farthest from the BPO. While the increase in ATMAC 12 relative to DTDMAC 18:18 with distance from the BPO could be due to more efficient degradation of ATMAC 12 once deposited in sediments closest to the outfall, this is not supported by suspended sediment compositions, which are in-line with underlying sediments as discussed below (Figure 3.11). This trend may also be explained by decreasing uses of ATMAC 12 in recent years, but no information is available on the use of ATMAC 12, and geochronologies are unavailable due to low concentrations in sediments (Chapter 4). Differential transport of QACs associated with different particle types may also explain this observation, as noted above.

While no significant changes in composition very close to the STP outfalls were observed for ATMAC 16 and ATMAC 18, significant (Table 3.7) decreases in the relative composition of behentrimonium (ATMAC 20 and 22) in sediment grab samples with distance from the BPO were observed (Figure 3.10). The decrease in the relative composition observed for these compounds are greater than any other QAC measured, with enrichment in the relative composition of ATMAC 20 and ATMAC 22 7.6 and 7.0 times higher, respectively than the relative composition of these compounds near Jones Inlet. This large degree of enrichment may suggest that these changes observed in Hempstead Bay are in part due to dramatic increases in the use of behentrimonium relative to DTDMAC 18:18 not seen for other QACs (Lara-Martín et al., 2010), as was suggested in Chapter 2. While there was not enough data east of the Jones Inlet for a separate analysis for ATMAC 20, the data was separated for ATMAC 22 and while there is a significant, non-zero relationship between ATMAC 22 normalized to DTDMAC 18:18 west of the inlet, this relationship does not extend beyond Jones Inlet.

Conceptual Model for QACs in sediments

A conceptual model for the behavior of QACs upon release from a source has been developed based on data from Chapter 2 and the more detailed sampling and analysis of the results from this chapter. In this model, the amount of each QAC present in sediments is comprised of a resistant phase as well as more reactive, labile pool. This model is informed by prior work on desorption of lab and field aged nonpolar hydrophobic contaminants (HOCs, Lamoureux and Brownawell, 1999; Ten Hulscher et al., 1999; Wu and Gschwend, 1988) as there has not been detailed work on desorption of QACs from sediment. The situation with QACs is likely even more complicated than it is for HOCs, given very non-linear sorption isotherms for organic cations and the suggestion that sorbed QACs exist in a continuum of binding domains with vastly different sorption energies which are subject to competitive cation-ion exchange (Brownawell and Westall, 1991; Brownawell et al., 1990). Desorption of QACs is likely most important in the water column where there are much higher water to sediment ratios and where the dissolved phase is likely well below equilibrium with sorbed phases. Once desorbed, biodegradation is likely an important removal process.

In this model, the resistant phase is not subject to much desorption and degradation as a particle is transported, and once surface coverages for sorbed QACs have reached the resistant phase, desorption rates of that QAC become exceedingly slow. In contrast, the labile pool is subject to more extensive desorption at rates and extents that are a function of hydrophobicity of the QAC and surface concentration, each of which affect sorption to sediments. As the hydrophobicity of QACs increases, the extent and rates of desorption from labile pools is likely to become increasingly low as more alkylated QACs are among the most hydrophobic organic compounds synthesized by man, and also strong cation exchangers, which further contributes to the sorption energy. Furthermore, the extent and rate of desorption of QACs must be a function of concentration of not only an individual QAC but the co-existence of other strongly sorbing QACs which compete for limited numbers of the strongest cation-exchange sites (Brownawell et al., 1990).

There have been few studies of the desorption of QACs from soils or sediments. Wagner et al. (1994) were able to show that desorption rate slowed dramatically over time as dodecylpyridinium (similar in solubility to ATMAC 12) was eluted off a soil column, with 16% still remaining after 1000 pore volumes were flushed through the column. In addition, many studies with nonpolar organic compounds have shown that desorption rates decrease with an increase in the time that sorbates are associated with particles and with increasing hydrophobicity (Wu and Gschwend, 1988). On the other hand, more soluble hydrophobic compounds found in field sediments can sometimes be much more resistant to desorption than more hydrophobic compounds (Ten Hulscher et al., 1999). Similarly, Lamoureux and Brownawell (1999) have observed greater, continued desorption of more hydrophobic polychlorinated biphenyls from field collected LIS sediments as compared to their less hydrophobic counterparts. It seems likely that for more soluble hydrophobic contaminants, once removed from the source of contaminants, readily desorbable fractions are lost to variable degrees before or after they become incorporated in sediment beds, leading to persistence of more resistant and very slowly desorbing phases. The relative size of a labile sorbed pool of sewage derived QACs that enters receiving waters may be related to the extent of sewage treatment before release, as well as initial concentrations. The effect of contaminant aging may also be important and lead to reduced desorbability as has been seen for nonpolar HOCs (Lamoureux and Brownawell, 1999; Ten Hulscher et al., 1999; Wu and Gschwend, 1988).

Based on a mass balance study by Clara et al. (2007), it is known that BACs, ATMACs and DADMACs can be extensively (up to 95%) biodegraded during sewage treatment, with the extent of degradation inversely proportional to chain length. During more extensive sewage treatment, the portion of the labile pool surviving sewage treatment is most likely quite small for the smallest QACs, such that only the resistant phase remains for these compounds upon release into receiving waters. In contrast, the largest QACs are not appreciably desorbed and degraded simply because they are so hydrophobic, and not because they reside in a resistant pool protected in some manner from desorption. For DTDMACs, removal from sewage influents in STPs can be entirely accounted for by loss to sewage sludge (Clara et al., 2007). QACs with intermediate hydrophobicity fall between these two extremes in that they have low enough sorption energies that some slow desorption can be expected, especially during transport in the water column, resulting in changes in composition that are observed with distance from the source as the labile pool is reduced. The size of the labile pool as well as the relative rate at which this labile pool is desorbed and possibly degraded is thought to be dependent upon the hydrophobicity and initial concentration of sorbed QACs. Smaller QACs are thought to have a smaller labile pool due to more extensive biodegradation during sewage treatment (Clara et al., 2007), and the residual labile pool that exists on particles that are deposited close to the source desorb at a faster rate than for more hydrophobic compounds, thus reaching a resistant phase relatively close to the source. Larger QACs are hypothesized to leave sewage treatment with a larger labile pool due to decreased biodegradability in STPs, and subsequent desorption and/or degradation of this labile pool is expected to occur over relatively longer time frames due to the more hydrophobic nature of these larger QACs.

Evidence for this model of the behavior of QACs in sewage-impacted sediments is best observed in the series of BAC homologs (Figure 3.10). There is no change in the relative composition of BAC 12 observed with distance from the source, and this model would suggest that this is because the labile pool of this compound was degraded during sewage treatment or very quickly upon release into receiving waters. The fraction of BAC 12 remaining after treatment is in a resistant phase and remains unchanged during transport throughout Hempstead Bay. In contrast, significant decreases in the relative composition of the largest BACs are observed within the first 5km of the BPO (Figure 3.10), as these compounds are thought to have larger and slower-desorbing labile pools. The smallest QACs in this study that see little to no change in sediment compositions with distance include BAC 12, possibly BAC 14, ATMAC 16 and ATMAC 18 (Figure 3.10). The largest QACs for which no compositional changes are observed, most likely due to extreme persistence include DTDMAC 16:16 and DTDMAC 18:18. QACs of intermediate hydrophobicity include DADMACs, larger BACs, ATMACs C20 and C22, and smaller DTDMACs.

This model does not take into account potential changes in the source of these QACs to the environment that may also affect the composition of QACs relative to DTDMAC 18:18, as has been suggested for some QACs. As noted above, sediments closest to the source are expected to reflect the most recent sewage signal, while sediments further from the source have taken a longer time to reach that point and would therefore reflect an older sewage signal. Therefore, any changes in the source of these compounds may be reflected in the closest sediments and not in sediments further away. This is best illustrated for behentrimonium, as noted above, where dramatic decreases in the relative composition of behentrimonium are observed with distance from the BPO. Source changes have been suggested for DADMACs, smaller BACs, behentrimonium, and smaller DTDMACs (Li, 2009, Chapter 4). Therefore, the decrease in the relative composition of these compounds may not be due solely to loss of the labile pool but may also reflect a source change. Consequently, for larger compounds like behentrimonium and smaller DTDMACs, the changes in composition may be only a result of a change in source and there may not be any desorption or degradation of these compounds occurring.

Suspended Solids

Additional support for the conceptual model detailed above can be found in data from suspended solids collected in West Bay. Almost all QACs were measured on suspended particles at the BPO (Table 3.5), and the more abundant homologs were measured in filters at the two stations from northern portions of West Bay (Figure 3.1b). Concentrations (ng/L) of individual QACs at the BPO were extremely consistent for replicates taken on the same day (Table 3.5), with more variation observed across sampling dates. Large DTDMACs and ATMAC 22 dominated the composition of QACs on all suspended solids particle samples (Table 3.5). Concentrations of QACs on suspended particles were higher in Hewlett Bay than in Oil City, with a larger number of individual QACs being measured in Hewlett Bay (Table 3.5) and only DADMAC 10:10, behentrimonium, and the largest DTDMACs being measured on suspended particles in Oil City (Table 3.5). While comparisons are limited, the concentrations of QACs on suspended particles at sites in northern West Bay are far less enriched as compared to underlying sediments than enrichments observed in samples collected within the sewage effluent boil at the BPO (Table 3.6). This would be consistent with suspended particulate material at these more remote sites being more dominated by local resuspension, although this cannot be explicitly concluded based on the few samples taken away from the BPO.

Support for the conceptual model defined above can be found in the composition of QACs on suspended solids compared to the underlying sediments, particularly for samples at the BPO. For the smallest and largest QACs, suspended solid concentrations at the BPO are similar to underlying sediments (Figure 3.11). This is consistent with the model, which suggests that after sewage treatment, the most soluble QACs are already in a resistant phase upon release to the environment and do not undergo additional desorption/degradation upon release into this environment. These results may also indicate that sediments beneath the outfall are dominated by sewage particles and not significantly impacted by transport of sediments from other parts of the Bay.

In contrast, for QACs of intermediate hydrophobicity, including BAC 16, BAC 18, ATMACs C16-C22, DADMAC 10:10 and DTDMAC 12:12, suspended solid compositions in the BPO plume are higher and more variable than the composition of these QACs in the underlying sediment. Based on the model described above, these enrichments compared to underlying sediment may suggest that these compounds of intermediate hydrophobicity are undergoing desorption and/or degradation before incorporation into underlying sediments. It cannot be concluded whether the processes controlling the loss of intermediate hydrophobicity compounds occurs in the water column or after deposition to the sediment bed. The similarity of composition for these compounds on suspended particles between replicates, but larger variability across sampling trips, may be related to a number of factors, including time variable releases from the BPO or that samples were obtained at various stages of desorption/degradation while in the water column.

When comparing the difference between the composition of each QAC relative to DTDMAC 18:18 in the suspended solid phase within the sewage effluent plume (R_{filter}) and the underlying sediment ($R_{sediment}$), it becomes clear that these intermediate hydrophobicity QACs stand out when this $R_{filter}/Rs_{ediment}$ ratio is plotted against the log of the critical micelle concentration (CMC) of each QAC as a measure of hydrophobicity (Figure 3.11). The CMC values used (mM) were obtained through literature or estimated by extrapolating the effects of adding CH_2 groups in a homologous series when literature values were not available (Kunieda and Shinoda, 1978; Tezel, 2009). There is little difference in compositions between suspended matter and sediment for either the most hydrophobic (CMC much less than 0.1mM) or least hydrophobic (CMC greater than 1-2mM) with $R_{filter}/R_{sediment}$ average values ranging between 0.36- and 1.77. However, for QACs of intermediate hydrophobicity, with log CMC's between 0.1 to 1mM, the values of $R_{filter}/R_{sediment}$ is seen to be higher, between 1.79 and 5.29. This clustering suggests that these differences are largely a function of hydrophobicity that is causing these deviations and supports the conceptual model presented above that was initially based on looking at changes in compositional patterns observed in sediments as a function of distance.

Comparisons between Hempstead Bay and Long Island Sound

It is informative to compare results of QAC compositions in Hempstead Bay and Long Island Sound (Chapter 3), where the compositions of each individual QAC relative to DTDMAC 18:18 was plotted versus distance from a dominant sewage source (Tallman Island STP outfall in LIS, Figure 3.12). These environments represent two potentially different sewage input scenarios: Hempstead Bay represents an environment that has received a relatively constant input of secondary treated sewage for over 60 years, while Long Island Sound sewage inputs include a large number of CSOs. These differences might be important if CSO sources are large enough, as it is known that CSOs can result in a higher proportion of smaller QACs preserved in sediments (Li and Brownawell, 2010). Other differences between the two environments are the deeper depths and greater volumes of LIS and that LIS samples were not collected within very close distances from sewage outfalls. In Figure 3.12, as described in Chapter 2, negative distances represent far WLIS samples from Li (2009) that are located to the west of the Tallman Island STP outfall. These samples are located near the mouth of the East River and are heavily impacted by multiple sewage outfalls as well as CSO inputs. It should also be noted that ATMAC 12 is not included in this figure due to previously noted issues in the purification steps of the method, and DTDMAC 12:12 is not included as data for this compound was not collected in LIS.

There is remarkably good agreement between the data sets for DADMACs, BACs, and ATMAC 16 and 18 (as well as ATMAC 20 and 22 at distances removed from point sources). The similarities include both trends with distance from sewage point sources, but also, surprisingly, the actual magnitude of the relative abundance of each QAC to DTDMAC 18:18. While the relative size of the initial labile pool may be different for these compounds in the two locations due to different levels of sewage treatment (samples in the CSO affected far western WLIS tend to have higher relative compositions than Hempstead Bay samples closest to the source), the fraction of the compounds that remains in the resistant phase appears to be the same. While a similar pattern is observed for behentrimonium, the far western WLIS samples are much lower than the Hempstead Bay samples. This has been explained in Chapter 2, and is thought to be a result of the dates that these samples were taken (1998 and 2004) being much earlier than the Hempstead Bay samples (2010-2011) and even the rest of the Long Island Sound samples (2008), and the rapid increase in use of these compounds in recent years is not reflected in the samples collected earlier. Interestingly, the relative proportion of behentrimonium in 2008 samples in LIS (none of which were collected within 5km of a sewage outfall) do not approach the high levels seen in samples very near to the BPO in Hempstead Bay (Figure 3.11), although their fractional compositions do match well with Hempstead Bay samples when adjusted for distance from a major sewage source. The extent to which this is due to a lag time in transport of a rapidly increasing source tracer or to differential desorption and loss during transport is unclear and hard to separate in this data.

The highest relative abundances of more labile BACs, DADMACs and ATMAC 16-18 show remarkably good agreement between the two estuaries, with maximum relative concentrations observed in LIS only for BAC 14, BAC 16 and especially ATMAC 18. Whether the average loading patterns for QACs in LIS are different from those in Hempstead Bay is not known. However, if CSOs result in an appreciably greater source of more degradable QACs to LIS, such signals do not appear to be preserved in sediments to any great or obvious extent in far western LIS sediments analyzed by Li (2009).

Among the most obvious difference between the two data sets is the patterns of changes seen in the composition of less alkylated DTDMACs (12:14-16:16), where the compositions relative to DTDMAC 18:18 in LIS do not change much with distance from the WLIS sewage sources but are 1.43-3.0 times more enriched than they are at distances beyond 5km from the BPO source in Hempstead Bay, especially for more soluble 12:12 and 14:16 homologs. There are many possible reasons for differences of these relatively persistent QACs in two water bodies, including differences in how close to sources samples were obtained, likely greater amount of exchange with large volumes of seawater for suspended and resuspended sediments in LIS, possible differences in the average composition of DTDMACs in STP effluents, and the possibility that CSO inputs discharge different compositions of DTDMACs sorbed to different types of particles. It has also been argued above and in dated sediment cores from Chapter 4 that there may have been recent increases in the relative input of DTDMACs with lower alkyl chain lengths owing to the increased use of coconut and other vegetable oil sources. The argument for these DTDMACs is then similar to ATMAC 20 and 22 in which some portion of the explanation for a drop in relative abundance with distance is due to slow dispersive transport of sediments contaminated with newer sources of contaminants. Another potential difference between Hempstead Bay and WLIS is that sediments in Hempstead Bay have higher organic matter contents and higher levels of QACs, especially the very strong cationic exchanging DTDMAC 16:18 and 18:18. In limited studies, Li (2009 and personal communication) found that acidic solvent extraction of QACs from highly contaminated CSO affected sediment was easier than for less organically enriched and much lower QAC concentration sediments from central LIS. It may be that lower chain length DTDMACs are effectively more strongly bound in particles in LIS than they are in Hempstead Bay. For now, the reasons for these relatively modest, but consistent differences in DTDMAC distributions are uncertain, but further research might explore these questions that are clearly important for understanding the conditions in which QACs act as conservative particle tracers.

3.4 Conclusions

In this study, observed enrichment in TOC as well as measurements of ΣQAC that are similar to other local, heavily sewage affected environments suggests that sewage-affected particles are being retained in Hempstead Bay. In addition, this study provides valuable insight into the behavior of QACs in a sewage-impacted estuary, both immediately after discharge as well as during transport away from the source. While the largest DTDMACs are shown to be extremely persistent in this environment, changes in the relative composition of QACs with intermediate hydrophobicity support the conceptual model outlined in this study in which labile pools exist that are desorbed and/or degraded during transport away from the source, and that the extent of this loss is inversely related to QAC hydrophobicity. The lack of change in the smallest QACs in the BPO plume or in sediments may indicate that labile portions of these compounds are desorbed/degraded during sewage treatment or soon after release into the environment, and small remaining portions of these QACs are resistant to further desorption and degradation and therefore persist throughout this environment. Decreasing levels of smaller DADMACs, larger BACs, behentrimonium and the smallest DTDMACs relative to DTDMAC 18:18 in sediment samples with distance from the BPO may also be due to recent increases in the use of these compounds. Increases in the relative composition of BACs 12 and 14 as well as ATMAC 12 with distance from the BPO are most likely not related to changes at the source and raise important questions about the possibility of differential transport of QACs in estuarine environments.

Data from suspended solids collected in the sewage effluent plume from the BPO support the conceptual model outlined and preferential desorption and/or degradation for QACs of intermediate hydrophobicity before they are preserved in the sediment bed. Extremely good agreement between Hempstead Bay and Long Island Sound QAC composition data (Chapter 2) as a function of distance from sewage sources suggest that the relative composition of the resistant phase may be similar in these different environments. There are subtle but consistent differences in DTDMAC compositions between the two regions that may be due to a variety of reasons, including differences in municipal and CSO sources of DTDMAC inputs, differences in sediment transport, or even how tightly bound these QACs are when LIS sediments are less contaminated with QACs and less enriched in organic matter. Increases in DTDMACs closer to the source in Hempstead Bay but not observed in LIS may be due to recent increases in the use of these compounds that is not reflected in older samples from LIS and the East River. This study provides strong evidence for a new model for the fate of QACs in sewage-impacted environments as well as support for the use of QACs as persistent tracers of sewage.

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Table 3.1 Coordinates and distance from the Bay Park STP outfall for samples in this study.

Station #	Latitude	Longitude	km
3	40.60388	-73.73302	6.37
4	40.60143	-73.73483	6.07
6	40.6043	-73.72897	6.69
8	40.58948	-73.71398	3.46
8.5	40.5908	-73.70678	2.82
9	40.58932	-73.68665	1.24
13	40.62337	-73.66127	3.64
14	40.61673	-73.65237	3.54
16	40.6119	-73.66635	2.16
18	40.61053	-73.66673	1.98
19	40.60755	-73.66685	1.77
21	40.59658	-73.6707	0.4
22	40.5963	-73.67495	0.05
24	40.59565	-73.67445	0.1
25	40.59323	-73.6779	0.4
26	40.59415	-73.6646	0.97
27	40.59662	-73.66315	1.05
30	40.59692	-73.65003	2.25
31	40.59592	-73.62742	4.07
33	40.5957	-73.61458	5.25
35	40.60535	-73.55098	11.54
37.2	40.60283	-73.51173	13.92
38.2	40.61123	-73.50273	15.03
40	40.63382	-73.5099	17.38
43	40.6379	-73.52532	17.38
46	40.64543	-73.54405	16.58
47	40.6426	-73.53745	16.09
48.4	40.62083	-73.53192	15.16
49.2	40.61565	-73.5239	14.31
55	40.61843	-73.67613	3.43
56	40.62438	-73.68648	4.76
61	40.60952	-73.69138	3.44
62	40.61787	-73.70023	4.06
63	40.61727	-73.69707	3.85
69	40.62438	-73.59463	8.92
72	40.63007	-73.65973	4.38
73	40.62817	-73.66098	4.17
74	40.6207	-73.6544	3.93
75	40.60715	-73.64247	3.91
79	40.6118	-73.63045	5.04
81	40.61538	-73.62473	5.73
85	40.62127	-73.60558	8.34
87	40.633	-73.59363	9.88
88	40.6346	-73.5874	10.25
89	40.63725	-73.56507	13.5
93	40.64691	-73.4632	20.92
95	40.65282	-73.44146	22.53
102	40.60099	-73.49468	19.63
107	40.6538	-73.44874	22.53
115	40.65355	-73.46869	21.24
105B	40.65524	-73.65524	24.62
1B	40.59648	-73.67562	0
2B	40.6119	-73.63177	8.03
3B	40.5954	-73.6375	3.22
94B	40.65196	-73.45262	21.89
EL2	40.6385	-73.55863	16.25
MR1	40.63535	-73.65733	5.05
MR2	40.63848	-73.65868	5.47
MR3	40.64425	-73.65799	6.2
NM	40.62797	-73.57972	11.93
Core 4, top	40.62707	-73.67445	5.2

Table 3.2 Coordinates, distance from the Bay Park STP outfall, and total suspended solids (TSS, when available) for suspended solid samples. Samples from the Bay Park STP outfall have been given coordinates of the outfall cement block.

Name	Date Collected	Latitude	Longitude	km from outfall	TSS mg/L
BP Outfall 1	09/16/11	40.596311	-73.675622	0	
BP Outfall 2	09/16/11	40.596311	-73.675622	0	
BP Outfall 3	10/12/11	40.596311	-73.675622	0	
BP Outfall 4	10/12/11	40.596311	-73.675622	0	
BP Outfall 5	6/6/12	40.596311	-73.675622	0	7.49
BP Outfall 6	6/6/12	40.596311	-73.675622	0	7.40
Oil City	10/12/11	40.62075	-73.654317	3.86	
Hewlett Bay	6/6/12	40.625631	-73.668872	4.49	5.33

Table 3.3 Total organic nitrogen (TON), total organic carbon (TOC), Fe, volume weighted mean particle diameter, DTDMAC 18:18 and ΣQACs in grab samples.

Station	TON %	TOC %	Fe ug/g	Mean Particle Diameter µm	DTDMAC 18:18 ng/g	ΣQACs ng/g
3	0.75	6.05	31700	25	7660	18100
4	0.51	4.41	33900	38.2	7220	15500
6	0.65	6.38	33100	21.9	10800	26600
8	0.04	0.4	9300	111	695	1620
8.5	0.17	1.64	13400	105	4960	11100
9	0.5	3.99	1750	59.2	13400	35000
13	1.05	7.66	28100	221	15300	38800
14	0.6	5.55	4890	57	21000	52600
16	0.52	4.93	23800	60.8	17300	43600
18	0.54	5.16	21600	68.5	15900	42200
19	0.63	5.3	27800	63.2	15500	40500
21	1.12	8.14	27200	121	22300	75900
22	0.18	1.87	14100	97.5	10800	31800
24	1.03	8.97	24900	254	35500	104000
25	0.56	5.05	26100	48.7	15500	41800
26	0.68	5.3	27700	69.4	13600	38700
27	0.73	6.7	30900	36.7	16500	47800
30	0.52	4.88	29800	39.4	14800	40500
31	0.45	4.28	20500	118	2250	6760
33	0.15	1.68	8250	139	673	1350
35	<.001	0.14	1970	149	<RL[a]	289
37.2	0.35	3.12	25200	44.3	1836	3440
38.2	0.01	0.22	2280	170	<RL	297
40	0.25	2.42	16200	60.9	1160	2300
43	NA[b]	NA	30100	NA	2590	4710
46	0.51	4.61	31800	25.3	3120	6060
47	0.39	4.04	29900	25	2450	5260
48.4	0.29	2.86	20300	56.9	1810	3320
49.2	0.01	0.3	4560	125	372	673
55	0.32	2.82	15700	109	5010	10200
56	0.58	4.93	29400	105	10900	25300
61	0.22	1.94	12900	92.4	3460	6740
62	0.24	2.21	19800	81.5	4570	10400
63	0.48	4.62	16300	97	3800	8580
69	0.37	3.31	25600	63.7	2650	4990
72	0.45	4.96	37200	36.5	18900	38500
73	0.55	5.33	36400	36.2	16800	40200
74	0.55	4.9	30100	47	14500	37800
75	0.56	5.27	27300	130	6580	21200
79	0.15	2.26	15300	88.1	997	2110
81	0.43	3.97	27800	70.1	3850	8140
85	NA	NA	25500	NA	1680	3380
87	0.33	3.08	25900	44	1520	3080
88	0.43	4.42	33800	25.7	2840	5620
89	0.42	3.93	28900	76.4	1940	3860
93	0.18	1.78	20800	NA	967	1900
95	0.41	3.97	24700	NA	922	1840
102	0.47	4.44	26400	NA	2140	4350
107	0.31	3.56	27700	NA	1410	2870
115	0.29	2.93	25100	NA	1230	2490
105b	0.22	1.92	16700	NA	670	1360
1B	0.54	4.51	25100	57.7	13800	34500
2B	0.35	3.17	23500	47.1	3260	6980
3B	0.67	5.72	28400	79.7	9180	24200
94b	0.35	3.28	22500	NA	1040	2110
EL2	0.23	3.72	18500	137	520	1330
MR1	0.49	5.95	39600	NA	14700	31900
MR2	0.44	6.4	42300	NA	9490	22200
MR3	0.61	8.17	51600	NA	4310	12200
NM	NA	NA	20300	NA	2370	3600

a. Levels measured were below reporting limits. b. not analyzed for this sample

Table 3.4 Concentrations (ng/g) of individual QACs measured in grab samples.

Sta[a]	DADMAC			BAC				ATMAC					DTDMAC						
	8:8	**8:10**	**10:10**	**12**	**14**	**16**	**18**	**12**	**16**	**18**	**20**	**22**	**12:12**	**12:14**	**14:14**	**14:16**	**16:16**	**16:18**	**18:18**
									ng/g										
3	10	31	144	74	391	258	480	43	167	157	234	1550	154	205	179	385	1360	4660	7660
4	9	23	131	63	244	158	342	21	103	110	164	1190	163	208	186	332	1100	3740	7220
6	10	49	226	121	624	393	659	65	294	319	218	1650	154	166	162	535	2060	8150	10800
8	3	<RL	12	<RL[b]	6	5	17	2	17	20	8	85	11	13	12	39	171	508	695
8.5	<RL	12	88	22	103	69	181	46	101	78	97	1080	111	121	104	226	625	3160	4960
9	20	60	412	88	375	<RL	909	26	147	193	653	6460	531	686	594	848	2140	7530	13400
13	10	48	388	46	302	267	891	38	108	180	488	4740	557	622	540	950	3220	10100	15300
14	13	67	572	57	420	382	1270	40	135	241	724	6210	767	912	725	1060	4560	13500	21000
16	18	77	715	82	455	369	1070	57	156	218	581	4880	700	766	591	984	3270	11400	17300
18	19	70	538	63	390	378	1020	20	137	206	674	6850	691	898	737	1030	3000	9600	15900
19	25	85	582	73	407	378	813	25	148	216	818	6860	780	615	574	926	2510	9190	15500
21	44	150	1060	200	900	706	1650	83	591	532	2650	21600	1130	1270	1050	1700	4490	13900	22300
22	48	105	466	182	563	350	793	72	175	185	623	6190	530	669	582	796	2080	6680	10800
24	80	226	1910	765	1520	970	2820	136	512	455	1690	21500	1770	1970	1790	2500	6370	21600	35500
25	18	65	446	69	403	358	959	21	147	197	727	7780	619	822	697	980	2590	9430	15500
26	<RL	59	526	72	523	465	1680	147	165	210	684	6830	799	867	730	1020	2790	7690	13600
27	33	101	665	117	553	535	1090	35	240	299	1040	9460	877	857	982	1130	3100	10220	16500
30	16	65	499	67	448	406	959	33	177	230	750	7300	644	798	696	985	2650	9050	14800
31	11	13	92	39	121	72	162	16	42	50	104	1010	103	126	111	175	535	1740	2250
33	2	2	14	<RL	9	5	17	9	<RL	<RL	6	66	12	13	11	27	108	383	673
35	0	0	<RL	30	74	49	114	0	17	0	0	0	0	0	0	5	<RL	<RL	<RL
37.2	0	3	18	0	35	15	57	28	<RL	26	<RL	88	34	28	24	61	260	951	1836
38.2	3	<RL	<RL	14	72	3	4	0	<RL	<RL	0	7	<RL	2	2	9	36	145	<RL
40	0	11	44	37	62	15	26	27	20	31	0	35	10	10	9	34	151	604	1163
43	6	4	28	22	33	20	60	0	<RL	20	8	88	30	39	36	78	317	1330	2590
46	0	9	66	21	67	36	66	0	27	46	0	93	35	34	32	83	490	1830	3120
47	0	<RL	32	8	49	29	97	39	<RL	<RL	<RL	101	47	40	36	92	363	1310	2450
48.4	0	<RL	22	13	28	6	27	30	33	38	0	46	21	15	15	49	248	951	1810
49.2	<RL	1	<RL	<RL	12	2	6	0	<RL	<RL	0	5	<RL	2	3	12	58	200	372
55	3	12	97	<RL	41	28	166	69	<RL	41	38	595	107	122	103	201	781	2810	5010

a. Station number b. Levels measured were below reporting limits

Table 3.4. continued

Sta[a]	**DADMAC**			**BAC**				**ATMAC**					**DTDMAC**						
	8:8	**8:10**	**10:10**	**12**	**14**	**16**	**18**	**12**	**16**	**18**	**20**	**22**	**12:12**	**12:14**	**14:14**	**14:16**	**16:16**	**16:18**	**18:18**
										ng/g									
56	<RL[b]	<RL	320	27	192	159	666	48	66	135	341	3280	361	414	360	511	1830	5650	10900
61	2	8	49	0	36	23	137	53	0	41	51	726	80	90	72	119	400	1450	3460
62	5	19	140	17	83	57	253	0	26	53	95	1160	145	175	132	231	774	2460	4570
63	0	9	73	0	38	38	189	<RL	0	42	73	1120	112	124	105	178	613	2070	3800
69	<RL	<RL	35	35	120	42	72	29	<RL	16	17	178	28	34	36	67	253	1410	2650
72	<RL	<RL	285	27	81	81	660	40	17	103	115	1260	321	460	432	877	3700	11200	18900
73	<RL	<RL	578	33	326	325	1280	89	78	191	519	5270	592	680	574	875	2930	9120	16800
74	12	50	424	44	320	334	1360	53	87	165	559	6270	719	783	629	854	2500	8160	14500
75	5	22	204	27	143	143	490	0	42	86	280	2650	236	249	237	351	1163	8320	6580
79	2	<RL	25	6	15	10	36	<RL	0	<RL	21	207	17	21	22	39	145	545	997
81	2	8	72	10	54	46	164	19	12	28	78	842	80	93	84	143	514	2060	3850
85	0	<RL	24	7	29	14	47	26	15	10	21	192	21	24	26	49	186	1040	1680
87	0	0	26	8	39	21	48	14	0	8	6	84	18	24	26	51	204	1000	1520
88	<RL	<RL	62	19	59	41	97	15	<RL	20	12	130	36	44	46	94	360	1760	2840
89	0	<RL	33	9	44	23	68	21	<RL	14	21	159	31	35	35	61	223	1160	1940
93	1	<RL	15	13	38	16	24	17	18	<RL	<RL	35	14	10	16	42	171	524	967
95	0	<RL	15	13	47	12	27	17	11	<RL	<RL	55	9	11	12	33	154	515	922
102	<RL	<RL	18	16	45	18	71	12	14	<RL	<RL	115	27	32	33	82	378	1360	2140
107	0	<RL	20	12	61	15	39	12	15	0	<RL	70	15	17	20	52	244	883	1410
115			27	17	45	18	40		13	0		57	13	14	17	44	205	749	1226
105B	4	<RL	47	17	25	9	14	11	12	<RL	<RL	21	5	5	8	23	108	391	670
1B	<RL	72	520	39	462	313	1030	83	143	93	477	4530	NM[c]	650	490	812	2530	8520	13800
2B	<RL	<RL	88	<RL	51	50	199	<RL	16	13	44	487	NM	100	70	148	558	1900	3260
3B	<RL	53	488	77	458	394	881	122	207	194	450	3430	NM	387	296	503	1650	5600	9180
94B	0	<RL	20	<RL	54	12	30	14	11	<RL	<RL	50	11	11	13	37	176	648	1040
EL2	2	<RL	31	25	96	49	35	0	17	19	17	75	19	21	18	28	78	283	520
MR1	11	37	261	45	158	163	585	59	36	86	104	1350	415	321	364	785	2760	9690	14700
MR2	<RL	23	220	38	240	268	645	36	25	0	80	1170	277	327	272	507	2030	6610	9490
MR3	5	25	266	70	309	212	278	25	28	0	38	633	245	271	204	334	1170	3770	4310
NM	0	<RL	22	8	32	18	41	0	<RL	10	<RL	74	12	17	20	45	190	742	2370
Core 4, top avg	<RL	12	124	<RL	102	74	286	24	47	79	144	1532	177	196	182	255	702	3306	5281

a. Station number b. Levels measured were below reporting limits c. Individual QAC was not measured for this sample

Table 3.5. Individual QAC concentrations (ng/L or ng/g, as indicated) for samples of suspended particles

		DADMAC			**BAC**				**ATMAC**					**DTDMAC**						
Sample	**Unit**	**8:8**	**8:10**	**10:10**	**12**	**14**	**16**	**18**	**12**	**16**	**18**	**20**	**22**	**12:12**	**12:14**	**14:14**	**14:16**	**16:16**	**16:18**	**18:18**
BP Outfall 1	ng/L	<RL	2.44	19.7	3.12	16.5	19.8	103	0.67	0.13	24.6	53.0	363	24.5	23.6	21.7	30.8	78.0	238	373
BP Outfall 2	ng/L	<RL	2.82	27.4	3.60	23.6	26.6	65.7	1.43	0.44	29.2	60.7	454	29.5	28.4	23.6	33.9	83.6	262	461
BP Outfall 3	ng/L	0	0.78	11.6	0.70	13.4	16.5	29.7	0	17.9	14.5	28.2	89.5	11.1	8.76	8.96	7.83	<RL	87.4	141
BP Outfall 4	ng/L	0	0.85	9.59	0.61	11.6	13.5	25.0	0	17.3	11.5	20.5	140	9.14	6.44	6.75	9.25	22.0	73.2	120
BP Outfall 5	ng/L	0	2	15.6	2.00	18.2	15.7	41.8	0.45	22.2	19.2	45.6	542	23.9	16.9	16.1	18.2	92.2	245	373
BP Outfall 5	*ng/g*	*40.2*	*256*	*2089*	*267*	*2436*	*2092*	*5576*	*60.5*	*2970*	*2566*	*6086*	*72370*	*3186*	*2257*	*2148*	*2424*	*12304*	*32760*	*49845*
BP Outfall 6	ng/L	0.35	2.18	14.4	2.31	19.9	15.8	37.1	0.45	22.5	18.1	42.1	400	20.6	16.3	11.6	19.7	78.8	219	355
BP Outfall 6	*ng/g*	*47.3*	*295*	*1950*	*312*	*2690*	*2140*	*5020*	*61.2*	*3040*	*2450*	*5690*	*54100*	*2790*	*2210*	*1570*	*2660*	*10700*	*29600*	*48000*
Oil City	ng/L	0	0	1.08	0	0	0	0	0	0	<RL	2.00	19.7	<RL	<RL	0.64	1.26	4.61	16.5	31.3
Hewlett Bay	ng/L	0		0.34	0.31	1.11	0.40	0.84	0.17	0.73	1.06	0.83	12.4	0.66	0.86	0.79	2.30	8.50	33.4	50.4
Hewlett Bay	*ng/g*	*0*	*<RL*	*63.0*	*58.5*	*208*	*75.3*	*158*	*31.6*	*136*	*199*	*156*	*2320*	*124*	*161*	*148*	*432*	*1600*	*6270*	*9460*

Table 3.6. Ratio of the composition of the suspended sediment sample over the average composition in the sediment. Values in parentheses are for samples with TSS data and are the concentrations on the suspended sediment divided by the concentrations in the underlying sediment.

Sample	DADMAC		BAC				ATMAC					DTDMAC						
	8:10	**10:10**	**12**	**14**	**16**	**18**	**12**	**16**	**18**	**20**	**22**	**12:12**	**12:14**	**14:14**	**14:16**	**16:16**	**16:18**	**18:18**
BP Outfall 1	1.01	1.25	0.76	1.14	1.93	3.79	0.41	2.96	4.50	2.32	1.63	1.73	1.15	1.25	1.20	1.13	1.04	NA[a]
BP Outfall 2	0.95	1.41	0.72	1.31	2.10	1.96	0.72	3.24	4.33	2.16	1.65	1.69	1.12	1.11	1.07	0.98	0.93	NA
BP Outfall 3	0.86	1.95	0.45	2.44	4.27	2.90	ND[b]	8.24	7.02	3.27	1.07	2.08	1.13	1.37	0.81	ND	1.01	NA
BP Outfall 4	1.09	1.89	0.46	2.47	4.10	2.86	ND	9.34	6.51	2.79	1.95	2.01	0.98	1.21	1.12	0.99	0.99	NA
BP Outfall 5	0.80 (2.07)	0.99 (2.37)	0.49 (1.07)	1.25 (3.17)	1.53 (3.88)	1.54 (3.85)	0.28 (0.77)	3.87 (9.47)	3.51 (8.78)	2.00 (4.94)	2.44 (5.87)	1.69 (3.15)	0.82 (2.10)	0.93 (2.33)	0.71 (1.79)	1.34 (3.40)	1.07 (2.72)	(2.55)
BP Outfall 6	0.95 (2.39)	0.96 (2.21)	0.59 (1.24)	1.44 (3.50)	1.63 (3.97)	1.44 (3.46)	0.29 (0.78)	4.12 (9.71)	3.48 (8.39)	1.94 (4.62)	1.89 (4.38)	1.53 (2.76)	0.84 (2.05)	0.71 (1.71)	0.81 (1.96)	1.20 (2.95)	1.00 (2.46)	(2.45)
BP Outfall Average	**0.94**	**1.41**	**0.58**	**1.68**	**2.59**	**2.42**	**0.43**	**5.29**	**4.89**	**2.41**	**1.77**	**1.79**	**1.01**	**1.10**	**0.96**	**1.13**	**1.01**	**2.50**
BP Outfall Std Dev	**0.10**	**0.39**	**0.12**	**0.56**	**1.14**	**0.84**	**0.18**	**2.52**	**1.38**	**0.47**	**0.41**	**0.19**	**0.14**	**0.22**	**0.19**	**0.13**	**0.04**	**0.05**
Oil City	ND	1.19	ND	ND	ND	0.15	ND	ND	ND	1.66	1.46	ND	ND	0.47	0.68	0.86	0.94	NA
Hewlett Bay	ND	0.28 (0.51)	ND	1.14 (2.04)	0.57 (1.02)	0.31 (0.55)	0.74 (1.32)	1.62 (2.90)	1.41 (2.52)	0.61 (1.08)	0.85 (1.51)	0.39 (0.70)	0.46 (0.82)	0.46 (0.82)	0.95 (1.69)	1.27 (2.27)	1.06 (1.90)	(1.79)

a. NA enrichment values for DTDMAC 18:18 are not available as data is normalized to DTDMAC 18:18 b. The individual QAC was not detected in this sample.

Table 3.7. P-values calculated from the ANOVA analysis of individual QACs normalized to DTDMAC 18:18 versus distance. Samples included are only those with Fe values greater than 2.25%. The test has been performed for all of the data and then with the data split into east and west of Jones Inlet. Significant results are highlighted in grey (p value ≤ .05).

Compound	All of HB	W of Jones Inlet	E of Jones Inlet
DADMAC 8:8	0.703		
DADMAC 8:10	1.30E-04		
DADMAC 10:10	1.43E-06	5.72E-06	0.305
BAC 12	0.193	0.965	0.020
BAC 14	0.800	0.447	0.005
BAC 16	9.12E-06	0.0103	0.367
BAC 18	3.79E-07	4.21E-04	0.539
ATMAC 12	2.69E-04		
ATMAC 16	0.407		
ATMAC 18	0.109		
ATMAC 20	1.38E-05		
ATMAC 22	8.09E-08	3.54E-07	0.793
DTDMAC 12:12	3.59E-08	3.76E-09	0.005
DTDMAC 12:14	5.06E-10	1.52E-09	0.021
DTDMAC 14:14	8.58E-09	1.90E-08	0.450
DTDMAC 14:16	1.11E-07	3.15E-09	0.124
DTDMAC 16:16	0.042	1.71E-04	0.006
DTDMAC 16:18	0.467	0.918	0.129

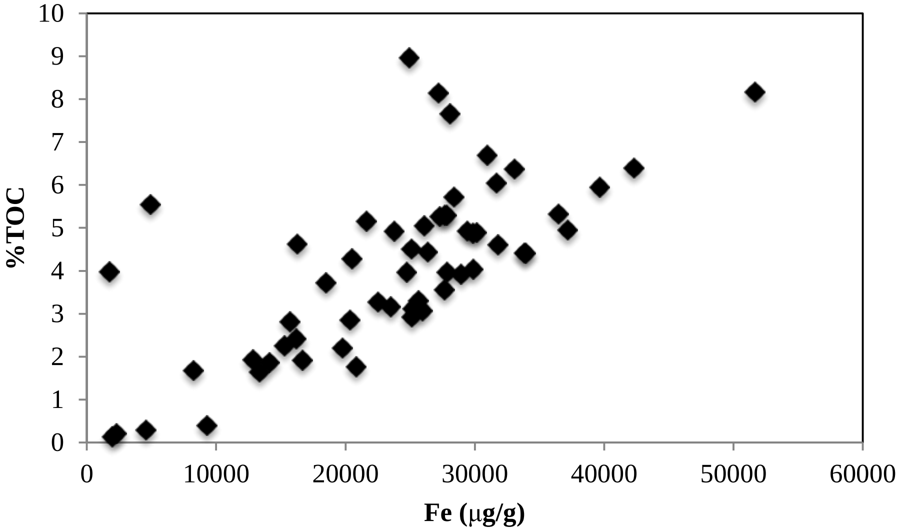
Figure 3.1 a) Sample locations for sediment grabs taken in Hempstead Bay and South Oyster Bay, NY as well as labels of major regions within Hempstead Bay. b) Locations of suspended solid samples taken in West Bay (yellow dots) as well as the outfall locations of the region's STPs (red dots). Suspended solids taken from the BPO are not indicated but were sampled in the outfall plume.

a)

b)

Figure 3.2. a) TOC (%) and b) volume weighted mean particle diameter (µm) versus Fe (µg/g).

a)



b)

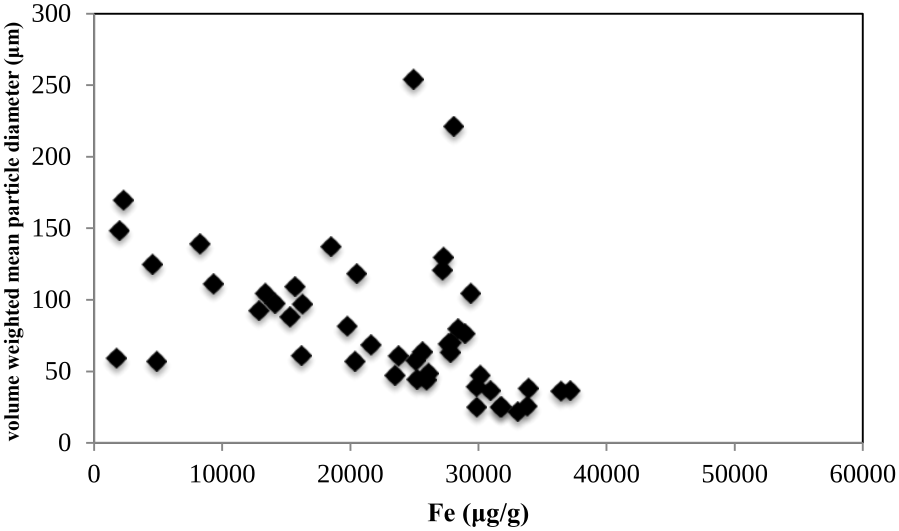


Figure 3.3. Grain size distributions for all samples, separated into classes with relatively distinct particle size distributions. The x-axis corresponds to the Krumbein phi scale ϕ, a modification of the Wentworth particle size scale. (Figure from Brownawell et al., 2013)

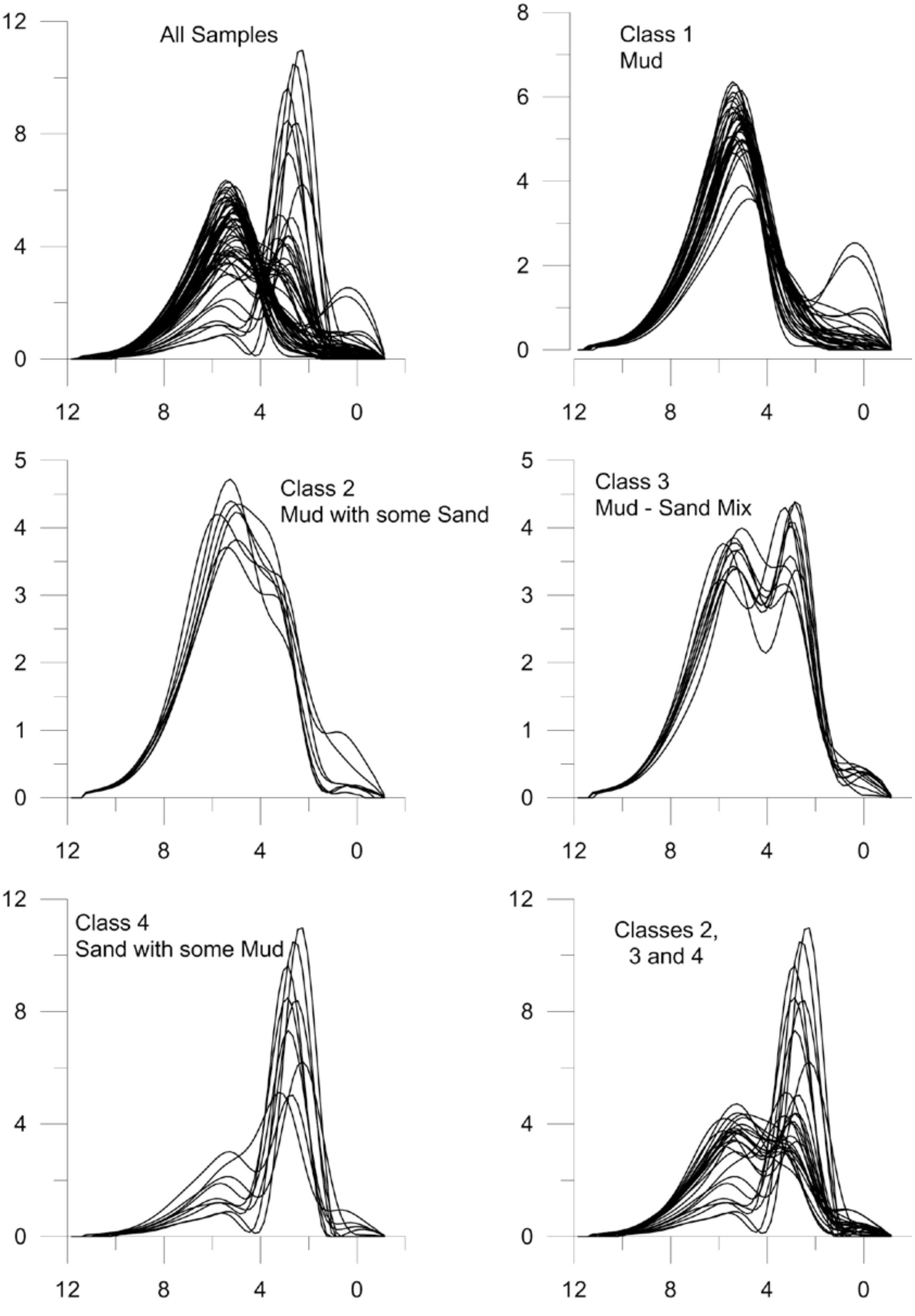


Figure 3.4 a)%TOC normalized to Fe plotted versus distance from the Bay Park STP outfall for all samples. b) the same data, but with a truncated y-axis to remove the two outliers.

a)

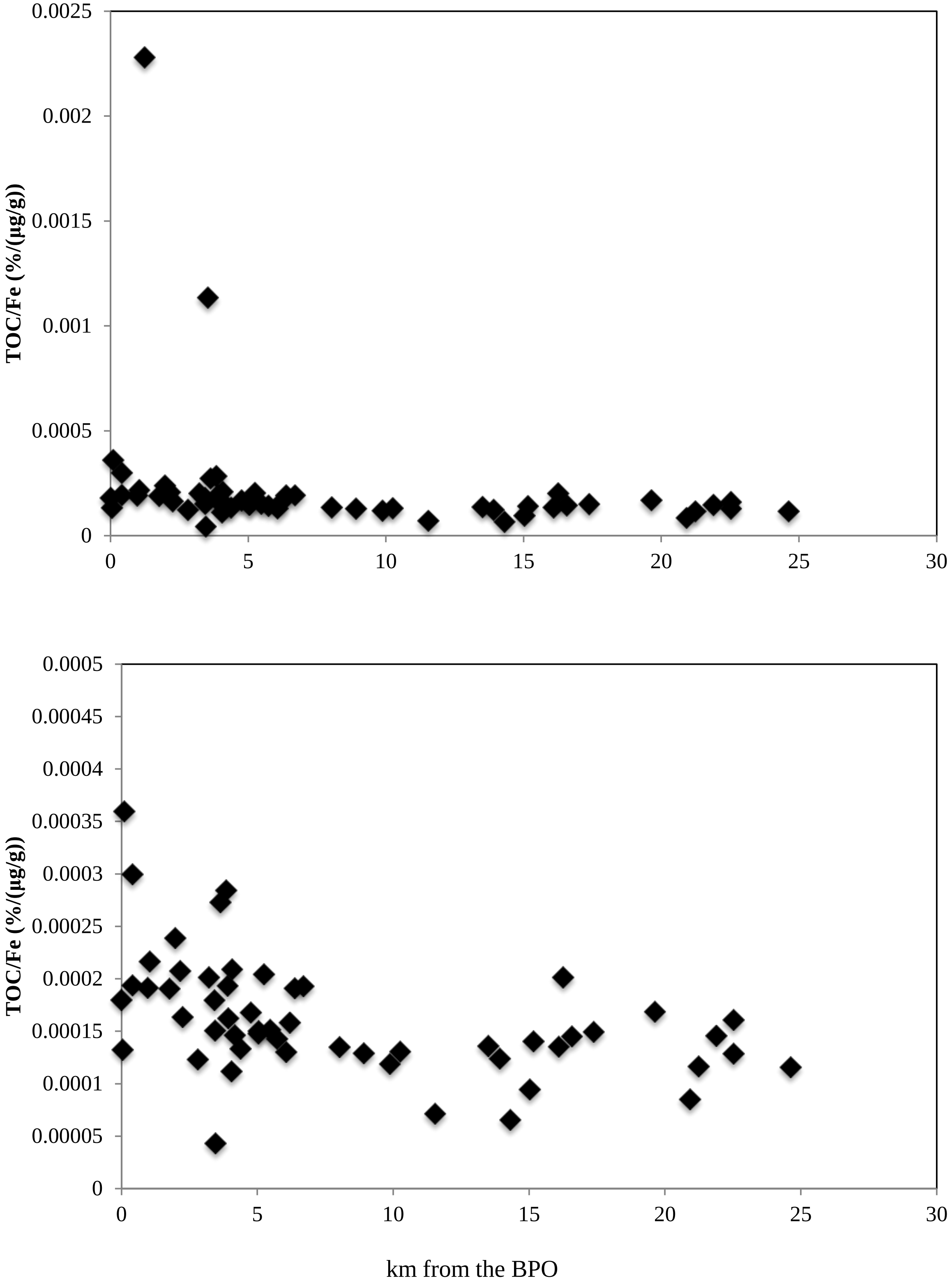


Figure 3.5. The ratio of TOC to TON plotted versus distance from the Bay Park STP outfall. Data points are those with Fe values greater than or equal to 2.25%. Samples from Mill River are noted with open black diamonds.

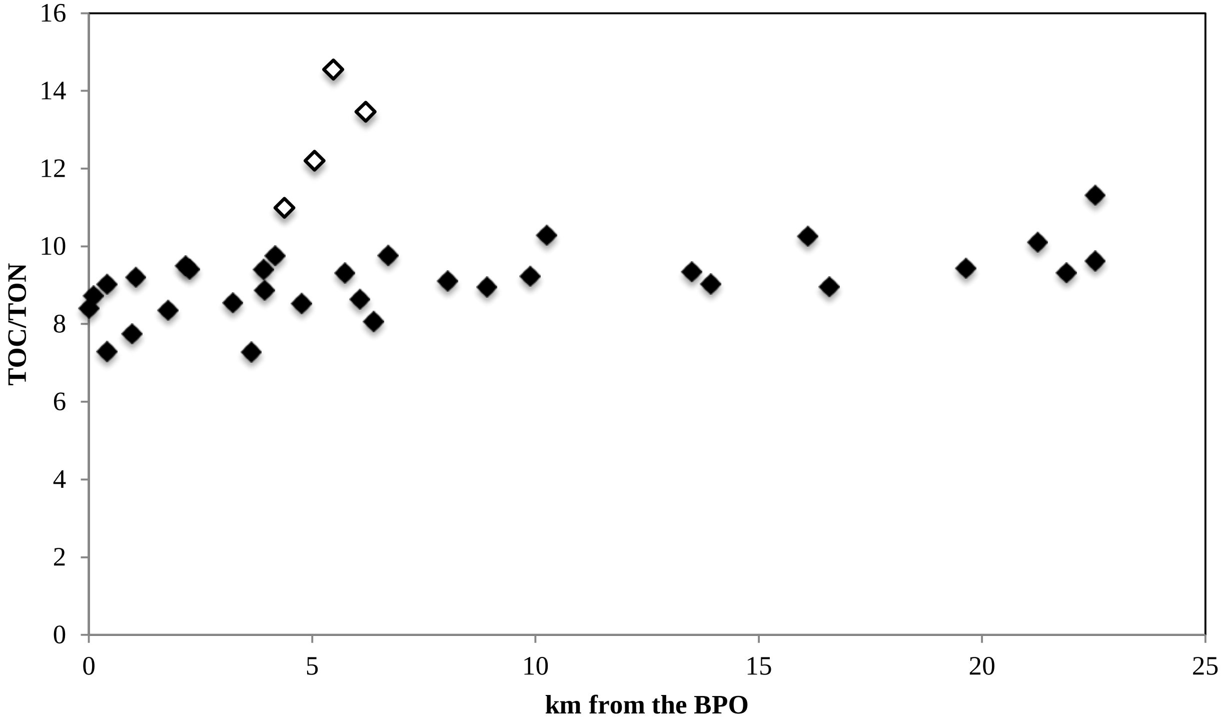


Figure 3.6. a) Total QACs (ng/g) in Hempstead Bay versus distance from the Bay Park outfall. b) Total QACs (ng/g) normalized to iron versus distance from the Bay Park outfall with the two outliers removed. c) Total QACs normalized to %TOC. d) Total QACs normalized to Fe for samples with Fe > 2.25%. Different sections of the Bay are differentiated with symbols.

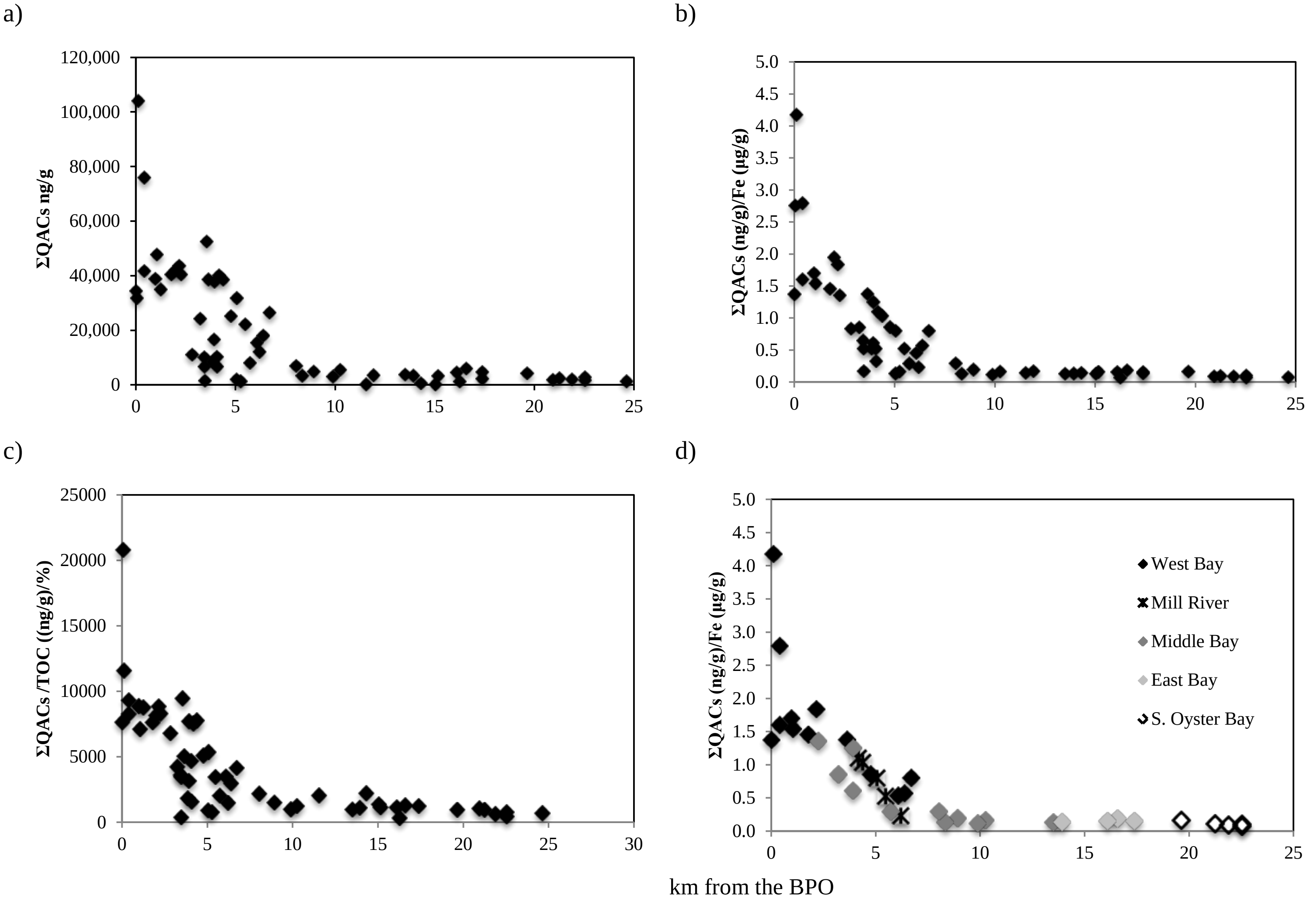


Figure 3.7. Total QAC concentrations normalized to %TOC in Hempstead Bay and other surrounding sewage impacted systems. The box represents the 25th to 75th percentile, and the line in the middle of the box represents the median, while the black dot represents the mean concentration of QACs in the system. Whiskers represent the 10th and 90th percentile.

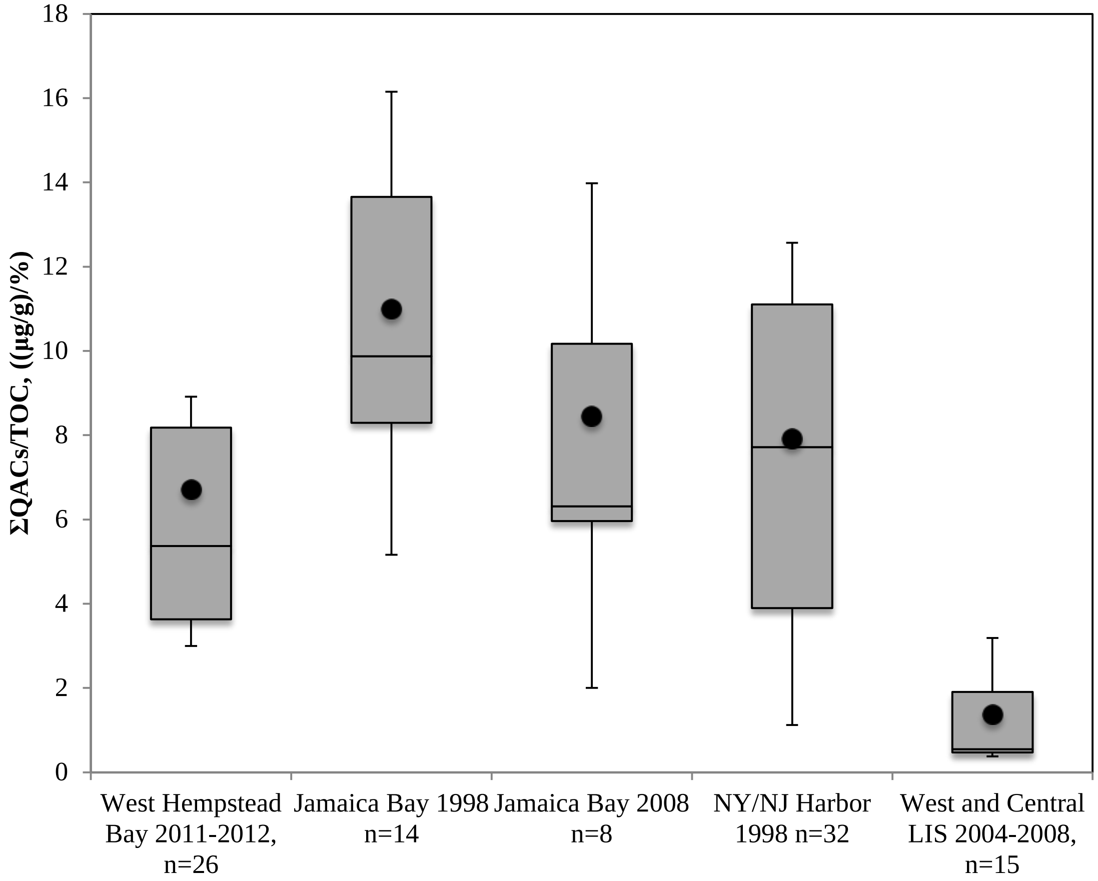


Figure 3.8. Samples with Fe > 2.25% for samples east of Jones Inlet (greater than 10km from the Bay Park STP outfall).

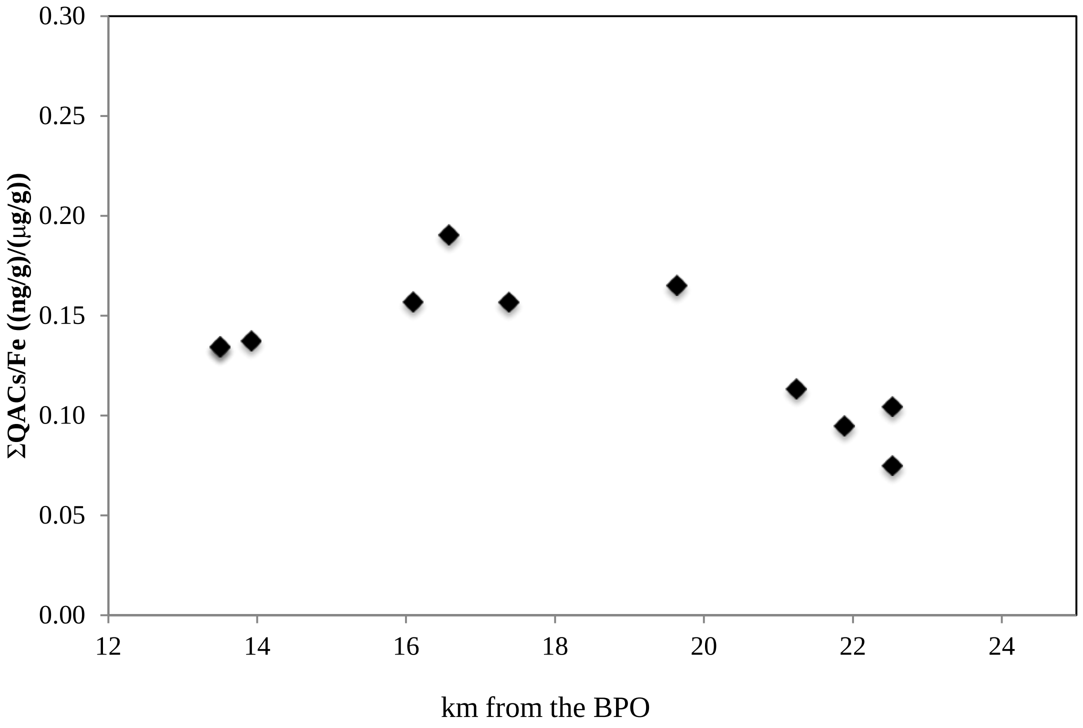


Figure 3.9. DTDMAC 18:18 divided by TAMAC 16:18:18 plotted against distance from the BPO (km).

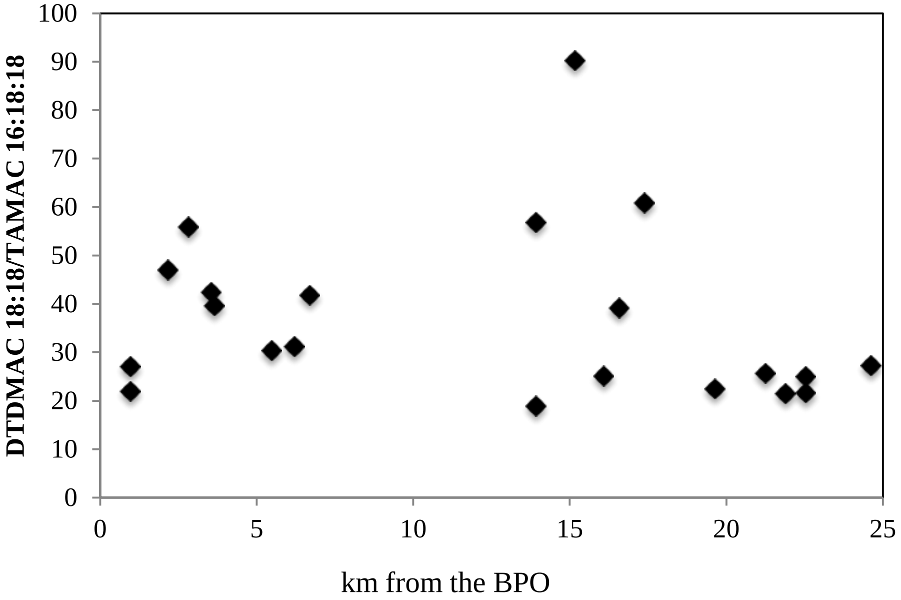


Figure 3.10. Individual QACs normalized by DTDMAC 18:18 in grab samples (black diamonds), suspended solid samples (open black diamonds) versus distance from the BPO. Samples plotted have Fe values greater than 2.25%, Mill River samples have been removed. The averaged top portions of Core 4 (Table 3.1) are also included for comparison purposes.

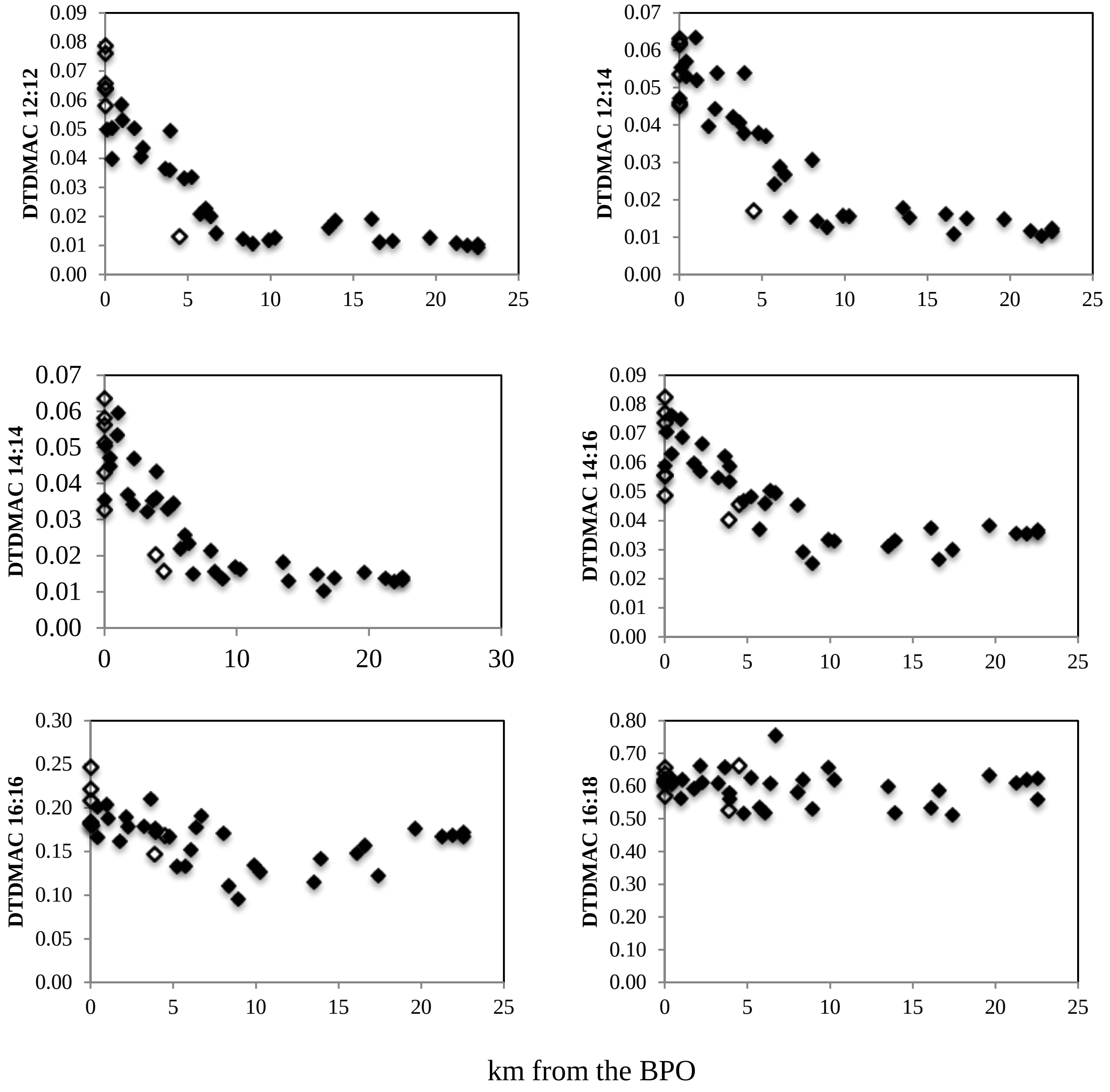


Figure 3.10. continued

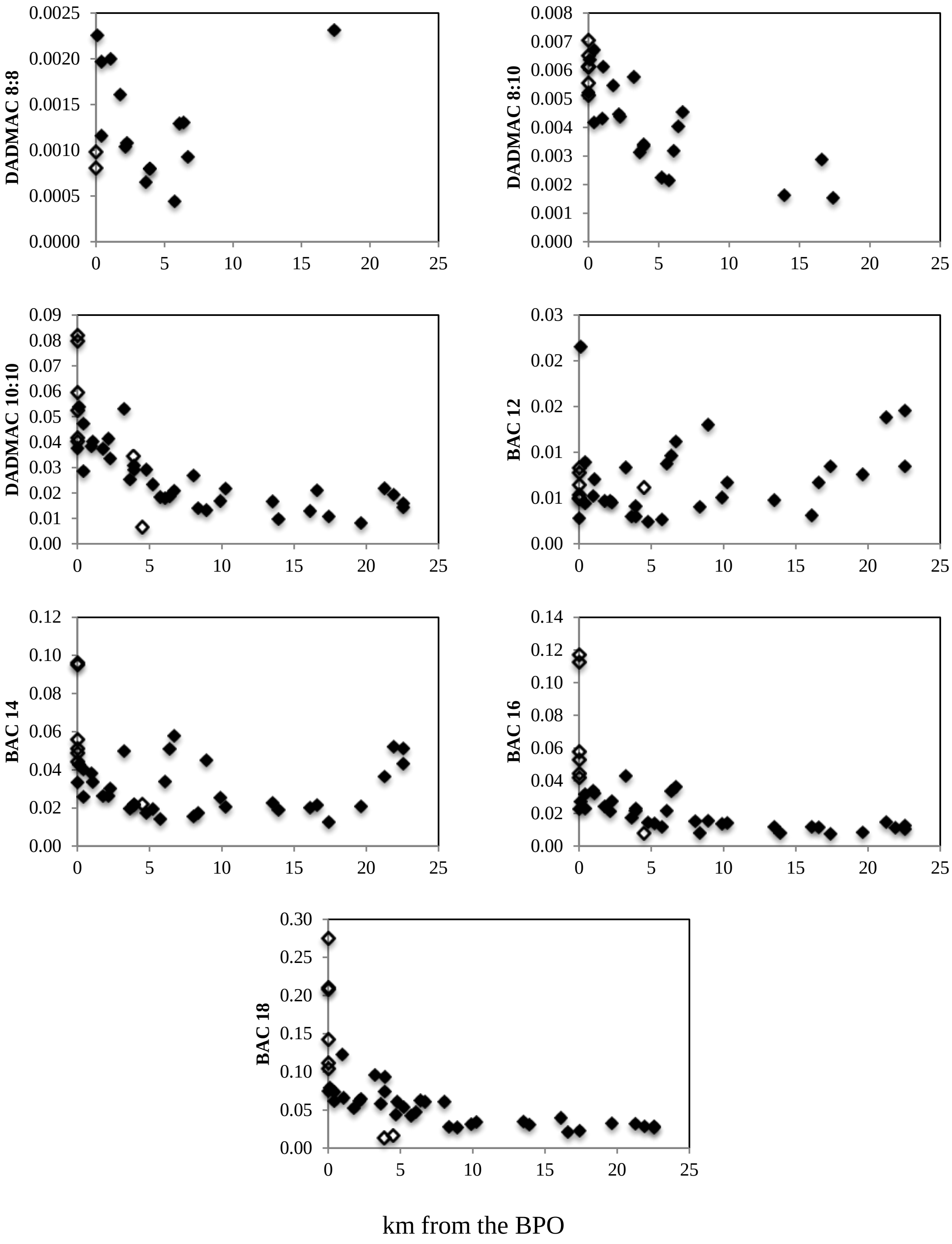


Figure 3.10. Continued

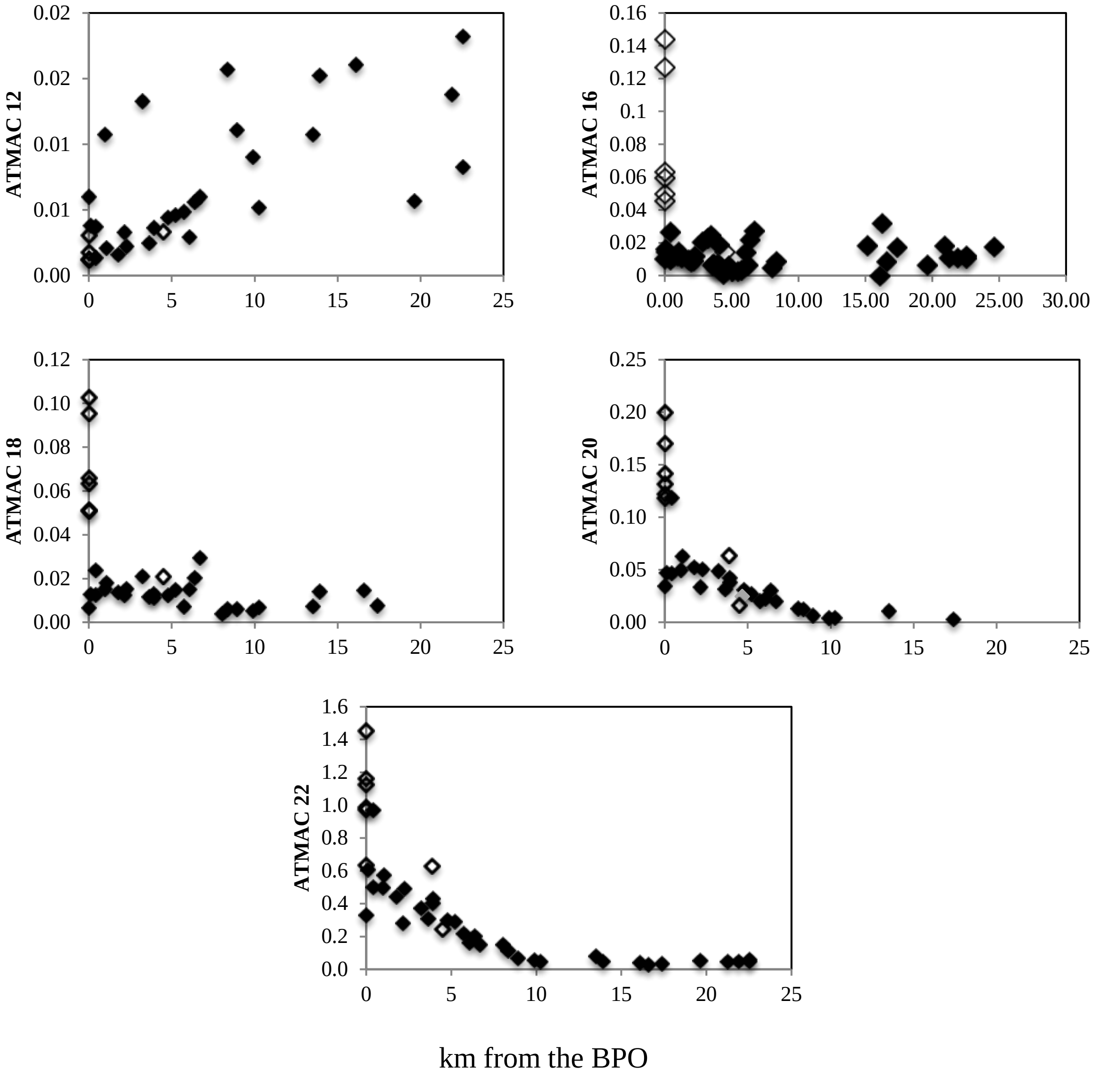


Figure 3.11 Enrichment of QACs on sewage affected suspended particles relative to underlying bedded sediments as a function of critical micelle concentrations (CMC, mM). The concentration of each QAC relative to DTDMAC 18:18 on filters from the BPO ($R_{filters}$) divided by the relative composition in the average of the underlying sediment samples ($r_{sediment}$).

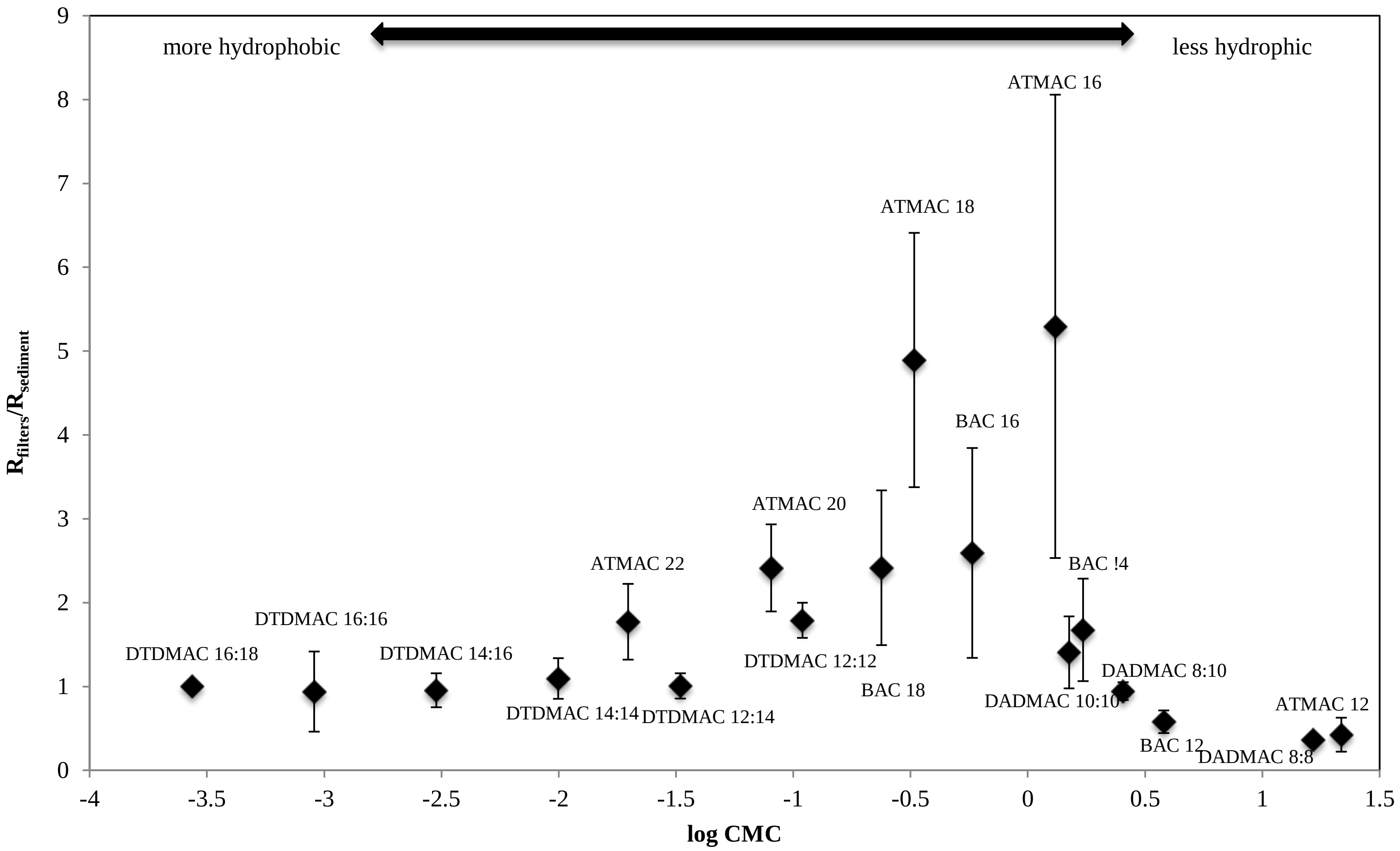


Figure 3.12. The relative composition of individual QACs normalized to DTDMAC 18:18 in sediments from Hempstead Bay (black diamonds) and LIS (2008, grey diamonds; 1998 and 2004 samples, open diamonds) with distance (km) from a major sewage source. Data for LIS can be found in Chapter 2 of this thesis. The 1998 and 2004 samples from LIS are heavily CSO impacted. Negative distances represent samples taken in East River west of the Tallman Island STP outfall.

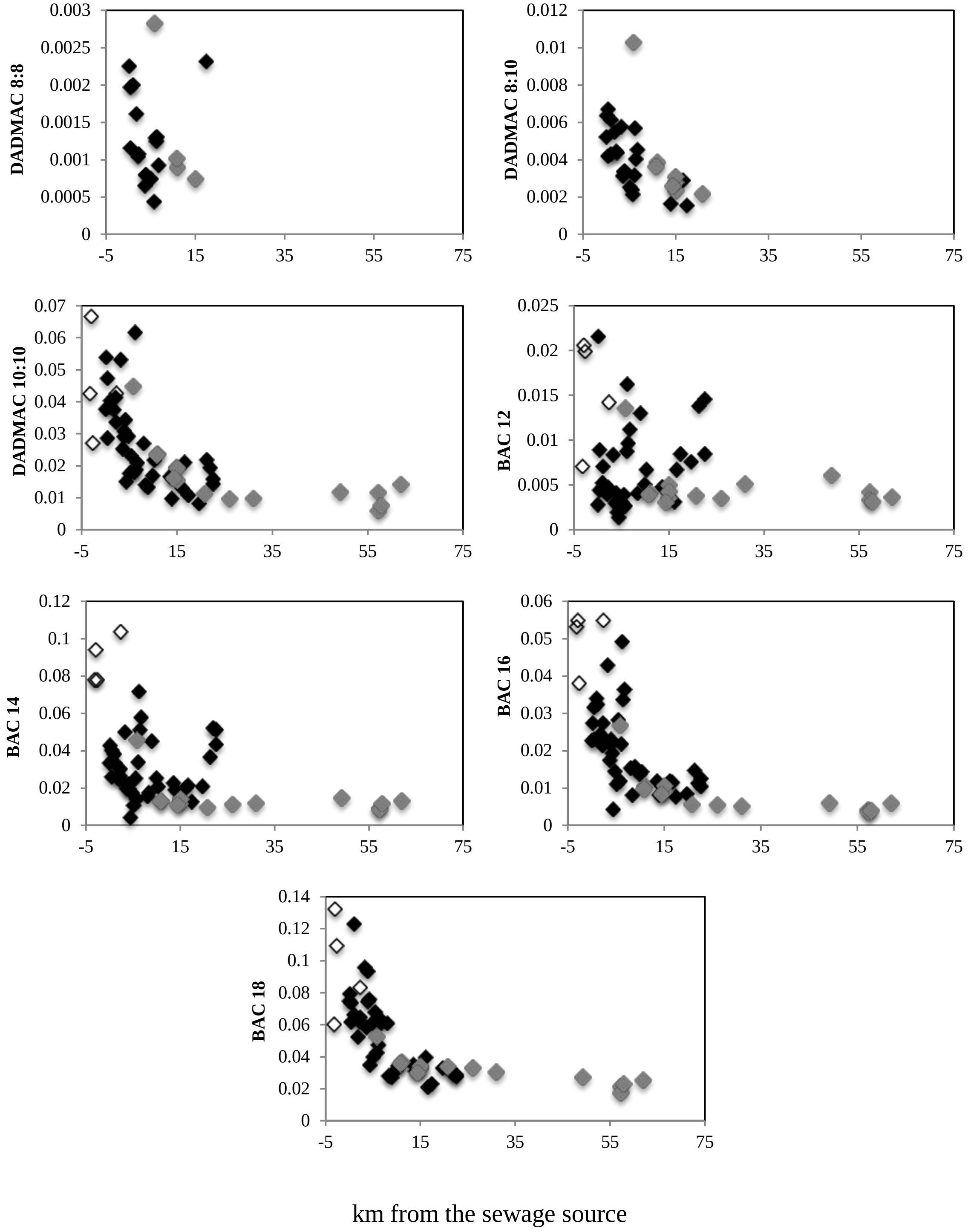


Figure 3.12 continued

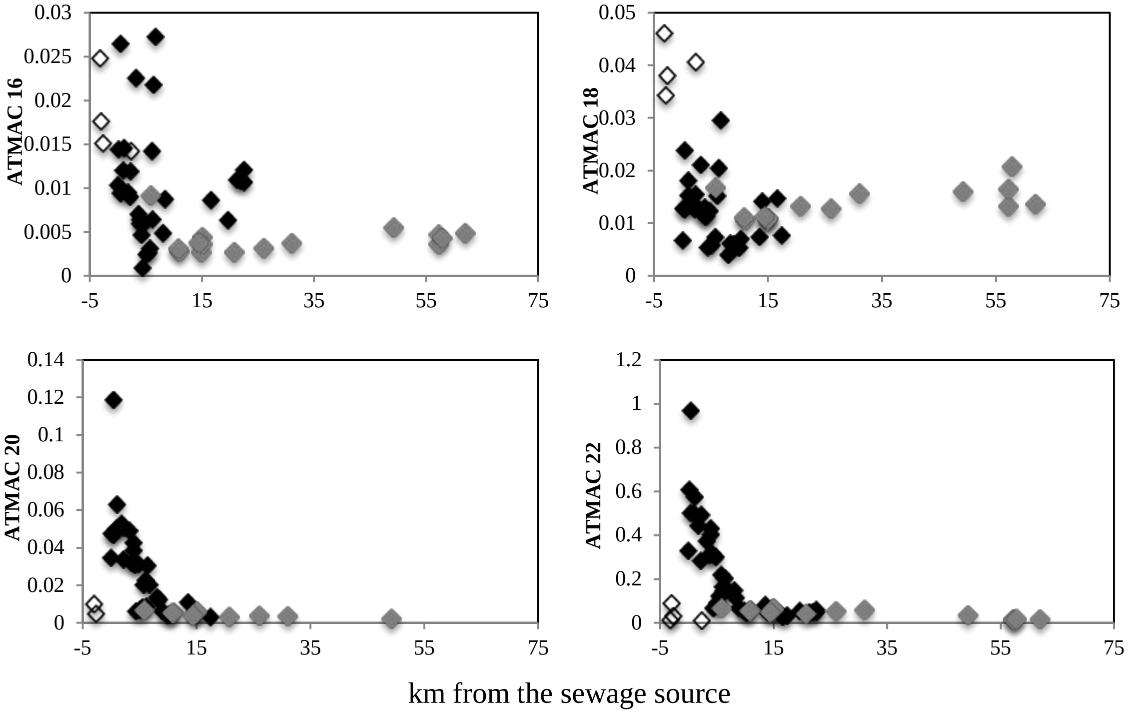
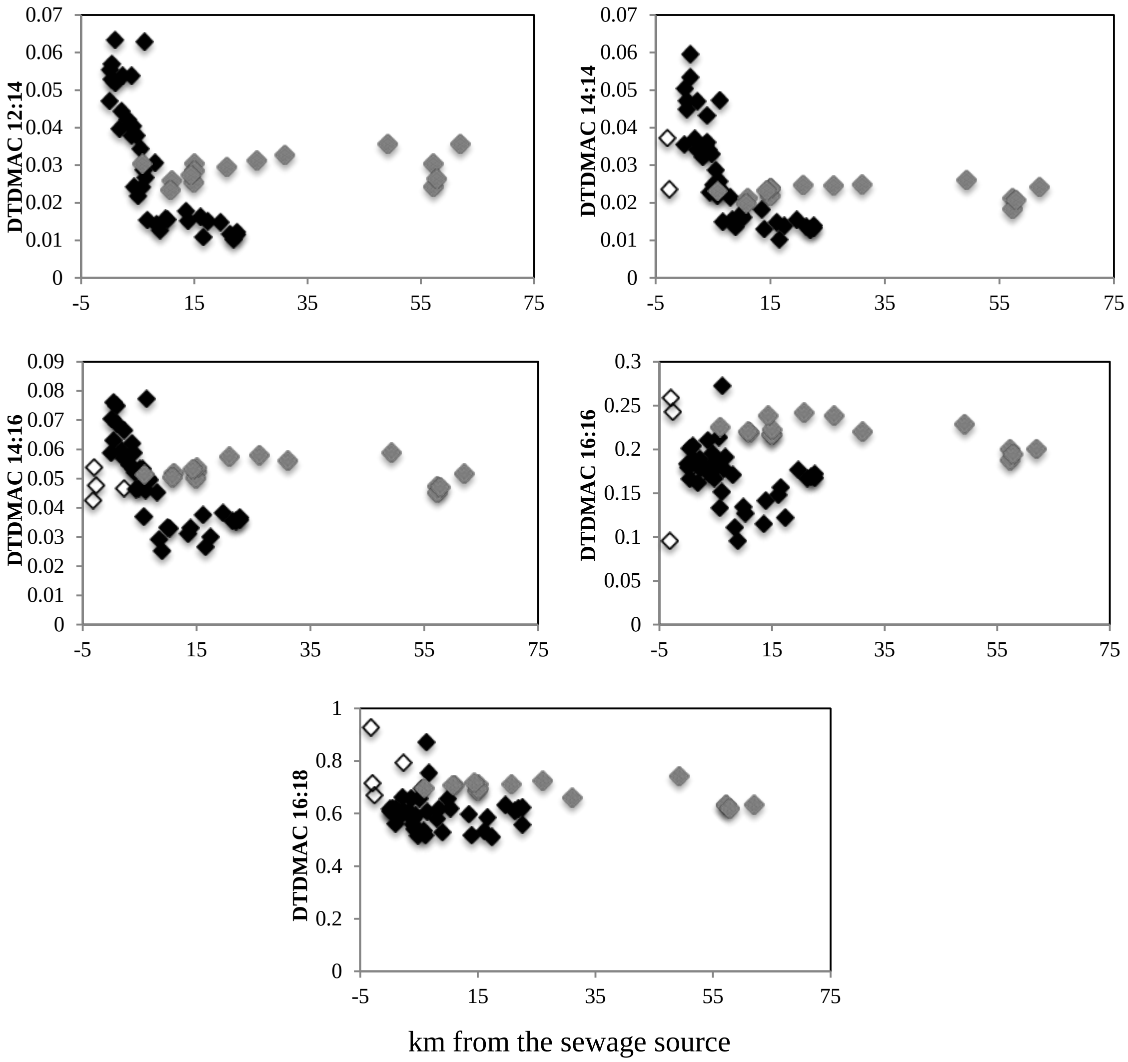


Figure 3.12. continued



CHAPTER 4: Geochronologies of quaternary ammonium compounds in sedimentary cores from sewage impacted, coastal New York estuaries.

4.1 Introduction

Quaternary ammonium compounds (QACs) are cationic surfactants that have been measured at very high concentrations relative to other well known organic contaminants in sewage-impacted estuaries (Li, 2009; Li and Brownawell, 2010). QACs are thought to be persistent in these environments (Li, 2009; Li and Brownawell, 2010), and while they are of concern due to high environmental concentrations, QACs have also been suggested as particle reactive tracers of sewage. In this study, sediment cores from two basins along the south shore of Long Island have been examined to better understand the persistence of these compounds once deposited in sediments as well as to gain insight into possible recent changes in production or use patterns.

Homologous series of three structurally distinct classes of QACs are considered in this study. Benzylalkyl dimethyl ammonium compounds (BACs) have only one long alkyl side chain (C12 to C18) as well as a benzyl group and are primarily used as biocides, sanitizers, and disinfectants (Boethling, 1984). Alkyltrimethyl ammonium compounds (ATMACs) have three methyl groups and one long alkyl side chain that can range from 12 to 22 carbons long. ATMACs are used as antimicrobials and in personal care products as well as in industrial applications (Lara-Martín et al., 2010; Li, 2009; Madsen et al., 2001). Dialkyldimethyl ammonium compounds (DADMACs) have two long side chains, and the class is often divided into two groups: DADMACs, which have side chains between 8 and 10 carbons long, and ditallowdimethyl ammonium compounds (DTDMACs) with side chains 12 carbons and longer. DADMACs are generally used in biocides and disinfectants, while DTDMACs are primarily found in products such as fabric softeners (Cross and Singer, 1994; Fernández et al., 1996; Schaeufele, 1984). DTDMACs are the largest and most hydrophobic of the QACs that have been targeted in this study.

As described by Li (2009), data on the production of QACs in the United States is difficult to obtain due to differences in nomenclature as well as changes in industry reporting requirements. Based on data from the United States International Trade Commission as well as a small number of geochronologies from Li (2009), some trends and first appearances have been established. BACs are the oldest of all of the QAC and were first discovered in the 1930's before the they were used in products beginning in the late 1940's (Schaeufele, 1984). USITC data (Table 4.1) also suggests an increase in BACs from the mid 1970's that continued until records stopped in the 1994. DTDMACs were first produced in the mid 1950s (Table 4.1, Levinson, 1999), with production peaking in the late 1980's followed by a decrease coinciding with a voluntary phase out of DTDMACs in Europe (Table 4 .1, Fernández et al., 1996). While sufficient detail is not available in recent industry data, geochronologies suggest that production has most likely remained relatively constant over the past several decades (Li, 2009). Smaller DADMACs were introduced as disinfectants in 1965 (Li, 2009) and geochronologies from Li's 2009 study suggest that release to the environment of these compounds may have continued to increase in use in recent years. ATMACs 16-18 tend to mirror trends of larger DTDMACs, although literature suggests first uses of these compounds (1940's) that precede the introduction of DTDMACs (Cruickshank and Squire, 1949; Li, 2009). ATMAC 20 and ATMAC 22, termed behentrimonium, have undergone an exponential increase in production over the last three decades related to their use in hair care products (Lara-Martín et al., 2010; Scientific Communication on Consumer Products, 2007).

The environmental persistence of QACs is important to understand not only due to high concentrations measured in the environment, but also because the largest QACs have been suggested as particle reactive sewage tracers that can be used to understand sources of other contaminants and lateral transport. Because of differences in loadings and composition as a function of time, QACs may also make excellent tools for sediment geochronology studies, both as time markers and as indicators of mixing. The extent to which individual QACs are deposited and then preserved in coastal sediments is a function of biodegradability, and it is known that more hydrophobic QACs are less biodegradable due to strong sorption to particles, the importance of which can be magnified at lower environmental concentrations due to strongly nonlinear sorption isotherms (Brownawell et al., 1990; Li and Brownawell, 2010). A number of studies have been conducted to understand the potential for biodegradation of QACs in the environment, although the results from these studies are often conflicting. A literature review (Ying, 2006) indicates that while oxic biodegradation is possible for QACs in spiked experiments, with biodegradation potential increasing as the length of the alkyl side chain decreases, QACs appear to be relatively persistent under anaerobic conditions. In sewage treatment plants (STPs), mass balances indicate that sorption of the largest QACs to particles is so strong that biodegradation does not occur, suggesting similar processes to be minimal in the environment (Clara et al., 2007). In addition, the importance of biodegradation in STPs is expected to increases as alkyl chain length decreases (Clara et al., 2007).

In the few environmental studies conducted to date, larger QACs have been suggested to be extremely persistent in the marine environment. Li (2009) noted relatively constant compositions of the largest QACs in the lower Hudson Basin that was suggested to provide evidence for stability and persistence in surface sediments. In Chapter 2 of this thesis, QACs were shown to persist over 70 km from major sources, with compositions of individual QACs remaining relatively constant, particularly for the largest QACs. QACs have also been found to be persistent in samples analyzed at a deep-water dumpsite 106 miles off of the New Jersey coast (Li, 2009). Core studies that utilized a limited number of comparisons from age matched cores indicate that down core, the four major classes of QACs are persistent in sewage impacted, highly depositional environments following burial (Li, 2009), although this does not rule out degradation in upper portions of the core. In addition, comparisons of DTDMAC 18:18 with the QAC impurities trialkylmethyl ammonium compounds (TAMACs), which are even larger and more persistent, indicate that DTDMAC 18:18 is very stable in sewage-impacted environments (Chapter 3).

While a small number of geochronologies have been analyzed for QACs (Lara-Martín et al., 2010; Li, 2009), studies from regions that have not experienced significant upgrades in treatment over time are lacking, as are studies examining sediment core profiles at distances removed from a primary source. In this study, sediment cores taken from two sewage-impacted bays on the south shore of Long Island, NY provide comparisons between two nearby embayments that have experienced different histories of sewage treatment. In addition, a core taken 15.5 km away from the dominant sewage source is also presented. Cores were investigated for trends in concentration and composition that can inform whether sediment depositional histories are preserved in selected muddy areas of Hempstead Bay and Jamaica Bay as well as provide more insight into the changes in the historical production of QACs. In contrast to cores studied in the past, the extent of secondary sewage treatment from Hempstead Bay sewage treatment plants has remained very similar since the area was sewered in 1951 and 1952 and it receives no CSO discharges. Geochronologies of cores taken in Jamaica Bay (JB), one beside a sewage outfall and one near a major CSO outfall, provide insight onto the affect of sewage treatment on QACs in the environment, both as a function of CSO inputs as well as STP upgrades that have occurred in JB. By combining data from Li (2009) with new Jamaica Bay cores presented in this study, we compare cores taken in the same location over 20 years to better understand the *in situ* behavior of QACs in Jamaica Bay. Geochronologies between bays are also compared to look for evidence of source changes.

4.2 Experimental

Core Locations and Sampling

Hempstead Bay (HB) is a heavily sewage impacted coastal lagoon located along the south shore of Long Island, NY that receives almost 60 million gallons per day (MGD) of treated wastewater. The largest of the STPs, Bay Park, came online in 1952 (Swanson, 2011), coinciding closely with the first appearances of QACs, and has been discharging at a fairly constant rate for the last 30 years, with current discharges of 49.9 MGD (Interstate Environmental Commission, 2010). This plant represents the largest source of sewage to the Bay. The second largest plant, Long Beach STP, was built in 1951 and discharges 5 MGD and is located 1km away from the Bay Park STP outfall (BPO), with these two plants creating a point source of sewage to the rest of Hempstead Bay. While there are three additional STPs that discharge into Hempstead Bay, these plants are much smaller than Bay Park STP and Long Beach STP and are either hydrodynamically separated from the rest of the Bay or represent only a very small, seasonal input (more details are available in the introduction of this dissertation). The concentrations and compositions of QACs measured within Hempstead Bay vary spatially (Chapter 3), and sediment core locations were selected at different distances from the BPO to characterize the history of inputs in different regions of the Bay. These cores represent the first geochronologies of QACs in a region that has received continuous input of sewage effluent from STPs that have undergone no major upgrades.

Hempstead Bay cores were collected on April 26, 2011 using a gravity corer on the R/V Pritchard (Table 4.1, Figure 4.1). The sediment water interface was thought to be successfully captured based on observations of a very thin surface oxic layer, as oxygen is not thought to penetrate very deeply in these environments, as well as visual inspections indicating the sediment surface had not been extensively disturbed. HB Core 1 was taken at the BPO while HB Core 2 was taken adjacent to an old sewage sludge loading facility located approximately 2.2 km north of the BPO (Figure 4.1). This sampling location was chosen to investigate the possibility that a 1976 explosion of sludge storage tanks at this facility represents a past or continuing source of QACs to West Bay. HB Core 3 was taken farther from the BPO (3.7 km) in the northern region of West Bay in an area that was expected to be highly depositional and heavily sewage-impacted based on previous sampling (Chapter 3). HB Core 11 was taken 15.5 km away from the BPO at the far northeastern edge of the East Bay portion of Hempstead Bay in a deeper area that prior grab samples suggested might be seasonally hypoxic and highly depositional. HB Core 11 also served as an end member for a site that had appreciably different QAC compositions in surface sediments (Chapter 3). While multiple cores were obtained from these and other sites, the four selected for QAC analysis were chosen based on differences in proximity to sources, length of the cores, and interpretations of x-radiographs of the cores to look for layering that would be indicative of high rates of burial and a lack of bioturbation (Appendix A3).

Cores were immediately frozen upon return to the lab and stored until sectioning. Radiographs were obtained before sectioning. Cores were allowed to slightly thaw before being sectioned using a solvent-washed serrated knife at 2cm increments from the surface to 30cm, and 4cm increments below 30cm. Samples for QAC analysis were stored in solvent washed glass jars and frozen until analysis while samples for radiochemistry were immediately weighed to get initial weights for water content.

Two additional dated sediment cores from Jamaica Bay were also analyzed in this study. Ten JB sediment cores collected in 2008 and geochronologies were characterized using ^{210}Pb and ^{137}Cs by Renfro, Cochran and colleagues (Renfro et al., 2010). The two cores analyzed for QACs were selected based on proximity to sewage effluent locations as well as ^{210}Pb geochronologies that indicated high rates of accumulation. JB Core 4 is located very near the outfall of the Jamaica plant discharging 80 MGD, while JB Core 7 is located very near the mouth of a creek dominated by the Paerdegaart Basin combined sewage overflow (CSO), one of the biggest CSO outfalls in New York City (Table 4.1, Figure 4.2). Core 4 was also analyzed because it is from Grassy Bay and very close in location to two cores collected in 1988 and 1996 with previously published data on nonylphenol ethoxylate metabolites (Ferguson et al., 2003) and QACs (Lara-Martín et al., 2010; Li, 2009). Jamaica Bay receives over 200 MGD of sewage, with upgrades to the Jamaica Bay sewage treatment plant occurring in 1963 and 1978. A more extensive review of Jamaica Bay and the sewage treatment plants in the Bay is provided in Ferguson (2003) and Li (2009) as well as in the introduction of this dissertation.

Sampling and sectioning information for Jamaica Bay cores taken in 1988 and 1996 are described elsewhere (Li, 2009). JB cores taken in 2008 were collected in August using a gravity corer on the R/V Pritchard with locations listed in Table 4.1 and shown in Figure 4.2. Cores were immediately frozen upon return to the lab. Cores were sectioned at 2cm intervals from the surface to 20cm, 4cm intervals from 20cm to 48cm, and 8cm intervals for the remaining length of the core.

QAC analysis

QACs were analyzed for the 2008 JB cores as described by Li and Brownawell (2009) and Lara-Martin et al. (2010). HB cores were analyzed for QACs using a similar method as described in Appendix A1, a variation of Li and Brownawell (2009) and Lara-Martin (2010). The two differences from previously published methods include the use of deuterated DTDMAC 12:12 as a surrogate standard as well as the use of only one machine run for all analytes. Sample recovery was based on spiked deuterated DTDMAC 12:12 and recoveries averaged 82% ± 18%. Precision for total QACs was based on extractions run in triplicate for a subset of samples and averaged 6.2% ± 5.5%.

^{210}*Pb Analysis and Dating*

Dried sub samples from each core section were ground using a mortar and pestle and stored in a 30 mL screw top Nalgene HDPE jar for counting. Samples were counted on a Canberra 3800 mm^2 germanium detector for 2-3 days to obtain sufficient counts such that estimated counting error was reasonable. Total ^{210}Pb activity was determined from the ^{210}Pb decay at 46.5 keV while the supported ^{210}Pb activity was determined from ^{214}Pb (a daughter of ^{226}Ra) at 352 keV. For the ^{210}Pb peak, counting efficiencies and a self-adsorption correction were determined using liquid standards of varying densities spiked with ^{210}Pb. For the 352 keV peak, detector efficiency was calculated using an IAEA sediment standard in the same jar type as used for the samples. The counts per minute/disintegrations per minute (cpm/dpm) conversion was determined using the known activity of ^{214}Pb in the IAEA-300 standard, counted in the same geometry as the samples.

A constant initial activity model was used to obtain sedimentation rates for the cores in this study, where the sedimentation rate for the each core was calculated to be the ratio of the decay constant of ^{210}Pb and the slope of the line formed by plotting the natural log of excess ^{210}Pb versus depth. 137Cs data was used to further refine dating for the cores in Jamaica Bay, but 137Cs data was inconclusive or not applicable for the Hempstead Bay cores. First appearances and peaks of QACs as well as other contaminants are used to further refine sedimentation rates. The total excess ^{210}Pb inventory relies upon measured dry bulk densities of sediments, and represents lower limits for many of these cores where there was still excess ^{210}Pb present in the lowest sections of the cores (Cochran et al., 1998).

4.3 Results and Discussion

4.3.1 Radiochemistry and Dating of Hempstead Bay Cores

Data for ^{210}Pb and ^{226} Ra is provided in Table 4.3, and profiles of unsupported ^{210}Pb are illustrated in Figure 4.3 for the four Hempstead Bay cores in this study. For HB Cores 1, 2, and 11, it is clear that the sampled depths were not deep enough to recover the full profiles of ^{210}Pb. All four cores analyzed have high inventories of ^{210}Pb (between 64 and 351 dpm/cm^2), which indicates that these are areas of high sediment deposition (Table 4.3, Figure 4.3). For comparison, spatially averaged ^{210}Pb inventories resulting from atmospheric deposition are estimated to be about 27 dpm/cm^2 (Bacon et al., 1994, Cochran et al. 1998, Turekian et al. 1977). Considering that much of this region is covered by sandier sediments, it is not surprising that there is a focusing of ^{210}Pb on fine grain sediments in muddy, depositional areas. Note that for HB Cores 1, 2 and 11, the calculated inventories are most likely underestimates for these sites because these cores did not penetrate deeply enough to approach equilibrium levels with ^{226}Ra.

For HB Core 1 and HB Core 2, excess ^{210}Pb does not decrease very much (HB Core 1) nor systematically (HB Core 2) with depth, indicating some combination of very rapid burial and apparently extensive mixing that makes dating impossible with this tracer (Table 4.3, Figure 4.3). Interestingly, there are higher measured dry bulk densities corresponding to the mid-core minimum of excess ^{210}Pb in HB Core 2, further indicating non-steady-state deposition of sediments at that site. Plotting the natural log of the excess ^{210}Pb against depth for HB Core 1 provides a very shallow slope resulting in an estimated 11 cm/yr sedimentation rate, however, this profile is most likely dominated by mixing. Based on geochronologies from Li (2009), a very pronounced peak in production of DTDMAC 18:18 should be evident in the late 1980's of the core. In addition, a smooth, exponential increase of ATMAC 22 over the last few decades has been noted (Lara-Martín et al., 2010; Scientific Communication on Consumer Products, 2007) and an increase in ATMAC 22 is apparent in the surface profiles of previously studied geochronologies (Lara-Martín et al., 2010; Li, 2009). While there is an increase in ATMAC 22 (normalized to DTDMAC 18:18) evident in HB Core 1, this increase is not exponential and is disturbed by mixing closer to the surface (Figure 4.6). Although there is no clear maximum of DTDMAC 18:18 in HB Core 1, there is the suggestion of a possible peak around 15cm (Figure 4.6). However, the relative abundance of ATMAC 22 at this same depth is much higher than would be expected for ATMAC 22 for the late 1980's, as ATMAC 22/DTDMAC ratios were less than 1% for that time period. This suggests that while sediments do reflect older contaminant signatures with depth for HB Core 1, mixing is most likely obscuring this signal. A more pronounced increase of ATMAC 22 toward the surface of the HB Core 2 is observed (Figure 4.6), which may suggest continuous deposition in the upper portion of this core, although concentrations reach a much higher than expected asymptote of ATMAC 22 at the bottom of the core that suggest lower portions of the core are either well mixed or rapidly depositional. These profiles, combined with ^{210}Pb data, suggest that HB Core 1 and HB Core 2 do not represent continuous geochronologies and as such will not be analyzed further.

However, there are two important points that can be made from examining QAC profiles in HB Cores 1 and 2. First, the concentrations of DTDMACs with depth vary little over the upper 20cm of Core 2 and fluctuate within a limited range with depth in Core 1 (Figure 4.6). These observations are consistent with relatively steady state inputs of the more prominent DTDMAC homologs to Hempstead Bay over time. This is important with respect to its use as a source tracer, applications of which are presented in Chapter 6. Secondly, the HB Core 2 data is from the site of a very large explosion and accidental discharge of two large sludge holding tanks in 1976. One of the reasons this site was sampled was to determine if there was a sedimentary record of this input of QACs to the area. The absence of any unusually high levels of QACs buried deeply in this cores provides evidence that contamination of this area was not a large source of QACS to this region, and that sewage inputs to the northern parts of West Bay and that inputs to are consistent with recent inputs from Reynolds Channel several km away.

^{210}Pb data for HB Core 3 and Core 11 suggest more continuous sedimentation that is less influenced by mixing in surface suctions (Table 4.3, Figure 4.3). As seen in Figure 4.3, the ^{210}Pb profile for HB Core 3 appears to have three distinct sedimentation regimes, with a more than factor of two drop seen in ^{210}Pb activity observed between 18-20 and 20-22 cm sections, which separates the upper two sedimentation regimes. Applying the slope of ln^{210}Pb versus depth for the upper two sediment intervals yields sedimentation rate estimates (.79 and .73 cm/yr, respectively) that are consistent with other sedimentation rates measured in cores from muddy depositional areas in Jamaica Bay that varied from 0.14 to 1.11 cm/yr (Renfro et al., 2010). While the sedimentation rates of the first two sections of HB Core 3 are similar, the third section (below 30cm) has a dramatic change in the slope of excess ^{210}Pb versus depth (Figure 4.3) that could indicate a period of high sedimentation rate or mixing. In this case, we have assumed this to be indicative of a high sedimentation rate in the past.

Due to complications in the ^{210}Pb profile, the dating of HB Core 3 was conducted in two ways. The first dating scheme is straightforward in that it assumes continuous sedimentation utilizing the three sedimentation rates as presented and largely ignores the drop in ^{210}Pb below 20cm. The second dating scheme takes into account the large difference in excess ^{210}Pb between the first two sections and assumes that it is related to a hiatus in sediment accumulation (which may have been tied to an erosional event). While the cause of this difference is unknown, in the second dating scheme, this gap has been accounted for by subtracting 23.7 years from the bottom of the first section (18-20cm) to obtain a date for the top of the second section (20-22cm). The age difference between the top two sections was approximated by calculating the expected value of the natural log of the excess ^{210}Pb for the 20-22cm section based on extrapolating the slope of the upper section to determine an expected ^{210}Pb activity. The difference between the expected value and the actual value observed for the 20-22cm section was calculated and converted into a time of 23.7 years based on the half life of ^{210}Pb. Utilizing this second dating model results in an estimated age at the midpoint of the 18-20cm section of 1987. If the discontinuity below that section was due to an erosional event, the timing would be consistent with Hurricane Gloria that hit Long Island in 1985. Similar large scale erosion of muddy sediment environments have recently been observed in Hempstead Bay as a result of the more recent Hurricane Sandy in Hempstead Bay (Brownawell, 2013).

To identify the best dating scheme to use, the profile of QACs with known time histories were plotted with and without the inclusion of this 23.7-year gap (Figure 4.7). Important profile characteristics used to compare the dating schemes include the first use of DADMACs in the mid 1960's, first large-scale use of DTDMAC in the mid to late 1950's, and the peak in DTDMACs in the mid 1980's. The profiles of behentrimonium ingredients ATMAC 20-22 are seen to be consistent with past geochronologies (Lara-Martin et al 2010), although these profiles are found in sediments after the mid 1980's and the dating of this portion of the core is not sensitive to assumptions about sedimentation changes that appear to have occurred just before that time. While QACs, specifically BACs, were introduced and first used in small quantities in the 1940's (Schaeufele, 1984), input of sewage to West Bay, and therefore QACs, to the region did not begin until 1951-1952. The first continuous deposition model yields first major appearances in Hempstead Bay that appear to be recent in time, with DTDMACs in the 1970's and DADMACs in the early 1980's (Figure 4.7). The large rise in BACs in the 1970's also appears to be too recent, although there are trace amounts of BACs seen significantly earlier/deeper in the sediment profile. These trace levels of BACs at depth could be due to a number of processes, including infilling of burrows by infauna that may have affected the sedimentary record prior to more widespread use of other QACs. In contrast, the second age model that incorporates a 23.7 year gap in the record is seen to better match expected dates of first appearances of BACs (early 1950's, corresponding to the beginning of the major portion of the record), the early 1960's for DADMAC disinfectants, and the late 1950's for DTDMAC (Figure 4.7).

The continuous ^{210}Pb record (Figure 4.3) and high sedimentation rate (2.55 cm/yr) observed for HB Core 11 suggests that bioturbation and mixing are most likely minimal and that this core comes from a highly depositional environment. This conclusion is also supported by observation of the gradient in time sensitive behentrimonium throughout this core. This core was obtained in a deeper area of the northeast corner of Hempstead Bay. Grab samples collected at or near this site were also devoid of benthic communities, with little evidence of an oxidized surface layer. This stands in contrast to most of the samples collected in this area where extensive amphipod mats were observed (Chapter 3).

4.3.2 Radiochemistry and Dating of Jamaica Bay Cores

JB Core 4 and JB Core 7 were dated based on ^{210}Pb data (Table 4.4, Figure 4.4) that was further refined with cesium data (Table 4.4, Figure 4.5). Dating of JB Core 4 was further constrained by analysis of a wide range of anionic and nonionic surfactants and pharmaceuticals with known dates of first production that have been analyzed by Pablo Lara Martin (unpublished and not shown here). Two cesium peaks were identified in both cores as well as most of the other eight JB Cores collected in 2008 for which Alisha Renfro analyzed for radiochemistry (Renfro et al., 2010; Table 4.4, Figure 4.7). The deeper Cs maximum is estimated to have occurred around 1963, a known peak in cesium atmospheric deposition due to bomb testing. The shallower peak is hypothesized here to coincide with record high levels of rain that occurred in 1984, resulting in extremely large CSO inputs, most likely due to increased runoff from land, for that year. The influence of this event on the profile of metals, particularly Zn, in a core taken at the approximate site of JB Core 4 was invoked by Bopp et al. (1993). Based on these two cesium peaks, as well as ^{210}Pb estimates of an overall average sedimentation rate of 1 cm/yr for both cores, the sedimentation rate for individual sections of the cores was refined, leading to more reasonable and consistent dating of the maximum and first appearances of DTDMAC, and the depth distribution of behentrimonium. These adjustments resulted in a sedimentation rate of 0.7 cm/yr until 16 cm, then 1.25 cm/yr for the remainder of the core for JB Core 4. Fore JB Core 7, a sedimentation rate of 1.44 cm/yr was estimated from the surface down to 34cm, beyond which a sedimentation rate of .8 cm/year was used.   These sedimentation rates resulted in the agreement between the cesium peaks and their expected dates, with the deepest cesium peak occurring at 1963 and 1962 for JB Core 4 and JB Core 7, respectively and the shallower peak occurring at 1985 and 1984, respectively.

4.3.3 QAC Concentration Profiles

QACs were measured in all sections from the HB Core 3, HB Core 11, JB Core 4 and JB Core 7 (Table 4.6 and 4.7), with the highest ΣQAC concentrations occurring in the Jamaica Bay cores (peak concentrations greater than 500 μg/g in JB Core 4 collected proximate to the Jamaica STP outfall, Figure 4.2, 4.8). The concentration of ΣQACs is lower in HB, with peak ΣQAC concentrations reaching subsurface maximum levels of 158 μg/g at HB Core 3 collected 3.7 km from the major sewage source at the BPO, with more constant concentrations around 30 μg/g measured in the upper 10 cm of the core (Figure 4.8). Concentrations of ΣQACs in HB Core 11 are much lower as compared to the other cores, with peak values of only 25 μg/g (Figure 4.8), consistent with a greater distance (15.5 km) from the source of sewage (BPO). Peak concentrations of ΣQACs in JB Core 7 were 150 μg/g. This site is affected by a number of STP outfalls in Jamaica Bay, the closest being the 26th Ward STP that empties into Jamaica Bay 4.5km away. As mentioned above, this site is likely influenced by one of the two largest CSO discharges into all of NY Harbor, located in Paerdegat Basin (Figure 4.2). Evidence of near steady-state inputs of ΣQACs over the last two decades in all four cores supports the use of these compounds as sewage tracers.

More highly alkylated DTDMACs (14:16-18:18) constitute a major portion of all cores (Figure 4.9-4.12), with DTDMAC 18:18 alone comprising 40-57% of total QACs measured. Concentrations of smaller DTDMACs (12:12-14:14) only comprise between 1.6-5.3% of the larger QAC concentrations and are similar to BAC concentrations at the surface. These lower alkyl chain length DTDMACs are graphed separately because they may come from vegetable oil based sources of these compounds (particularly coconut, Cross and Singer, 1994), and because they have sediment profiles that co-vary with each other more than other DTDMACs. After DTDMACs, BACs constitute the second largest portion of the total QACs, although at the surface, behentrimonium becomes increasingly important. Surface concentrations of DADMACs and ATMACs C16-C18 are similar and much lower than those observed for behentrimonium and the largest QACs (Figures 4.9-4.12).

DTDMACs

A peak in total DTDMACs is observed in all four cores related to the known peak in DTDMACs in the mid-to late 1980's (Figure 4.9-4.12). Portions of the cores closer to the surface indicate a more steady state input of DTDMACs to both basins over the past two decades (Figures 4.9-4.12), providing additional support for the use of these compounds as sewage tracers. While there is some variation and indication of a decrease in the surface profiles of the larger DTDMACs in JB Core 4 collected in 2008 (Figure 4.11), this is not seen in any of the other cores from this study nor in time series of sediment grab samples collected in 1998, 2003 and 2008 at a nearby site (Li, 2009). The preponderance of evidence from these studies is that inputs of DTDMACs from STPs likely peaked by 1990 and declined as a result of reformulations driven by the phase out in Europe and have remained relatively constant at about 20% of peak levels since the mid 1990's.

First appearances of DTDMACs are expected in the mid-1950's, and this is consistent with first readily observable appearances of DTDMACs in both JB cores and HB Core 3. Relatively small concentrations of DTDMAC are observed in sections dated prior to this time, but their relative abundances are very low and seem more likely related to processes that mix sediment sections either in the field or potentially during sediment core processing. Interestingly, a peak in DTDMACs around 1984 is detected in both JB cores corresponding to the secondary maximum in ^{137}Cs. Whether or not the same processes control both of these tracers is not clear. If greater CSO discharges in 1984 were a factor in controlling the profiles of DTDMAC in Jamaica Bay cores, it would represent a source that would not be important in Hempstead Bay, which has no CSO outfall.

Local minima in Jamaica Bay DTDMAC and other QAC (Figure 4.11, 4.12) concentrations in the 1970s likely reflect complex balances between rising production volumes during this time period (Table 4.1) and known sewage upgrades. The evidence for effects of STP upgrades on the loadings of composition of NPEO and QACs has been discussed in prior work on cores collected near JB Core 4 (Ferguson et al., 2003). The similar geochronologies between the two Jamaica Bay cores raises questions as to how much the local CSO input near JB Core 7 is affecting that site. It is interesting to note that the concentration profiles of smaller DTDMACs (12:12-14:14) increase in relative abundance in comparison to DTDMAC 14:16-18:18 concentrations approaching the surface of the three sediment cores closest to a source of sewage. This may be due to a more recent industrial move towards the use of plant-based oils for the alkyl side chains, resulting in an increase in these shorter side-chained DTDMACs. Another possibly explanation would be that the relative decrease with depth is related to *in situ* degradation as was observed for NP1EO in a 1996 core described by Ferguson et al. (2003).

There is a strong primary (JB Core 7, Figure 4.11) or secondary (JB Core 4, Figure 4.12) maximum in shorter alkyl chain DTDMACs in Jamaica Bay centered around 1970, and the relative abundance of these compounds to DTDMAC 14:16-18:18 is much higher deeper in the two Jamaica Bay cores. This feature may be related to the STP upgrades, as greater biodegradation of DTDMAC 12:12-14:14 in STPs would result in greater removal of the more biodegradable components after the STP upgrades occurred. The higher abundance of these potentially biodegradable homologs in JB Core 7 might also be related to the proximity of this site to a major source of less treated CSO effluent. This can be contrasted with observations of DTDMAC compositions in HB Core 3, where the level of sewage treatment has remained much more constant over time. In HB Core 3, the relative abundance of DTDMAC homologs measured deep in the core are similar to those seen at depths corresponding to the late 1980's and 1990's.

DADMACs

The concentration of total DADMAC disinfectants increases consistently towards the surface for all cores except HB Core 11, the site farthest from a sewage source where there is considerable noise in the data. These are among the most soluble QACs measured in this work, and appreciable levels are only seen for the most hydrophobic 10:10 homolog. This increase is consistent with a similar increase in DADMACs in geochronologies presented by Li and has been attributed to increases in the use of DADMACs (Li, 2009). First appearances of DADMACs in the three older cores are close to the known first appearances around 1965, although, as suggested above, slightly older first detections may be a result of smearing during sampling of the cores.

ATMACs

The concentration profiles of ATMAC 16-18 closely mirror the profiles of larger DTDMACs (Figures 4.9-4.12), consistent with these compounds often occurring as impurities in DTDMAC formulations (Cross and Singer, 1994). However, ATMAC 16-18 were also widely used in personal care products and it appears that some of the rise in behentrimonium in hair care products comes at the expensive of ATMAC 16-18, as these compounds are more irritating to the skin and can not be used in as high percentages as behentrimonium (Lara-Martín et al., 2010). If these compounds are primarily introduced associated with DTDMAC as impurities, it is not clear why they are not elevated in proportion to DTDMAC in deeper sections of the two JB cores when the level of treatment was less (Figures 4.11-4.12), as ATMAC 16 and 18 are highly biodegraded during biological sewage treatment (Clara et al., 2007).

First appearances of behentrimonium (ATMAC 20 and especially ATMAC 22) in the early 1980's as well as exponential increases towards the surface are in agreement with previous studies (Lara-Martín et al., 2010; Li, 2009) where 3-4 year doubling times in concentrations between the early 1980's and mid-to-late 2000's were reported. The large increases over the last few decades observed in all of the cores analyzed in this work are broadly consistent with these earlier reports, which must reflect rapidly growing use in hair care products (Lara-Martín et al., 2010; Li, 2009).

BACs

Measurements of BACs throughout all cores is in agreement with USITC data (Table 4.1) suggesting BACs were the first QACs used, with first appearances occurring in the late 1940's to early 1950's (Li, 2009; Schaeufele, 1984). Trace levels of BACs (as well as ATMAC 16-18, another early use QAC) are observed in HB Core 3 and JB Core 4 around the 1930's, which is not only prior to known uses of BACs but before there was discharge of sewage in West Hempstead Bay, which started in 1951. The appearance of QACs at low levels in sediments dated before 1951 has been mentioned, but may be due to mixing by benthic organisms, errors in dating deeper in the cores, or to some extent issues related to smearing of sediments during collection, transport or extrusion of the sediment cores. The composition of BACs deep in these two sediment cores is dominated by BAC 18, which is interesting because this homolog is used in personal care products rather than in present day disinfectant mixtures. Similarly, enrichment of BAC 18 was also noted in the deepest sections of a core from the Hackensack River (Li, 2009). The reason for increases in BACs towards the surface observed in HB Core 3 is not clear, as similar increases were not observed in the concentration profiles of other cores.

4.3.4 Comparison of core profiles to QAC loading data

An estimate of the loading of total DTDMACs and BACs to Jamaica Bay and Hempstead Bay from STPs was calculated by multiplying the production levels for each compound obtained from USITC reports, as found in Table 4.1, by the average daily sewage discharge calculated for each year that USITC data was available, as the latter is assumed to be a proxy for the population of people in the sewer shed. The Bay Park STP was used to approximate HB loadings, representing an unchanged sewage source that has had no upgrades since it was built, while the Jamaica Bay STP flow data (Ferguson et al., 2003) was used to approximate JB loadings and represents a source of sewage that has experienced multiple upgrades. Loading data and core concentrations were then normalized to the year of peak loading for each compound. Plots of the estimated loading for DTDMACs and BACs overlaid with core profiles for total DTDMACs and total BACs in Hempstead Bay Core 3 appear to be consistent with each other (Figure 4.13 and 4.14). Unfortunately, the hypothesized erosional gap in HB Core 3 coincides with an important time period in the production data, and HB Core 11 does not extend far enough for much comparisons (Figure 4.12). The first data point in HB Core 3 after the erosional gap does deviate slightly from this profile, but this might be the result of mixing between the two sections on either side of the erosional event after deposition resumed.

In contrast, the effects of upgrading the level of sewage treatment may be seen when comparing the profiles of the loadings of DTDMACs and BACs with the corresponding core profiles in Jamaica Bay (Figure 4.13, Figure 4.14). The general shape of the core profiles agrees with the loadings data after 1978 (Figure 4.13 and 4.14), which corresponds to the last upgrade at the Jamaica Bay STP, but before 1978, it is evident for both total BACs and total DTDMACs that the core profiles deviate from the shape of the loadings profile (Figure 4.13 and 4.14). The difference between the core profile and the loadings profile is much larger for BACs than for DTDMACs, and this may be due to BACs being smaller, less hydrophobic, and more biodegradable in STPs (Clara et al., 2007) and would therefore may be more affected by increased treatment. These differences, in contrast to HB, are consistent with different concentrations and compositions of QACs being deposited and preserved before and after the STP upgrade

4.3.5 QAC Compositions

Evidence for DTDMAC persistence from TAMACs

To determine the relative persistence of DTDMAC 18:18 in HB Core 3 and HB Core 11, concentrations of trialkyl methyl ammonium compounds (TAMACs) were calculated using peak area integration and response factors derived from DTDMAC 18:18 standards (following the approach in Chapter 3). TAMACs are impurities in QACs, and in this analysis, it is assumed that DTDMAC is the most important source of TAMACs and that the percentage of TAMAC in DTDMAC formulations have remained similar over time. With three long alkyl side chains, TAMACs are even more hydrophobic and particle reactive than DTDMAC 18:18 and are expected to be even more persistent in the environment. The ratio of the most abundant TAMAC (16:18:18) and DTDMAC 18:18 is relatively constant throughout both cores in Hempstead Bay (Figure 4.15), consistent with DTDMAC 18:18 being extremely persistent once deposited in this environment.

In the remainder of this study, individual QACs have been normalized to DTDMAC 18:18 to better understand the behavior of individual QACs in these environments. DTDMAC 18:18 has been shown in numerous studies (Li, 2009; Li and Brownawell, 2010, Chapter 2, Chapter 3) to be extremely hydrophobic and persistent in marine environments. In addition, comparison to the extremely persistent TAMACs in both this study as well as Chapter 3 of this dissertation confirms the persistence of this compound. DTDMAC 18:18 is the most abundant of all QACs, and normalizing individual QACs to DTDMAC 18:18 can give an indication of how smaller QACs are behaving relative to this extremely persistent compound.

Matched Cores

To gain additional insight into the persistence of individual QACs in Jamaica Bay, data from Li (2009) was combined with data from JB Core 4 to investigate the possibility of *in situ* degradation that might be occurring over a span of 20 years (1988-2008) in approximately the same location. This is similar to what was done by Ferguson et al. (2003) and Li (2009), but with additional data from the 2008 JB Core 4 from this study and a focus on individual compounds as opposed to larger classes.

As can be seen in Figure 4.16, there is remarkably good agreement for individual QACs normalized to DTDMAC 18:18 for almost all QACs throughout the length of the cores. This suggests that these QAC are extremely persistent once deposited in this environment, even for the smallest QACs and over long time frames, although the possibility of degradation at the surface of these cores cannot be ruled out. While the profile of most individual QACs agreed extremely well between the different dates, increased variation is observed down core for BAC 14, BAC 16 and ATMAC 16 and 18 (Figure 4.16). These compounds have been noted previously (Chapter 2, Chapter 3) for their intermediate hydrophobicity that is associated with unique behavior compared to other QACs. For example, they are relatively enriched in fresh sewage derived particles relative to surficial sediments under the plume at the BPO in Hempstead Bay (Chapter 3). It is argued in Chapters 2 and 3 that these compounds may be among the most desorbable and biodegradable in receiving waters and perhaps even sediments due to labile pools that are not as extensively degraded in STPs as compared to smaller QACs. Most of the differences in the profiles for these three compounds are observed before 1978, the time of the final JB STP upgrade. It is unclear whether the depletion of these compounds was the result of processes occurring prior (local heterogeneity of depositional environments) or following burial (*in situ* degradation). In either case, there may have been a higher labile pool of sorbed QACs being deposited to the JB Core 4 site before the upgrade.

4.3.6 Individual QAC compositions

Inter-basin composition comparisons

The compositions of individual QACs relative to DTDMAC 18:18 are remarkably similar across cores and basins from this study (Figure 4.17) with sites being closest to point sewage sources being the most similar. These similarities are consistent with the hypothesis that a portion of the QACs entering the environment are extremely persistent once deposited in these depositional, sewage impacted environments, and may also suggest similar sewage signatures for both Bays. The strong agreement between basins as well as the lack of evidence of *in situ* degradation observed for most QACs in the matched cores discussed above may suggest that trends seen for individual QACs in relation to DTDMAC 18:18 discussed below may be due to reasons other than *in situ* degradation, including source changes. It should be noted that the strong agreement observed across all cores is also good evidence to support the revised dating used for these cores, as is particularly evident for bottom sections of DTDMAC 12:14 and DTDMAC 14:14 (Figure 4.17).

HB Core 11 is enriched in BACs 12-16 as well as ATMAC 16 and ATMAC 18 relative to DTDMAC 18:18 as compared to the other cores from this study and is greatly depleted in ATMAC 20 and 22. Reasons for enrichment of the former QACs are currently unknown, but could include additional sources east of the study area or differential transport of different QACs (e.g. different compositions on different sediment types). The depletion of behentrimonium may be related to their more recent introduction into the environment and the possibility of slow dispersal of contaminated sediments through many resuspension and deposition events (Chapter 2). The lack of enrichment of even the smallest QACs in the CSO affected JB Core 7 is also interesting in comparison to Li's findings (2010) of enrichment of smaller QACs in more CSO impacted regions. This lack of enrichment could indicate that even though proximal to a CSO, treated sewage is still the dominant source of QACs to this area.

As has been noted before, the oldest portions of the cores from Jamaica Bay provide some insight into the effect of sewage treatment plant upgrades on QACs. For the smaller DTDMACs, ATMAC 18, and BACs, decreases in these compounds relative to DTDMAC 18:18 are observed at the time of the increase in the level of sewage treatment at the Jamaica Plant. This is consistent with increased treatment affecting the deposition and preservation of QACs, especially for the smaller compounds.

DTDMACs

The composition profiles of individual DTDMACs are quite similar between all cores from this study (Figure 4.17), with the exception of depletion of the most soluble homologs 12:14-14:16 that are depleted near the surface of HB Core 11 located 15.5 km from the BPO. This depletion may be due to fractionation of DTDMAC homologs in Hempstead Bay during transport, with loss the result of the desorption of more soluble homologs, as observed in Chapter 3. Depletion of smaller DTDMAC homologs could also be due to slow dispersal of contaminated sediments within the environment, as noted above for behentrimonium. In other cores, smaller DTDMACs, including DTDMAC 12:12, DTDMAC 12:14 and DTDMAC 14:14, have increasing compositions towards the surface when normalized to DTDMAC 18:18 (Figure 4.15. 4.17). One potential explanation for the increases in these smallest QACs relative to DTDMAC 18:18 is a recent trend away from animal fats as the source of the side alkyl chains for surfactants like DTDMACs in favor of plant oils with shorter side chains. Li (2009) did not look at the compositional changes of individual QACs in his study, but closer inspection of the data from that study does suggest a similar increase for the smallest DTDMACs when compared to DTDMAC 18:18. As is noted above, the largest DTDMACs (14:16-16:16) have uniformly steady compositions relative to DTDMAC 18:18 in all four cores, once again suggesting persistence of these compounds once deposited.

DADMACs

Increasing compositions of DADMAC 8:10 and DADMAC 10:10 relative to DTDMAC 18:18 towards the surface over the last several decades is evident in all cores from this study (Figure 4.8). A similar increase in DADMACs was observed in the concentration profiles, as noted above (Figures 4.9-4.12), as well as by Li (2009). As the use of DADMACs has increased in recent years, Li (2009) suggested that this increase in use is most likely the reason for the trends observed. DADMAC is sometimes referred to as a fourth generation QAC biocide, being used in place of or in combination with BACs and early generation ethyl-BACs (Schaeufele, 1984).

BACs

The composition of BACs relative to DTDMAC 18:18 increases from the 1990's to the present for all BACs in all cores, although this increase is very small for BAC 18. An increase in BACs was not seen in cores from Li's study (2009), although Li's study focused on BACs as a group, and as BAC 18 dominates the BAC concentrations, trends in smaller BACs would have been obscured.

ATMACs

While the relative compositions of both ATMAC 16 and ATMAC 18 appear to be in a relatively steady state since the peak of QACs in the late 1980's (Figure 4.17), ATMAC 20 and ATMAC 22 exhibited large increases towards the surface relative to DTDMAC 18:18 in all cores from this study. As noted above, this is in line with noted recent uses as well as increases in environmental concentrations of these compounds in recent decades, as noted by Lara-Martin et al. (2010).

4.4 Conclusions

This study provides additional geochronologies for QACs in marine, sewage-impacted environments. In particular, the analysis of cores from Hempstead Bay represent environments with unchanging degrees of sewage treatment as well as at a location 15.5 km away from the source. Peaks in DTDMACs in the late 1980’s for all cores are consistent with previous findings and USITC data. Additionally, the profiles of these and other cores are consistent with a steady-state input of DTDMACs to these basins between the early 1990’s and the time at which cores were collected (2008-2011), which may simplify interpretations based on the use of these compounds as particle reactive sewage tracers. Trends of increasing DADMACs, smaller DTDMACs, smaller BACs and behentrimonium relative to DTDMAC 18:18 were consistently observed and may indicate a change in use for these compounds. Comparisons of the relative composition of QACs in cores from nearby sites in Jamaica Bay collected across a span of 20 years indicate that *in situ* degradation is not likely controlling the profiles for even the smallest, most biodegradable QACs following burial, although some variation is observed for between cores for compounds with intermediate hydrophobicity. In addition, comparisons of DTDMAC 18:18 with TAMACs provide additional evidence for the persistence of DTDMAC compounds in the environment, assuming the primary source of TAMACs is as impurities in DTDMAC formulations and the fraction remaining constant over time. Agreement in the composition of individual QACs in cores closer to point sources of sewage in both Jamaica Bay and Hempstead Bay is interesting and may suggest that the sewage signature is similar for these neighboring regions.

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Table 4.1 USITC data for total DTDMAC and BAC sales and production. (United States International Trade Commission, 1953-1994).

year	DTDMAC production	DTDMAC sales	BAC production	BAC sales
	1000's of pounds			
1953			1383	1329
1954			1176	1036
1955			1445	1289
1956			598	595
1957			579	565
1958			826	797
1959			2197	2135
1960			1459	1350
1961			3462	3128
1962	15386	13260	1341	1283
1963	19075	17686	926	940
1964	13223	15798	4704	4557
1965	12894	13349	4599	4705
1966	18387	17840	4900	4315
1967	20675	20577	4934	4876
1968	16460	16420	5995	5803
1969	19172	17373	8814	8641
1970	24486	22762	7392	5926
1971	26133	24458	8559	6836
1972	31383	28322	8082	6507
1973	29672	29180	11850	9744
1974	36992	31960	11130	9961
1975	46539	35132	8803	8498
1976	43087	41805	10650	8093
1977	60348	55477	8459	7684
1978	57506	39833	10272	8096
1979	52126	52349	11175	11046
1980				
1981	47765	47118	15771	15357
1982	66392	66389	17658	16731
1983	57160	56964	17923	16274
1984	69685	61974	15908	14863
1985	65232	64398	15083	11137
1986				
1987	75008	72925	7044	5511
1988	79222	78358	8014	6433
1989	75396.2	69495.8	8111.4	7438.2
1990	84297.4	78144	26602.4	14471.6
1991	83694.6	76322.4	19690	13983.2
1992	78716	78845.8	19866	13299
1993	52819.8	0	25007.4	12399.2
1994	58997.4	0	21566.6	13230.8

Table 4.2 Core coordinates.

Core	Latitude (N)	Longitude (W)
HB Core 1	40°35.759	73°40.516
HB Core 2	40°36.721	73°39.987
HB Core 3	40°37.399	73°39.668
HB Core 11	40°38.555	73°32.253
JB Core 4	40°37.926	73°48.214
JB Core 7	40°37.207	73°53.495

Table 4.3 Sediment properties and data for ^{226}Ra and ^{210}Pb and the inventory of ^{210}Pb in cores from Hempstead Bay.

Depth cm	Dry Bulk Density g/cm^3	^{226}Ra dpm/g	^{210}Pb dpm/g	^{210}Pb$_{xs}$ dpm/g	^{210}Pb$_{xs}$ Inventory dpm/cm^2
HB Core 1					
1	0.26	1.49	10.74	9.25	4.65
3	0.37	2.71	9.71	7.00	7.85
5	0.38	3.49	12.07	8.58	5.77
7	0.38	2.61	8.94	6.32	6.07
9	0.35	2.95	9.97	7.02	6.25
11	0.35	2.79	9.51	6.73	4.84
13	0.35	3.16	11.13	7.97	4.87
15	0.36	5.10	15.67	10.57	5.27
17	0.38	2.58	8.42	5.84	5.20
19	0.43	3.08	11.16	8.08	6.04
21	0.55	2.32	9.05	6.73	8.20
23	0.56	2.21	8.58	6.37	7.73
25	0.55	2.74	10.28	7.54	7.65
27	0.51	2.62	9.98	7.36	5.66
29	0.54	2.57	10.07	7.50	13.18
32	0.58	2.66	10.12	7.46	14.55
36	0.52	2.85	10.94	8.09	13.26
40	0.60	2.19	8.48	6.29	14.11
43.5	0.62	2.30	9.05	6.75	14.59
Total Inventory					**155.73**
HB Core 2					
1	0.34	1.49	9.39	7.90	7.90
3	0.34	2.07	10.97	8.90	8.90
5	0.38	1.79	8.25	6.46	6.46
7	0.47	1.70	7.64	5.94	5.94
9	0.52	1.96	7.67	5.70	5.70
11	0.56	2.07	6.22	4.15	4.15
13	0.58	2.15	5.98	3.83	3.83
15	0.58	2.13	6.53	4.39	4.39
17	0.54	2.28	6.78	4.50	4.50
19	0.53	1.95	5.82	3.86	3.86
21	0.65	2.02	4.89	2.86	2.86
23	0.62	1.74	5.07	3.33	3.33
25	0.57	2.48	6.25	3.77	3.77
27	0.56	2.21	6.26	4.06	4.06
29	0.52	2.16	6.20	4.04	4.04
32	0.51	0.75	6.86	6.11	6.11
36	0.52	0.91	6.17	5.25	5.25
39.5	0.54	0.78	8.17	7.40	7.40
Total Inventory					**92.47**

Depth cm	Dry Bulk Density g/cm^3	Ra dpm/g	^{210}Pb dpm/g	^{210}Pb$_{xs}$ dpm/g	^{210}Pb$_{xs}$ Inventory dpm/cm^2
HB Core 3					
1	0.26	1.35	8.88	7.53	3.94
3	0.45	2.10	7.62	5.52	4.96
5	0.44	2.05	7.46	5.40	4.72
7	0.46	1.91	7.35	5.43	4.94
9	0.47	1.79	6.62	4.83	4.56
11	0.48	3.68	7.21	3.53	3.36
13	0.47	1.86	6.36	4.50	4.19
15	0.48	1.90	6.25	4.35	4.13
17	0.47	1.88	5.80	3.92	3.71
19	0.57	2.27	5.18	2.91	3.31
21	0.69	2.24	3.52	1.29	1.78
23	0.68	2.17	3.47	1.30	1.76
25	0.72	2.21	3.29	1.08	1.55
27	0.63	2.49	3.60	1.11	1.39
29	0.59	2.12	3.03	0.91	1.07
32	0.55	1.88	2.61	0.73	1.59
36	0.67	2.17	2.82	0.65	1.75
40	0.63	2.48	3.37	0.89	2.23
44	0.54	1.57	2.23	0.67	1.43
48	0.62	2.55	3.22	0.67	1.65
52	0.65	2.47	3.02	0.54	1.41
56	0.60	2.20	3.13	0.93	2.23
60	0.65	2.03	2.61	0.59	1.53
64	0.63	3.82	2.89	-0.93	-2.32
68	0.61	2.24	3.07	0.83	2.02
72	0.65	2.16	2.25	0.09	0.24
77	0.60	2.25	2.66	0.41	0.99
Total Inventory					**64.13**
HB Core 11					
1	0.28	1.49	9.03	7.54	4.21
3	0.38	1.72	10.74	9.02	6.78
5	0.35	2.03	12.74	10.72	7.58
7	0.39	1.68	9.34	7.66	5.90
9	0.39	1.88	10.11	8.23	6.48
11	0.41	1.74	10.87	9.13	7.58
13	0.43	1.79	8.78	6.99	6.03
15	0.44	1.55	8.65	7.10	6.29
17	0.46	1.83	9.30	7.47	6.83
19	0.44	1.75	8.80	7.05	6.17
21	0.42	1.70	8.88	7.18	6.03
23	0.43	1.80	9.51	7.72	6.69
25	0.46	1.51	8.53	7.02	6.51
27	0.46	1.73	8.93	7.19	6.65
29	0.47	1.83	7.50	5.67	5.32
32	0.49	1.62	7.94	6.33	12.31
36	0.49	1.85	8.31	6.46	12.76
40	0.50	1.64	8.22	6.58	13.04
44	0.47	1.72	7.56	5.84	10.97
48	0.48	1.90	8.21	6.31	12.14
52	0.50	1.79	5.98	4.19	8.34
56	0.51	1.61	6.65	5.04	10.25
60	0.51	1.89	5.80	3.91	7.97
64	0.51	1.86	5.55	3.70	7.61
Total Inventory					**190.44**

Table 4.4 Sediment properties and data ^{210}Pb and the inventory of ^{210}Pb in cores from Jamaica Bay (Renfro et al., 2010).

Depth (cm)	**Dry Bulk Density (g/cm^3)**	**^{210}Pb$_{xs}$ (dpm/g)**	**^{210}Pb$_{xs}$ Inventory (dpm/cm^2)**	**^{137}Cs (dpm/g)**	**Depth (cm)**	**Dry Bulk Density (g/cm^3)**	**^{210}Pb$_{xs}$ (dpm/g)**	**^{210}Pb$_{xs}$ Inventory (dpm /cm^2)**	**^{137}Cs (dpm g^{-1})**
JB Core 4					**JB 7**				
1	0.2	22.4	8.07	0.0	1	0.4	20.8	16.0	0.00
3	0.2	23.0	8.05	0.0	3	0.5	22.9	21.6	0.00
5	0.2	19.7	7.48	0.0	5	0.5	17.5	16.9	0.00
7	0.2	15.9	7.91	0.0	7	0.5	15.5	16.1	0.00
9	0.2	15.0	6.86	0.0	9	0.5	17.9	17.8	0.00
11	0.2	16.6	7.48	0.0	11	0.5	9.7	9.7	0.00
13	0.2	17.9	7.43	0.0	13	0.5	15.2	15.5	0.00
15	0.2	10.6	4.16	0.0	15	0.5	12.9	13.1	0.00
17	0.2	13.9	5.30	0.0	17	0.5	14.3	15.0	0.00
19	0.2	16.3	6.67	0.3	19	0.5	13.1	13.6	0.00
22	0.3	9.1	9.21	0.0	22	0.5	10.3	22.1	0.00
26	0.2	7.2	7.02	0.0	26	0.6	7.9	20.1	0.00
30	0.2	12.2	11.7	0.0	30	0.6	9.1	22.8	0.15
34	0.2	9.0	7.73	0.6	34	0.6	7.7	19.6	0.26
38	0.2	9.4	8.90	0.6	38	1.1	3.9	17.0	0.00
42	0.2	9.4	8.39	0.6	42	1.0	5.6	22.4	0.06
46	0.3	3.1	3.79	0.9	46	0.7	4.8	14.2	0.29
52	0.5	4.6	17.0	0.2	52	0.9	4.4	30.4	0.35
60	0.5	3.7	14.3	0.0	60	0.8	4.0	26.9	0.22
68	1.3	3.0	29.8	0.0					
Total Inventory			**187**		**Total Inventory**			**351**	

Table 4.5 Individual QAC concentrations (ng/g) measured in HB Core 1 and HB Core 2. Dates were not assigned for these cores.

Core	Depth cm	DADMAC			BAC				ATMAC				DTDMAC						
		8:8	**8:10**	**10:10**	**12**	**14**	**16**	**18**	**16**	**18**	**20**	**22**	**12:12**	**12:14**	**14:14**	**14:16**	**16:16**	**16:18**	**18:18**
		ng/g																	
HB Core 1	0-2	<RL[a]	50	306	68	289	204	622	85	128	429	4370	403	502	428	574	1820	6270	9470
	2-4	12	43	304	171	372	253	666	241	262	408	4450	501	494	402	546	1700	5030	9600
	4-6	<RL	27	193	34	156	107	284	46	70	130	1310	216	230	174	229	692	2590	5200
	6-8	14	40	320	107	328	227	540	159	143	290	2660	401	344	254	352	1120	4100	8030
	8-10	<RL	46	299	71	312	192	499	95	128	253	2260	264	293	257	376	1190	4230	5460
	10-12	12	41	343	101	364	280	732	182	204	408	3,110	451	365	296	468	1590	4470	7610
	12-14	<RL	66	486	91	448	260	969	157	212	536	4050	490	508	435	617	2070	5800	9050
	14-16	23	72	437	140	527	385	1210	195	257	674	5040	596	600	489	726	2610	7640	14500
	16-18	<RL	42	319	71	270	190	581	76	123	284	2560	280	327	303	467	1660	5700	8510
	20-22	<RL	19	143	93	193	106	368	84	136	162	1450	218	208	184	309	1160	4310	6120
	24-26	<RL	<RL	136	25	91	82	247	32	82	64	537	121	160	140	257	922	3330	5660
	28-30	<RL	<RL	182	31	131	91	279	41	87	59	577	143	169	175	332	1250	4160	5780
	34-38	<RL	<RL	125	28	99	66	233	39	85	34	298	84	112	121	272	1120	3800	6810
	42-45	<RL	20	130	32	122	88	266	38	95	45	379	80	127	132	312	1330	426	6470
HB Core 2	0-2	<RL	43	354	43	234	211	620	81	124	312	2780	380	397	326	464	1460	4930	7970
	4-6	<RL	25	213	30	146	132	441	38	95	180	1490	<RL	<RL	<RL	420	1090	4930	7610
	8-10	<RL	22	205	23	92	81	341	28	88	84	709	166	207	189	362	1460	4780	6240
	12-14	<RL	18	144	<RL	44	39	199	11	60	29	307	84	128	124	295	1250	4040	5270
	16-18	<RL	35	224	30	91	78	364	32	95	53	488	173	215	197	451	2020	6190	9210
	20-22	<RL	21	173	23	54	40	240	<RL	65	30	334	113	164	151	352	1510	4650	6450
	26-28	<RL	38	252	32	86	74	417	21	100	65	530	157	237	220	560	2820	8310	10700
	30-34	<RL	51	289	34	121	91	493	22	125	73	583	174	289	239	642	3200	4120	12700
	34-38	20	78	427	111	285	195	881	77	255	147	1010	321	440	366	974	5070	11900	17100
	38-41	17	61	336	56	198	164	859	75	263	128	842	315	444	413	1120	4150	13400	20000

a. levels measured were below reporting limits

Table 4.6 Individual QAC concentrations (ng/g) for HB Core 3 and HB Core 11. Dates are estimated as described in the text.

Date	Depth	DADMAC			BAC				ATMAC				DTDMAC						
	cm	8:8	8:10	10:10	12	14	16	18	16	18	20	22	12:12	12:14	14:14	14:16	16:16	16:18	18:18
HB Core 3											ng/g								
2010	0-2	<RL[a]	34	332	34	211	228	877	47	134	411	4640	418	432	382	696	2460	8340	14200
2007	2-4	<RL	25	249	30	129	120	646	33	124	167	1800	299	301	321	727	2730	8840	11900
2005	4-6	<RL	26	234	25	90	82	559	15	97	107	1260	261	292	304	743	2580	8860	13000
2000	8-10	<RL	28	238	19	88	68	577	20	107	71	836	261	301	348	933	3980	12800	16100
1995	12-14	<RL	37	250	28	125	65	692	21	174	49	495	236	418	462	1500	6430	22400	33400
1992	14-16	<RL	33	167	<RL	107	67	520	34	187	27	210	197	496	534	1800	6810	19700	27400
1990	16-18	<RL	37	212	37	144	90	1440	41	400	47	130	474	804	1070	3480	16100	52300	84400
1987	18-20																		
1963	20-22	<RL	<RL	65	23	82	62	763	20	129	11	40	372	409	600	1620	7140	21000	28400
1961	22-24																		
1958	24-26	0	0	<RL	<RL	<RL	10	126	<RL	23	0	7	69	71	99	318	1520	4460	5070
1952	28-30	0	<RL	<RL	<RL	<RL	8	54	0	10	0	8	6	5	22	98	473	1560	2020
1947	34-38	0	0	<RL	0	19	<RL	65	29	47	0	<RL	6	2	30	141	664	1840	1200
1946	42-46	0	<RL	16	<RL	19	14	77	0	25	0	<RL	<RL	<RL	28	83	397	1190	1290
1944	50-54	0	<RL	<RL	0	26	28	192	<RL	49	<RL	<RL	8	8	46	142	673	1600	2350
1942	58-62	0	<RL	<RL	0	<RL	<RL	58	0	21	0	<RL	<RL	<RL	23	38	139	375	406
1940	66-70	0	<RL	<RL	0	0	<RL	23	0	<RL	0	<RL	<RL	0	<RL	7	<RL	<RL	0
1938	74-80	0	<RL	<RL	0	0	0	13	0	<RL	0	<RL	<RL	0	<RL	<RL	<RL	<RL	0
HB Core 11																			
2011	0-2	0	4	36	19	72	42	85	22	44	13	140	33	37	47	96	411	1350	2460
2010	2-4	<RL	6	26	22	45	28	68	21	41	9	112	27	28	40	82	348	1300	2210
2009	4-6	<RL	4	38	19	58	33	71	20	42	10	131	30	32	40	86	364	1370	2580
2008	6-8	<RL	3	24	15	40	26	61	19	37	<RL	75	27	28	39	87	377	1250	2260
2007	8-10	<RL	7	47	19	56	31	89	22	41	7	118	36	38	50	113	488	1610	2800
2007	10-12	<RL	3	32	13	48	31	89	17	44	7	99	34	37	51	108	465	1640	2860
2006	12-14	<RL	4	28	<RL	44	33	68	20	36	7	70	28	28	37	82	334	1250	2290
2005	14-16	0	2	30	13	41	29	73	20	36	<RL	72	30	33	42	89	373	1370	2740
2004	16-18	<RL	2	35	<RL	42	27	63	16	36	<RL	60	29	32	41	90	389	1370	2510
2003	20-22	<RL	6	51	26	72	43	147	25	54	10	111	50	55	75	171	761	2070	3710
2000	26-28	<RL	4	36	21	65	40	107	27	43	<RL	80	39	48	63	149	684	1910	3280
1998	30-34	<RL	3	19	<RL	51	31	86	26	43	<RL	65	32	43	53	130	604	2050	3510
1995	38-42	<RL	4	16	17	41	28	91	23	43	<RL	32	30	43	57	139	651	2190	3870
1992	46-50	<RL	5	31	23	78	51	211	25	72	<RL	13	54	79	108	285	1110	3907	6670
1989	54-58	2	8	42	36	122	67	363	24	101	<RL	9	101	187	234	629	2510	8160	14100
1986	62-66	<RL	5	29	41	128	76	421	24	101	7	15	90	127	206	538	2740	8840	13900

a. levels measured were below reporting limits

Table 4.7 Individual QAC concentrations (ng/g) in JB Core 4 and JB Core 7. Dates are estimated as described in the text.

Date	Depth (cm)	DADMAC		BAC				ATMAC				DTDMAC					
		8:10	10:10	12	14	16	18	16	18	20	22	12:14	14:14	14:16	16:16	16:18	18:18
									ng/g								
JB Core 4																	
2008	1	93	525	185	702	488	1,960	286	466	351	3,320	1,040	1,050	2,250	8,250	26,100	34,300
2005	3	71	500	137	510	463	2,240	235	588	0	2,840	1,190	1,150	2,790	11,600	34,800	46,200
2002	4	58	420	163	724	587	2,520	281	750	0	3,480	1,170	1,120	3,030	12,700	49,700	63,000
1999	7	72	495	201	746	715	2,950	261	996	487	3,740	980	1,130	3,930	17,700	73,000	93,000
1997	9	44	302	91	448	393	1,390	136	533	155	1,270	412	449	1,710	7,470	32,000	44,400
1994	11	100	449	222	645	679	2,040	250	922	130	821	652	707	2,780	12,600	50,700	66,100
1991	13	98	496	242	814	878	3,630	365	2,160	0	818	717	1,010	4,200	20,500	83,500	109,000
1988	15	75	538	194	605	691	4,310	429	3,920	266	376	2,800	1,990	7,720	44,400	182,000	251,000
1986	17	65	374	171	335	532	3,960	333	3,200	263	264	3,520	2,220	7,990	39,600	156,000	232,000
1985	19	55	330	168	0	412	3,560	264	2,500	223	227	1,210	2,190	7,240	37,300	156,000	255,000
1982	22	62	369	192	330	463	3,970	197	2,270	179	123	1,400	1,930	5,700	27,700	114,000	192,000
1979	26	39	284	147	317	367	2,930	104	917	63	72	853	1,210	3,760	16,600	64,000	82,300
1976	30	0	153	185	361	346	2,810	101	595	0	55	888	1,200	3,470	14,900	55,900	70,900
1973	34	47	437	1,050	1,320	1,360	8,870	432	2,420	158	202	3,440	4,490	10,700	47,200	121,000	140,000
1970	38	0	299	739	1,100	909	5,270	227	1,490	0	67	3,380	3,820	7,000	26,900	92,500	113,000
1966	42	0	190	895	2,210	1,390	6,320	508	2,040	0	0	2,880	2,860	5,830	24,300	95,000	116,000
1963	46	0	96	797	2,090	1,140	4,070	389	2,140	0	0	846	1,470	4,840	23,600	102,000	127,000
1958	52	0	35	197	291	140	825	91	299	0	0	156	296	946	3,710	10,700	13,000
1952	60	0	0	0	17	0	177	0	0	0	0	0	0	0	128	411	560

Table 4.7 Continued

Date	Depth (cm)	DADMAC		BAC				ATMAC					DTDMAC					
		8:10	**10:10**	**12**	**14**	**16**	**18**	**12**	**16**	**18**	**20**	**22**	**12:14**	**14:14**	**14:16**	**16:16**	**16:18**	**18:18**
										ng/g								
JB Core 7																		
2007	1	21	193	42	218	100	483	0	60	90	51	824	434	413	856	3,320	9,040	15,900
2006	3	29	209	42	255	113	471	0	43	98	48	702	351	389	824	3,430	8,640	14,700
2005	5	0	212	31	110	59	427	53	53	52	0	431	257	293	719	3,070	8,320	12,200
2003	7	0	194	40	140	79	474	20	64	107	96	822	253	286	730	3,270	8,830	13,200
2002	9	22	196	38	169	108	635	0	0	110	42	624	317	391	982	4,680	11,900	19,000
2000	11	0	161	19	168	75	503	0	0	110	38	573	271	344	982	4,660	12,100	19,400
1999	13	0	200	65	240	92	663	0	0	123	49	655	332	383	1,180	5,980	14,300	22,600
1998	15	0	139	64	235	94	504	0	54	163	34	472	246	299	986	5,020	14,300	22,200
1996	17	0	150	23	162	82	515	0	0	114	0	351	232	303	1,050	4,900	14,300	22,800
1995	19	23	184	65	286	126	640	0	0	144	25	335	281	351	1,250	5,660	17,000	26,500
1993	22	23	157	43	200	114	663	0	34	199	16	175	287	361	1,310	6,460	18,700	24,600
1990	26	0	166	42	143	117	698	0	0	290	13	67	324	418	1,690	7,460	22,000	35,700
1987	30	24	163	38	187	130	947	0	49	570	18	36	624	540	2,040	9,840	28,900	49,100
1984	34	24	211	79	318	246	1,590	0	64	746	35	45	436	861	2,990	14,700	41,900	85,700
1979	38	0	79	31	127	57	556	0	0	139	0	0	181	291	861	3,960	9,680	17,500
1974	42	0	70	49	118	57	449	0	0	56	0	0	194	218	548	2,240	65,000	9,170
1969	46	0	54	150	255	144	1,100	0	57	191	0	13	421	445	1,150	4,240	12,000	16,800
1962	52	0	147	122	270	132	802	0	43	176	0	0	177	273	1,080	5,000	15,200	19,000
1952	60	0	37	88	168	65	521	0	0	134	0	0	31.0	103	544	2,500	6,890	8,530

Figure 4.1 Locations for HB Core 1, HB Core 2, HB Core 3 and HB Core 11 in Hempstead Bay on the south shore of Long Island, NY.

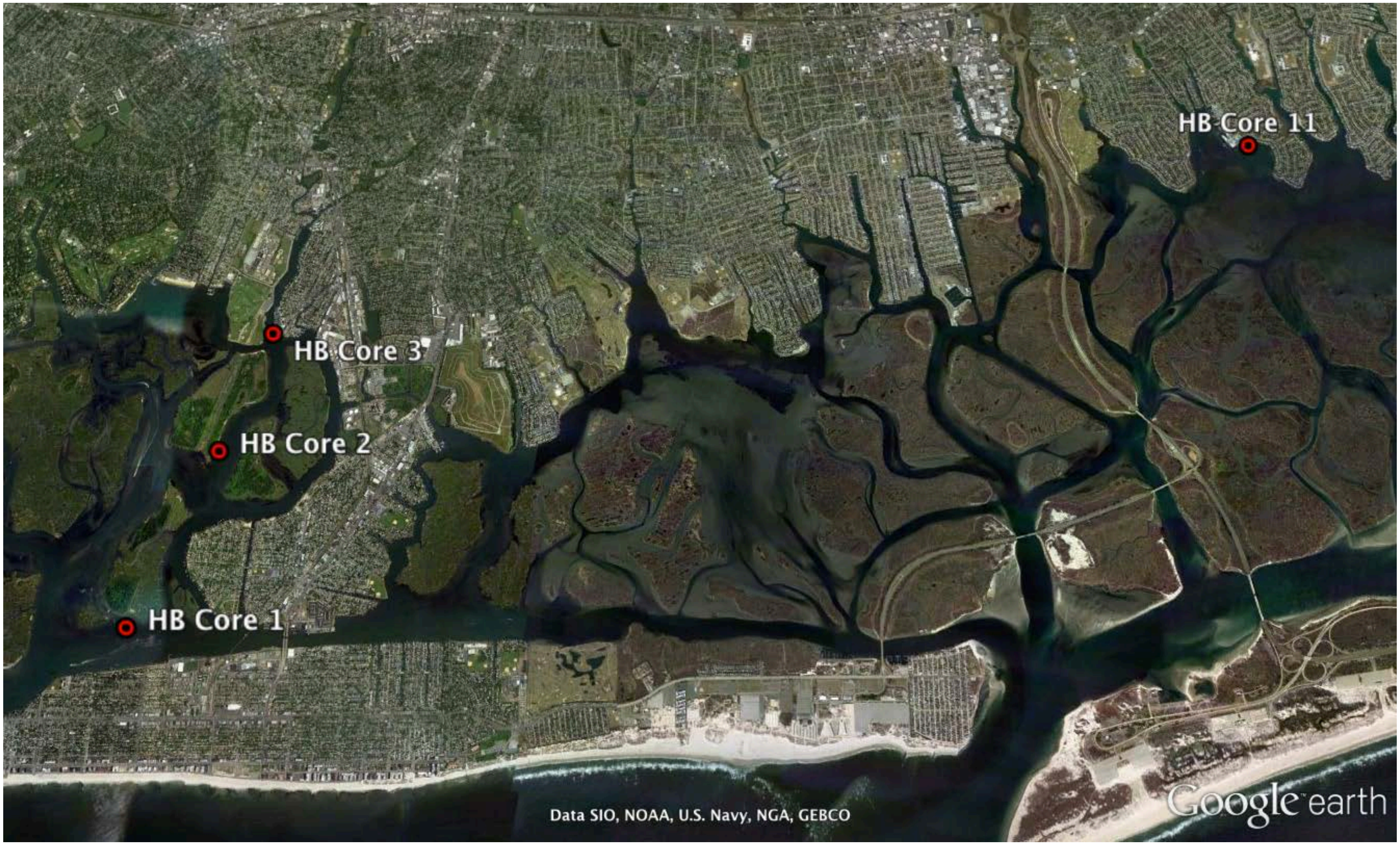


Figure 4.2 Jamaica Bay core locations (yellow dots) and major STP and CSO outfalls (red dots).

Figure 4.3. The ln ($^{210}Pb_{excess}$) for HB Core 1, HB Core 2, HB Core 3 and HB Core 11 plotted versus depth (cm) in the cores from Hempstead Bay.

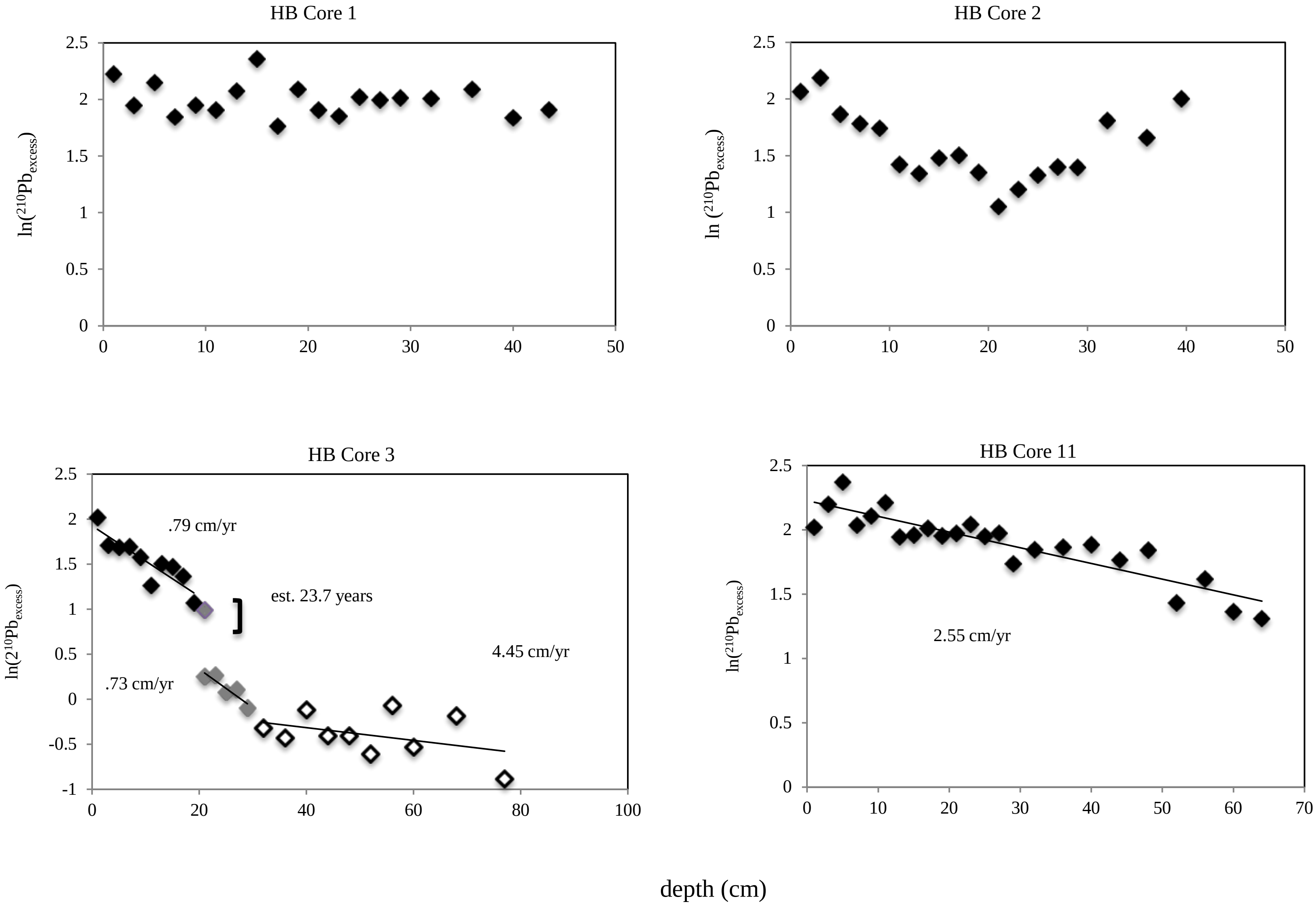


Figure 4.4. The ln ($^{210}Pb_{excess}$) for JB core 4 and JB core 7 from 2008 versus depth (cm) in the core (data reproduced from Renfro et al., 2010). Sedimentation rates were on average 1 cm/yr for both cores, see text for final dating adjustments.

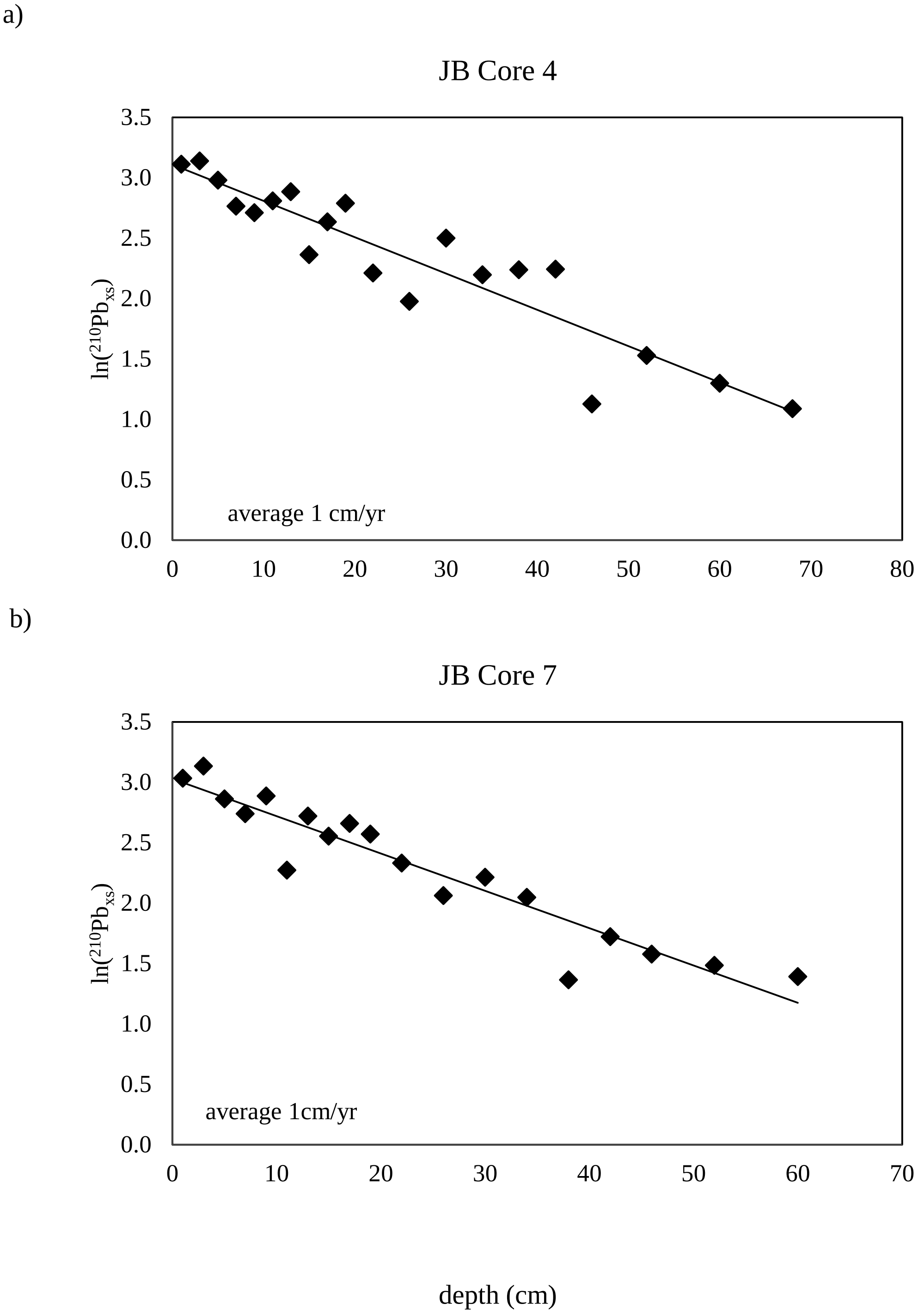


Figure 4.5. ^{137}Cesium values (dpm/g) plotted with depth for JB Core 4 and JB core 7 from 2008 (Renfro et al., 2010).

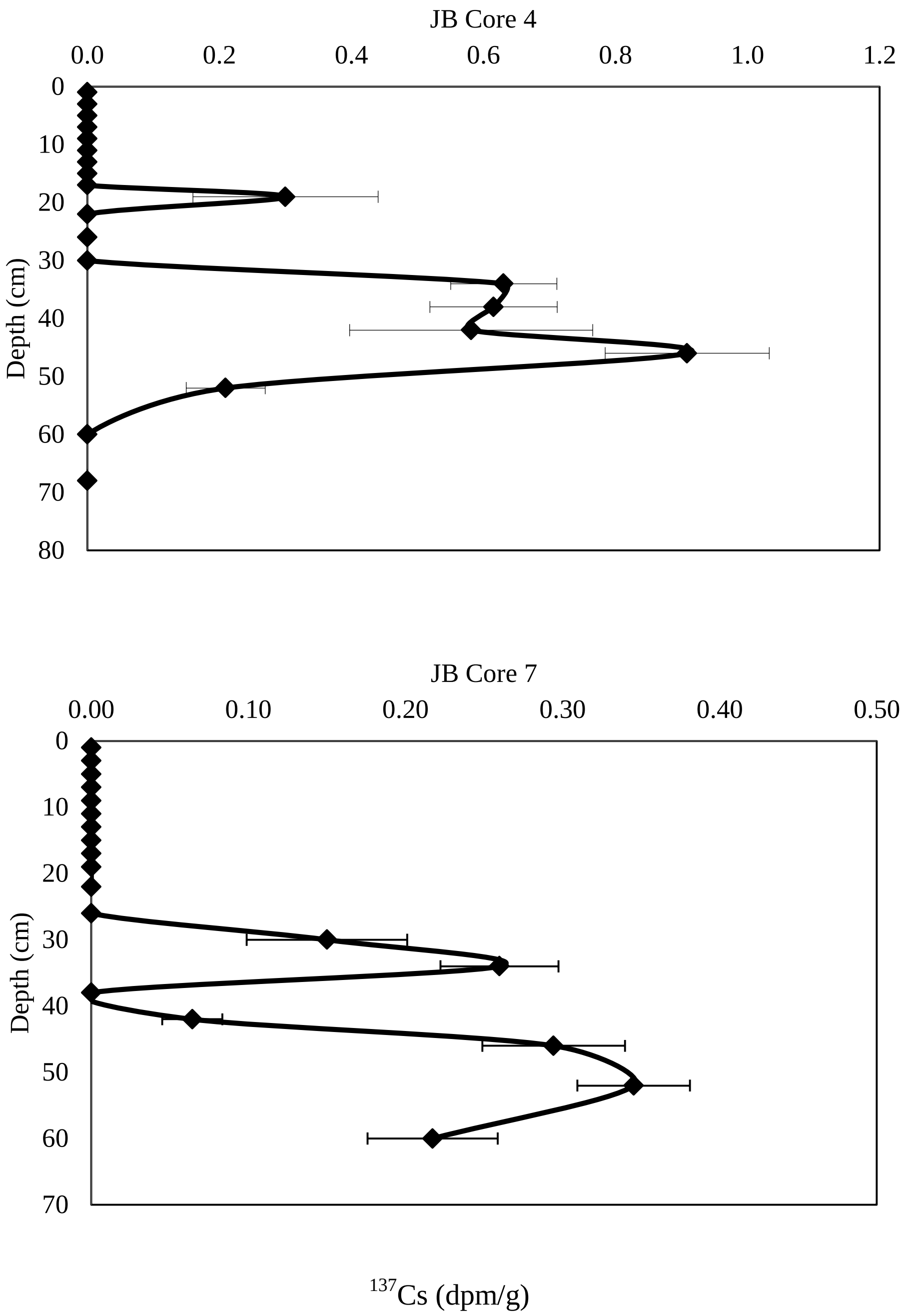


Figure 4.6. Core profiles of DTDMAC 18:18 (ng/g) and ATMAC 22 normalized to DTDMAC 18:18 in a) HB Core 1 and b) HB Core 2.

a)

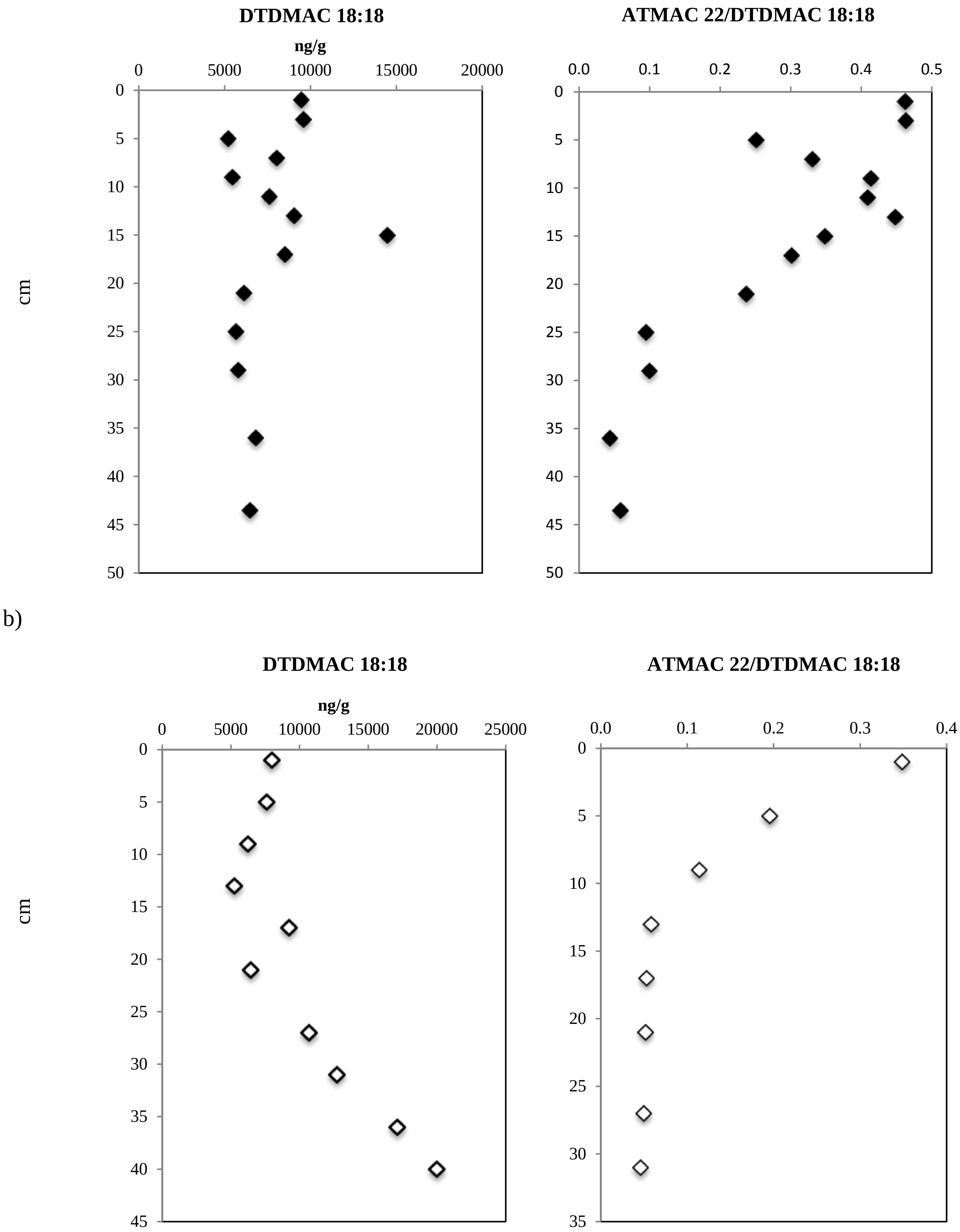


Figure 4.7. A comparison of the two dating schemes for HB Core 3, a) cores dated without accounting for the gap in ^{210}Pb activity, and b) cores dated subtracting 23.7 years between the first two sections to account for the gap in ^{210}Pb activity. Details for each dating scheme can be found in the text.

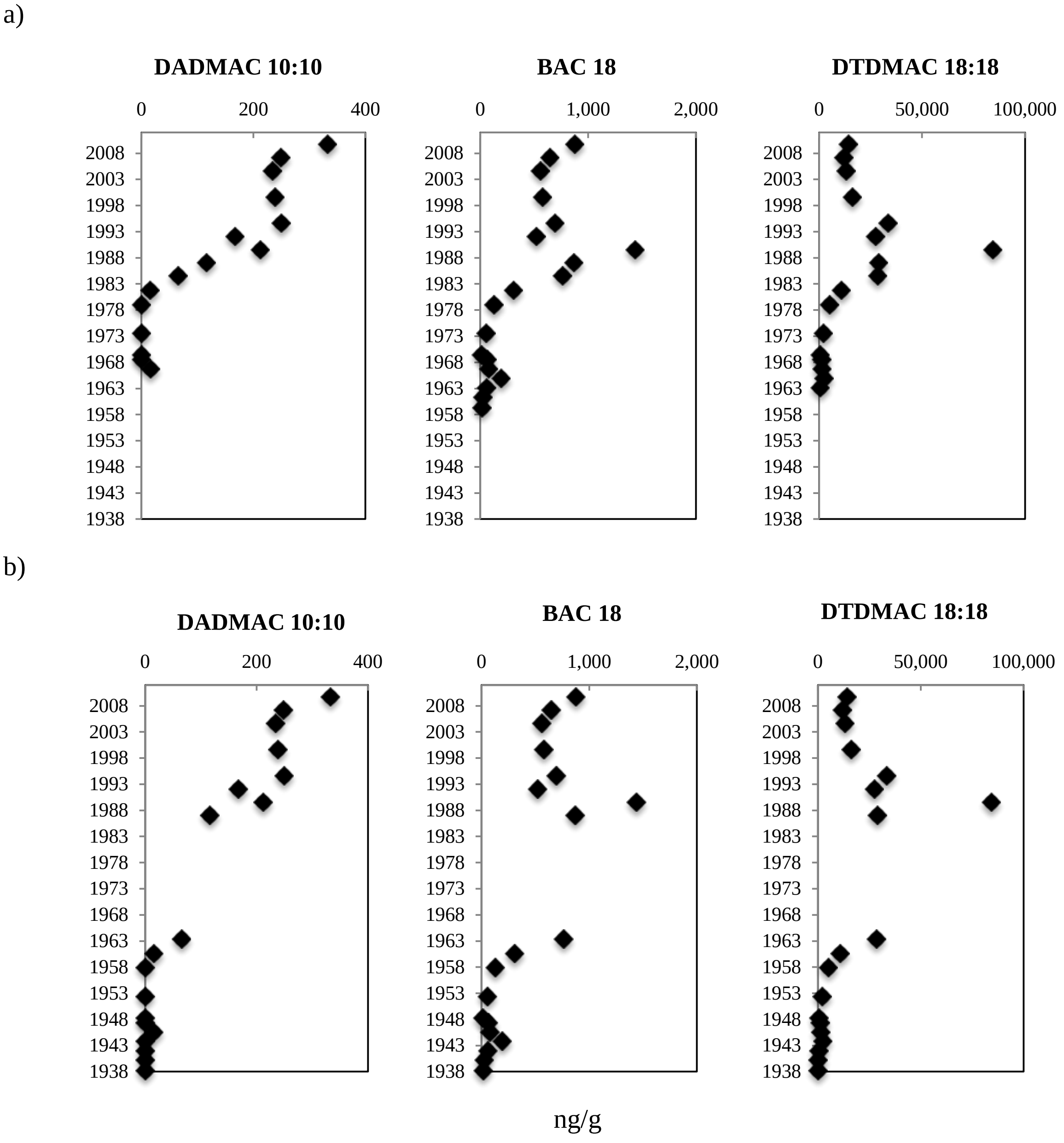


Figure 4.8. Total QACs (ng/g) versus time (years) years for HB Core 3, HB Core 11, JB Core 4 and JB Core 7.

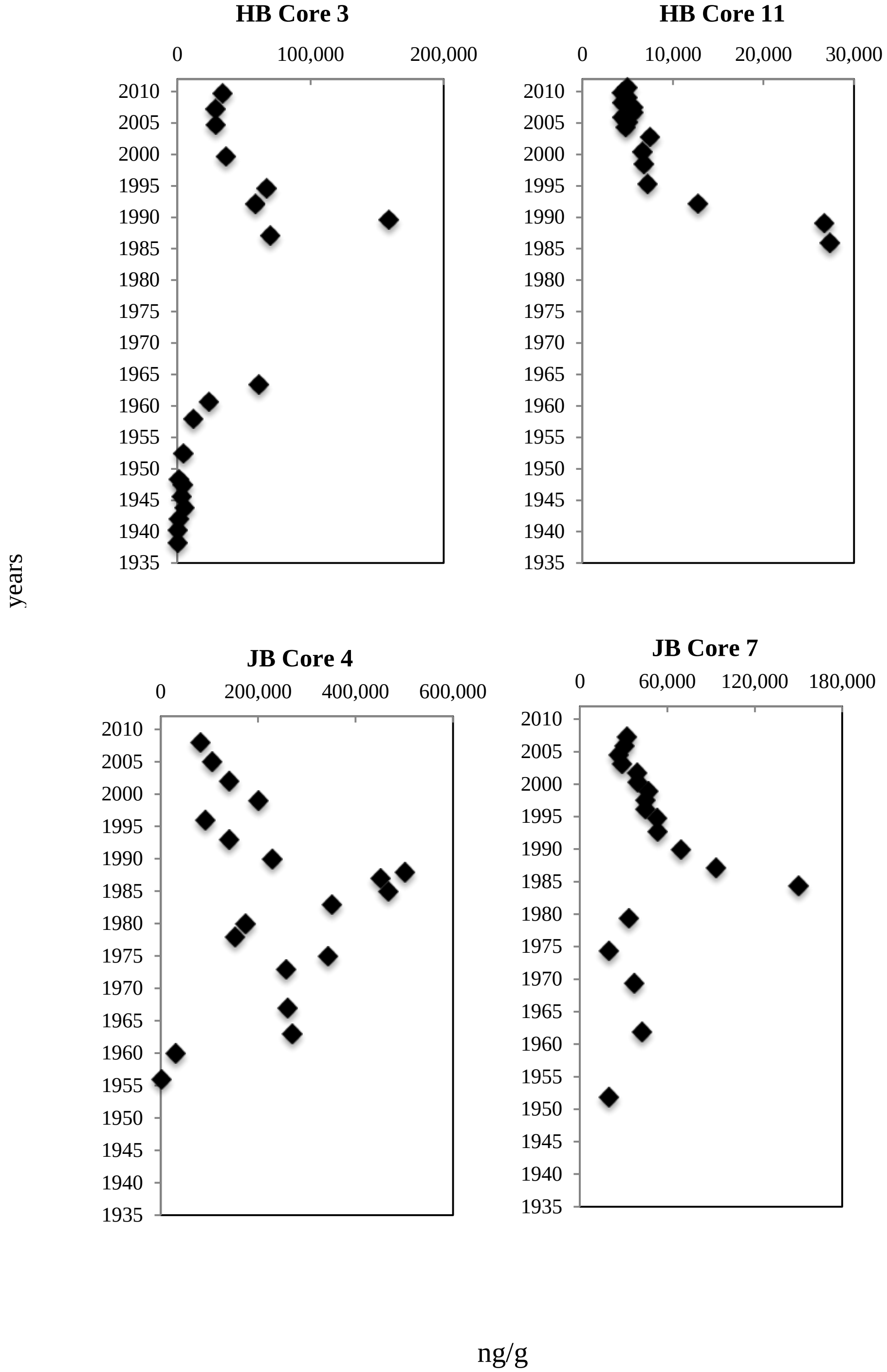


Figure 4.9. Concentration profiles (ng/g) of total DADMACs, total BACs, ATMACs 16-18, ATMACs 20-22, DTDMACs 12:12-14:14 and DTDMACs 14:16-18:18 versus time (years) in HB Core 3 using the second dating method as described in the text.

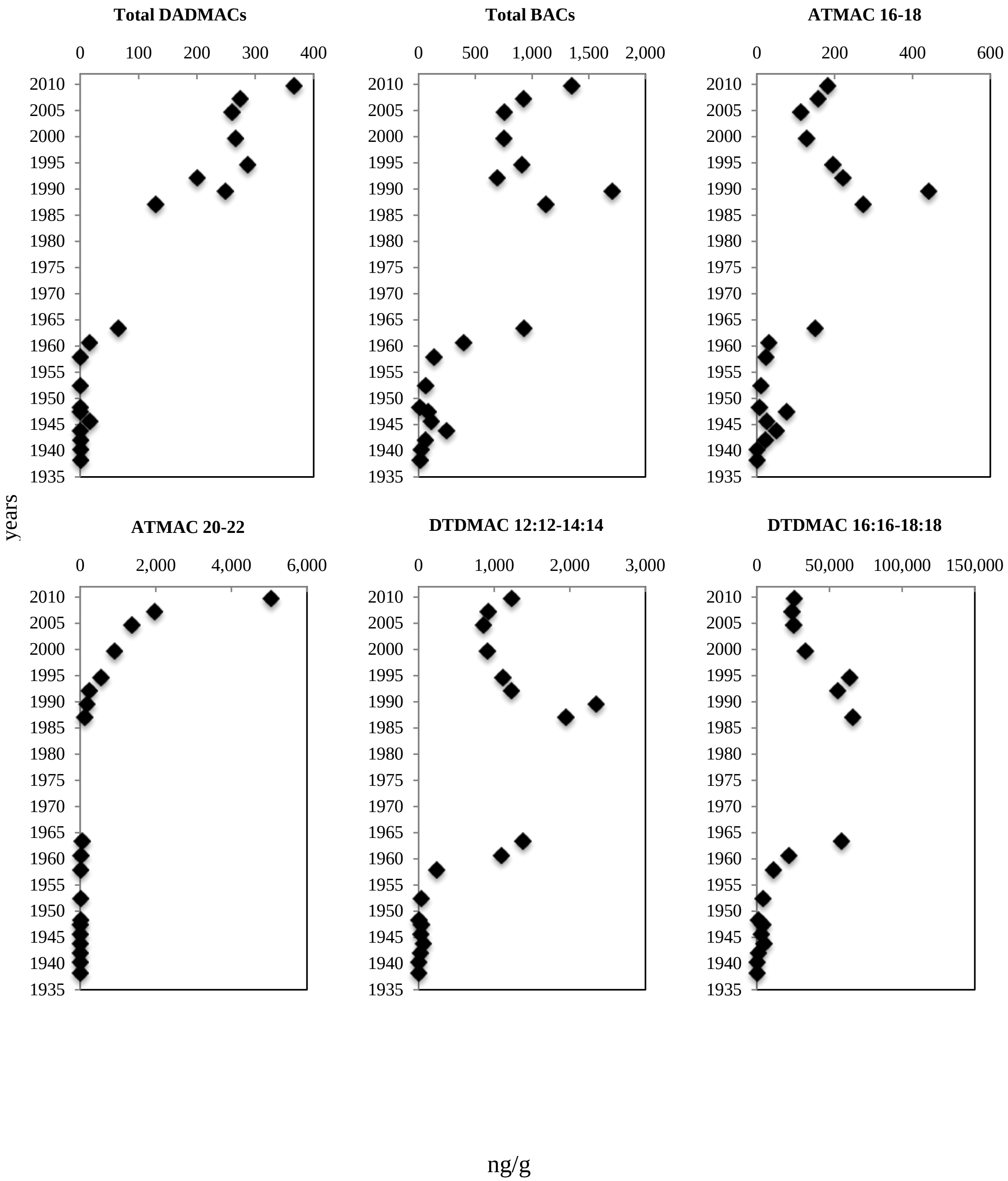


Figure 4.10. Concentration profiles (ng/g) of total DADMACs, total BACs, ATMACs 16-18, ATMACs 20-22, DTDMACs 12:12-14:14 and DTDMACs 14:16-18:18 in HB Core 11.

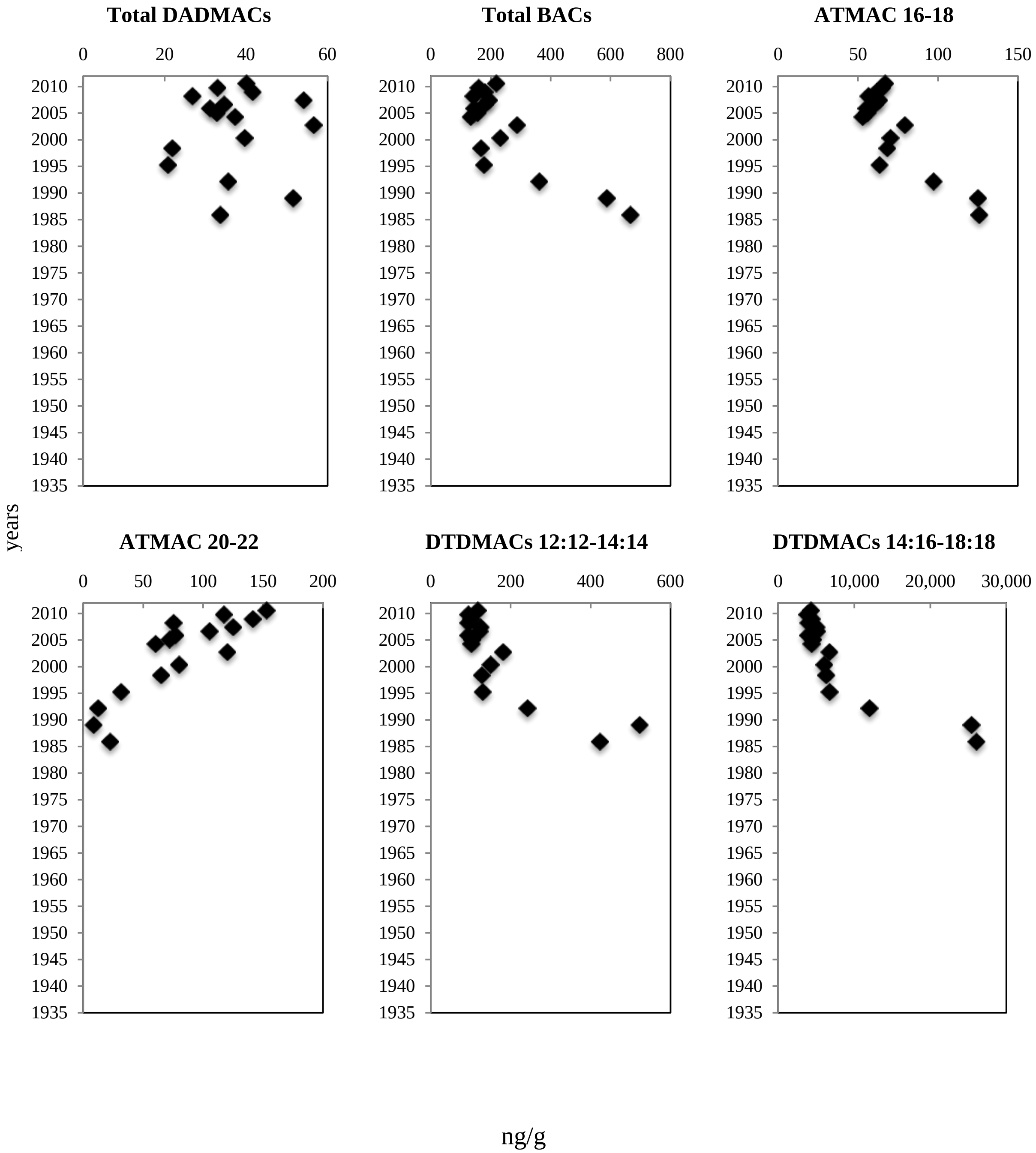
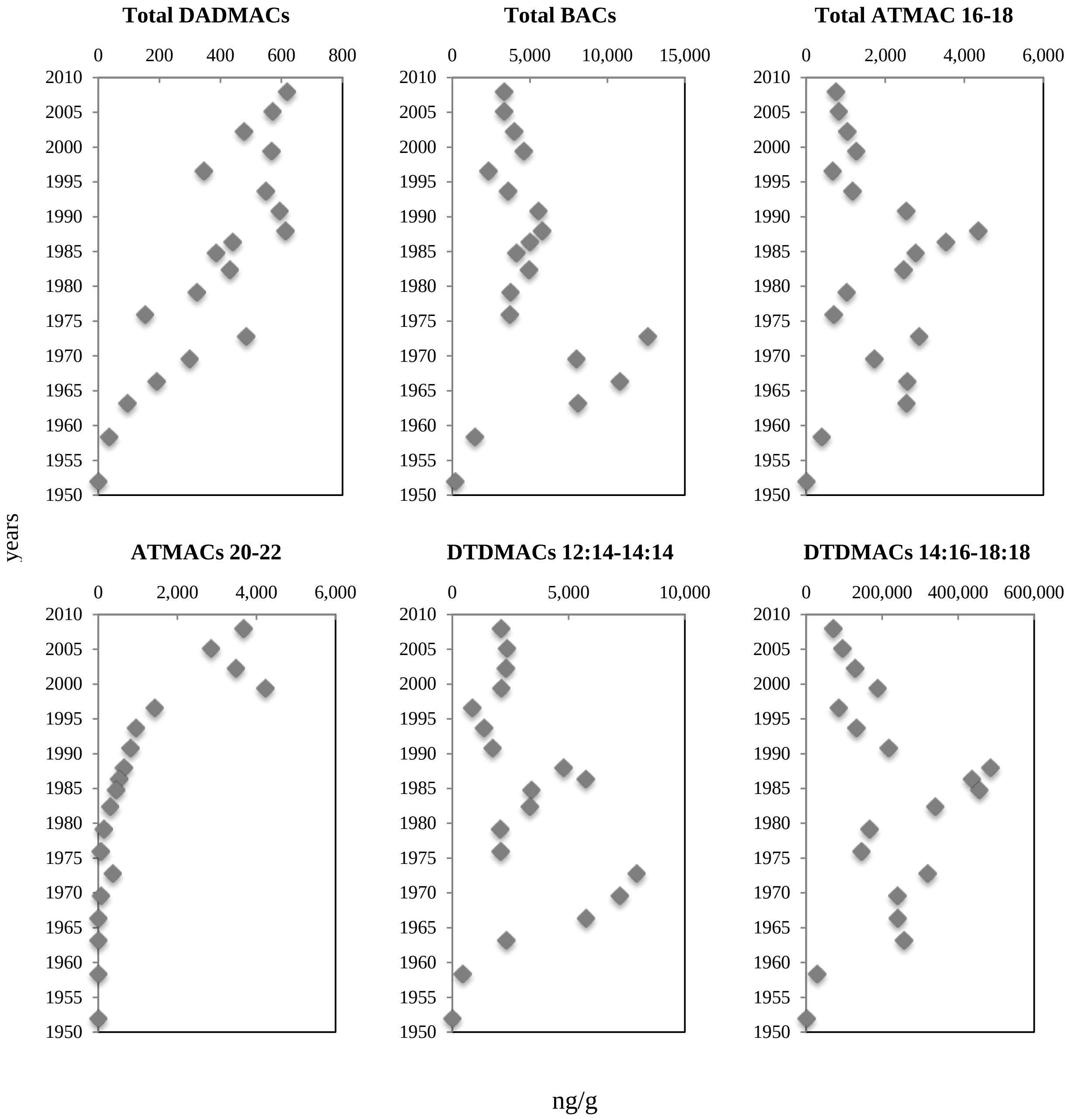


Figure 4.11. Concentration profiles (ng/g) of total DADMACs, total BACs, ATMACs 16-18, ATMACs 20-22, DTDMACs 12:12-14:14 and DTDMACs 14:16-18:18 in JB Core 4.



Total DADMACs

Total BACs

Total ATMAC 16-18

ATMACs 20-22

DTDMACs 12:14-14:14

DTDMACs 14:16-18:18

Figure 4.12. Concentration profiles (ng/g) of total DADMACs, total BACs, ATMACs 16-18, ATMACs 20-22, DTDMACs 12:12-14:14 and DTDMACs 14:16-18:18 in JB Core 7.

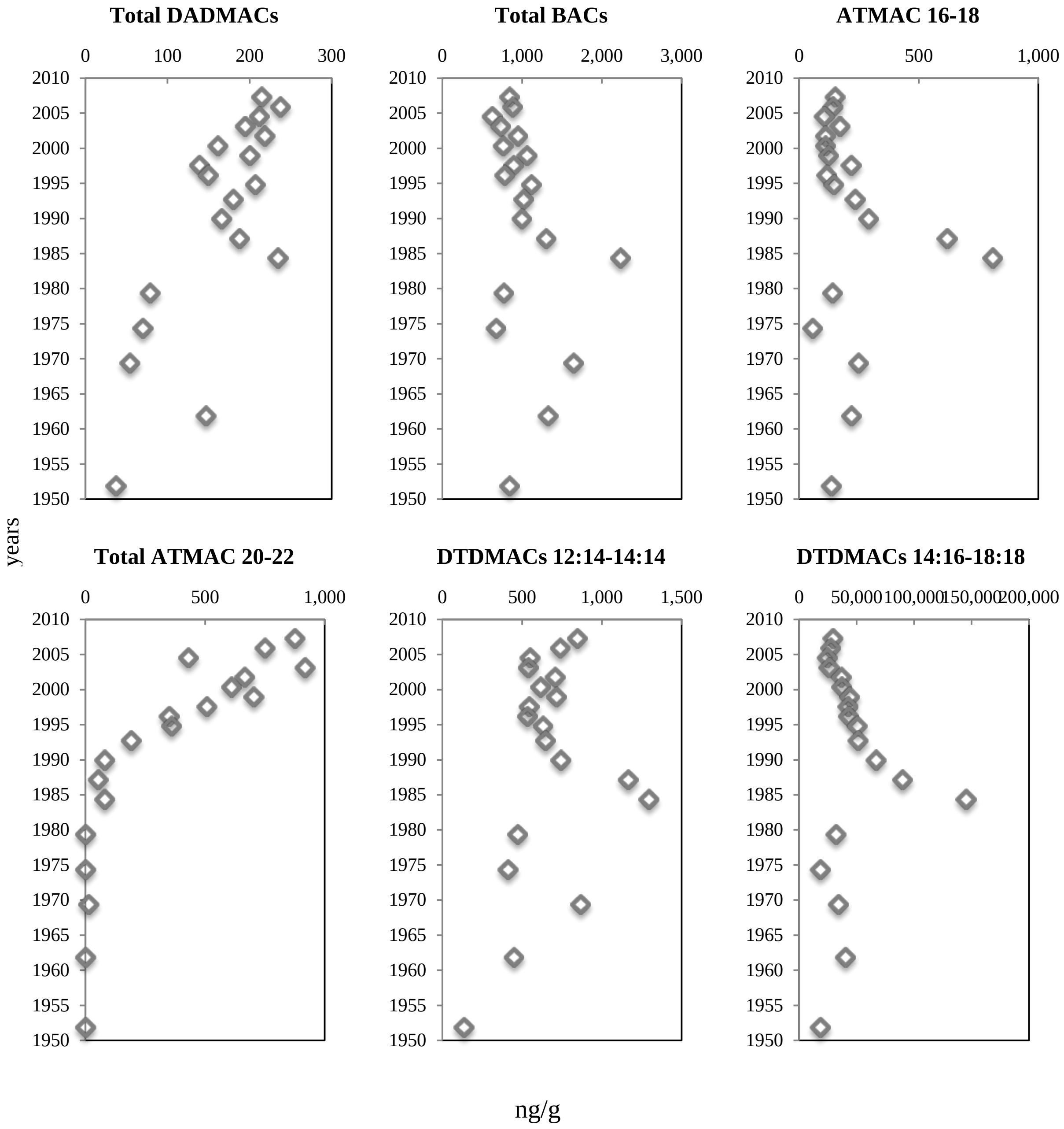


Figure 4.13. Loading data (yearly average of plant discharge per day multiplied by the annual reported production) for total BACs for a) Hempstead Bay and b) Jamaica Bay, shown plotted versus time (years) in black diamonds. Open diamonds represent core profiles. Data has been normalized to the year of peak loading.

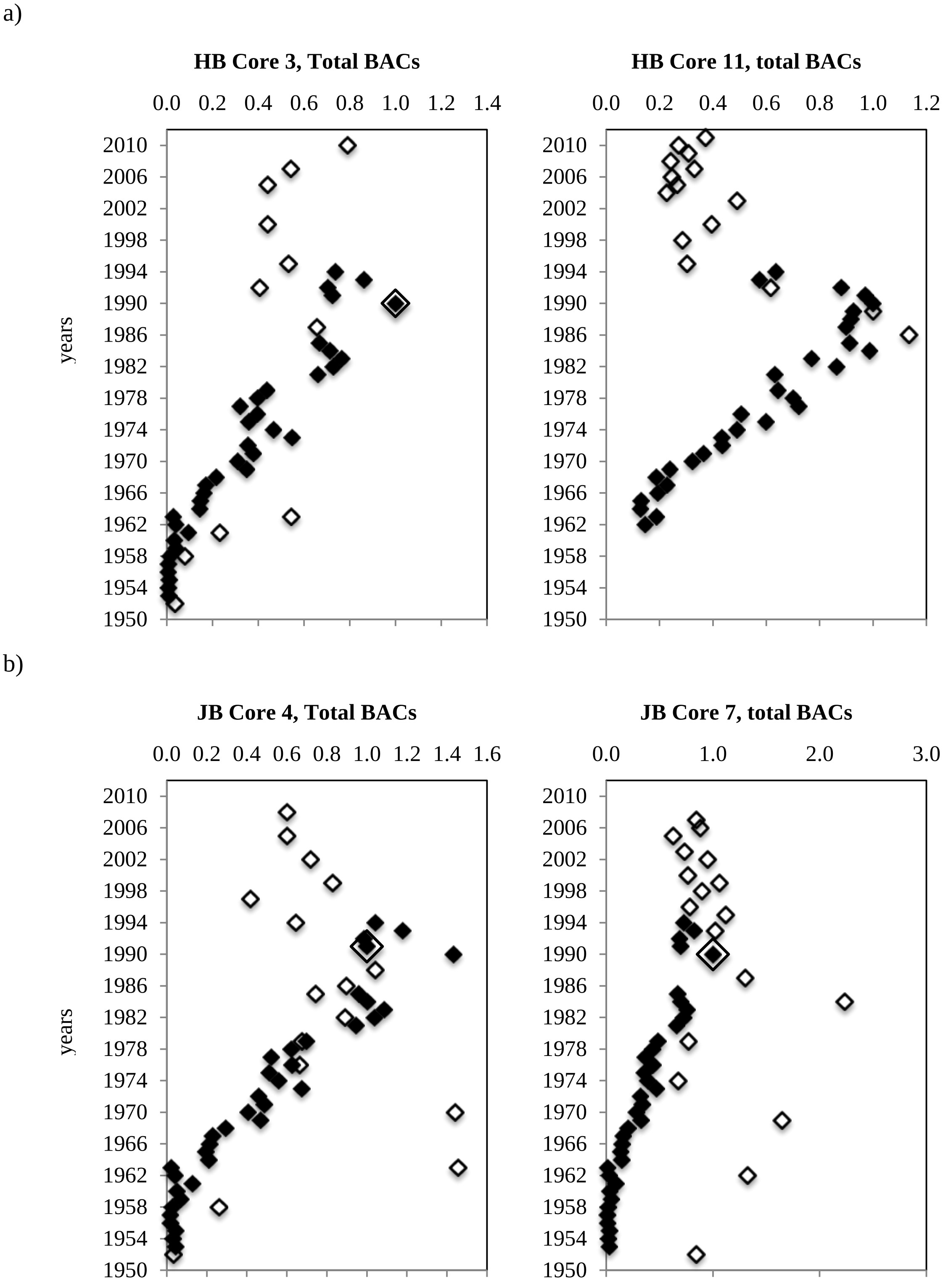


Figure 4.14. Loading data (yearly average of plant discharge per day multiplied by the annual reported production) for total DTDMACs for a) Hempstead Bay and b) Jamaica Bay, shown plotted versus time (years) in black diamonds. Open diamonds represent core profiles. Data has been normalized to the year of peak loading.

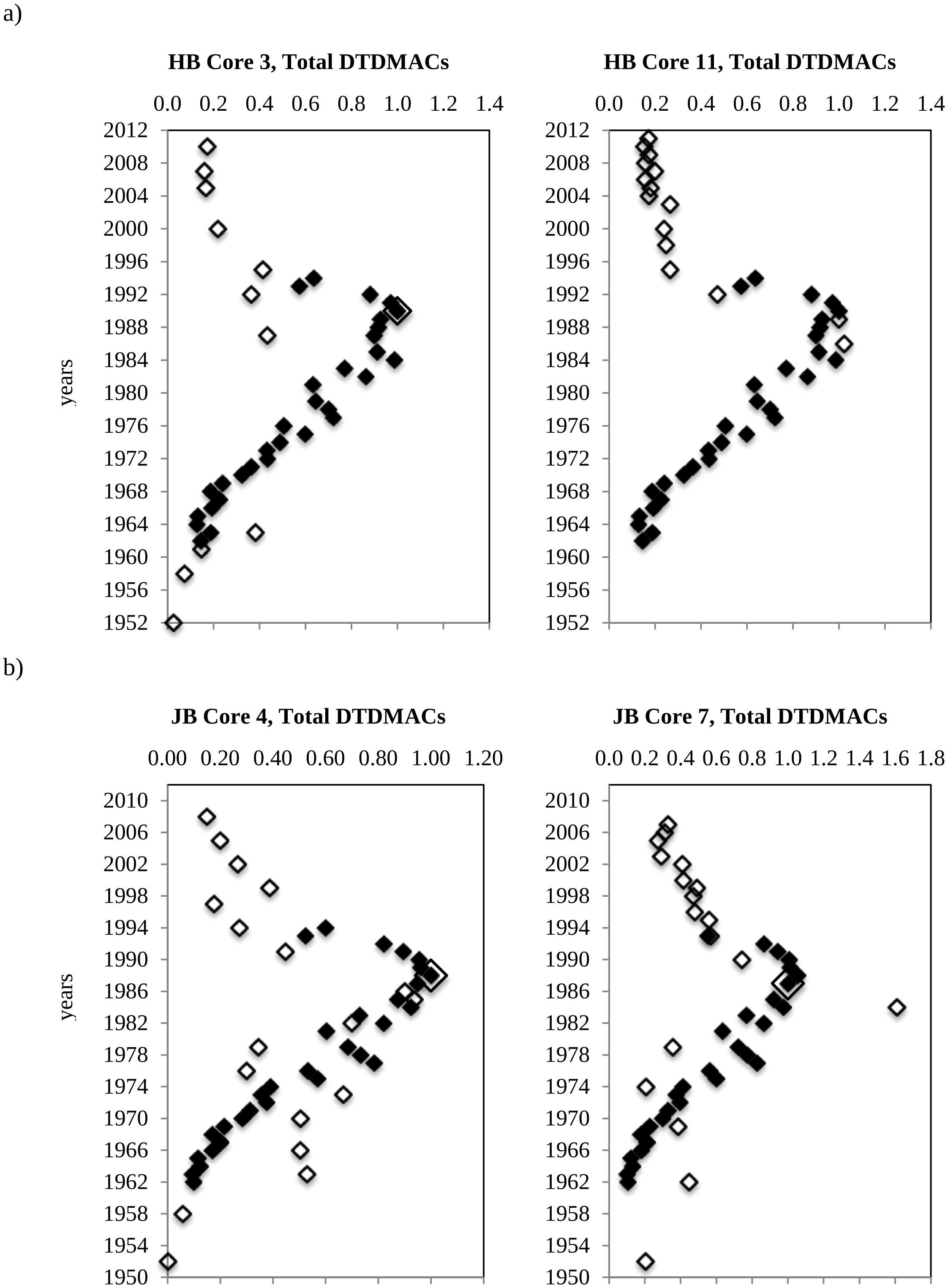


Figure 4.15. DTDMAC 18:18 normalized to TAMAC 16:18:18 versus time (years) in HB Core 3 and HB Core 11.

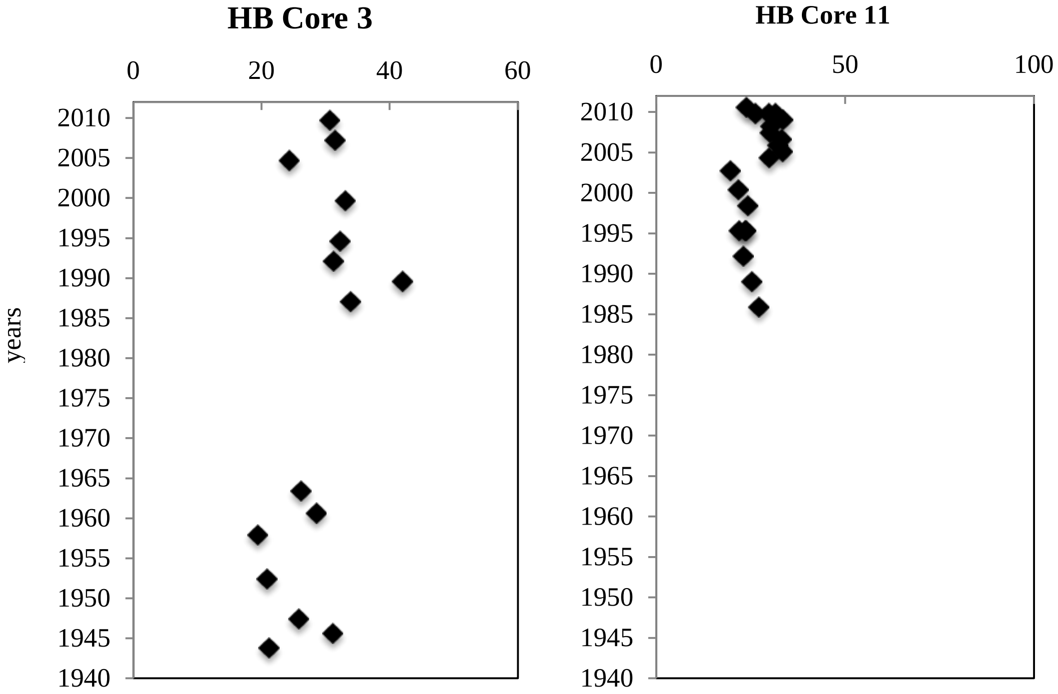


Figure 4.16. Individual QAC compositions normalized to DTDMAC 18:18 versus time (years) at the JB Core 4 location for three time periods (Li 2009) (filled black diamonds = 1988, grey diamonds = 1996, empty black diamonds = 2008).

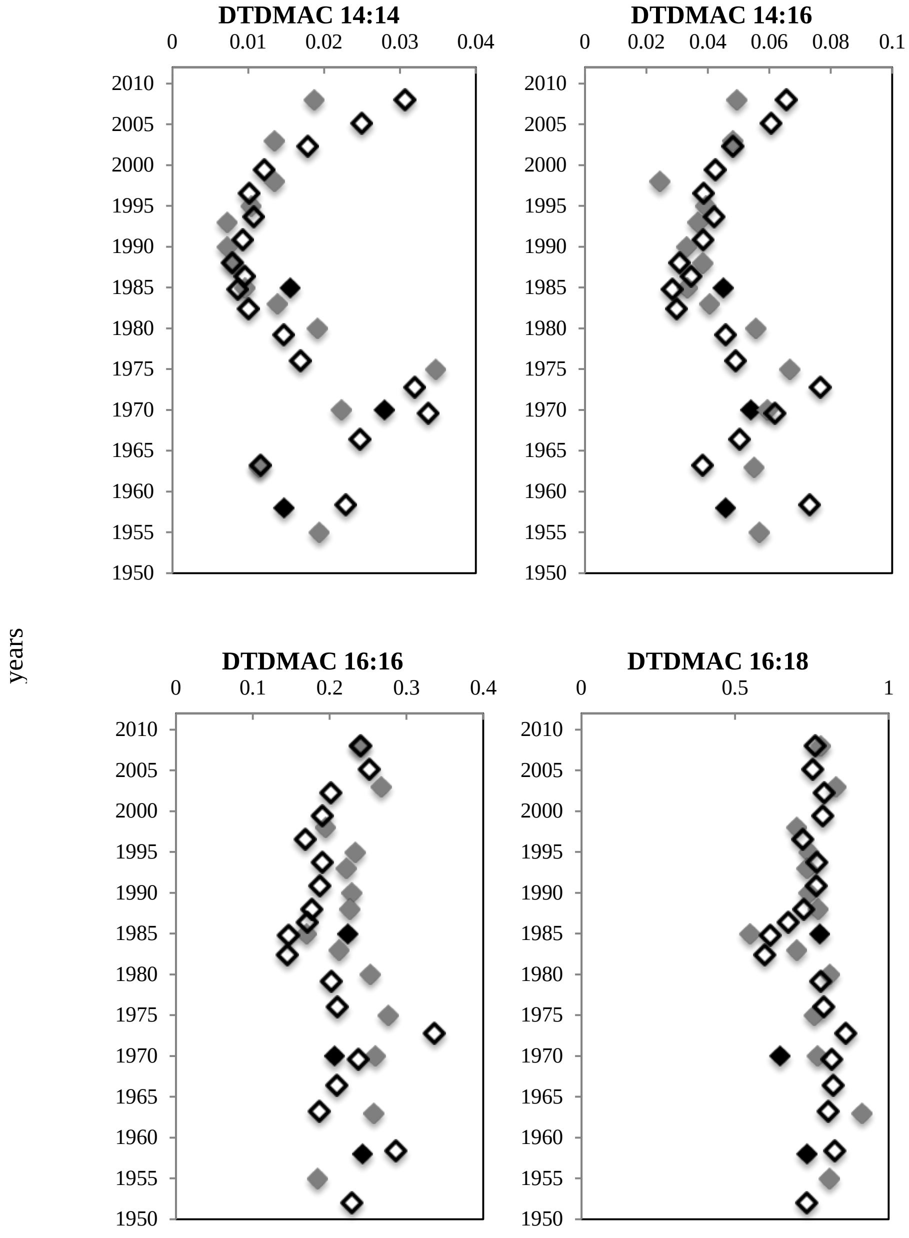


Figure 4.16 continued

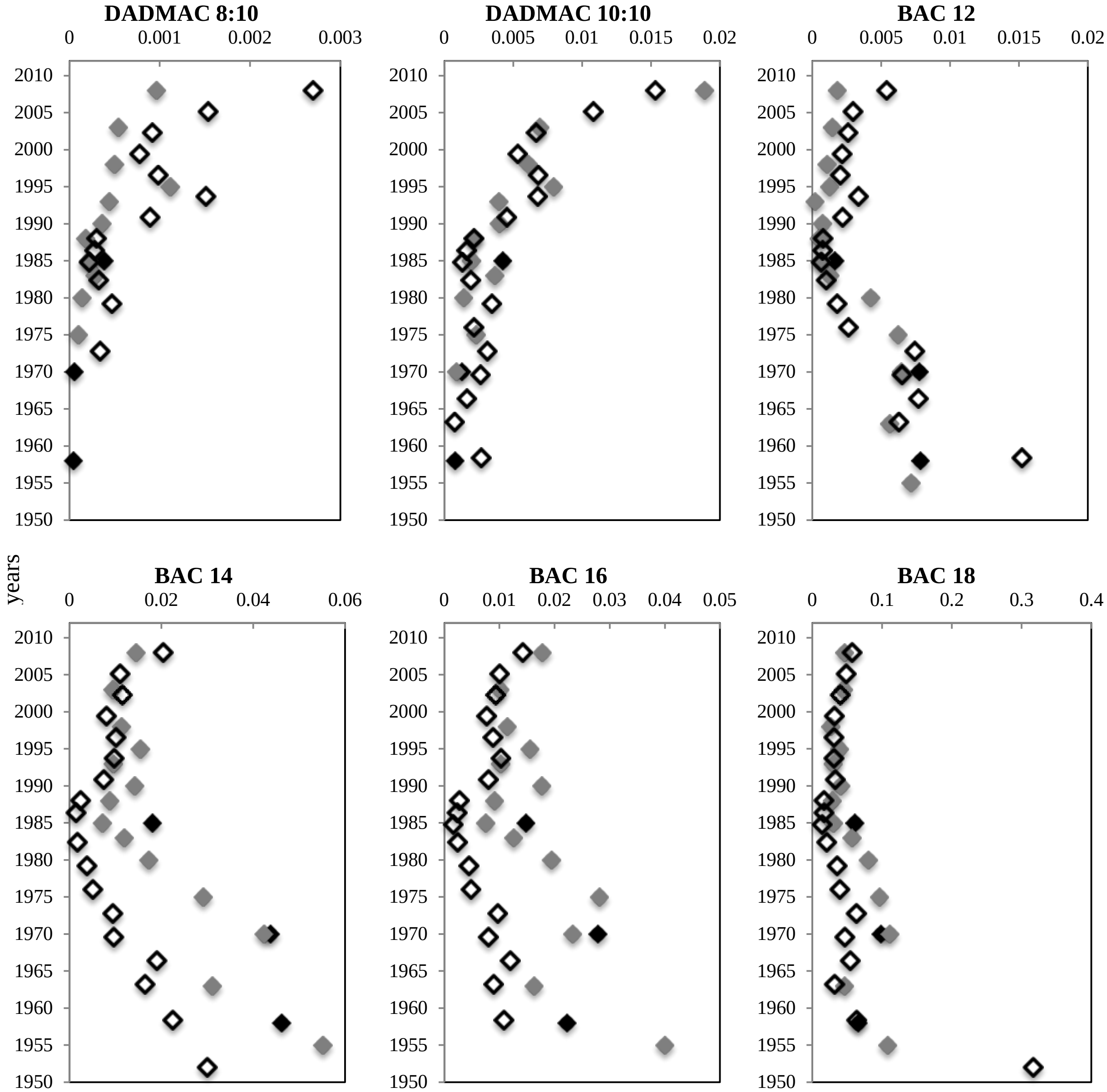


Figure 4.16. continued

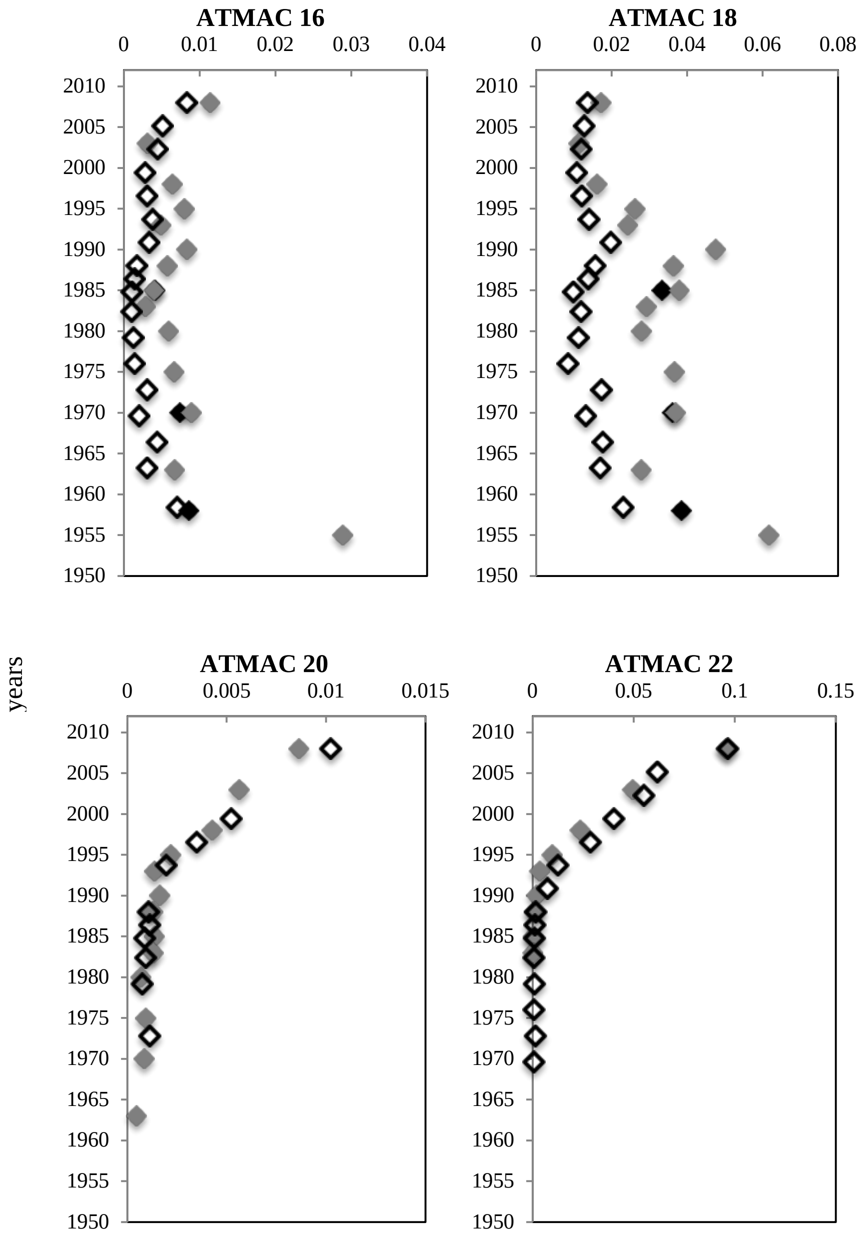


Figure 4.17. Overlay of the composition of individual QACs relative to DTDMAC 18:18 versus time for cores from Hempstead Bay (HB Core 3 (open red diamonds) and HB Core 11, (orange diamonds) and Jamaica Bay (JB Core 4 (open black diamonds) and JB Core 7 (light blue diamonds) (Li 2009)).

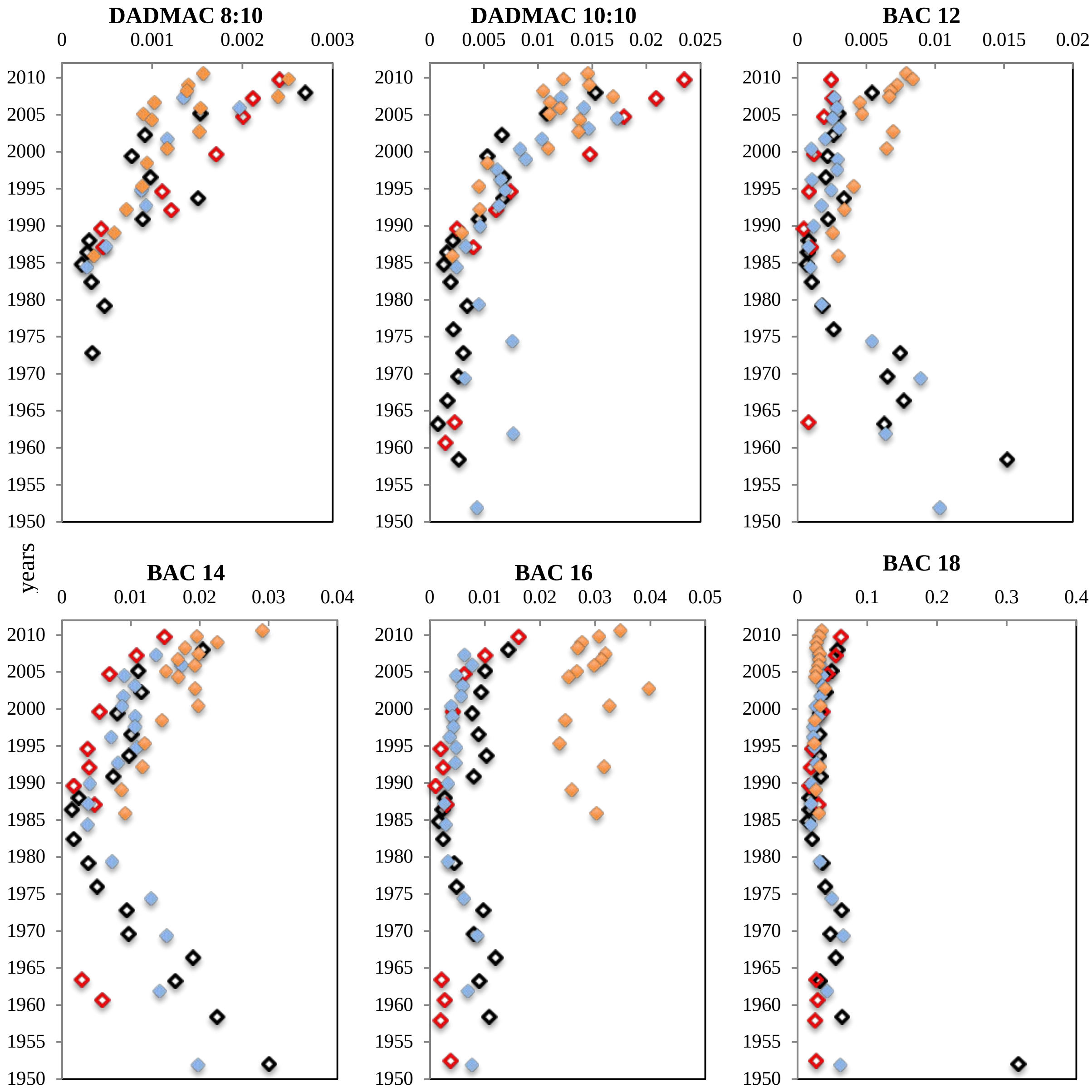


Figure 4.17. continued

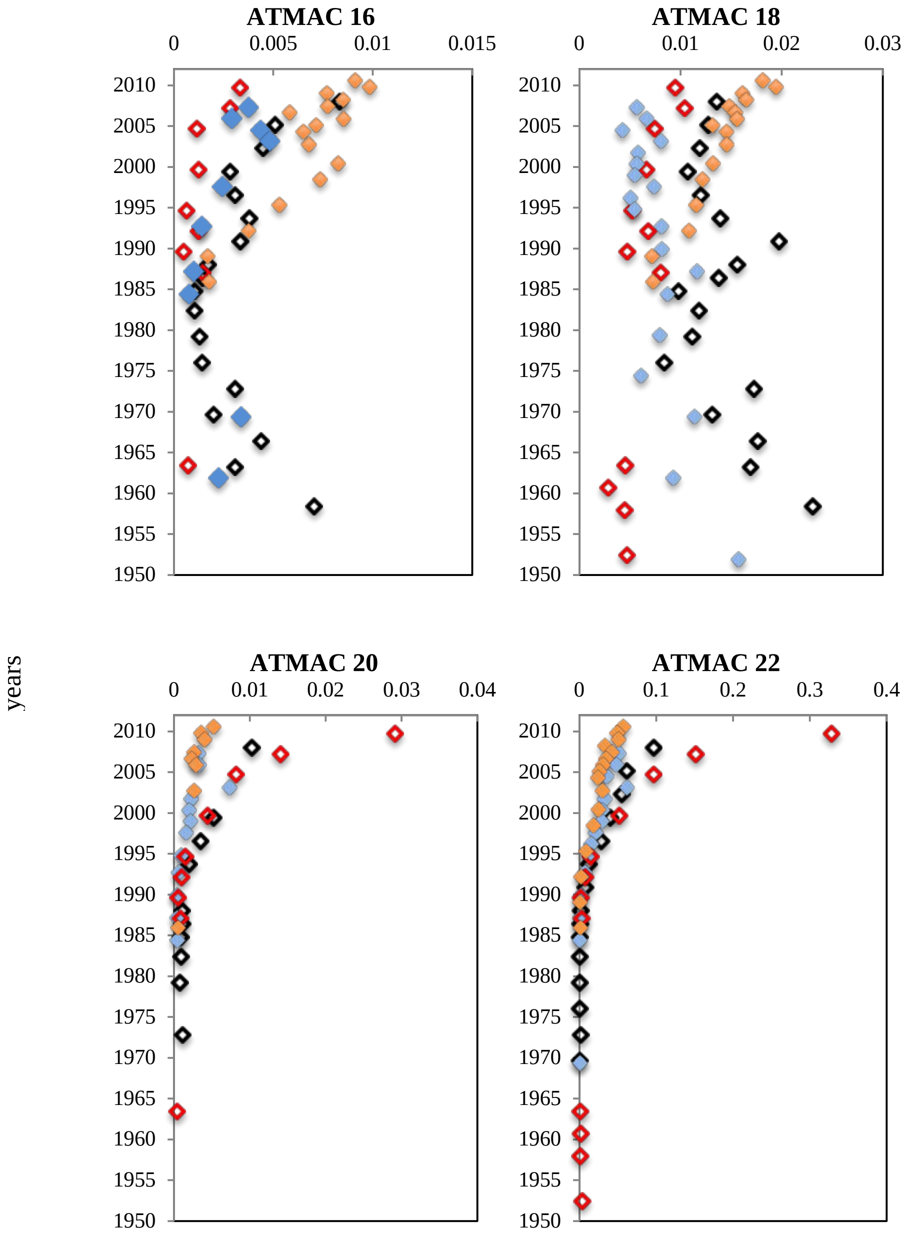
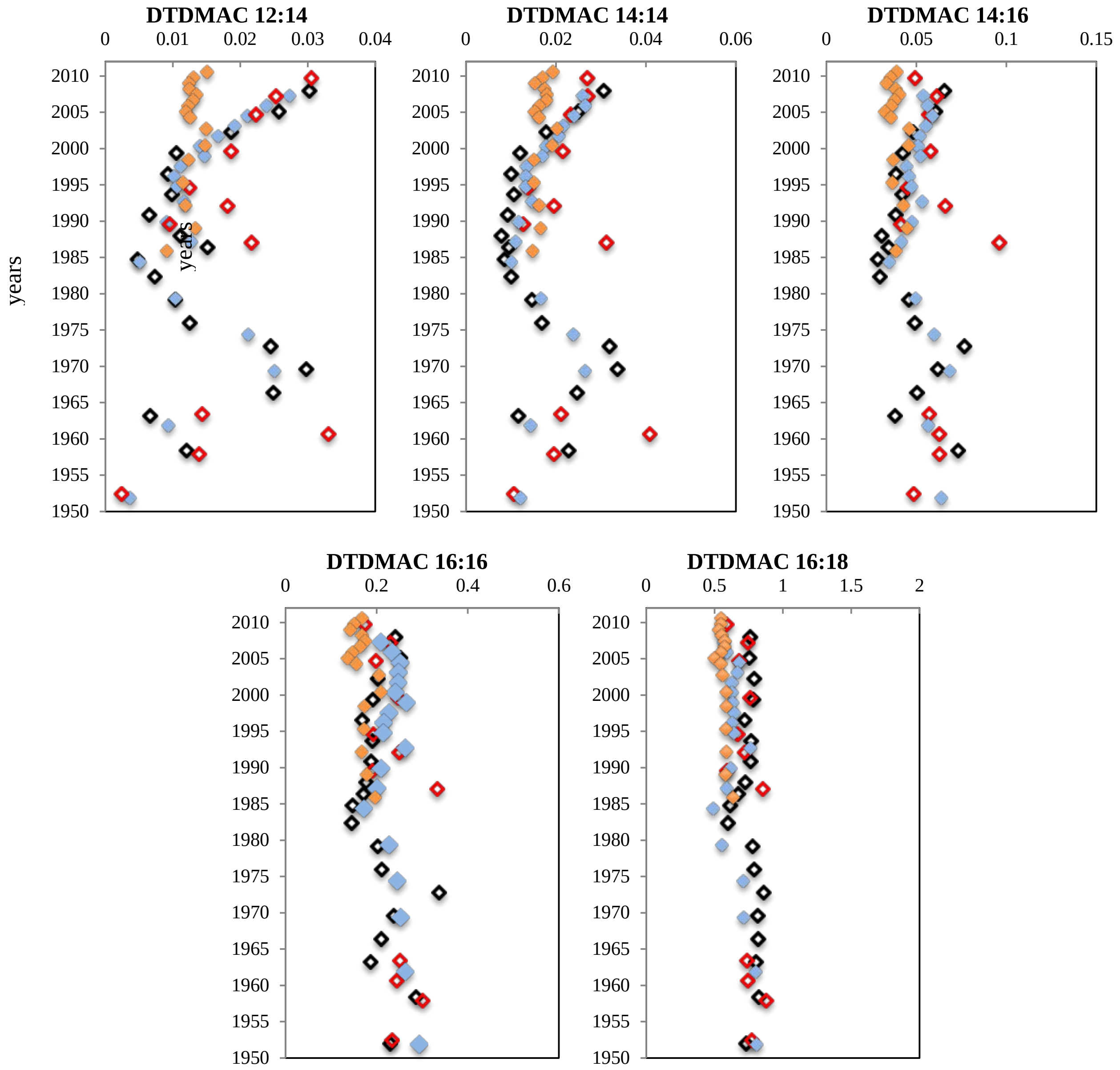


Figure 4.17 continued



CHAPTER 5: Quaternary ammonium compounds (QACs) as tracers to assess sources of di-ethylhexyl phthalate and metals in sediments of Hempstead Bay, NY, an urban coastal lagoon.

5.1 Introduction

Urban, sewage impacted estuaries are enriched in a wide variety of contaminants. Sewage is one possible source of contaminants to these estuaries, yet additional point and non point sources exist, and it is important to understand the source and fate of these contaminants for management purposes. Hempstead Bay, NY is one such sewage-impacted estuary located along the south shore of Long Island, NY (Figure 5.1).

Previous studies have employed sewage tracers to better understand the source and fate of sewage-derived, particle reactive contaminants in sewage-impacted settings (Chalaux et al., 1995; Fernandez et al., 1991; Hatcher and McGillivary, 1979; Sanudo-Wilhelmy and Flegal, 1992; Takada et al., 1992a, 1994; Valls et al., 1989; Venkatesan and Kaplan, 1990). Tracers used to track inputs and transport of sediments or particles affected by sewage should possess several qualities, including high particle reactivity, persistence in the environment, sewage as a dominant source to the environment of interest, a low natural background, and a well known time history of release into the environment. Past compounds used as sewage tracers include silver (Ag) (Lamoureux et al., 1996; Sanudo-Wilhelmy and Flegal, 1992), trialkylamines (Chalaux et al., 1995; Fernandez et al., 1991; Valls et al., 1989), coprostanol (Hatcher and McGillivary, 1979; LeBlanc et al., 1992; Takada et al., 1994; Venkatesan and Kaplan, 1990),and linear alkylbenzenes (Takada and Ishiwatari, 1987; Takada et al., 1992a, 1992b, 1994), yet many of these have been either shown to degrade in some environments (Lamoureux et al., 1996; Maldonado et al., 1999) or have been decreasing in environmental concentrations in recent years (i.e. Ag).

Quaternary ammonium compounds (QACs) are cationic surfactants that have been suggested as a tracer of sewage affected particles (Li and Brownawell, 2010). QACs are an extremely particle reactive class of surfactants that have been measured at extremely high levels in the marine environment (Lara-Martín et al., 2010; Li, 2009; Li and Brownawell, 2009, 2010), often times representing the highest measured organic contaminant in any given sample (Li and Brownawell, 2010). Ditallowdimethyl ammonium chloride (DTDMAC) 18:18 is the most hydrophobic of the QACs that have been targeted for analysis and are considered to be extremely particle reactive and persistent in the environment (Li, 2009; Li and Brownawell, 2010). Li and Brownawell (2010) suggest that a relatively uniform composition of QACs in the New York/New Jersey Harbor complex is consistent with QACs being extremely stable once associated with sediments. QACs have already been employed as sewage tracers in studies to investigate the sources of compounds like polybrominated diphenyl ethers, polychlorinated biphenyls, and nonylphenol ethoxylates (Li, 2009), and have been shown to have high correlations with the traditional sewage tracer silver (Li and Brownawell, 2010).

In this work, QACs, and in particular DTDMAC 18:18, are used to apportion sources of trace metals as well as the hydrophobic organic contaminant di-ethylhexyl phthalate (DEHP) in Hempstead Bay. Particle reactive trace metals have been measured in many urban estuarine sediments at levels that exceed sediment quality criteria levels (Fairey et al., 1998; Hyland et al., 1999; Long et al., 2002; McGee et al., 1999; Mecray and ten Brink, 2000) and are known to have a variety of potential point and non-point sources. Some of these potential sources have been identified in other local estuaries and include sewage and industry (Buck et al., 2005; Mecray and ten Brink, 2000; Rozan and Benoit, 2001; Sanudo-Wilhelmy and Flegal, 1992), as well as atmospheric deposition and runoff (Cochran et al., 1998; Mecray and ten Brink, 2000; Wolfe et al., 1991) in addition to potentially localized sources such as marinas.

Diethylhexyl phthalate (DEHP) is another particle reactive contaminant that is known to occur at higher concentrations in estuarine or coastal sediments near urban or sewage sources (Dargnat et al., 2009; McDowell and Metcalfe, 2001; Swartz et al., 1986; Vitali and Macilenti, 1997). DEHP is a plasticizer that has been previously measured in urbanized marine environments (Bartolome et al., 2005; Fromme et al., 2002; Giam et al., 1978; Lin et al., 2003; McDowell and Metcalfe, 2001; Peterson and Freeman, 1982), and there has been concern about this compound in the environment due to the potential for DEHP to cause acute toxicity and endocrine disruption for aquatic organisms (Call et al., 2001; Patyna et al., 2006; Rhodes et al., 1995; Shimada and Yamauchi, 2004; Staples et al., 1997). While estimates of the octanol-water partition coefficient (K_{ow}) of DEHP vary widely, log K_{ow} values between 4.20-8.90 (Staples et al., 1997) with a suggested value of 7.73 (Staples, 2003) indicate that sediments should be the main repository for DEHP.

Possible sources of DEHP to urbanized environments include point (sewage, landfills) (Dargnat et al., 2009; Swartz et al., 1986; Vitali and Macilenti, 1997) and non-point (atmospheric deposition, runoff) (Bjorklund et al., 2009; Ebinghaus and Xie, 2006; Giam et al., 1978; Staples et al., 1997) sources. While some have implied sewage to be a dominant source of DEHP to urbanized environment (Fauser et al., 2009; Vitali and Macilenti, 1997), often by measuring decreases in DEHP down stream from sewage treatment plants (STPs) (Chaler et al., 2004; Dargnat et al., 2009; McDowell and Metcalfe, 2001; Swartz et al., 1986), source apportionment of DEHP has not been explicitly addressed.

This work relies on QAC data presented in Chapter 3, in which the distribution of QACs in Hempstead Bay was presented. This study found decreasing levels of QACs with distance from the major sewage inputs within the Bay, as well as a correlation between QACs and total organic carbon, which was found to be enriched as compared to other locally studied basins. These results suggest that sewage is being significantly retained within Hempstead Bay. In this work, we will look at the distribution of trace metals and DEHP in Hempstead Bay, NY as a function of distance from the major sewage outfall in the region. Trace metals and DEHP will be correlated with QACs, and in particular DTDMAC 18:18, to determine the importance of sewage as a source of these contaminants to Hempstead Bay. In addition, the relationship between DEHP and DTDMAC 18:18 will be used to assess the relative persistence of DEHP in this environment.

5.2 Experimental

Study area and sample collection

Hempstead Bay (HB), NY is a sewage-impacted estuary located along the south shore of Long Island between Jamaica Bay and Great South Bay (Figure 5.1). HB is divided into three main sections: West Bay, where the four major sewage outfalls, most of the industry, and the largest landfill (which also borders Middle Bay) are located, Middle Bay, and East Bay (Figure 5.1). South Oyster Bay, located to the east of East Bay, was also sampled to provide additional spatial coverage (Figure 5.1). Pines Brook (in this report, referred to as Mill River (MR)) is a small stream that feeds into the northern region of West Bay near the Bay Park sewage treatment plant (STP) and the major industrial region of the Bay (Figure 5.1). It is the largest stream that feeds into West Bay. MR was sampled based on reports from the Town of Hempstead that this area has had periodic troubles with low oxygen and receives significant amounts of storm water discharge.

A majority of the residences surrounding HB have been sewered since 1952 by plants employing secondary treatment, aside from a small number of houses adjacent to Jones Inlet that still use septic systems (Swanson et al., 2013). Five sewage outfalls discharge into Hempstead Bay, including Bay Park STP (49.9 million gallons per day (MGD)), Long Beach STP (5 MGD), West Long Beach STP (0.6 MGD), Lawrence STP (1.3 MGD) and Jones Beach STP outfall (0.05 MGD) (Interstate Environmental Commission, 2010). All of these sewage outfalls except for the Jones Beach STP outfall are located in West Bay. West Long Beach STP outfall is located very close to the mouth of Rockaway Inlet and the discharge is most likely quickly flushed out of the channel. Lawrence STP outfall is located in a small creek on the western edge of HB and the impact of the discharge is most likely contained within the creek. Jones Beach STP outfall represents a very small seasonal discharge into East Bay and is not expected to represent a significant source of sewage to the region. The two largest outfalls, Bay Park STP outfall (BPO) and Long Beach STP outfall, are located within 1 km of each other along Reynolds Channel along the south side of West Bay and effectively serve as a point source of treated sewage to the rest of Hempstead Bay.

Like other areas of the South Shores Estuary Reserve, the bottom of the Western Bays are largely covered with sandy sediments due to shallow depths and strong tidal and wind driven currents. The study plan was to focus on identifying sites with muddy, more depositional sediments that would better represent recent inputs and allow spatial comparison of sediments with more similar properties. In planning sampling locations, results from multi beam side scan were utilized to select candidate areas that were most likely to be depositional. In order to capture spatial variability, some sandier samples were also collected and analyzed for this study. In addition, samples close to marinas, landfills and former industrial sites were also targeted to represent additional potential contamination sources of metals and DEHP (Figure 5.1). Sample coordinates can be found in Table 3.1. Samples were collected with a modified Van Veen sampler or a similarly constructed Petite Ponar, and the top 5 cm were collected and stored in solvent cleaned glass jars. Samples were immediately frozen upon return to the lab. The distance of each sample from the BPO was calculated in Google Earth using the shortest distance between the outfall and the station along major channels.

Materials

Materials for the QAC extraction and analysis can be found in Appendix A1. Ethyl acetate (GC^2 grade), methanol (GC^2 grade), hexane (GC^2 grade) and toluene (GC^2 grade) used in the DEHP extraction were all Burdick and Jackson brand purchased from VWR (Radnor, PA). Supelclean LC-Florisil SPE columns cartridges were purchased from Sigma Aldrich (St. Louis, MO). The Di-ethylhexyl phthalate standard was part of the Method 8061 phthalate ester mix from Restek (Bellefonte, PA). Di-ethylhexyl phthalate-3,4,5,6-d_4 (d_4-DEHP) and chrysene-d_{12} was purchased from Cambridge Isotope Laboratories (Andover, MA).

QAC extraction and analysis

QACs were extracted based on the method presented in Li and Brownawell (2009 and 2010) and Lara-Martin et al. (2010) with two exceptions. The first includes using deuterated DTDMAC 12:12 as the surrogate standard so that native DTDMAC 12:12 can be analyzed in these samples. In addition, the HPLC method has been simplified to one run for analysis of all compounds. The full method is outlined in Appendix A1. In short, 100 mg of freeze-dried sediment was extracted using acidic methanol in a heated sonication bath. Extracts were cleaned up using a chloroform/water liquid-liquid extraction as well as a final weak ion exchange resin clean up step. Analysis was performed with an HPLC-ToF-MS using electrospray ionization in positive ionization mode. Sample recovery was based on spiked deuterated DTDMAC 12:12 and recoveries averaged 100% ± 19%. Precision for total QACs was based on extractions run in triplicate for a subset of samples and averaged 9.8% ± 6.37%.

DEHP extraction and analysis

A method was developed to effectively extract DEHP from sediments while minimizing blank levels. The extraction method is based on Ferguson et al. (2000), with an optimized Florisil clean-up method based on work by Bartolome et al. (2005). To minimize blanks, all glassware and sand was muffled at 450°C for at least four hours prior to use. Stainless steel columns were sonicated in hexane before use.

For the extraction, between 0.5 and 1.0 grams of freeze dried sediment were loaded into a 150 mm stainless steel column (4.6mm i.d.) fitted with 0.2µm stainless steel frits (Alltech Chromatography, Deerfield, IL) already loaded with clean sand, after which the sediment was spiked with d_4-DEHP and the column was filled with additional clean sand. The column was placed in a heated (55°C) sonication bath and methanol was run through the column at 0.5 mL/minute for 7 minutes for a total of 3.5 mL methanol. The extract was blown to dryness under a gentle stream of nitrogen.

Samples extracts were cleaned up using pre-packaged Supelclean LC-Florisil SPE columns with a bed weight of 1g and a volume of 6 mL. The columns were conditioned with 15 mL of ethyl acetate followed by 10 mL of hexane, a key step in minimizing procedural blanks. Samples were resuspended in 0.5 mL of hexane and loaded onto the column. Another 0.5 mL of hexane was used to rinse the remaining sample from the test tube and onto the column. Columns containing the sample were then washed with 12 mL of 4:1 mixture of hexane: toluene before being eluted with 5 mL of ethyl acetate. The ethyl acetate was blown to dryness under a gentle stream of nitrogen before being resuspended in hexane for analysis.

DEHP was analyzed using a Varian CP-3800 gas chromatograph with a Saturn 2200 ion trap mass spectrometer. A fused silica Phenomenex (Torrence, CA) Zebron ZB-5MS capillary column (30m x 0.25mm internal diameter) coated with a 0.25 µm film of 95% dimethylpolysiloxane and 5% phenyl-arylene was used to separate compounds. d_{12}-Chrysene was used as an internal standard for quantification, and calibration curves were run daily. The injection port was kept at 280°C. The run began with a one minute hold at 50°C, after which the temperature was increased to 305°C at a rate of 10°C/minute with a final 8 minute hold for a total run time of 34.50 minutes. Data was acquired from 45-450 m/z after a 4.75 minute delay in full scan mode.

Extraction recoveries of deuterated DEHP using this column extraction method were 115% ± 53%, and the reproducibility of the DEHP extraction procedure was 7.6%. Extraction recoveries for nine samples were below the first standard of d_4-DEHP but are still included in this calculation as peaks were three times the blank. Average blank levels for this method were below reporting limits based on the lowest standard of the calibration curve. Four samples were also below reporting limits and as such are not reported here. The area calculated for each sample reported is at least three times the average of the two method blanks for the run.

Metal extraction and analysis

Descriptions of metal extraction and analysis can be found in Chapter 3.

Statistical Analysis

Statistical analyses were used to determine if there was a significant relationship between each metal and distance from the BPO outfall and DTDMAC 18:18. An ANOVA was used to determine if a relationship existed between metals and distance and the F-statistic determined from this test was then used to obtain a p-value. For the relationship between metals and DTDMAC 18:18, a Type II regression was used as an independent variable could not be explicitly assumed. From the Type II regression coefficients, an F-statistic was calculated and the corresponding p-value is reported. A Spearman Rank Correlation test was also performed for metals and distance and metals and DTDMAC 18:18 and a correlation coefficient (Spearman's rho) and corresponding p-value were determined. The relationship for each metal and either distance or DTDMAC 18:18 was considered significant if both the F-test statistic and Spearman's rho were significant (p value 0.05 or less). Statistics were only performed for samples with Fe > 2.25% and Mill River samples were excluded.

5.3 Results and Discussion

5.3.1 QACs in Hempstead Bay

QACs were detected throughout Hempstead Bay at concentrations above detection limits, as presented in detail in Chapter 3, with concentrations ranging from 289 – 104,148 ng/g and generally decreasing with distance from the BPO (Figure 3.5). For many more soluble QACs, a progressive relative loss with distance was observed (Chapter 3). Together, these observations are consistent with a major BPO source, with a few samples impacted by the Lawrence STP outfall in a localized, isolated cove in far Western Hempstead Bay. The compositions of DTDMAC compounds with the longest chain lengths were consistent throughout HB, suggesting persistence of these compounds during transport, a conclusion further supported by similarity in distributions of DTDMAC 18:18 and an even more hydrophobic trialkylmethylammonium compound (TAMAC 16:18:18, Chapter 3). DTDMAC 18:18, which existed in the highest relative abundance (on average, comprising 44% of total QACs), was chosen to use as a sewage tracer for this study.

5.3.2 DEHP

DEHP in Hempstead Bay

DEHP was detected in all but four samples analyzed throughout Hempstead Bay, with concentrations ranging from 140 – 9,440 ng/g (Table 5.1) and decreasing with distance from the Bay Park STP outfall (Figure 5.2). These measurements fall within the range of published measurements in marine sediments, which range from 180 – 29,000 ng/g (Bartolome et al., 2005; Fromme et al., 2002; Giam et al., 1978; Lin et al., 2003; McDowell and Metcalfe, 2001; Peterson and Freeman, 1982). All samples measured are above the threshold effect level (118 ng/g) described by MacDonald et al. (1996), and 10 samples were above the probable effects level of 2,647 ng/g, all located in the West Bay region of HB.

The relationship between DEHP and DTDMAC 18:18 in Hempstead Bay was investigated, and the strong relationship observed (R^2 of .94, Type II regression) is consistent with sewage being the dominant source of DEHP to HB (Figure 5.3). This strong relationship also suggests that DEHP is persistent in this environment. No relationship is observed between DEHP and Fe, suggesting that the distribution of DEHP in HB, as well as the relationship between DEHP and DTDMAC 18:18, is not simply controlled by grain size.

A relatively constant ratio of DEHP to DTDMAC 18:18 with distance from the BPO suggests a common source and similar fate (Figure 5.4). If, as hypothesized, DTDMAC 18:18 is a relatively conservative particle tracer, it would also suggest that DEHP is also very strongly particle associated and not appreciably lost or degraded during transport. Estimates on the half-life of DEHP in oxidized sediments are rare, but Staples et al. (1997) suggested a half-life of greater than 100 days, while Staples et al. (2003) suggested a conservative estimate of 229 days for modeling purposes. Anaerobic degradation rates are expected to be significantly slower than aerobic degradation rates (Staples et al., 1997). In contrast, Fauser et al. (2009) used a half life of just 0.4 days in aerobic sediments and 1 day in anaerobic sediments when modeling the fate of DEHP in a Danish fjord; these estimated degradation rates appear to be unreasonably fast.

Additional evidence for sewage as a source of DEHP: the Palos Verdes shelf

Swartz et al. (1986) provide additional data that has been further analyzed in this study wherein DEHP can be compared to a persistent, particle reactive sewage tracer in a sewage-impacted coastal environment. The Los Angeles Sanitation District outfalls that discharge onto the Palos Verdes shelf represented a unique sewage source from 1950 until the 1980’s (Eganhouse et al., 2000). During this time, large loadings of the very stable pesticide metabolite 4,4-dichlorodiphenyldichloroethylene (4,4’-DDE) were introduced into the waste stream, with releases peaking in the late 1960’s/early 1970’s (Eganhouse and Pontolillo, 2000; Eganhouse et al., 2000). This resulted in 4,4’-DDE being discharged onto the Palos Verdes shelf, and a plume of DDE along a 60 meter isobath has since been measured down current (north) of the outfall (Swartz et al., 1986). Similar to DEHP, DDE has a log K_{ow} that is reported to range from 5.63 to 6.96 (Shen and Wania 2005), indicating that the reservoir of DDE is most likely located in the sediment and can serve as a unique sewage tracer of this particular sewage source.

DEHP and 4,4’-DDE were both measured by Swartz et al. (1986) along a transect away from the sewage outfall. In this study, we have used these reported values to assess the relationship between DEHP and 4,4’-DDE, with 4,4’-DDE representing a stable and particle reactive sewage tracer. Figure 5.5 shows the progressive decrease in both DEHP and 4,4’-DDE with distance from the sewage outfall. As seen above with DTDMAC 18:18, the log of the concentration DEHP was plotted against the log of the concentration of 4,4’-DDE (Figure 5.6), and a strong relationship (R^2 values of .92 and .76 for 1980 and 1983 data, respectively) is observed between DEHP and 4’4-DDE, once again consistent with a shared source, sewage.

While the ratio of DEHP to DTDMAC 18:18 was consistent throughout HB, (Figure 5.4), the ratio of DEHP/DDE decreases with distance away from the outfall along the Palos Verdes shelf (Figure 5.7). Such differences might be due to a combination of factors including less advanced treatment at the Los Angeles plant, deeper water depths (60m) along the California coast, and the fact that the release of DDE prior to 1983 was far from steady state. The input of 4,4’-DDE into the waste stream decreased significantly starting in the early 1970’s (Eganhouse and Pontolillo, 2000; Eganhouse et al., 2000) and would result in 4,4’-DDE concentrations increasing with distance from the source, which could have resulted in decreasing DEHP/4,4’-DDE ratios if DEHP levels remained steady. The ratio of DEHP/4’4-DDE decreases steadily with distance until the sample furthest from the source, where a sharp increase in the DEHP/4’4-DDE ratio is observed (Figure 5.7). There are two plausible explanations for this increase. The first could be the introduction of an additional source (ex. atmospheric deposition) at this point, which is most remote from the outfall (DEHP concentrations of 140-440 ng/g), which would provide an additional input of DEHP to the environment but not 4,4’-DDE. The second explanation could be blank problems, as blanks are a known issue in DEHP analysis and are particularly important at extremely low concentrations (Blount et al., 2000; Giam et al., 1975; Lin et al., 2003; Schwarzenbach et al., 2003).

Evidence from Hempstead Bay and Southern California indicate that in the two sewage-impacted environments studied here, sewage has the potential to be the dominant source of DEHP in sewage impacted estuarine and coastal waters. These studies represent the first empirical evidence that we know of that supports sewage as the dominant source in an urbanized environment. These findings may not hold true in all human impacted environments, as regions far from sewage sources, as suggested in Palos Verdes, may have additional sources of DEHP that are locally more important. HB results lead us to hypothesize that DEHP is also very persistent and stable in an estuarine environment.

5.3.3 Metals in Hempstead Bay

Metal concentrations in Hempstead Bay ranged from .04 – 2.14 μg/g for Ag, .07-.97 μg/g for Cd, 1.28 – 332 μg/g for Cu, 1750-51600 μg/g for Fe, .11 – 17.2 μg/g for Mo, 44.7 – 379 μg/g for Mn, 4.02 – 316 μg/g for Pb, and 9.76 – 636 μg/g for Zn (Table 5.1). The wide range of Fe values observed reflects the variation of sediment types sampled while attempting to obtain wide spatial coverage of the region. However, 50 and 38 samples had Fe values greater than 1.5% and 2.25% respectively, an indication that a majority of samples were fine-grained, muddy sediments. This assumption is further discussed in Chapter 3.

Metals were normalized to Fe and compared to crustal abundance values (also normalized to Fe) (Taylor and McLennan, 1995) to explore the degree of enrichment in HB. All metals except for Mn (discussed below) were enriched in all samples from this study (Table 5.2). The average enrichment factors for all samples for Ag, Cd, Cu, Mn, Mo, Pb and Zn were 20.3, 9.2, 2.8, 0.6, 2.8, 3.5 and 2.6, respectively (Table 5.2). HB Metal concentrations are similar to measurements in other local estuaries for these metals (Table 5.3, Figure 5.8) with some exceptions. While Fe values were very similar to other studies of fine grain deposits in the region, indicating similar sediment types, Cd and Mo levels were somewhat elevated and Mn levels were much lower in HB. In light of the correlation between total organic carbon and DTDMAC 18:18 as well as results that indicate that sewage is significantly retained within the Bay from Chapter 3, increased sewage-derived organic matter would lead to reducing conditions in the most sewage impacted regions of the Bay. Enrichment in Cd and Mo and depletion in Mn has been observed by others in sulfidic sedimentary conditions (Adelson et al., 2001; Brownawell et al., 2009; Morford et al., 2005; Nameroff et al., 2002) and would explain the differences observed between these studies.

Strong correlations with Fe (Figure 5.8) were observed for all metals in this study, indicating that grain size does affect the distribution of these metals in HB. It should also be noted that while most of the data from the EPA's Coastal Assessment Program agrees with the results obtained here, low Fe values indicate that most of the EPA's samples were sandy sediments (Figure 5.8) and may explain why concentrations from that monitoring program, which emphasized randomized station selection, are at the lower end of those observed in this study. The effects range low (ERL, blue line) and effects range medium (ERM, red line) values put forth by Long et al. (1995) are overlaid in Figure 5.8 for Ag, Cu, Mn, Pb and Zn. ERL and ERM values for Cd are not shown as they are significantly above the highest samples measured here. While several samples have values of these metals that are above ERL levels, the only samples that are above ERM levels are those found in Mill River, aside from one Pb sample from the upper east corner of East Bay.

Anthropogenic metals

Sewage as a source

Ag, Cu, Pb and Zn are traditionally considered to be anthropogenically mobilized metals that have been measured at enriched concentrations relative to background levels in local estuaries (Table 5.3), with sewage representing one potential source of these metals to HB. These metals are all enriched in HB (Table 5.3), with Ag having the highest average enrichment value. This is hypothesized to be due to large amount of sewage being discharged into HB and very low natural backgrounds for Ag, as sewage is often considered the dominant source of Ag to the environment (Sanudo-Wilhelmy and Flegal, 1992). As shown in Figure 5.8, while all metals showed a correlation with Fe, Ag showed the most varied response, and this may be due to sewage having a stronger influence on Ag distribution than grain size. While Cd may also have anthropogenic sources, it is not as particle reactive in seawater as other metals such as Pb, Cu and Ag, and it's distribution in HB is most likely controlled by redox conditions, as discussed above.

Metals were normalized by Fe to account for some of the effect of grain size on metal distributions. The impact of normalizing to Fe can be seen in Figure 5.9 for two representative metals. Plots of Fe normalized metals provide a better indication of the relationship between metals and distance from the source as well as metals with DTDMAC 18:18. Samples were further restricted by limiting analyses to only those samples with Fe values greater than 2.25% (to further select for fine-grained sediments that would be found in more depositional areas; Chapter 3) and removing MR samples, leaving 33 samples in the final analysis. In the case of Ag, increasing the cut-off to higher Fe concentrations makes little difference in the relationship between Fe normalized concentrations and distance, while for Pb, increasing the cutoff leads to a decreased number of samples that have concentrations falling above or below the trend line. The effects of reducing the number of samples considered by increasing Fe concentration cutoffs to 1.5 and 2.25% is more pronounced for some of the other metals, including Zn, and the redox sensitive Cd and Mn.

Ag, Cu and Zn were the only metals with a statistically significant relationship with distance from the BPO, and this relationship was not sensitive to Fe normalization (Table 5.4). After removal of an outlier in East Bay that were not reflective of mean conditions in HB, the relationship between both Pb and Pb/Fe and distance were statistically significant (p values of .0093 and .016, respectively). While both Cd and Cd/Fe showed some relationship with distance (i.e. the type II regression was statistically significant), it did not meet our stringent requirement for statistical significance. Interestingly, Fe normalization did not result in substantial improvements in the strength of the correlations (either p or rho). While the data for Cu and Zn indicates very slight decreases with distance from the BPO, indicative of very weak sources of these metals, a statistically significant relationship between these metals and the BPO indicate that sewage may serve as at least a minor source of Cu and Zn metals to Hempstead Bay.

More metals (Ag, Cd, Cu, Pb and Zn, with and without iron normalization using both tests, Table 5.5) were significantly correlated with DTDMAC 18:18 than with distance from the BPO. In almost all cases, metals appear to have a stronger relationship with DTDMAC 18:18 than with distance (lower p-value, larger rho). A stronger relationship between metals and DTDMAC 18:18 than with distance from the source may be due to their distributions being controlled by recent patters of deposition of sewage derived contaminants and sewage derived organic matter that might affect local redox conditions.

Ag has the steepest slope of all metals when plotted against DTDMAC 18:18 (Figure 5.10a), indicating the greatest dependence on sewage as a source, a result consistent with prior use of Ag as a sewage tracer. For Cu, Pb and Zn, while significant correlations do indicate sewage is one source of these metals to HB, the shallow slopes observed for the linear regression compared to the enrichment of these metals indicates that other sources must play a role in the distribution of these metals in Hempstead Bay. While the significant correlation between Cd and DTDMAC 18:18 indicates that sewage may serve as one source of Cd to Hempstead Bay, redox conditions as a result of greater sewage-derived organic enrichment in sediments near to the BPO may also cause this relationship. The relatively well-mixed signature of these metals in Hempstead Bay may also be a result of long-term redistribution of sediments and metals deposited long ago when metal inputs were greater and less regulated.

Other sources

In addition to sewage, there are other sources that may be contributing to excess metals in Hempstead Bay. One localized source that is most likely confined to West Bay is Mill River. Upon closer inspection of samples from MR (Figure 5.10, 5.11), Cu, Pb and Zn levels in MR increase with decreasing DTDMAC 18:18 values and increased distance from the Bay Park sewage outfall (i.e. up the river). This negative correlation, in contrast to the relationships observed in the rest of Hempstead Bay, suggests that sewage is not controlling the distribution of metals in MR. Samples taken near marinas and industrialized areas in Hempstead Bay do not indicate that these local, potential sources represent important inputs of metals to this region. Atmospheric deposition most likely also serves as an important source of these metals to Hempstead Bay, as suggested by Cochran et al. (1998) for Long Island Sound.

Confounding Factors

Interpretations of the data to assess the sources of metals within Hempstead Bay is confounded by a number of potential differences between metals and DTDMAC 18:18 that may exist in the environment. The method of transport of metals may be different than DTDMAC 18:18, particularly for those metals which may not be as particle reactive. Metal distributions may also be affected by seasonal influences related to mobilization of metals from sediment pore waters that have been documented to affect certain metals (Riedel et al., 1997). Time histories may also differ and would complicate the interpretation of observed trends. For example, while data from Chapter 4 of this thesis indicates that inputs of DTDMAC 18:18 to Hempstead Bay and Jamaica Bay have been fairly constant since the early 1990’s, Bopp et al. (1993) noted that metal inputs to the sewage-impacted Jamaica Bay peaked in the 1970’s and declined throughout the 1980’s and into the 1990’s due to a combination of STP upgrades and increased efforts to regular the use and release of metals in the United Sates.

Non-anthropogenic metals

Cd, Mn, and Mo are considered to be redox sensitive metals, and Mn and Mo are not traditionally thought of as metals affected by anthropogenic sources. The high levels of Cd and Mo and low levels of Mn observed in this study are similar to those measured in the highly eutrophied Forge River, NY (Table 5.3) where there is strong seasonal hypoxia and rates of sediment sulfate reduction. Elevated levels of Mo and Cd are likely a result of these redox sensitive metals being scavenged from the dissolved phase from the highly reducing and sulfidic sediments found in HB (Morford et al., 2005; Nameroff et al., 2002). Mn, which is present in relatively low abundance compared to other sites, has been found to be preferentially mobilized from sediments under reduced sedimentary conditions (Morford et al., 2005). When comparing Cd, Mn and Mo with and without Fe normalization to DTDMAC 18:18, Cd was the only metal with a significant relationship (Table 5.5), and no significant correlation between these metals and distance from the BPO was found (Table 5.4), although all of the higher concentrations of Mo are associated with stations with somewhat elevated levels of DTDMAC (Figure 5.10). While redox conditions are thought to be a major control on the distribution of Cd, Mn, and Mo, sewage sources of Cd cannot be discounted.

5.4 Conclusions

Quaternary ammonium compounds are highly elevated in Hempstead Bay and decrease in a consistent manner away from the major sewage source around the BPO. Organic enrichment of sediments was also seen to be greater in stations nearest to the sewage outfalls. In this study, we were able to show a strong correlation between DEHP, a particle reactive organic contaminant, with DTDMAC 18:18, an extremely stable and persistent sewage tracer, in Hempstead Bay as well as with 4,4’-DDE on the Palos Verdes shelf. To our knowledge, these studies represent the first empirical evidence for sewage as a dominant source of DEHP in an environment. Based on the linear relationship with DTDMAC, we hypothesize that DEHP is also very persistent in this environment in HB, with little loss to desorption or degradation during transport from the BP STP outfall. Decreasing ratios of DEHP and 4,4’-DDE in California with distance from the Los Angeles Sanitation District outfall may be due to the non-steady state inputs of 4,4’-DDE that preceded the sediment sampling. An increase in the DEHP/4,4’-DDE relationship for the point furthest from the outfalls may represent a new source of DEHP, but could also be attributed to blank problems. For metals in HB, Ag, Cd, Cu, Pb and Zn have significant relationships with DTDMAC 18:18 in HB, indicating that sewage is a possible source of these metals to HB. Sewage appears to be one of the most dominant sources of Ag to HB, while having a smaller impact on Cu, Pb and Zn. Cd correlations with DTDMAC 18:18 may be related to sewage-associated changes in redox conditions, but sewage may also represent a continuing source of Cd in Hempstead Bay. Mn and Mo distributions in HB appear to be driven mainly be redox conditions. These applications further demonstrate the important information about sewage-derived contaminants that can be gained through the use of QACs as tracers of sewage.

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Table 5.1. Concentrations of DEHP and metals in HB samples.

Station	DEHP	Ag	Cd	Cu	Fe	Mn	Mo	Pb	Zn
	ng/g	µg/g							
3	1460	1.16	0.82	52.4	31700	265	5.42	51.2	153
4	1180	0.8	0.82	64.8	33900	305	4.11	46.1	145
6	2080	1.38	0.88	69.5	33100	230	17.2	52.9	174
8	235	0.18	0.19	11.9	9300	127	0.57	14.7	42.1
8.5	946	0.5	0.32	20.3	13400	171	0.77	24.9	62.1
9	2460	0.07	0.07	2.59	1750	55.8	0.11	5.0	9.76
13	3660	1.58	0.9	89	28100	202	10.8	48.7	184
14	4320	0.1	0.14	5.04	4890	88.8	0.22	7.44	24
16	3700	1.01	0.5	36.9	23800	368	1.09	45.4	116
18		0.77	0.48	48.8	21600	185	2.8	40.8	114
19	2190	0.84	0.47	61.4	27800	346	2.52	46.2	123
21	4960	1.56	0.67	64.3	27200	233	7.7	50.2	157
22	3800	0.93	0.42	31.5	14100	140	1.89	32.7	90.3
24	9440	0.68	0.88	81.9	24900	205	11.4	60.9	204
25	3010	1.11	0.49	50.6	26100	339	1.38	54.2	138
26		1.05	0.63	56.3	27700	322	1.94	61	145
27	4470	2.14	0.69	66.1	30900	266	3.87	66	166
30	2890	1.17	0.84	65.5	29800	283	3.71	58.3	165
31		0.56	0.61	26.1	20500	239	1.6	30.9	94.3
33	235	0.17	0.25	10.9	8250	91.2	0.87	13.1	37.1
35		0.04	0.27	4.22	1970	44.7	0.11	4.02	12.3
37.2	361	0.51	0.42	25.4	25200	303	2.98	40.5	98.8
38.2		0.05	0.09	1.28	2280	63.2	0.15	5.2	10.3
40	294	0.28	0.31	25.3	16200	237	0.95	54.8	72.4
43	523	0.59	0.5	39.6	30100	361	1.73	128	121
46	584	0.74	0.75	63.3	31800	279	3.88	46.3	144
47	512	0.7	0.76	44.9	29900	270	2.01	13.1	135
48.4	140	0.44	0.54	20.7	20300	194	1.44	12.8	81.5
49.2		0.09	0.19	6.01	4560	79.4	0.27	6.91	22.2
55		0.72	0.24	28.2	15700	136	1.27	30.7	68.9
56		0.86	0.87	56.9	29400	208	4.29	48	154
61		0.46	0.29	19.6	12900	138	1	21.7	57.8
62		0.76	0.4	32	19800	161	1.54	35.4	84.2
63		0.55	0.31	23.1	16300	141	1.14	26.2	64.6
69		0.53	0.51	47.1	25600	194	2	41.1	129
72		0.81	0.82	128	37200	241	4.1	85.6	226
73		0.79	0.75	108	36400	242	3.83	59.5	202
74		0.81	0.77	72.5	30100	218	2.49	49.6	168
75		0.97	0.76	60	27300	194	8.96	45.8	147
79		0.22	0.28	16.6	15300	103	3.69	14	48.3
81		0.66	0.85	43.2	27800	208	2.46	42.9	114
85		0.39	0.43	33.7	25500	203	1.77	33.3	95.5
87		0.52	0.65	55.5	25900	215	1.72	32.7	131
88		0.8	0.78	84	33800	254	4.78	70.4	181
89		0.56	0.74	42.3	28900	223	3.52	50.9	120
93		0.34	0.47	29	20800	244	1.22	34.9	83
95		0.39	0.35	43.3	24700	275	1.67	38.6	114
102		0.65	0.54	35.6	26400	225	2.49	56.9	130
107		0.53	0.46	47.9	27700	269	1.77	46	129
115		0.5	0.57	45	25100	192	4.05	35.3	125
105b		0.28	0.41	38.3	16700	187	1.31	28.7	130
1B	2810	1.05	0.44	43.8	25100	270	1.39	55	120
2B	803	0.44	0.3	28.2	23500	265	1.4	29.2	81.1
3B	1790	0.96	0.55	47.6	28400	379	2.19	54.9	139
94b		0.38	0.34	36.6	22500	218	1.55	38	106
EL2		0.39	0.62	33.6	18500	89.1	2.65	82.4	126
MR1		1.51	n.r.	193	39600	220	4.45	143	259
MR2		1.19	0.76	253	42300	186	5.7	190	352
MR3		1.38	0.97	332	51600	169	9.69	316	636
NM		0.47	0.49	40.4	20300	183	1.54	44.4	105

Table 5.2. Enrichment factors for metals measured in Hempstead Bay. Calculated as (metal/Fe, sample)/(metal/Fe, crustal abundance) (Taylor and McLennan 1995).

Station	Ag	Cd	Cu	Mn	Mo	Pb	Zn	Station	Ag	Cd	Cu	Mn	Mo	Pb	Zn
3	25.6	9.3	2.3	0.5	4	2.8	2.4	**63**	23.9	6.8	2	0.5	1.6	2.8	2
4	16.6	8.6	2.7	0.5	2.8	2.4	2.1	**69**	14.4	7.1	2.6	0.4	1.8	2.8	2.5
6	29.3	9.6	2.9	0.4	12.2	2.8	2.6	**72**	15.2	7.9	4.8	0.4	2.6	4	3
8	13.7	7.3	1.8	0.8	1.4	2.8	2.2	**73**	15.2	7.4	4.1	0.4	2.4	2.9	2.7
8.5	26	8.4	2.1	0.7	1.3	3.3	2.3	**74**	18.7	9.1	3.4	0.4	1.9	2.9	2.7
9	26.3	14.4	2.1	1.9	1.5	5	2.7	**75**	24.9	9.9	3.1	0.4	7.7	2.9	2.7
13	39.5	11.5	4.4	0.4	9	3	3.2	**79**	10.1	6.6	1.5	0.4	5.6	1.6	1.6
14	13.8	10.5	1.4	1.1	1.1	2.7	2.4	**81**	16.6	10.8	2.2	0.4	2.1	2.7	2
16	29.6	7.5	2.2	0.9	1.1	3.3	2.4	**85**	10.7	6	1.9	0.5	1.6	2.3	1.8
18	25	7.9	3.2	0.5	3	3.3	2.6	**87**	14.1	9	3	0.5	1.5	2.2	2.5
19	21.1	6	3.1	0.7	2.1	2.9	2.2	**88**	16.6	8.3	3.5	0.4	3.3	3.6	2.6
21	40.1	8.9	3.3	0.5	6.6	3.2	2.8	**89**	13.6	9.2	2	0.5	2.8	3.1	2
22	46	10.6	3.1	0.6	3.1	4.1	3.2	**93**	11.6	8	2	0.7	1.4	2.9	2
24	19.1	12.5	4.6	0.5	10.7	4.3	4	**95**	11.1	5.1	2.4	0.6	1.6	2.7	2.3
25	29.7	6.8	2.7	0.8	1.2	3.6	2.6	**102**	17.4	7.3	1.9	0.5	2.2	3.8	2.4
26	26.5	8.1	2.8	0.7	1.6	3.9	2.6	**107**	13.3	6	2.4	0.6	1.5	2.9	2.3
27	48.3	8	3	0.5	2.9	3.7	2.6	**115**	14	8.1	2.5	0.4	3.8	2.5	2.4
30	27.4	10.1	3.1	0.6	2.9	3.4	2.7	**105b**	11.8	8.9	3.2	0.7	1.8	3	3.8
31	19.1	10.6	1.8	0.7	1.8	2.6	2.3	**1B**	29.2	6.3	2.4	0.6	1.3	3.8	2.4
33	14.4	10.7	1.8	0.6	2.5	2.8	2.2	**2B**	13.1	4.5	1.7	0.7	1.4	2.2	1.7
35	15.4	49	3	1.3	1.3	3.6	3.1	**3B**	23.7	7	2.3	0.8	1.8	3.4	2.4
37.2	14.3	5.9	1.4	0.7	2.8	2.8	1.9	**94b**	11.8	5.4	2.3	0.6	1.6	3	2.3
38.2	14.3	13.8	0.8	1.6	1.5	4	2.2	**EL2**	14.8	11.9	2.5	0.3	3.3	7.8	3.4
40	12.3	6.8	2.2	0.9	1.4	5.9	2.2	**MR1**	26.7		6.8	0.3	2.6	6.3	3.2
43	13.6	5.9	1.8	0.7	1.3	7.5	2	**MR2**	19.6	6.5	8.4	0.3	3.1	7.8	4.1
46	16.3	8.4	2.8	0.5	2.8	2.5	2.2	**MR3**	18.8	6.7	9	0.2	4.4	10.7	6.1
47	16.3	9	2.1	0.5	1.6	0.8	2.2	**NM**	16.4	8.7	2.8	0.5	1.8	3.8	2.6
48.4	15.1	9.4	1.4	0.6	1.7	1.1	2	**average**	**20.3**	**9.2**	**2.8**	**0.6**	**2.8**	**3.5**	**2.6**
49.2	13.8	15	1.8	1	1.4	2.7	2.4								
55	32	5.4	2.5	0.5	1.9	3.4	2.2								
56	20.6	10.5	2.7	0.4	3.4	2.9	2.6								
61	25	8.1	2.1	0.6	1.8	2.9	2.2								
62	27	7.3	2.3	0.5	1.8	3.1	2.1								

Table 5.3. Comparison of metal concentrations found in this study to those from other local studies as well as crustal abundances (Taylor and McLennan, 1995)
(n = number of samples, ranges indicate studies where the number of samples reported varied for individual metals).

Location	Date Collected	n	Reference		Ag	Cd	Cu	Fe	Mn	Mo	Pb	Zn
								µg/g				
Hempstead Bay	2011-2012	60	This work	Mean	*0.701*	*0.536*	*54.1*	*23700*	*212*	*3.09*	*50.1*	*128*
				Std Dev	*0.428*	*0.233*	*55.2*	*9970*	*78.6*	*3.13*	*47.1*	*90.4*
				Median	*0.657*	*0.501*	*43.2*	*25300*	*217*	*1.97*	*44.9*	*122*
Western, Central LIS	2008	16	Chapter 1, this thesis	Mean	1.06	0.824	70.6	38600	1030	1.69	50.5	131
				Std Dev	0.463	0.324	19.1	3430	226	0.347	15.7	20.5
				Median	0.924	0.712	67.6	38800	974	1.68	44.8	126
Western LIS	summary	141-453	Mitch and Anisfield 2010	Mean	0.54	0.63	89.0	27000	803	n.r.[a]	57.0	164
				Std Dev	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
				Median	0.97	1.18	116	26200	883	n.r.	87.0	183
Central LIS	summary	145-323	Mitch and Anisfield 2010	Mean	0.31	0.21	51.7	25800	722	n.r.	37.0	113
				Std Dev	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
				Median	0.71	0.92	83.8	24400	691	n.r.	45.6	137
LIS (depositional sites)	1996-1997	98	Mecray and Buchholtz ten Brink 2000	Mean	0.44	0.25	59.5	33100	1010	n.r.	47.7	146
				Std Dev	0.321	0.177	27.3	8550	433	n.r.	18.1	46.1
				Median	0.42	0.17	56.9	32900	903	n.r.	42.0	144
Western, Central LIS	1988	7	Cochran et al. 1991	Mean	n.r.	n.r.	107.1	37000	803	n.r.	108.6	216
				Std Dev	n.r.	n.r.	27.8	3850	165	n.r.	34.7	31.3
				Median	n.r.	n.r.	115.0	38500	800	n.r.	112.0	215
Forge River, NY	2006	13	Brownawell et al. 2009	Mean	0.79	1.20	87	36000	390	9	66	200
				Std Dev	0.13	0.56	31	4400	130	6.4	15	58
				Median	0.84	1.20	88	37000	350	8.3	66	200
NY/NJ Harbor Complex	1998	111	Adams and Benyi, 2003	Mean	1.8	0.97	80	20000	520	n.r.	97	190
				Std Dev	1.3	0.99	82	11000	210	n.r.	81	130
				Median	1.9	0.75	62	19000	480	n.r.	88	170
Hudson River	1994-1996	31	Feng et al. 1998	Mean	2.23	1.00	77.8	34400	n.r.	n.r.	81.5	182
				Std Dev	1.50	0.566	31.7	5600	n.r.	n.r.	33.5	40.6
				Median	2.08	0.77	68	35100	n.r.	n.r.	82.0	180
Jamaica Bay	1981-1984	71	Seidemann, 1991	Mean	n.r.	0.86	33.3	n.r.	n.r.	n.r.	55.7	71.3
				Std Dev	n.r.	0.97	60.7	n.r.	n.r.	n.r.	78.0	76.7
				Median	n.r.	0.53	14.1	n.r.	n.r.	n.r.	30.5	43.0
Jamaica Bay	1978	52	Ramondetta and Harris, 1978	Mean	n.r.	3.15	85.7	n.r.	n.r.	n.r.	115	196
				Std Dev	n.r.	3.32	117	n.r.	n.r.	n.r.	121	256
				Median	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
Crustal Abundance	n/a		Taylor and McLennan 1995		0.05	0.10	25.0	35000	600	2	20	71

a. value not reported

Table 5.4. The p-value of the ANOVA as well as Spearman's Rho and associated p-value ($p \leq 0.05$) for the relationship between individual metals and distance from the BPO outfall for samples with Fe> 2.25%, without MR. A relationship was considered significant if values from both the F-test and Spearman's Rank Correlation were significant; these metals are highlighted in grey. The ANOVA analysis for Pb and Pb/Fe was found to be significant (p = .0093 and .016 respectively) when an outlier in East Bay was removed.

Metal	ANOVA	Spearman Rank Correlation		Metal	ANOVA	Spearman Rank Correlation	
	p-value	Rho	p-value		p-value	Rho	p-value
Ag	7.89E-05	-0.74	8.32E-07	Ag/Fe	1.93E-05	-0.81	1.33E-08
Cd	0.036	-0.28	0.12	Cd/Fe	0.02	-0.34	0.06
Cu	3.00E-05	-0.45	0.01	Cu/Fe	0.01	-0.50	3.0E-03
Fe	0.47	-0.03	0.89				
Mn	0.41	-0.15	0.40	Mn/Fe	0.61	-0.08	0.64
Mo	0.14	-0.15	0.41	Mo/Fe	0.12	-0.15	0.41
Pb	0.55	-0.44	0.01	Pb/Fe	0.58	-0.44	0.01
Zn	4.92E-06	-0.42	0.02	Zn/Fe	0.02	-0.50	3.0E-03

Table 5.5. The p-value of the F-test statistic as well as Spearman's Rho and associated p-value ($p \leq 0.05$) for the relationship between individual metals and the concentration of DTDMAC 18:18 for samples with Fe> 2.25%, without MR. A relationship was considered significant if values from both the F-test and Spearman's Rank Correlation were significant; these metals are highlighted in grey.

Metal	F-test p-value	Spearman Rank Correlation		Metal	F-test p-value	Spearman Rank Correlation	
		Rho	p-value			Rho	p-value
Ag	8.46E-07	0.83	2.71E-09	Ag/Fe	2.16E-07	0.86	1.49E-10
Cd	3.18E-05	0.39	0.02	Cd/Fe	8.21E-06	0.37	0.03
Cu	1.67E-06	0.55	1.05E-03	Cu/Fe	9.49E-08	0.53	1.72E-03
Fe	4.34E-04	0.29	0.29				
Mn	1.90E-04	0.26	0.14	Mn/Fe	1.96E-04	0.10	0.60
Mo	1.51E-05	0.26	0.15	Mo/Fe	6.03E-06	0.23	0.21
Pb	8.15E-05	0.58	4.29E-04	Pb/Fe	6.22E-05	0.53	1.57E-03
Zn	4.43E-07	0.56	6.68E-04	Zn/Fe	5.06E-09	0.55	9.76E-04

Figure 5.1. Sample locations in Hempstead Bay. Yellow dots correspond to sample locations, while red dots are the STP outfalls.

Figure 5.2. DEHP (ng/g) versus distance (km) from the Bay Park STP outfall in Hempstead Bay.

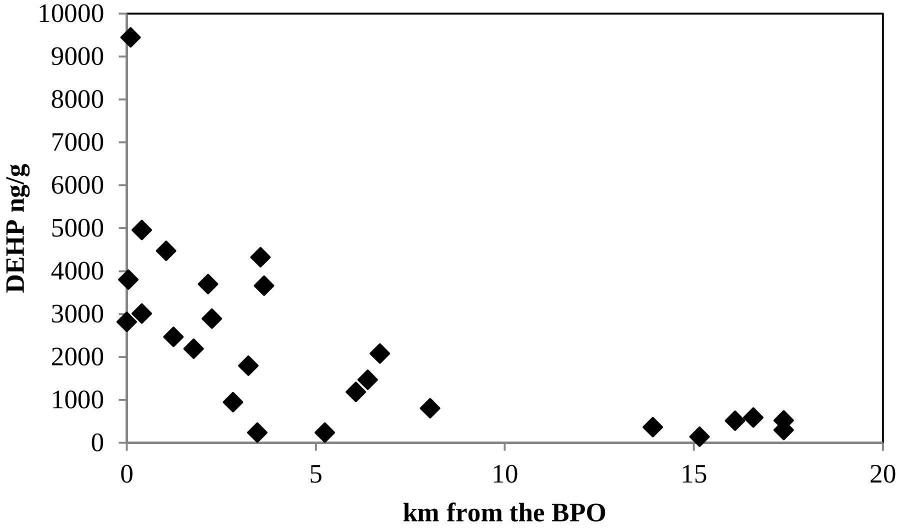


Figure 5.3. DEHP (ng/g) versus DTDMAC 18:18 (ng/g) in Hempstead Bay.

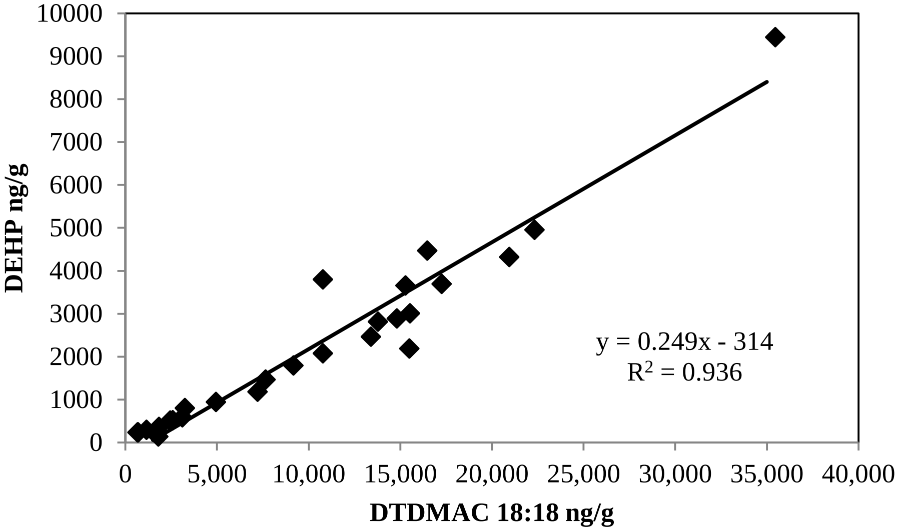


Figure 5.4. DEHP/DTDMAC 18:18 versus distance (km) from the Bay Park STP outfall.

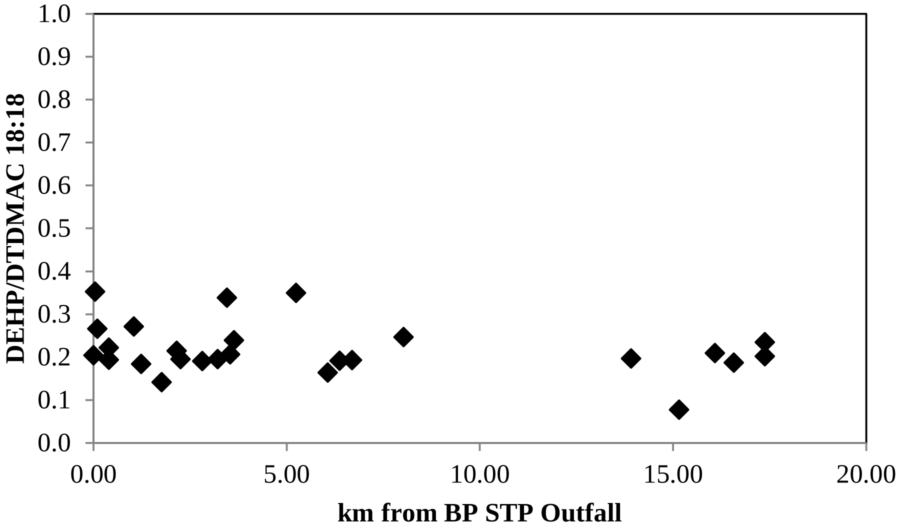


Figure 5.5. DEHP versus distance (km) from the sewage outfall along the Palos Verdes shelf.

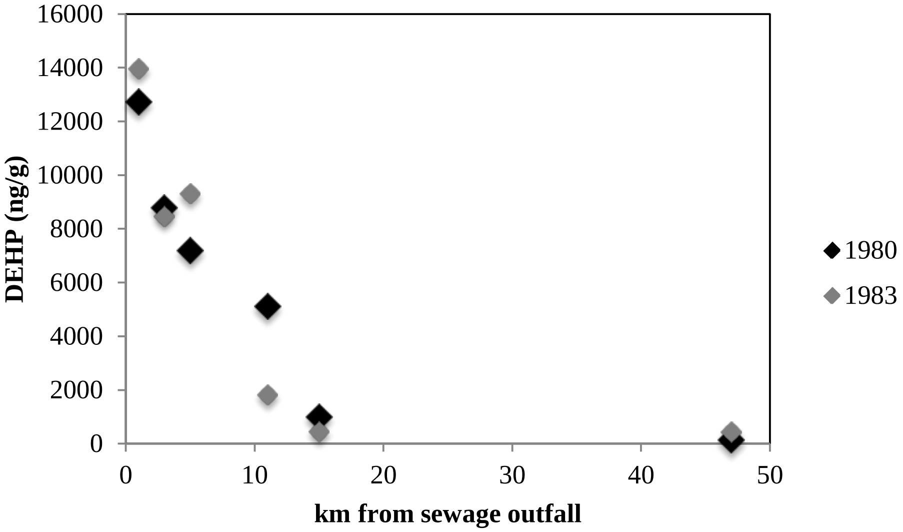


Figure 5.6. The log of DEHP (ng/g) versus the log of 4,4'-DDE (ng/g) along the Palos Verdes shelf. (Swartz et al., 1986)

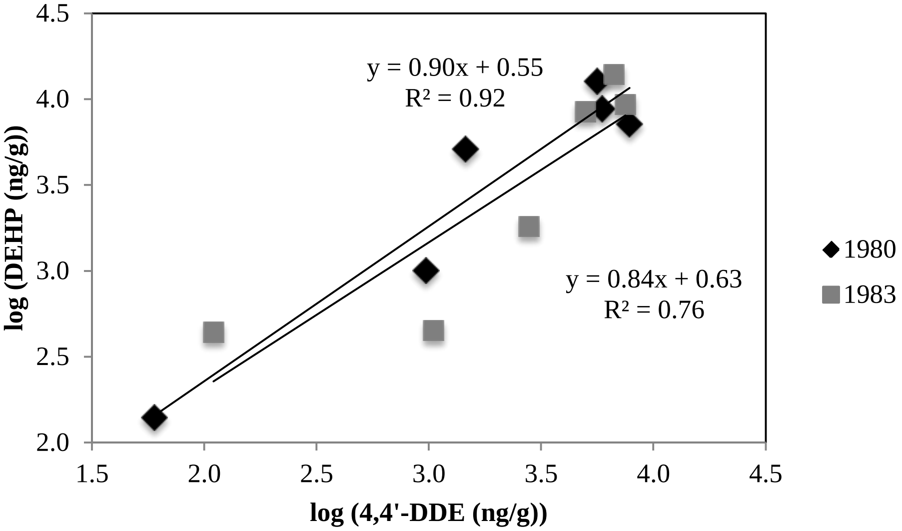


Figure 5.7. DEHP/4,4’-DDE versus distance (km) from sewage source.

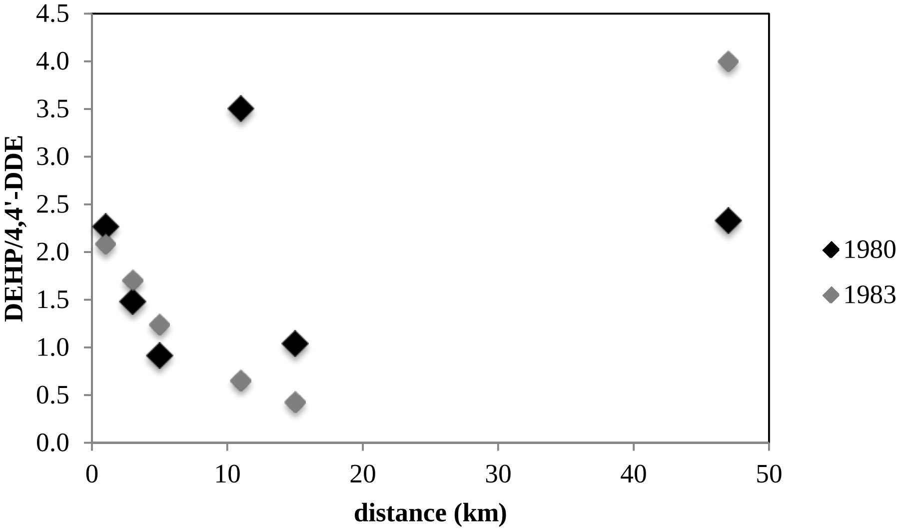


Figure 5.8. Anthropogenic metals versus Fe with data from EPA's Coastal Assessment Program (2000-2005) as well as ERL and ERM values. Blue solid lines are ERLs, red are ERMs. Cadmium values are all below ERL values, and Mo does not have ERL and ERM values.

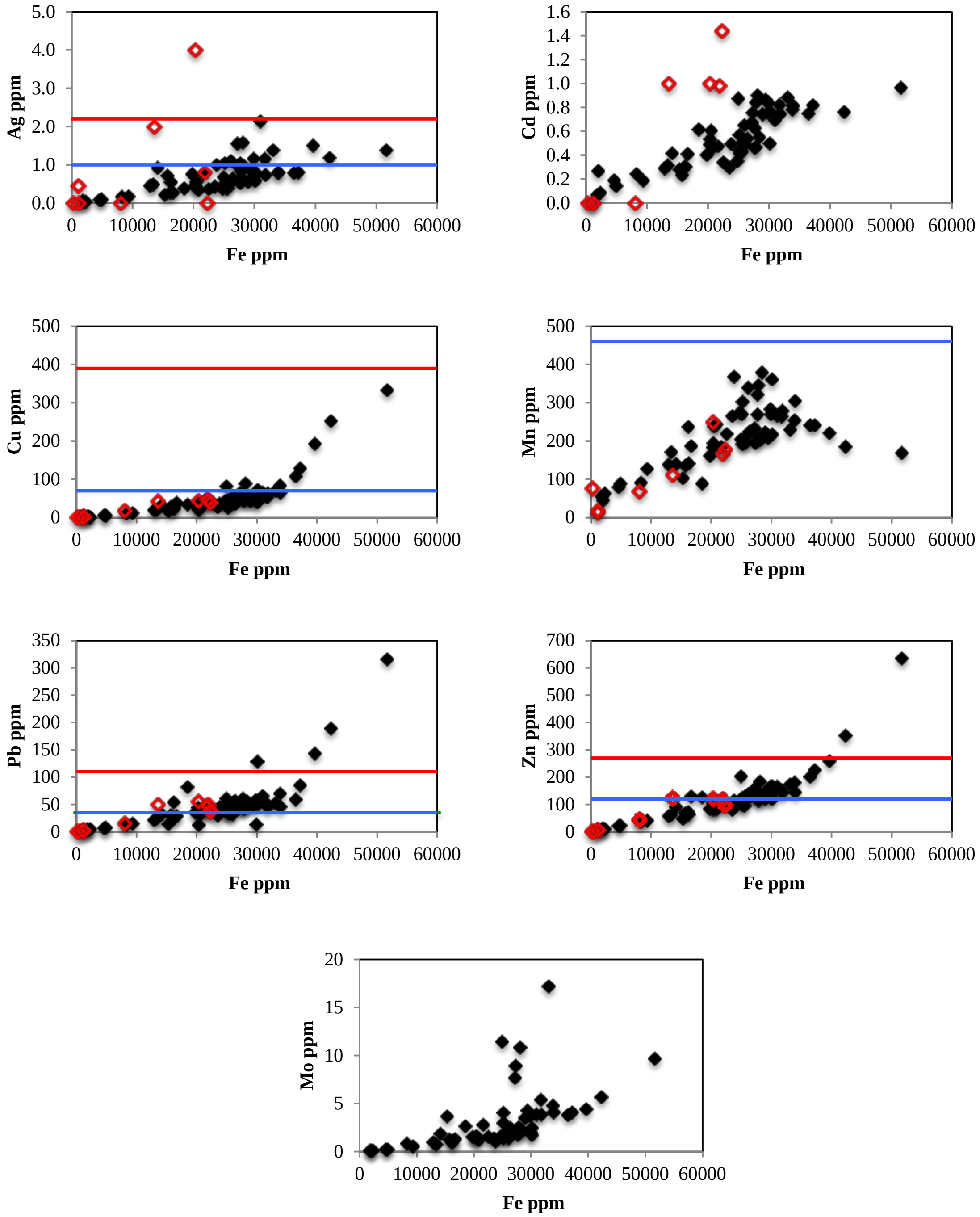


Figure 5.9. Representative anthropogenic metals, silver (Ag) and lead (Pb) with distance (km) from Bay Park STP outfall.

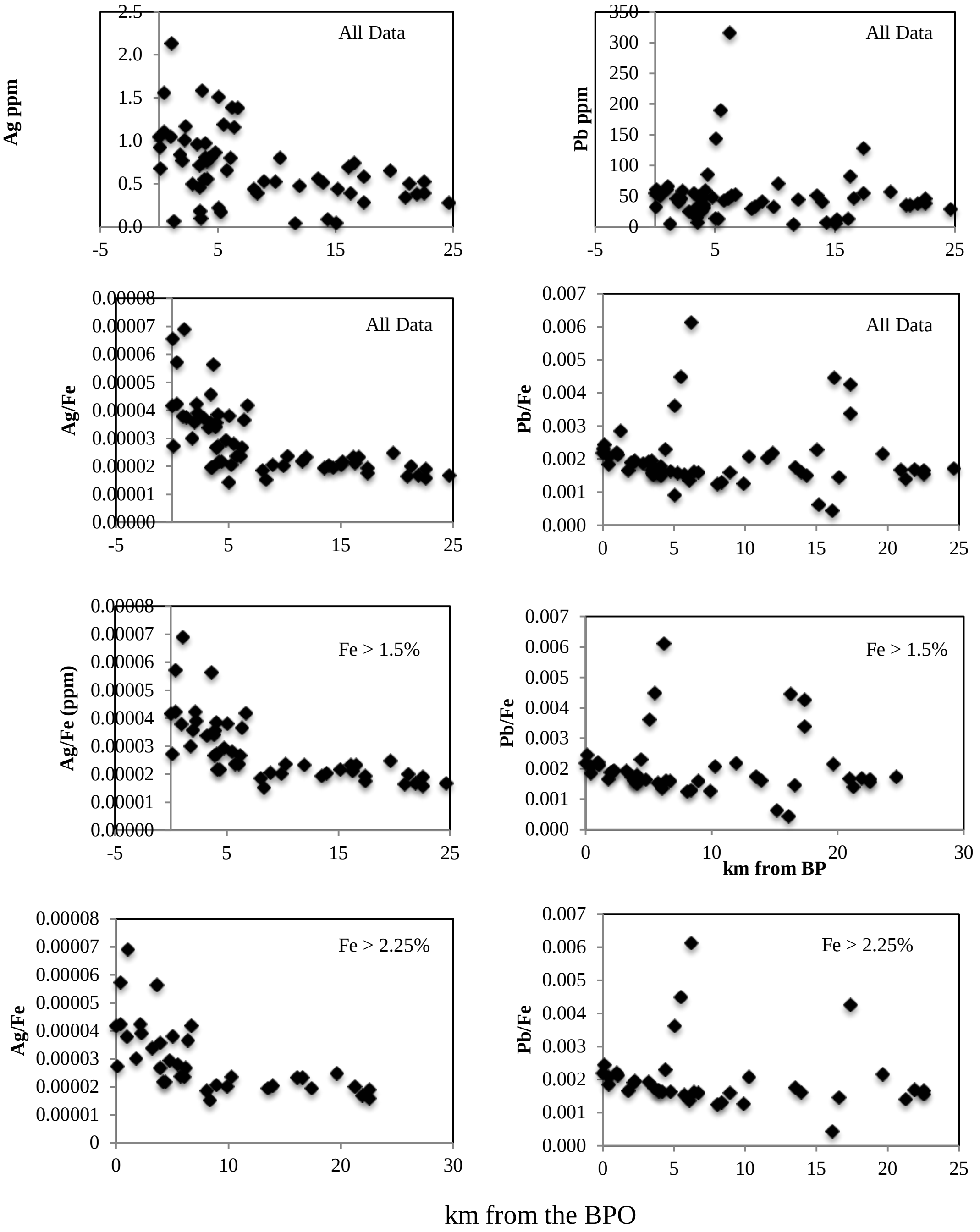


Figure 5.10. Concentration of metals for samples with Fe greater than 2.25% that have been normalized to Fe plotted against DTDMAC 18:18 (ng/g). Mill River samples are in grey.

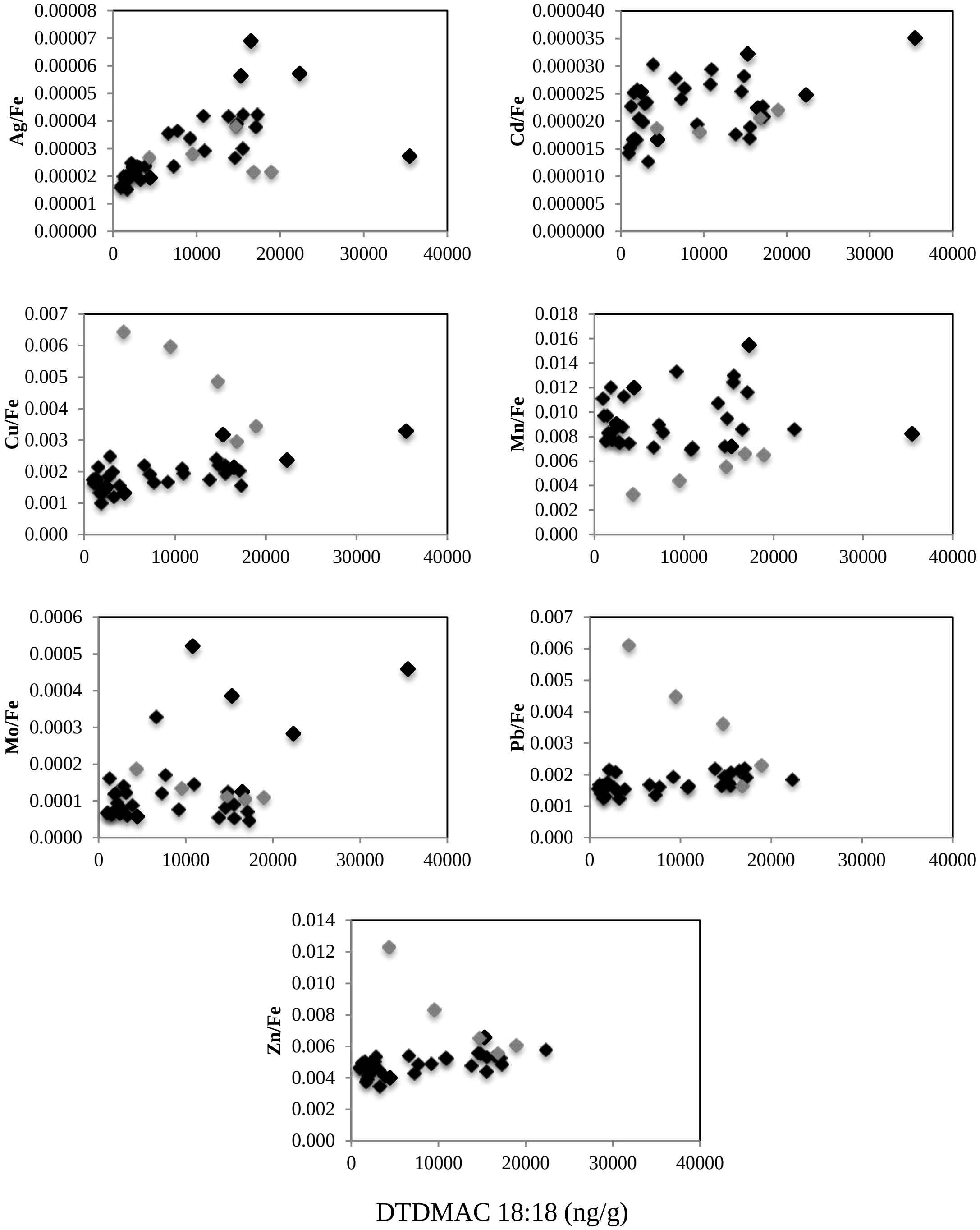
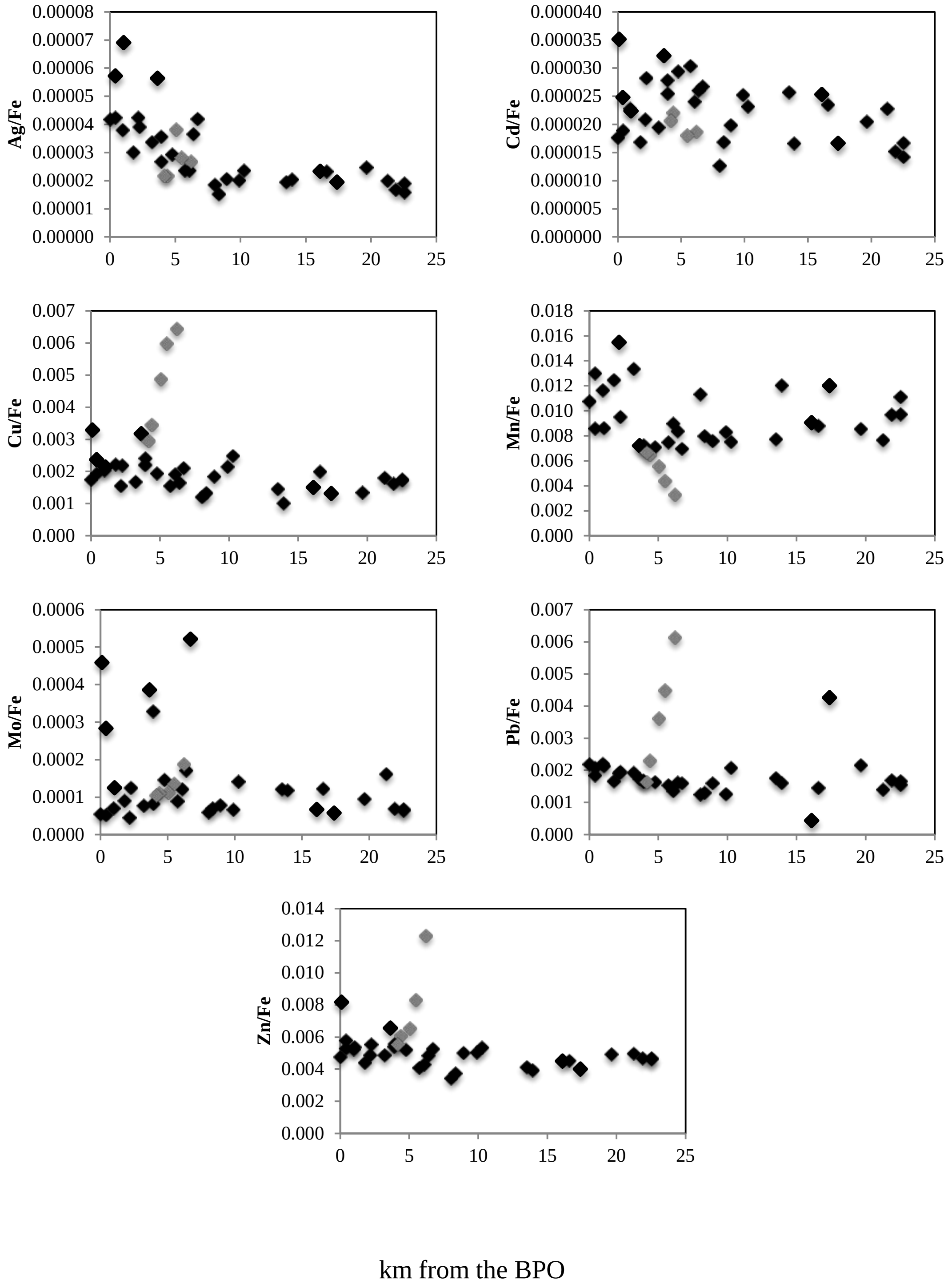


Figure 5.11. Concentration of metals for samples with Fe greater than 2.25% that have been normalized to Fe plotted against distance (km) from the Bay Park STP outfall. Mill River samples are in grey.



CHAPTER 6. The oxic and anoxic degradation of quaternary ammonium compounds in estuarine sediments.

6.1 Introduction

Quaternary ammonium compounds (QACs) are cationic surfactants used in a wide variety of applications, including disinfectants, personal care products, and fabric softeners. Understanding the environmental fate of QACs is important due to their high environmental concentrations as well as their potential to serve as a sewage tracer. In this study, the potential for biodegradation of QACs in oxic and anoxic sewage-impacted sediments is investigated to gain additional insight into the fate of these compounds once released into the aquatic environment.

QACs are comprised of a positively charged nitrogen atom with four substituents and are divided into three major classes: benzylalkyl dimethyl ammonium compounds (BACs) and alkyltrimethyl ammonium compounds (ATMACs), which have only one long alkyl side chain, and, dialkyldimethyl ammonium compounds (DADMACs), which have two long alkyl side chains. The largest DADMACs (C12:C12-C18:C18) have traditionally been referred to as ditallowdimethyl ammonium compounds (DTDMACs). DTDMACs are the largest and most hydrophobic of all of the QACs in this study and have been measured at extremely high concentrations in sewage impacted estuaries (ΣQACs from 1-114 μg/g, Li and Brownawell, 2010). ATMACs and BACs are the smallest and therefore most soluble and least hydrophobic QACs and are typically considered to be more toxic than the larger DTDMACs (Garcia et al., 2001; Pantani et al., 1995; Singh et al., 2002; Utsunomiya et al., 1997). More detailed information on the history, use, and toxicity of these compounds can be found in the introduction of this dissertation (Chapter 1).

As noted above, there is considerable concern about QACs in sewage-impacted environments due to their extremely high environmental concentrations, and understanding the potential for biodegradation of QACs in the environment is crucial in conducting risk assessments. In addition, if QACs are to be used as particle reactive sewage tracers, more research on the environmental persistence of these compounds is necessary. Literature attempting to understand the biodegradation of QACs is conflicted, with wide ranges of biodegradability reported for the same compound (Boethling, 1984). This is in part due to several issues associated with QACs, including strong non-linear adsorption isotherms for QACs in sediments (Boethling, 1984; Brownawell et al., 1990; Li, 2009; Li and Brownawell, 2010; Madsen et al., 2001) such that the experiments using high spike concentrations may not be representative of smaller concentrations in the environment when QAC adsorption is thought to be strongest, as well as toxicity associated with high spiking levels, particularly for ATMACs and BACs (Boethling, 1984; van Ginkel and Kolvenbach, 1991; Madsen et al., 2001). Degradation may also be greater at higher concentrations due to the ability of the bacterial communities to use high levels as an energy source. In addition, there is a wide range of methods that have been used to understand biodegradation and may result in highly variable results (Boethling, 1984; Cross and Singer, 1994).

QAC degradation is closely tied to their physical properties, with the smallest QACs (BACs and ATMACs) considered to be more biodegradable than the larger DTDMACs (Boethling, 1984; Cross and Singer, 1994), and degradation being inversely proportional to chain length (Boethling, 1984; van Ginkel and Kolvenbach, 1991). Acclimation has also been found to be extremely important for the biodegradation of QACs (Cross and Singer, 1994; Federle and Pastwa, 1988; Games et al., 1982). The major degradation pathway for QACs is thought to be through n-dealkylation at the C-N bond (García et al., 2000; Tezel et al., 2012; Ying, 2006), with studies suggesting that this degradation is first order (Games et al., 1982). Studies indicate that degradation intermediates (tri, di and monoalkylamines, Nishiyama et al., 1995) are not persistent (Games et al., 1982; Nishiyama et al., 1995), suggesting that once primary biodegradation occurs, ultimate biodegradation should be fairly rapid.

Studies using sewage sludge spiked with QACs have found BACs, ATMACs and DTDMACs to be readily biodegradable (García et al., 2001; Gerike, 1978; van Ginkel and Kolvenbach, 1991; Nishiyama et al., 1995; Sullivan, 1983), yet a mass balance study in a sewage treatment plant (STP) indicates that this is not the case for DTDMACs (Clara et al., 2007). In this study by Clara et al. (2007), loss of BACs, ATMACs and DADMACs was a result of both adsorption onto particles as well as biodegradation, while the loss observed for DTDMACs was thought to be only a function of adsorption onto particles, which has been suggested in other studies (Martinez-Carballo et al., 2007). There are far fewer studies on the anoxic degradation of QACs, but most conclude that QACs are far less biodegradable, if at all, under these conditions (Brownawell et al., 2013; Garcia et al., 1999; García et al., 2000; Ying, 2006).

Experiments to understand the biodegradation of QACs under environmental conditions are once again scarce and conflicting. While some have found that biodegradation is only a function of the fraction of ATMAC 12 not adsorbed onto sediments in a settled sediment column (Shimp and Young, 1988), others have suggested that for both ATMACs and DTDMACs, the portion sorbed to sediments has no affect on biodegradation (Larson and Vashon, 1983) and that they are readily biodegradable in river water. A review of data available for ATMACs by Cross and Singer (1994) suggests that ATMACs should be readily biodegradable in sediments and should not accumulate, yet measurements of these compounds in this dissertation and elsewhere (Lara-Martín et al., 2010; Li, 2009; Li and Brownawell, 2010) suggest otherwise. Additionally, a study by Federle and Pastwa (1988) suggests that larger QACs (ATMAC 18, DTDMAC 18:18) can be mineralized in acclimated sediments from a pond that has been exposed to QACs, but un-acclimated control sediments were unable to degrade the compounds, highlighting the importance of acclimation in the biodegradation of QACs.

It is apparent that while there are numerous studies on the biodegradation of QACs, these studies are often in conflict and leave many unanswered questions on the persistence of these compounds in the environment. Studies by Li and Brownawell (2010) and in Chapter 3 of this dissertation have suggested that the relatively stable composition of the largest QACs throughout sewage-impacted environments indicates that these compounds are persistent in muddy, depositional sediments, although changes were observed in the composition of smaller QACs in Chapter 3, suggesting the possibility of degradation of these compounds in the environment. In addition, measurements of QACs at distances greater than 70km from the major sources in Long Island Sound (Chapter 2) indicate that QACs are persistent to great distances. Matched cores taken over a span of 20 years also indicate that little *in situ* degradation is occurring once these compounds are buried under anoxic conditions (Li, 2009, Chapter 4), but cannot rule out the possibility of degradation of QACs in surface sediments. In fact, many of the more potentially labile QACs have sediment profiles that often increase towards the sediment water interface (Chapter 4).

In this study, the degradation of QACs in sediments taken adjacent to the Bay Park STP outfall (BPO) in Hempstead Bay is investigated under both oxic and anoxic conditions. Past incubations of sediment to study biodegradation of contaminants with slurries of sulfidic marine muds from organically enriched urban estuaries have resulted in a buildup of toxic metabolites from organic matter decomposition (sulfide and ammonia) as well as decreases in pH caused in large part by oxidation of iron and perhaps other metal sulfides (Ferguson and Brownawell, 2003) that could negatively impact the results of the study. In Ferguson and Brownawell (2003), pre-oxidation of reduced Jamaica Bay mud prior to oxic incubations reduced the rate of acid formation but did not stop a substantial drop in solution pH (pH change from 6.2 to 2.8) over a couple month time scale. In this work, we have employed the use of open plug incubations as described by Aller and Mackin (1989) in which extremely thin plugs of sediment are incubated in a tank full of oxic seawater. In this set up, the small length scale of the sediment allows for fairly rapid diffusion-limited oxidation of the sediments, as well as diffusion of toxic metabolites out of the sediment. In addition, losses to desorption for these particle reactive compounds are most likely less important than in dilute slurries, given the retardation of diffusive transport through porous media, although QACs possess high sorption coefficients at environmentally relevant low concentrations. Due to cost restrictions, this same method was not applied for the anoxic incubation, which instead were conducted in sealed tubes immersed in anaerobic mud. This study attempts to accurately determine the biodegradation potential of QACS in both fully oxidized as well as anoxic sediments. The potential for a difference in degradation of strongly sorbed, aged QACs from freshly spiked QACs is also investigated. This work aims to provide a more realistic understanding of the fate and persistence of QACS in sewage-impacted environments.

6.2 Experimental

6.2.1 Incubation Setup and Execution

Four incubations in total were performed, including one incubation under anoxic conditions using sediment from the BPO (2012), two incubations under oxic conditions using sediment from the BPO (2011 and 2012), and one incubation under oxic conditions using sediment from the East Bay (2012; Figure 5.1). Data from the East Bay incubation was affected by poorly constrained initial conditions, and are therefore presented in Appendix A2.

Incubation Sediments

Surface sediments for the incubations were taken from Hempstead Bay, NY, a sewage-impacted lagoonal estuary. Hempstead Bay is a unique environment in which all of the sewage inputs are focused in one region of the Bay. The dominant outfall in this region is the Bay Park sewage treatment plant (STP) outfall which discharges 49.9 million galls per day (MGD) (Interstate Environmental Commission, 2010) and is located only 1km away from the smaller Long Beach STP outfall which discharges 5 MGD. More information on Hempstead Bay is available in Chapters 1, 3, 4 and 5.

Sediments were collected for these incubations proximal to the BPO to represent highly acclimated, sewage-impacted muds (Figure 5.1), as acclimation has been shown to be important in the degradation of QACs (Cross and Singer, 1994; Federle and Pastwa, 1988; Games et al., 1982). Collection for the 2011 BPO oxic incubation occurred in October of 2011, and collection for the 2012 BPO oxic and anoxic incubations occurred in June of 2012. Sediments (top 5cm) were collected using a ponar grab sampler and stored in solvent washed glass jars and refrigerated (4°C) upon return to the lab. Experiments were begun within two weeks of sediment collection.

Sediment Spiking

Clean, empty glass jars were spiked with individual standards of d-34 ATMAC 12, d-25 DTDMAC 12:12, and d-3 DTDMAC 18:18 at appropriate levels to obtain final concentrations of 20 μg/g dry weight each. The amount of each standard needed was calculated based on the amount of wet sediment needed to fill sample disks, assuming a fifty percent water weight. After introducing the spike to the glass jar, the solvent was allowed to evaporate while turning the jars to distribute the standards across the glass surface. Evaporation was aided by blowing nitrogen gas into the jar. After the solvent was completely evaporated, between 35-205 g of sediment was added to the jars and seawater from Stony Brook Harbor (10mL or less) was added to the sediment to create a thick slurry. The jars were then placed on a rotating wheel for six hours.

Anoxic Incubation

When sediments had been spiked, the slurry was pipetted into 4mL screw top amber glass vials. Snap cap vials (2mL) were also filled with the slurry for porewater sulfate monitoring. The vials were then placed into a small cooler that was filled with mud to ensure complete anoxic conditions and left at room temperature (20-25°C) for the duration of the experiment. At each desired time point, two samples as well as one snap cap vial were removed. The samples were immediately frozen while the snap cap vial was immediately centrifuged at 8,000 rpm for 10 minutes to separate the sediment from the pore water. The pore water (about 1mL) was then removed with a pipette, preserved with HCl, and stored in the refrigerator until analysis.

Oxic Incubations

After spiking, sediment for oxic incubations was placed in a Teflon centrifuge tube and quickly centrifuged to remove excess water such that sediment to be loaded into plugs was sufficiently cohesive (porosity between 0.80 and 0.85). Excess seawater was then decanted, and the sediment was added to the disks. If needed, a portion of the decanted seawater was added back into the centrifuge tube to obtain the desired sediment water content.

Oxic incubations were conducted using plug incubations, as outlined by Aller and Mackin (1989). For these experiments, large polycarbonate cylindrical tanks (18.8L) were used to hold seawater and plugs were placed on the bottom. Plug containers were made of polycarbonate bottle caps (Figure 5.2a) that were made negatively buoyant with a small washer covered with paraffin wax until the depth of the disk was 2-3mm, the maximum thickness for which molecular diffusion from overlying seawater would oxidize sediments. The plug containers also had a lip on one side that facilitated raising and lowering them into the tanks. The plug containers and tanks were soaked in Stony Brook Harbor seawater for one week before the experiment was begun to minimize any potential leaching of contaminants from them into the sediments.

To begin the experiment, tanks were placed on a large stir plate and filled with Stony Brook Harbor seawater and allowed to come to room temperature. Sediment was placed into the sample containers using a spatula until flush with the rim of the disk (Figure 5.2b). Disks were then carefully placed into the tank using long tweezers. To ensure that entire water column remained oxic, a magnetic stir bar was placed in the bottom of each tank in a small dish and air was bubbled into the water using an aquarium bubbler attached to a glass pipette that was attached to the side of the tank (Figure 5.2c). Complete oxidation of the sediment, noted by a color change from blank to grey, was seen in two days or less (Figure 5.2b). The water temperature varied from 21-24°C throughout the course of the experiments.

Sampling of plugs as a function of time

At each time point a disk was carefully removed using long tweezers. The sediment was then gently scraped off the disk using a metal spatula into a screw top vial and immediately frozen. Samples were then freeze-dried and extracted according to the QAC method described below and in Appendix A1. The 2012 BPO oxic incubation was stopped at 58 days because benthic organisms had sufficiently redistributed the sediment throughout the tanks such that sample collection was no longer possible. Evidence of the loss of fine grained sediment from the plugs was observed around 30 days into the incubation by a distribution of fine sediment on the bottom of the tank, most likely a result of meiofaunal activity (Aller and Aller, 1992).

6.2.3 Sample Analyses

QAC Extraction and Analysis

QACs were extracted based on the method outlined in Appendix A1 with two modifications. In short 0.1 grams of freeze-dried sediment was extracted using acidic methanol in a heated sonication bath. Extracts were then cleaned up using a chloroform:water extraction as well as an anionic exchange resin to remove additional matrix. Between the 2011 and 2012 incubations, it was determined that the method for QAC extraction and purification that has been well tested for other QACs did not result in complete recovery of ATMAC 12 and its deuterated analog. It was determined that this loss occurred during the seperatory funnel extraction and appears to be more problematic in low matrix extracts. To overcome this problem, 36 µg of linear alkylbenzene sulfonate (LAS) was added to the 30mL sample as an ion-pair reagent to the seperatory funnel during the chloroform:water liquid-liquid extraction, as suggested in other studies (Gerike et al., 1994; Martinez-Carballo et al., 2007), to allow for the quantitative extraction of ATMAC 12. In addition, no surrogate standards were used in these extractions because the deuterated QAC standards were spiked in the experiment, so extraction recovery information is not available. Analysis was performed on an HPLC-ToF-MS using electrospray ionization in positive ionization mode. Precision, determined from time point triplicates from the 2012 BPO oxic and anoxic incubations, was 9% ± 5% for total QACs.

Sulfur Analysis

Porewater samples were diluted one hundred times before analysis. Samples were analyzed on an Ultima 2C ICP Optical Emission Spectrometer from Horiba Scientific using a one-point standard of sodium sulfate.

Statistical Analysis

Statistical methods were applied to determine if a significant loss was observed for each compound over the course of the oxic incubation experiments. Based on results from TAMAC analyses discussed below, only the first 30 days of the 2012 BPO oxic incubation were used in these analyses. For the each data set (2011 and 2012), an ANOVA linear regression was performed to determine if the slope of the data was significant by calculating an F statistic. The corresponding p-values are reported below, p-values below 0.05 were considered to be significant. The sign (positive or negative) of the slope is also reported.

6.3 Results and Discussion

Data for the deuterated QACs (Tables 6.1-6.2) indicates that the method used for spiking was successful in homogenously distributing the deuterated QACs onto the sediments, as concentrations of the spiked deuterated DTDMAC 12:12 and DTDMAC 18:18 were extremely close to the targeted spike concentrations of 20 μg/g (Tables 6.1, 6.2 and 6.3). The measured initial concentrations of deuterated ATMAC 12 in the 2012 BPO oxic and anoxic experiments were between 15.3 and 22.1 μg/g, but only 5.92 μg/g for the 2011 incubation. This increased recovery of spike was due to the use of LAS to increase the extraction efficiency of ATMAC in the 2012 analyses. However, high precision was obtained for native and deuterated ATMAC 12 even when apparent recoveries were low in 2011, and therefore, results for the earlier data set are presented here.

No significant loss of any QACs were indicated in the closed anoxic experiments, with extremely good reproducibility and homogeneity observed between samples. Concentration data for the oxic incubations using plugs exposed to a large volume of seawater indicated some loss for almost all compounds over the course of the experiment. However, those losses may be the result of multiple processes, including biodegradation, diffusive loss of QACs in pore water, and later in the 2012 incubations, the possibility of size dependent fractionation of sediment after plugs were colonized with animals. By using TAMAC data to better understand these processes as well as normalizing to DTMDAC 18:18, no degradation was observed in most QACs, native or spiked. Exceptions included significant losses observed for the smallest QACs, including ATMAC 12, deuterated ATMAC 12 and BAC 12.

6.3.1 Anoxic Incubation Results

As noted above, no significant loss was observed for any of the QACs measured in this experiment (Table 6.1, Figure 6.3). These results are in line with the lab batch degradation studies conducted under anaerobic conditions (Garcia et al., 1999; García et al., 2000; Ying, 2006) as well as the STP mass balance study (Clara et al., 2007) and a study of anaerobically digested sludges (Brownawell et al., 2013) that suggest that degradation of QACs under anoxic conditions is considerably less than under oxic conditions. Sulfate levels in porewater (Table 6.2, Figure 6.4) decrease for the first 16 days of the experiment before leveling off, and may suggest later inhibition of sulfate reducers as a result of build-up of toxic metabolites. The sulfate data also suggests that future anoxic experiments should be conducted using the plug incubation approach. The results from this anoxic incubation are consistent with the hypothesis that QACs are not likely to be degraded to a significant extent once buried under muddy, anoxic conditions due to a combination of low oxygen and a high fractionation of QACs sorbed. However, additional work is required to test this hypothesis for both longer time periods and under more realistic conditions that allow diffusive exchange of reactants and products related to mineralization of organic matter under sulfate reducing conditions.

In addition to the lack of QAC degradation observed during the anoxic incubation, this experiment provided additional information about the reproducibility and homogeneity of spiking and sampling in these incubations. Very good reproducibility (the relative standard deviation of all time points for each individual QAC was averaged for all of the QACs sampled across all time points and found to be 14% ± 3) was observed among all data points throughout this experiment (Table 6.1, Figure 6.3). This agreement suggests that the spiking method employed was sufficient to homogenously spike all of the sediment and that analytical procedures used are reproducible enough to observe modest decreases in concentration over time.

6.3.2 Oxic Incubation Results

The oxic incubations were successful in mimicking a highly oxidized environment, with complete oxidation of the plugs observed by a color change (black to grey) in the sediment by day 2 in both experiments. Data from the 2011 BPO oxic incubation can be found in Table 6.2 and Figure 6.5. Due to analytical issues, only single data points are presented for time points 0 and 2 in this experiment. While no loss is observed for most of the QACs in this shorter experiment, loss is apparent for ATMAC 12, deuterated ATMAC 12, and possibly deuterated DTDMAC 12:12 and deuterated DTDMAC 18:18 (BAC 12 was not measurable in this study as instrument detection limits were higher during the time period of those analyses). It should also be noted that in this study, LAS was not used in the QAC extractions, so comparisons between ATMAC 12 in the 2011 and 2012 BPO oxic incubations should be done cautiously.

In contrast to the 2011 BPO oxic incubation, the 2012 incubation (Table 6.3, Figure 6.6) indicates loss in all QACS measured, although many of these losses are focused in the latter (30 days and beyond) portions of the incubation. Sediments were not sieved and seawater was not filtered before use in either experiment, and because of this, organisms grew in most of the plugs after they were introduced into the incubation tanks. While the presence of these organisms is similar to what may be observed in oxic sediments, the lengthened incubation time of the 2012 experiment allowed for sufficient growth of these organisms such that infaunal activity could be observed beginning around 30 days and resulted in extensive sediment redistribution throughout the tank. First, there was an increase in fine sediment seen at the bottom of the tanks, and near the end of the experiment, small piles of sediment were observed. Because of this, the losses observed in this experiment (Figure 6.6) may be due to factors other than biodegradation, including diffusion into overlying waters over this longer time course and fractionation of different particle sizes and types that may have occurred after 30 days related to a possible loss of fines. It is likely that there was a very small loss of fine sediments prior to 30 days, however, and if that fine sediment contained a significant portion of clays with the greatest binding affinities for QACs, it may have had a disproportionate effect on the results.

The design of these incubations also sought to better understand potential differences in biodegradation of fresh and aged QACs, as QACs have been suggested to become increasingly associated with stronger sorption sites during aging (Li and Brownawell 2009, Fernandez 1996), and may therefore be less biodegradable. To better understand the data, the ratio of the deuterated spikes (d34-ATMAC 12, d-25 DTDMAC 12:12 and d3-DTDMAC 18:18) to their native counterparts was determined, with trends in either direction indicating preferential loss of one or the other. As is evident in Figure 6.8, there are no clear trends for differences in behavior of the spiked and native QACs in either the 2011 or 2012 incubations. This suggests that on these time scales, the degradation or lack thereof of spiked and aged QACs may be comparable. However, the deuterated spikes were not added at trace levels, totaling nearly 60 μg/g, similar to the total QAC concentrations in these samples. The high levels of DTDMAC spikes added may have perturbed the system as these compounds are expected to be especially good competitors for strong cation exchange sites with less alkylated or more soluble homologs.

TAMACs as tools to elucidate the likelihood of biodegradation

Little change in the extremely hydrophobic DTDMAC homologs was observed in the 2011 oxic incubation, but modest but seemingly continuous decreases in the concentration of even the most hydrophobic QAC studied, DTDMAC 18:18, were observed in the 2012 experiment (Figures 6.5, 6.6). To better understand the processes that are controlling the loss of DTDMACs and other QACs observed in the oxic incubations, TAMAC concentrations were estimated for each of the BPO oxic incubations (Table 6.5). TAMACs, which can have 15-17 more CH_2 groups than DTDMAC 18:18, are expected to be even more hydrophobic and particle reactive, and exist in DTDMAC formulations as impurities (van Leeuwen et al., 2010). They should be even less biodegradable than DTDMAC. TAMACs were analyzed based on known masses and estimated retention times and their concentrations were estimated assuming the response factors from DTDMAC 18:18. There was no clear loss of TAMAC 16:18:18 (the most abundant TAMAC) observed in the 16-day 2011 BPO oxic incubation nor was there a pronounced change in DTDMAC 18:18 as a function of time when normalized to TAMAC 16:18:18 (Figure 6.7a). In contrast, in the longer 2012 BPO incubation, loss of TAMAC 16:18:18 was observed, especially after 30 days, consistent with the first appearances of benthic organisms and enhanced sediment redistribution in the tank. Although there is variability in estimated TAMAC levels, particularly on days 9 and 16, there is a downward trend in TAMAC levels observed over the first 30 days, suggesting the possibility of small amount of loss of fine sediments observed at the bottom of the tanks that might be responsible for loss of other QACs in this incubation. When DTDMAC 18:18 measured in the 2012 oxic incubation is normalized to TAMAC 16:18:18, there is no evidence for relative loss of DTDMAC 18:18 over the first thirty days. There appears to be a slight increase in the DTDMAC/TAMAC ratio after 30 days, which is also seen for other QACs. If this trend is real, this may be due to different QACs being differentially enriched in different particle types. It may be that the shape or size of QACs and relative binding efficiencies for different sorption sites are quite different. Future studies should look at the composition of QACs on different particle size and mineral types, as this might also help explain some of the compositional changes of QACs observed in Hempstead Bay (Chapter 3).

Normalized BPO Oxic Incubation Results

To better understand the extent of biodegradation occurring in the BPO experiments, QACs were normalized to DTDMAC 18:18, for reasons discussed in other chapters, as well as to minimize analytical variability between samples. The focus was placed on the first 30 days before infaunal activity in the 2012 experiment resulted in extensive sediment redistribution. To help elucidate which QACs were experiencing significant loss, an ANOVA was performed for each individual QAC for the 2011 and 2012 oxic experiments. This analysis used the log of the composition (R, individual QAC divided by DTDMAC 18:18) of the remaining QACs at each time point (log (R_t/R_0), and the slope of the data was considered significantly less than zero if the slope was negative and the p-value was less than 0.05.

As is evident in Figure 6.9, significant loss (Table 6.6) is only observed for the smallest QACs, especially ATMAC 12 and deuterated ATMAC 12. Variations in the extent of ATMAC 12 lost between incubations (and the lack of a significant degradation for ATMAC 12 in the 2011 experiment) may be a result of the use of different sediments taken at different times of the year as well as the use of LAS in the 2012 experiment. While there is significant loss indicated for BAC 14 in the 2011 experiment (Table 6.6), there is no loss observed in the 2012 incubation, and Figure 6.9 does not suggest that this compound is being considerably biodegraded in this time frame. It is unclear if BAC 12 is being biodegraded in the 2012 incubation, as an initial loss is indicated over the first time points, but considerable noise in later time points make interpretation difficult. Data suggests that many of the losses observed in the 2012 experiment (Figure 6.6), with much of the loss occurring after 30 days, are likely due to modest losses of very fine clay rich particles that may possess a high fraction of the cation exchange capacity sediments. These results are contrary to varying reports in the literature as reviewed above, and indicate that aged as well as spiked compounds are not significantly degraded over a weeks to month time scale, even under ideal, completely oxidized environmental conditions. Loss of the smallest QACs are in agreement with the literature that suggests that biodegradability decreases with increasing side chain lengths (Boethling, 1984; van Ginkel and Kolvenbach, 1991) and that ATMACs and BACs should be the most biodegradable QACs (Boethling, 1984; Cross and Singer, 1994), if they are not present in resistant sorbed phases as has been hypothesized in Chapters 2 and 3. In mass balance studies of Austrian sewage treatment plants, ATMAC 12 was the most biodegraded (over 99%), followed closely by BAC 12 (94%), and other homologs were degraded to lesser extents inversely proportional to alkyl chain length.

6.4 Conclusions

Results from this study indicate that most QACs are not significantly degraded over approximately a one month time scale under oxic conditions or a three month time scale under anoxic conditions. This is not surprising for native QACs present at low concentrations, but appears to also be true for recently spiked DTDMACs (12:12 and 18:18). The few QACs where significant loss was observed under oxic conditions (ATMAC 12 and BAC 12) were the smallest of all of the QACs, consistent with studies suggesting that biodegradability is inversely proportional to chain length and greatest for ATMACs and BACs. Relatively high levels of QACs spiked may have led to cation exchange of these more soluble QACs and increased bioavailability of these compounds. Thus, experiments should be conducted with trace levels of spikes, especially for QACs like DTDMAC 18:18 which may outcompete other QACs for strong sorption sites. While these results do bear on future assessments on the environmental fate and risk of these compounds, the lessons learned should prove valuable for future experiments to better understand conditions where QACs may or may not persist when associated with bedded or suspended sediments.

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Table 6.1 The concentration (ng/g) of individual QACs measured in the 2012 BPO anoxic incubation.

Days	DADMAC			BAC				ATMAC						DTDMAC							deuterated		
	8:8	8:10	10:10	12	14	16	18	12	14	16	18	20	22	12:12	12:14	14:14	14:16	16:16	16:18	18:18	DTDMAC 12:12	ATMAC 12	DTDMAC 18:18
	ng/g																						
0	9	31	218	31	203	161	484	235	16	100	112	482	5210	371	495	424	771	1830	4050	6210	20900	19600	22700
0	8	27	179	28	158	130	391	182	14	90	97	392	3940	299	392	315	643	1700	3870	6510	21300	17300	22900
0	10	30	207	28	194	149	410	204	14	89	106	430	4410	316	431	353	686	2090	4740	7750	23600	22100	26500
2	7	26	172	27	156	118	351	179	13	67	96	367	3680	277	356	293	667	1980	4020	6460	19100	18500	21600
2	7	26	170	29	162	121	372	166	12	70	96	357	3710	288	370	309	575	1500	3910	6180	21200	19020	21600
4	8	26	197	27	154	104	319	162	11	60	106	324	3670	252	312	291	675	2050	3580	6000	18800	16800	20000
4	7	27	185	28	165	124	361	179	12	76	94	359	3570	282	358	297	561	1460	3790	6400	19700	17300	21000
9	8	27	187	28	173	138	396	200	13	88	114	388	3980	304	393	331	705	1940	3890	6360	22000	20300	23000
9	7	26	184	32	161	126	359	177	9	99	126	362	3720	278	349	301	568	1460	4470	7090	22400	21400	24300
16	7	25	169	23	141	101	295	154	7	55	87	306	3190	233	313	259	491	1300	4030	6330	19000	17300	21600
16	0	0	174	0	171	116	344	190	16	78	96	362	3060	260	326	304	409	970	2380	4030	12900	12500	11800
30	7	27	175	30	164	120	382	193	13	77	114	397	3900	296	391	329	616	1720	3760	5790	18800	16900	20300
44	7	26	181	19	142	116	393	180	17	90	118	381	3880	303	373	312	583	1510	4000	6630	19400	18200	21700
44	8	33	254	26	208	165	479	208	14	140	143	532	3650	368	481	287	558	1410	3870	6720	19300	16900	20700
44	6	24	171	25	161	125	381	168	16	69	115	373	3730	289	354	300	547	1530	3960	6140	19700	17900	22000
58	7	25	169	22	138	120	371	190	12	61	95	371	3650	288	363	306	584	1550	3600	6470	19400	16000	20400
58	7	26	174	20	145	114	388	190	12	87	106	383	3840	302	384	318	599	1590	3780	6090	19100	17000	21000
72	7	28	186	26	156	138	407	204	14	80	114	418	4640	325	415	397	863	2070	3530	5960	12000	17000	21700
72	8	35	230	33	207	196	584	231	18	89	124	512	5320	405	514	437	835	2080	4230	6790	20900	17800	21800
86	7	28	194	29	159	136	416	197	15	92	117	428	4100	332	413	336	654	1640	4000	6570	21400	20100	22700
86	8	28	196	26	158	137	379	199	12	76	105	400	3620	295	379	298	547	1570	4040	6910	22800	20100	24800

Table 6.2 The concentrations (ng/g) of individual QACs measured in the 2011 BPO oxic experiment. <RL denotes samples that are below the first standard.

Days	DADMAC			BAC				ATMAC						DTDMAC							deuterated		
	8:8	8:10	10:10	12	14	16	18	12	14	16	18	20	22	12:12	12:14	14:14	14:16	16:16	16:18	18:18	ATMAC 12	DTDMAC 12:12	DTDMAC 18:18
	ng/g																						
BPO Oxic 2011																							
0	13	24	205	<RL	198	109	441	160	0	64	137	327	3350	247	251	253	385	1130	3750	7870	5920	27000	24700
2	<RL	27	184	<RL	182	113	430	146	0	57	112	264	3280	203	238	230	345	1010	3420	6180	4250	22500	21100
5	0	21	149	25	130	92	353	58	<RL	64	111	259	3310	188	199	243	310	976	3150	4540	5010	20200	19100
5	<RL	25	187	52	159	133	418	52	<RL	60	90	305	3910	222	239	271	358	1120	3680	5230	3230	19600	19500
8	<RL	20	164	29	140	122	380	<RL	<RL	65	110	287	3750	203	235	288	358	1090	3650	5030	2560	19500	20000
8	<RL	24	202	37	177	154	422	61	<RL	74	114	0	4010	215	232	271	361	1120	3690	5080	4130	20200	21500
11	<RL	<RL	130	<RL	136	97	377	<RL	0	0	87	349	4000	210	217	222	349	1090	3740	5000	2060	22100	23200
11	<RL	<RL	112	<RL	126	103	376	<RL	0	0	119	323	3700	200	216	216	347	1100	3710	4890	1860	20000	20800
16	0	27	185	25	162	104	420	59	0	48	76	268	3850	205	220	278	371	1120	3690	5070	1760	19000	20800
16	<RL	24	177	43	128	107	378	<RL	<RL	64	102	282	3500	202	218	280	350	1090	3570	5050	1940	18200	20700

Table 6.3 The concentrations (ng/g) of individual QACs measured in the 2012 BPO oxic incubation. <RL denotes samples that are below the first standard.

Days	DADMAC			BAC				ATMAC						DTDMAC							deuterated		
	8:8	8:10	10:10	12	14	16	18	12	14	16	18	20	22	12:12	12:14	14:14	14:16	16:16	16:18	18:18	DTDMAC 12:12	ATMAC 12	DTDMAC 18:18
	ng/g																						
0	8	29	209	38	199	149	395	284	21	92	118	432	2950	303	406	342	695	834	3000	4970	19600	15300	21100
0	10	33	245	29	212	171	473	308	26	97	132	485	2820	365	474	538	953	884	3000	5050	20400	15600	21700
0	11	40	288	47	266	217	594	389	23	120	159	619	3500	451	568	499	1000	934	3450	5980	24300	17000	21900
2	<RL	17	119	7	56[a]	90	268	62	0	57	69	256	2270	133	200	205	457	790	2930	6740	15600	4550	15800
2	<RL	35	247	17	184[a]	185	504	141	21	111	134	495	4150	247	388	386	594	1280	4200	7260	28300	10900	29300
4	<RL	34	260	12	173[a]	169	470	77	0	98	159	449	2800	224	355	358	548	802	3530	4620	15900	3520	17300
4	<RL	29	238	4	60[a]	165	476	94	0	100	130	459	3130	229	371	373	585	971	3360	5600	19300	4720	21500
9	<RL	42	276	28	111[a]	171	518	112	0	116	132	499	3370	249	418	432	623	1010	3620	5970	21000	3820	22100
9	<RL	24	151	10	59[a]	86	301	54	0	62	164	256	3550	138	210	218	403	815	2790	4690	15900	3380	17200
16	<RL	20	154	16	145[a]	93	347	40	0	98	122	315	2220	165	265	265	424	736	2540	4080	12400	2110	13700
16	<RL	32	262	14	111[a]	141	501	70	0	91	139	427	2670	243	388	362	566	885	3010	5170	17900	2860	17600
30	<RL	32	263	15	136[a]	144	580	56	0	111	170	751	2110	302	697	316	498	820	2760	4460	16000	2160	15000
30	<RL	14	117	4	0	56	247	28	0	62	80	209	1680	129	213	217	342	648	2330	3930	11500	1940	11300
44	<RL	10	71	5	240[a]	35	153	21	0	30	43	119	1230	82	124	126	189	538	1780	2930	8430	1400	7880
44	<RL	13	96	0	0	44	172	17	0	36	53	143	1870	93	154	151	220	659	2290	3890	12700	1970	11200
44	<RL	9	70	3	0	39	152	21	0	30	45	127	1770	78	130	129	205	610	2150	3410	11300	1710	9360
58	<RL	9	69	5	0	25	121	20	0	34	53	99	1220	69	106	107	156	573	1900	3390	10400	1750	9220
58	<RL	0	65	0	0	30	148	18	0	29	58	157	1390	87	169	162	149	454	1600	2640	8100	1520	7280

A. samples were below the first standard but peaks were at least 5 times the blank and were therefore included.

Table 6.4 Sulfate concentrations (mg/L) and relative standard deviation (RSD) in pore water from the 2012 BPO anoxic incubation.

Time Point	Conc (mg/L)	RSD
0	7.535	0.71
2	7.209	2.03
9	5.533	2.16
16	4.603	2.44
30	5.891	3.03
44	4.528	0.78
58	5.949	2.11
72	5.802	0.6
86	4.432	1.5

Table 6.5 Estimated TAMAC 16:18:18 concentrations (ng/g) in the BPO Oxic Incubations

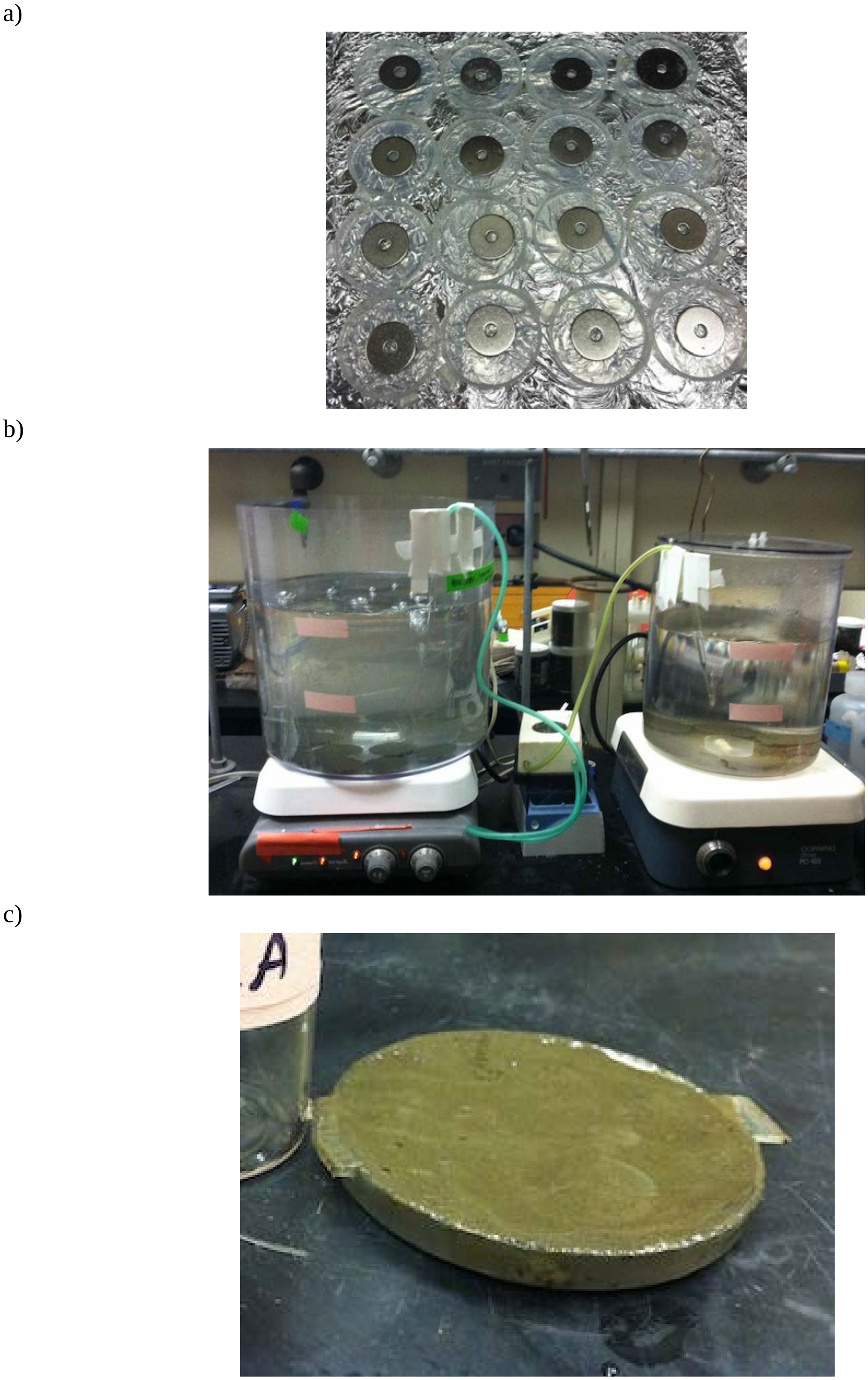
Time Point	2011 BPO Oxic Incubation	Time Point	2012 BPO Oxic Incubation
0	188	0	235
2	176	0	256
5	141	0	282
5	178	2	281
8	171	2	376
8	176	4	310
11	193	4	303
11	190	9	357
16	179	9	150
16	157	16	209
		16	388
		30	265
		30	177
		44	90
		44	110
		44	103
		58	102
		58	77

Table 6.6. Statistics for the Bay Park oxic incubations, including the p-value from the ANOVA analysis and the sign of the slope of all of the data for each incubation.

QACs	2011 BPO		2012 BPO	
	p-value	sign of slope	p-value	sign of slope
DADMAC 8:10	0.76		0.87	-
DADMAC 10:10	0.82	-	0.74	+
BAC 12	N/A		0.38	-
BAC 14	0.02	-	0.98	+
BAC 16	0.11	-	0.49	-
BAC 18	0.20	-	0.32	+
ATMAC 12	0.23	-	0.02	-
ATMAC 16	0.6	-	0.36	+
ATMAC 18	0.43	-	0.32	+
ATMAC 20	0.39	-	0.6	+
ATMAC 22	0.94	-	0.23	-
DTDMAC 12:12	0.36	-	0.88	-
DTDMAC 12:14	0.81	+	0.43	+
DTDMAC 14:14	0.27	+	0.84	-
DTDMAC 14:16	0.14	+	0.35	-
DTDMAC 16:16	0.10	+	0.32	+
DTDMAC 16:18	0.17	+	0.26	+
d34-ATMAC 12	6.38E-04	-	0.01	-
d25-DTDMAC 12:12	0.11	-	0.34	-
d3-DTDMAC 18:18	0.66	-	0.17	-

Figure 6.1 Location of sediments and sewage outfalls in Hempstead Bay, NY. The orange dot at the BPO represents both the location of the outfall as well as the location of the sediments used in the Bay Park incubations while the yellow dot is the location of the sediments taken for the East Bay incubation as described in Appendix A2.

Figure 6.2 a) Disks used to hold sediment for oxic plug incubations; note that weights are covered by a uniform layer of paraffin wax. b) entire set up of oxic incubations c) a plug filled with sediment after being sampled from the incubation tank.



a)

b)

c)

Figure 6.3. Representative QAC concentration (ng/g) plots for the BPO anoxic incubation. Error bars are the range for duplicates except for time points 0 and 44, which are the standard deviation of triplicates. Time point 30 as well as time point 16 for BAC 12 only represent single data points.

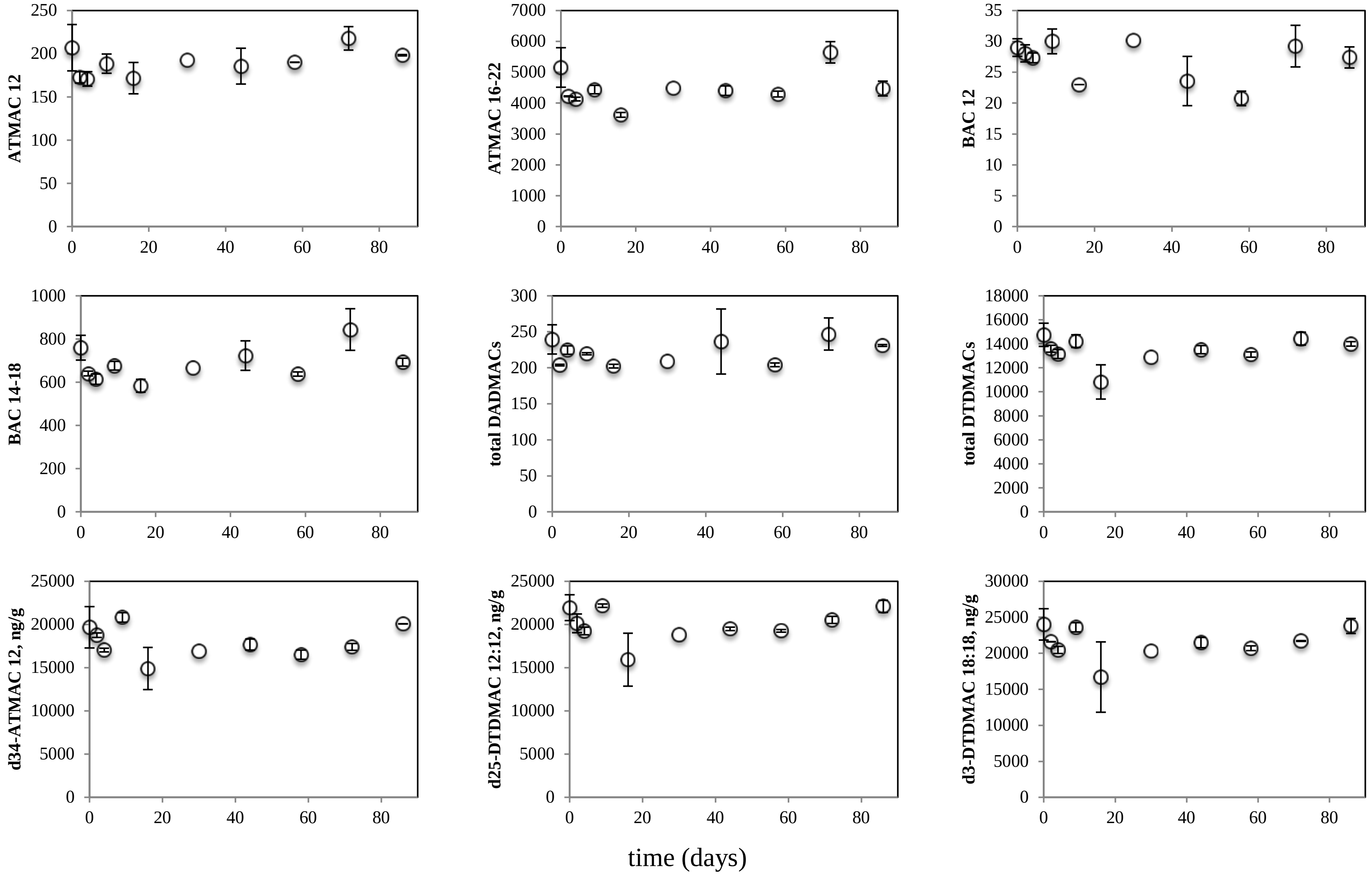


Figure 6.4. Sulfate concentrations in pore water from the BP anoxic incubation.

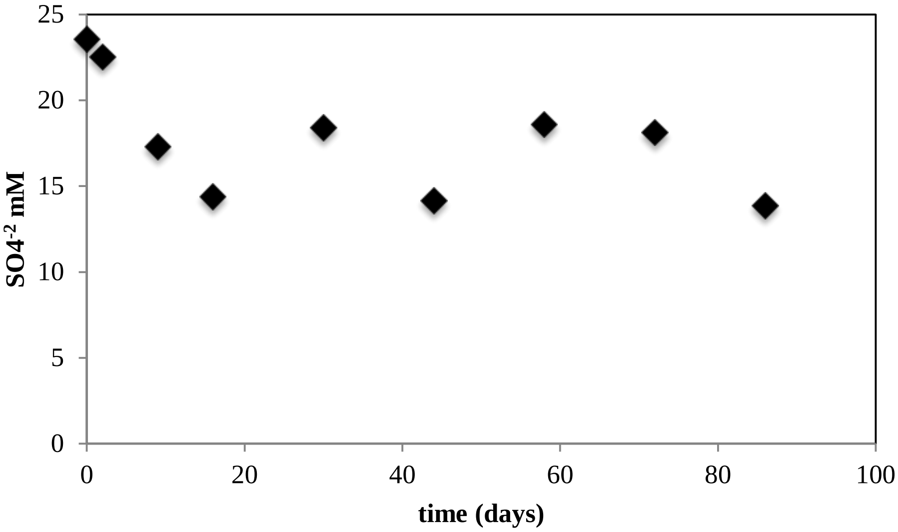


Figure 6.5. Representative QAC concentration (ng/g) plots for the 2011 BPO oxic incubation. Error bars are the range for duplicates except for time points 0 and 2 for all QACs as well as time points 8 and 16 for ATMAC 12, which represent only one data point. BAC 12 was present at levels below instrument detection and is therefore not presented here.

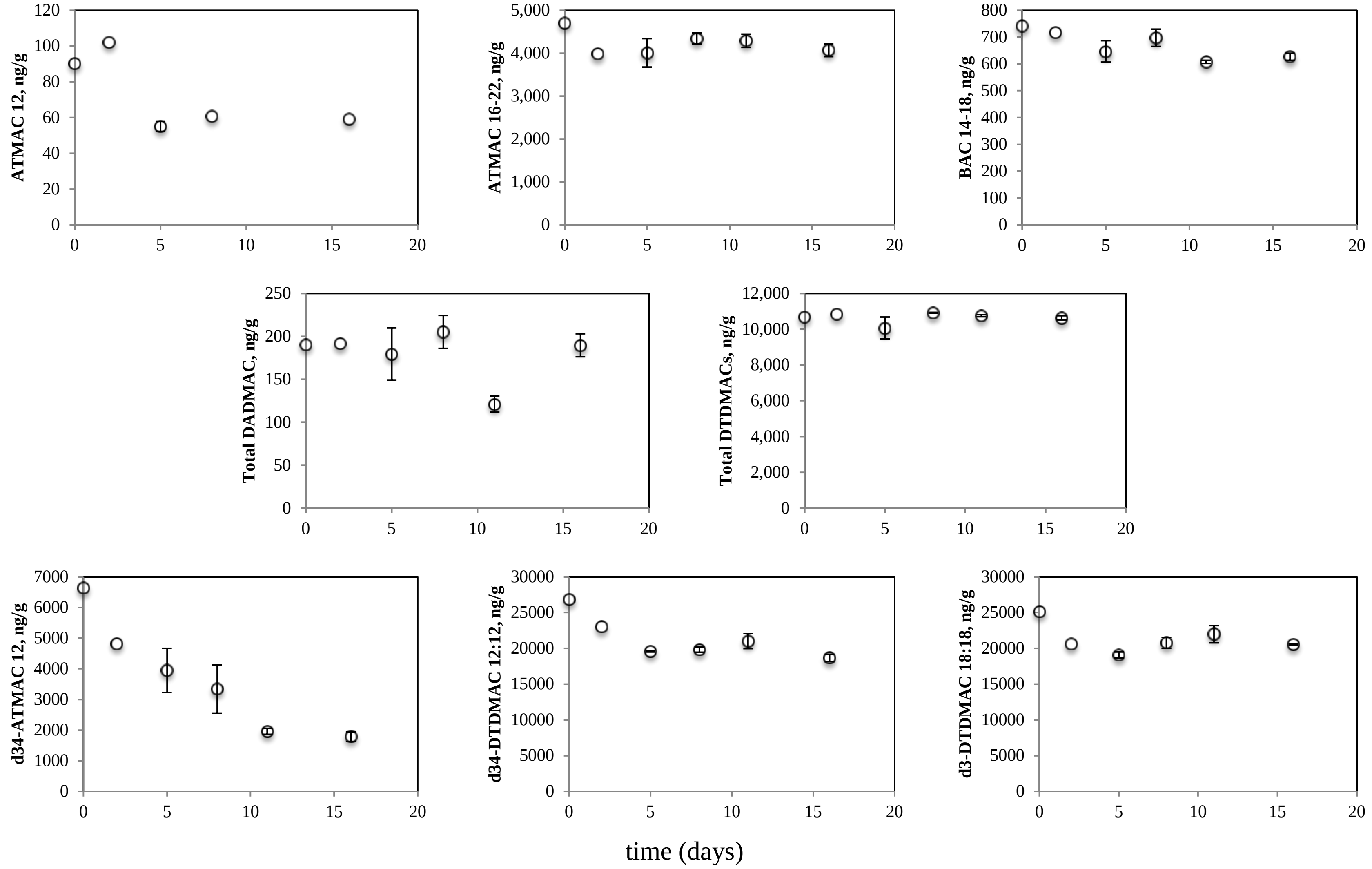


Figure 6.6. Representative QAC concentration (ng/g) plots for the 2012 BPO oxic incubation. Error bars are the range for duplicates except for time points 0 and 44, which are the standard deviation of triplicates with one exception (BAC 12 time point 44 error bars represent the range of duplicates and time point 58 represents one data point). Extensive redistribution of the sediment due to infaunal growth and activity was observed after the first thirty days, so later time points (noted in grey) should be carefully interpreted.

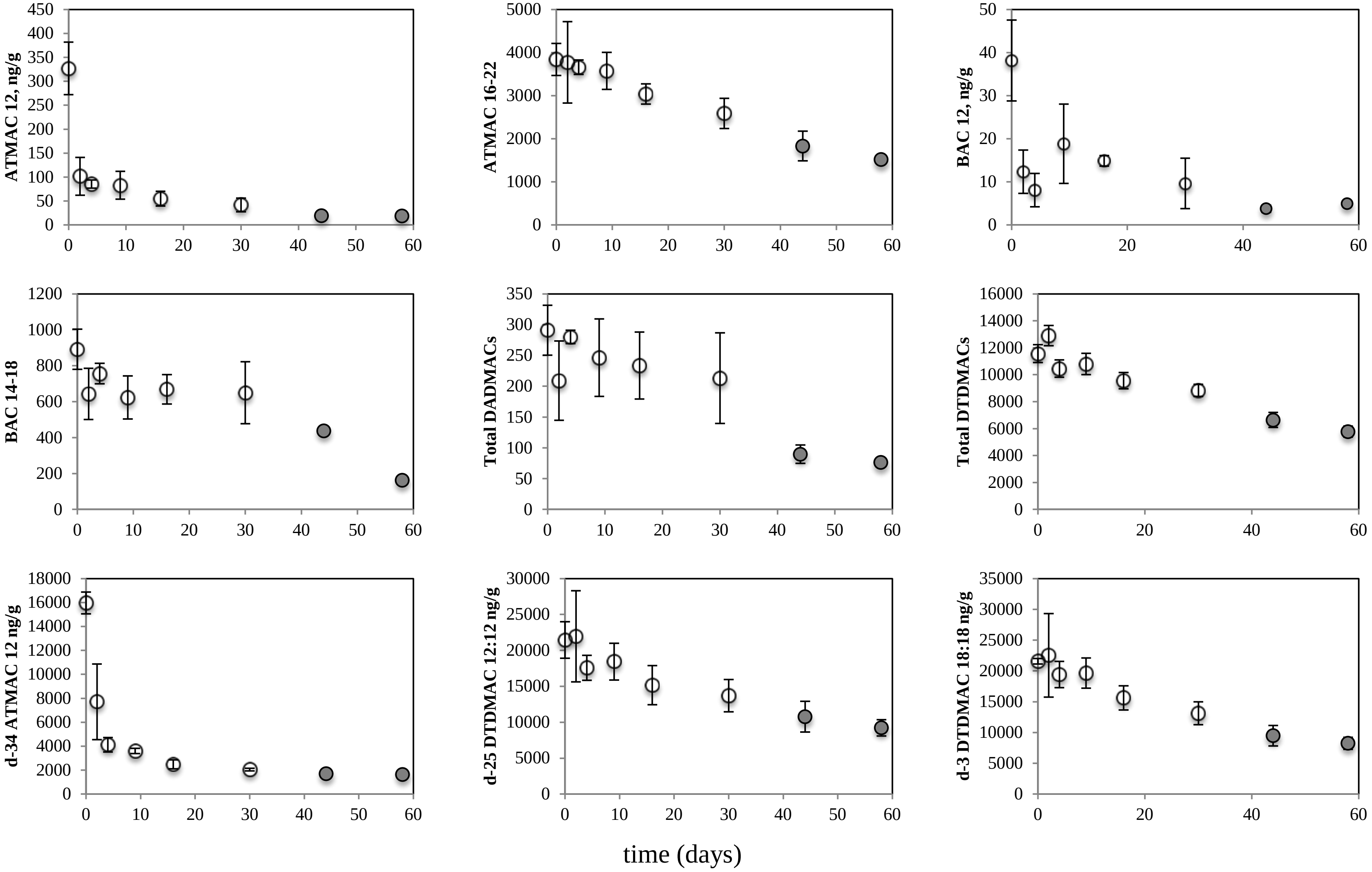


Figure 6.7. TAMAC 16:18:18 concentrations (ng/g), DTDMAC 18:18 concentrations, and DTDMAC 18:18 normalized to TAMAC 16:18:18 for the a) 2011 and b) 2012 BPO incubations. Again, note that the data for time points beyond 30 days is likely affected by sediment redistribution resulting from in growth of benthic infauna and subsequent sediment losses from the plugs to the tanks.

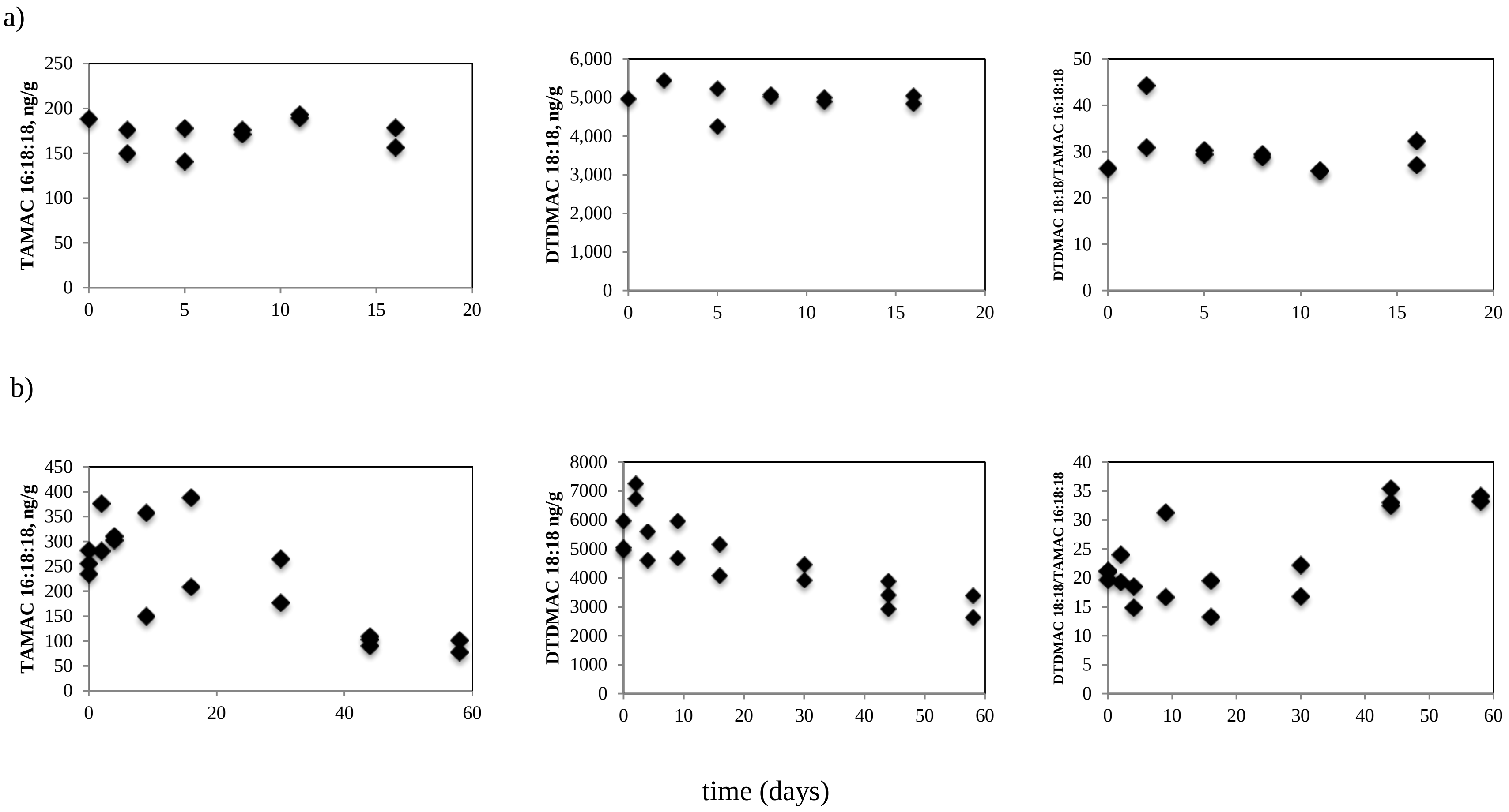


Figure 6.8 The ratio of deuterated to native compounds for ATMAC 12, DTDMAC 12:12 and DTDMAC 18:18 for the a) BPO oxic 2011 incubation and b) 2012 BPO oxic incubation.

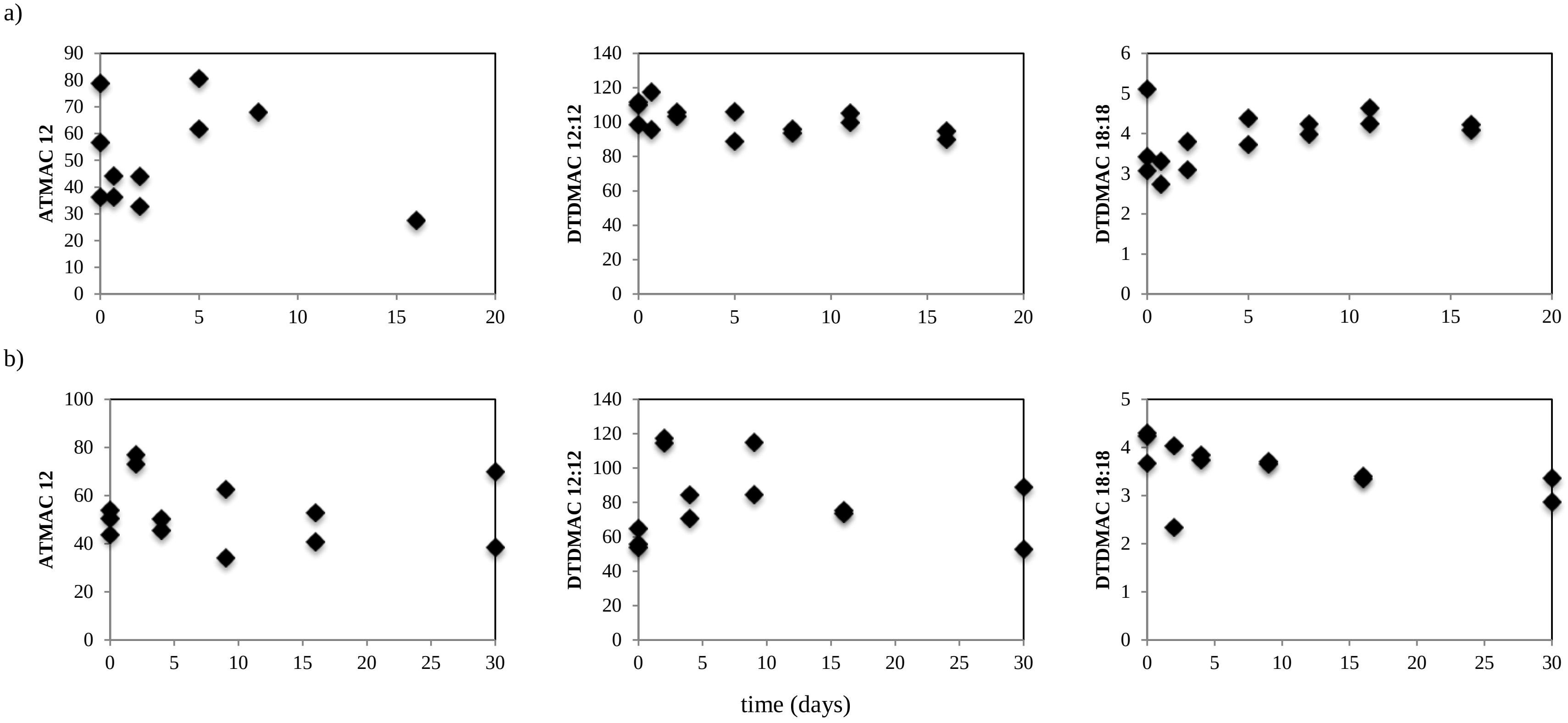
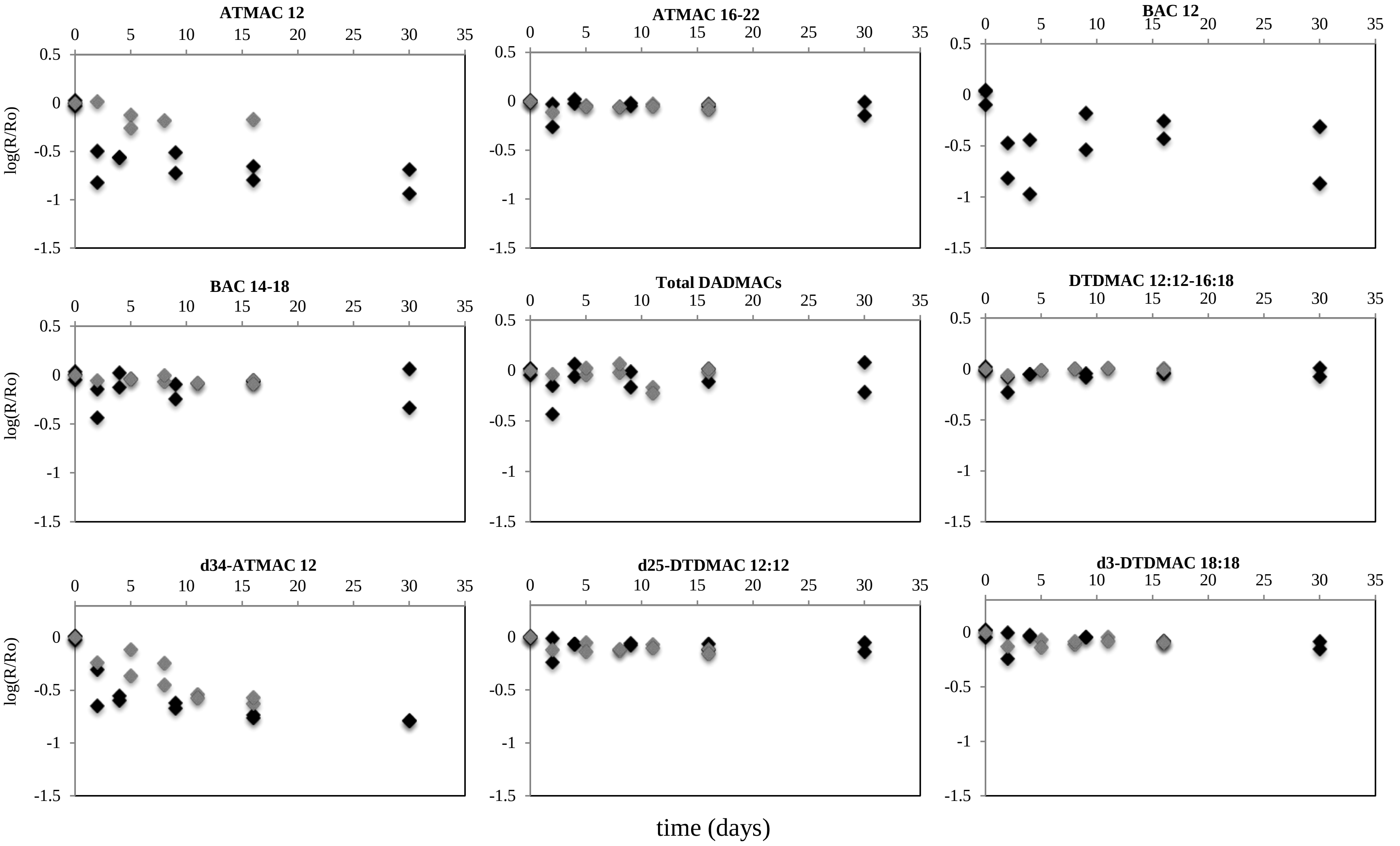


Figure 6.9. Combined results from all BPO oxic (2011 = grey, 2012 = black) experiments expressed as the log of the composition (R) (concentration divided by DTDMAC 18:18) at each time point over the average composition for ATMAC 12, ATMAC 16-22, BAC 12, BAC 14-18, total DADMACs, DTDMAC 12:12-16:18, as well as deuterated ATMAC 12, DTDMAC 12:12 and DTDMAC 18:18. BAC 12 was only reliably quantified for the 2012 incubation due to issues with LC-MS sensitivity.



CHAPTER 7. Summary

One of the main objectives of this dissertation was to better understand the distribution and fate of quaternary ammonium compounds (QACs), a class of cationic surfactants that have received attention due to high levels in the environment as well as the suggestion that they be a new class of particle reactive sewage tracers. In addition, this dissertation compared the distribution of QACs in Hempstead Bay and Long Island Sound (LIS) to better understand the sources and geochemical fate of metals and di-ethylhexyl phthalate (DEHP). In this chapter, the major findings of this thesis are summarized and discussed.

Measurements of QACs in LIS and Hempstead Bay provide two additional studies on the occurrence of QACs in the United States. While levels of QACs in the LIS study are lower than those found in the New York/New Jersey harbor complex (Li, 2009), this is most likely a result of more flushing in LIS as well as a majority of samples over 15km from major sources. Average total QAC concentrations in Hempstead Bay are much higher than in LIS, and concentrations of total QACs in the West Bay region of Hempstead Bay are similar to QACs measured in nearby, sewage-impacted regions including Jamaica Bay and the New York/New Jersey harbor complex. The high levels of QACs measured in Hempstead Bay, in addition to total organic carbon enrichment relative to other local systems thought to be in part a result of sewage derived organic matter, suggests that sewage affected particles are not being flushed out of the region and are instead being retained within the Bay. These results are in agreement with data from Swanson et al. (2013), which cites excessive macroalgae growth, high concentrations of total nitrogen, reduced light penetration, elevated chlorophyll a, and harmful algal blooms as additional evidence that sewage from sewage treatment plants (STPs), and in particular Bay Park STP, is significantly retained within the Bay.

Measurements of the distribution of QACs in LIS provide one of the first studies of QACs with distance from a focused source. This study provided evidence suggesting that sewage originating in western LIS (WLIS) is the dominant source of sewage to this environment, despite additional smaller STPs located along the shores of Connecticut and Long Island. With this understanding, the measurement of QACs over 70km from WLIS as well as the relatively steady composition of the largest QACs throughout the sampling transect indicates that these compounds are extremely persistent for great distances from a major sewage source. Similar findings of persistence in Hempstead Bay provide additional support to the LIS study. In addition, comparisons of DTDMAC 18:18 with trialkyl methyl ammonium chlorides (TAMACs), impurities in QACs thought to be more particle reactive and persistent than QACs, do not indicate significant desorption or degradation of DTDMAC 18:18 with distance from the dominant sewage source in Hempstead Bay. These studies together provide strong support that larger QACs are extremely persistent in the environment and can be used as incredibly powerful tracers of sewage-affected sediments.

In contrast to the largest QACs, significant changes in smaller, less hydrophobic QACs relative to DTDMAC 18:18 were found in both Long Island Sound and Hempstead Bay. The conceptual model used to explain these changes is outlined in Chapter 3, but, in brief, this model suggests that many QACs enter the system as a combination of very resistant phases not thought to be subject to much desorption or degradation during transport, and a labile pool. The size of the labile pool as well as the relative rate at which this labile pool is desorbed and possibly degraded is thought to be dependent upon the hydrophobicity and initial concentration of sorbed QACs. For the smallest QACs, sewage treatment may result in complete removal of the labile pool, such that only a resistant phase remains and no changes in composition are observed in the environment. In contrast, larger QACs like the more alkylated DTDMAC homologs are not appreciably desorbed and degraded simply because they are so hydrophobic. QACs with intermediate hydrophobicity fall between these two extremes in that they have low enough sorption energies that some slow desorption can be expected, especially during transport in the water column, resulting in changes in composition that are observed with distance from the source as the labile pool is reduced. The size of the labile pool as well as the relative rate at which this labile pool is desorbed and possibly degraded is thought to be dependent upon the hydrophobicity and initial concentration of sorbed QACs. Suspended solids data provides additional support for this model, as the greatest changes in composition between suspended solids and underlying sediments was observed for QACs of intermediate hydrophobicities in Chapter 3.

When data from LIS and Hempstead Bay (Chapters 2 and 3) are plotted together, there is remarkably good agreement between the data sets for DADMACs, BACs, and ATMAC 16 and 18 (as well as ATMAC 20 and 22 at distances removed from point sources) in both trends with distance from sewage point sources and the actual magnitude of the relative abundance of each QAC to DTDMAC 18:18. Differences between the basins observed in relative DTDMAC compositions may be complex and have been speculated upon in Chapter 3. Additional research is needed on the potential for differential transport of QACs in these basins

Large changes in the composition of ATMAC 20 and ATMAC 22 in both LIS and Hempstead Bay are thought to be predominantly due to an increase in the use of behentrimonium in consumer products (Lara-Martín et al., 2010; Li, 2009). If this is true, the changes observed provide evidence for the transport of particles within these basins. It is thought that the distribution of QAC contaminated sediments is controlled by many resuspension and desorption events and that, on average, the sewage contaminated sediments found further from the source have undergone more resuspension events with longer timescales involved in their transport to the sites where they are accumulating. With this assumption, the higher relative abundance of behentrimonium approaching the source is related to their recent increases in use. There may be insights into sediment transport processes that can be obtained from studying the distribution of relatively stable contaminants with different time histories of release into the environment.

The first geochronologies of QACs from dated sediment cores from environments with known histories of sewage treatment provide an indication of the history of QAC inputs to Hempstead Bay. These geochronologies, in addition to two sediment cores from Jamaica Bay, indicate that there have been relatively steady state inputs of DTDMAC 18:18 to both of these sewage impacted basins from the early 1990’s to the time of collection (2008-2011), which may simplify interpretations based on the use of these compounds as particle reactive sewage tracers. In addition, comparisons of DTDMAC 18:18 with the extremely hydrophobic DTDMAC impurities trialkylmethyl ammonium compounds (TAMACs) provide additional evidence for the persistence of these compounds in the environment and their use as tracers of sewage affected particles.

The geochronologies presented in Chapter 4, in addition to geochronologies reported by Li (2009) and Lara-Martin et al. (2010) and past USITC data suggest that there may have been recent increases in the use of DADMACs, smaller BACs, smaller DTDMACs and ATMACs 20-

22. These findings suggest that at least a portion of the changes in relative composition observed with distance from major sewage sources in LIS and Hempstead Bay may be due to changes in the use and source of these QACs to the environment. Profiles of the relative composition of QACs over a span of 20 years taken in the same relative location indicate that *in situ* degradation may not be occurring for even the smallest, most biodegradable QACs, although some variation is observed down core for compounds with intermediate hydrophobicity, and surface degradation cannot be ruled out. Agreement in the composition of individual QACs in cores closer to point sources of sewage in both Jamaica Bay and Hempstead Bay may suggest that the sewage signature is similar for these two basins.

The first known lab experiments to understand the potential for oxic and anoxic degradation of QACs in sewage-impacted sediments provide additional evidence for the persistence of QACs once deposited in these sewage-impacted environments, as no loss was observed for almost all QACs aside from the smallest compounds. The use of thin plugs in an open incubation allowed for the study of QAC degradation in highly reduced sediments that would have been difficult to do without changes in pH using sealed incubations of sediment slurries. No differences in QAC degradation were observed for the native compounds as compared to spiked deuterated QACs in these experiments, but additional work is needed to study longer time incubations. Future studies should employ lower level of spikes, as competitive ion exchange in this work may have had an impact on the bioavailability of more soluble QACs. Additional work is also needed to better understand the anoxic degradation of QACs in both longer time periods and under more realistic conditions that allow diffusive exchange of reactants and products related to mineralization of organic matter under sulfate reducing conditions. Because loss of QACs is likely to be slow in experiments with high sediment to water ratios, the use of 14C-labeled QACs to identify degradation products would also provide more accurate descriptions of the rates of QAC transformations and allow form identification of important metabolites.

Chapters 2 and Chapter 5 provide examples of the use of QACs, and in particular DTDMAC 18:18 to aid in source allocation of metals. A significant correlation between DTDMAC 18:18 and Ag, Cd, Cu, Pb and Zn was observed in LIS, suggesting that WLIS, and possibly the sewage emanating from WLIS, serves as at least one source of these metals to LIS. Significant correlations were also found between DTDMAC 18:18 and Ag, Cd, Cu, Pb and Zn in

Hempstead Bay, although sewage appears to only be a dominant source for the traditional sewage tracer Ag, and have a smaller impact on Cu, Pb and Zn, with Cd distributions hypothesized to be a function of sewage-derived redox conditions within the Bay. Current metal distributions may also be affected by long term redistribution of historical sediment contaminated from time periods when metal loadings from STPs were much greater, before the Clean Water Act. Additionally, increasing levels of Cu, Pb and Zn in Mill River, a small tributary in the northern part of West Bay, with decreasing levels of DTDMAC 18:18 suggests additional sources of these metals in this stream which is likely impacted by both boating activities and urban storm run-off. Factors that may affect the use of QACs to determine the source of metals in these environments include the possibility of different time histories and methods of transport within these basins. Additional research should be conducted to determine if the distributions of metals in sediments in areas like WLIS and Hempstead Bay are more controlled by transport of contaminated sediments or through processes that may include recycling and scavenging of metals mediated through transport in dissolved phases.

The application of QACs to determine the source as well as geochemical fate of DEHP in Hempstead Bay represent the first empirical evidence, to our knowledge, for sewage as a dominant source of DEHP in the environment. Based on the linear relationship with DTDMAC 18:18, DEHP is suggested to be very persistent in this environment in Hempstead Bay, with little loss to desorption or degradation during transport from the BPO. As with metals, differential time histories of DEHP and DTDMAC 18:18 may complicate these results, so additional research on the time histories of DEHP should be undertaken to better understand the correlations observed.

This dissertation provides important new information on the distribution and fate of QACs in sewage impacted marine environments. Evidence from this dissertation indicates that DTDMAC 18:18 is extremely persistent in depositional environments and has had steady state inputs to both Hempstead Bay and Jamaica Bay since the 1990's. This new information is extremely useful for the application of this compound as a sewage tracer. Additional information about the fate of smaller QACs with distance from a source indicate that while changes in composition with distance from primary sources do occur, these smaller compounds can also be extremely persistent once more labile fractions are desorbed and or degraded during transport. Matched cores in Jamaica Bay suggesting little evidence for *in situ* degradation of these compounds after burial and incubation data indicating little to no degradation of all but the smallest QACs under oxic and anoxic conditions provides additional support for the potential for smaller QACs to be persistent in the environment. Important information on possible historical changes in the use of QACs may aid in the interpretation of distributions of QACs. Applications of DTDMAC 18:18 as a sewage tracer in both Long Island Sound and Hempstead Bay not only provides important information about metals and DEHP in these environments, but highlights how useful these compounds can be as sewage tracers in estuarine environments.

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Appendix A1: Extraction and analysis of quaternary ammonium compounds.

The method used for the extraction and analysis of QACs is based on a procedure described by Li and Brownawell (2010) and modified by Lara-Martin et al. (2010). The method used for QAC analyses in Chapters 2-6 is presented below.

Materials

Solvents including methanol (GC^2 and HPLC grade), chloroform (GC^2), acetonitrile (GC^2) and 2-propanol (GC^2) were purchased from VWR (Radnor, PA). Standards for QACs (alkyltrimethyl ammonium bromides (ATMACs) C12, C14, C16 and C18, benzylalkyl ammonium bromides (BACs) C14 and C16, dialkyldimethyl ammonium bromides (DADMACs) C10:C10, C12:C12, C14:C14, C16:C16 and C18:C18) were purchased from Sigma-Aldrich (Milwaukee, WI) and Pfaltz & Bauer Inc (Waterbury, CT) as described by Li and Brownawell (2009), and the internal standard tridodecylamine was purchased from Acros Organics (New Jersey). Deuterated standards of d34-dodecyltrimethyl ammonium bromide (d34-ATMAC 12) and d25-didodecyldimethyl ammonium bromide (d25-DTDMAC 12:12) were purchased from CDN Isotopes (Quebec, Canada). All glassware was solvent washed with methanol and then baked in a muffle furnace at 450°C for at least four hours prior to use.

Extraction Method

Before extraction, sediment was freeze-dried and then homogenized using a mortar and pestle. To begin, approximately 0.1g of sediment was weighed into a 10mL test tube and the weight recorded. For filter samples, the filter was placed directly into the 10mL test tube. Surrogate standards (deuterated DTDMAC 12:12 and deuterated ATMAC 12) were then spiked into the test tube. For the extraction, 10mL of 1% HCl methanol (GC^2 grade) was added to the test tube which was then placed in a 60°C sonication bath for 1 hour. Sediment samples were then centrifuged at 1000 RPM for 5 minutes while filter samples were centrifuged for a total of 15 minutes to ensure all particles were removed from the extract. The supernatant was decanted into a 30 mL test tube and the extraction was repeated twice more for a total of 3 extractions. The final 30mL extract was brought to dryness under a gentle stream of nitrogen in a heated (50°C) water bath.

Extract Cleanup

The extract was first cleaned up using liquid-liquid extraction in a 60 mL seperatory funnel. The sample was first resuspended in a total of 20 mL, at which point 36 μg of LAS was added if needed for improving recovery of native and deuterated ATMAC 12 (Chapter 5). For each extraction, 10 mL of chloroform was added to the seperatory funnel and wrist shaken for 1 minute before recovering the chloroform. The extraction was repeated two additional times for a total of 30 mL of choloroform used. The collected chloroform (30mL total) was then blown to dryness under a gentle stream of nitrogen in a heated (50°C) water bath.

The final cleanup employed an anionic exchange resin (about 3g, AG-1X2 resin, Bio-Rad, Hercules, CA) loaded into a 6mL glass SPE column containing a Teflon frit (Supelco, Bellefonte, PA) on a vacuum manifold. The resin was stored in HPLC grade methanol overnight and then conditioned with an additional 50 mL of HPLC grade methanol before use. The extract was resuspended in 2.5 mL of GC^2 grade methanol and then eluted with GC^2 grade methanol at about 3mL/min for a final volume of 15 mL. Samples were then concentrated or diluted as needed before analysis.

QAC Analysis

QACs were analyzed using a high pressure liquid chromatography-time of flight-mass spectrometer. Separation and analysis of QACs employed the use of a Luna C18 column (Phenomenex; 150x2.00 mm, 5 μm) attached to a Waters Alliance 2695 LC paired with a LCT mass spectrometer with a Z-spray ESI source (Micromass, Manchester, UK). Samples were often run at multiple dilutions to ensure detection of all QACs within the calibration curve, and an internal standard (tridodecylamine) was added to each sample at 5ng/mL before analysis. Injections were 10 μl.

For the chromatographic separation of QACs, mobile phases included solvent A, a 95:5 acetonitrile:water mix with 10mM ammonium acetate and solvent B, 2-propanol with 0.1% formic acid. The HPLC gradient began by holding a mixture of 90% solvent A and 10% solvent B for 6.2 minutes before changing to 50% solvent A and 50% solvent B over 2 minutes. These conditions were held for 12 minutes before being changed back to 90% solvent A and 10% solvent B over 1 minute and then holding at 90% solvent A and 10% solvent B for an additional 4 minutes to complete the run. The column oven temperature was held at 45°C throughout the run and a 0.25 mL/minute flow rate was used.

Analysis of QACs was conducted using electrospray ionization in positive ionization mode with a capillary voltage of 2800V and a cone voltage of 55V. The instrument was internally calibrated daily and a lock-mass (leucine enkephalin) was infused throughout each run as described elsewhere (Benotti. et al., 2003). QACs were identified using the M+ ion as well as retention times from chromatographic separation. Quantification employed the use of a 6-point calibration standard (0.1 – 35 ng/mL) and responses were normalized to the internal standard. For QACs without standards, response factors were approximated using the most closely eluting QAC (i.e. the response factor for DADMAC 10:10 was used for both DADMAC 8:8 and DADMAC 8:10; BAC 12 and 18 were based on BAC 14 and 16 respectively, ATMAC 20 and 22 were based on ATMAC 18, and DTDMACs 12:14, 14:16, and 16:18 relied upon interpolations of response factors of the nearest homologs that included 12:12, 14:14, 16:16, and 18:18).

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Appendix A2: East Bay Oxic Sediment Incubation

An experiment was conducted using sediment from the East Bay region of Hempstead Bay, 10 km from the Bay Park STP outfall (BPO) (Figure 6.1). The purpose of this experiment was to determine if proximity to a major source would have an impact on the biodegradability of the native and spiked QACs in the sediments. Methodologies for set up and spiking of the incubation can be found in Chapter 6. This data has not been included in Chapter 6 as the quality was not deemed to be of sufficient quality. As seen in the 2012 BPO oxic incubation, infaunal growth and activity was noted in this incubation occurring around 18 days after the start of the experiment. In addition, the time zero data point is most likely not representative of the starting conditions of sediments in the incubation, possibly due to fractionation during the spiking procedure that resulted from centrifuging the spiked slurries and then not completely re-homogenizing the sediments before placing them in incubations disks. This inconsistency is evidenced by the fact that the spiked deuterated ATMAC 12 values are much lower than targeted (20 μg/g) in the time 0 data points and also as compared to the rest of the experiment (Table A2.1). As this experiment was designed to be preliminary, with fewer data points than the BPO oxic incubation, restricting the data to time points from 2 to 16 days (excluding time 0 as well as time points after infaunal growth and sediment redistribution became substantial) results in a very limited data set that was not of the same quality as the data presented in Chapter 6, and is therefore presented here as an appendix.

The greater variability of this data set can be observed in Figure A1.1, and perhaps some but not all of the variability might be attributed to lower concentrations of some of the less abundant QACs in the sediment as a result of the distance of this sediment from the dominant source in the region. When focusing on data points 2 through 16, no loss is suggested for any of the QACs, including the smallest QACs. While there are losses evident in later time points, these data cannot be confidently interpreted due to the fact that loss and redistribution of fine sediments occurred as benthic infauna grew in. The absence of pronounced loss of most QACs in this experiment is in agreement with experiments from

Chapter 6. The lack of degradation observed for native ATMAC 12 in this experiment over the 2-16 day time frame, in contrast to the significant lost observed in Chapter 6, may be due to the variability of the data and the short time frame. It was also seen in the oxic BPO experiments that most of the observed loss of ATMAC 12 occurred over the first two days. Persistence of more soluble QACs in East Bay sediments might also be expected if there was decreased biological and chemical availability of QACs that have persisted during transport to East Bay in comparison to Bay Park.

When the ratio of the deuterated spikes (d34-ATMAC 12, d-25 DTDMAC 12:12 and d3-DTDMAC 18:18) to their native compounds is plotted (Figure A1.2), there are indications of a preferential loss of the deuterated DTDMACs over their native counterparts in 2 to 16 day time frame. Explanations for this include the higher relative concentrations of the deuterated QACs as compared to both native QACs and sediment organic matter than in the BPO incubations as well as the aforementioned potential for decreased biological and chemical availability of native QACs after transport. TAMACs were also measured in this experiment, although no loss over time was observed for these compounds, in contrast to the 2012 BPO oxic incubation (Figure A1.3).

Table A2.1 The concentrations (ng/g) of individual QACs from the East Bay oxic incubation. <RL denotes measurements that were below the reporting limits for this analysis.

Days	DADMAC			BAC				ATMAC					DTDMAC							d34-	d25-	d3-
	8:8	**8:10**	**10:10**	**12**	**14**	**16**	**18**	**12**	**16**	**18**	**20**	**22**	**12:12**	**12:14**	**14:14**	**14:16**	**16:16**	**16:18**	**18:18**	ATMAC 12	DTDMAC 12:12	DTDMAC 18:18
	ng/g																					
0	<RL	<RL	18	6	52	30	26	139	10	10	10	130	20	27	26	64	213	1065	1894	6026	24539	19173
0	<RL	<RL	20	6	47	24	25	139	18	18	9	124	19	25	26	60	197	986	1756	5542	22917	18340
2	<RL	<RL	11	<RL	49	24	20	34	8	8	9	97	14.3	22.2	18	46	220	810	1265	5836	16088	12632
2	<RL	<RL	10	<RL	29	17	17	29	5	8	7	97	12.6	18.9	18	42	213	627	1158	5316	17193	11301
4	<RL	<RL	12	<RL	29	20	23	45	7	9	10	144	16.8	26.8	26	60	283	631	1248	9109	21243	11641
4	<RL	<RL	12	<RL	39	24	24	49	6	10	12	149	17.6	27.5	28	61	285	623	1247	8407	19047	11563
16	<RL	<RL	26	<RL	<RL	<RL	<RL	<RL	<RL	40	<RL	90	<RL	<RL	<RL	42	256	715	1245	4560	20257	11487
16	<RL	<RL	21	<RL	46	14	22	47	9	13	9	162	20	27	30	60	185	777	1314	4960	15183	12452
44	<RL	<RL	11	<RL	31	21	23	23	6	13	10	105	16.6	24.4	22	49	235	587	<RL	3971	15556	<RL
44	<RL	<RL	16	20	79	39	32	32	10	24	16	160	21.9	29.2	26	68	314	546	1026	3656	15248	6384
86	<RL	<RL	18	<RL	23	15	33	22	11	23	11	98	25.9	28.5	19	47	225	489	979	4127	18536	5479
86	<RL	<RL	23	<RL	18	27	83	12	7	15	6	57	13.2	13.5	11	26	139	393	823	2510	12679	4015

Figure A2.1. Representative QAC concentration (ng/g) plots for the EB oxic incubation. Error bars are the range for duplicates except for time point 16 for ATMAC 12, BAC 14-18, and deuterated DTDMAC 18:18. Extensive redistribution of the sediment due to infaunal growth and activity was observed after 16 days, so later time points should be cautiously interpreted.

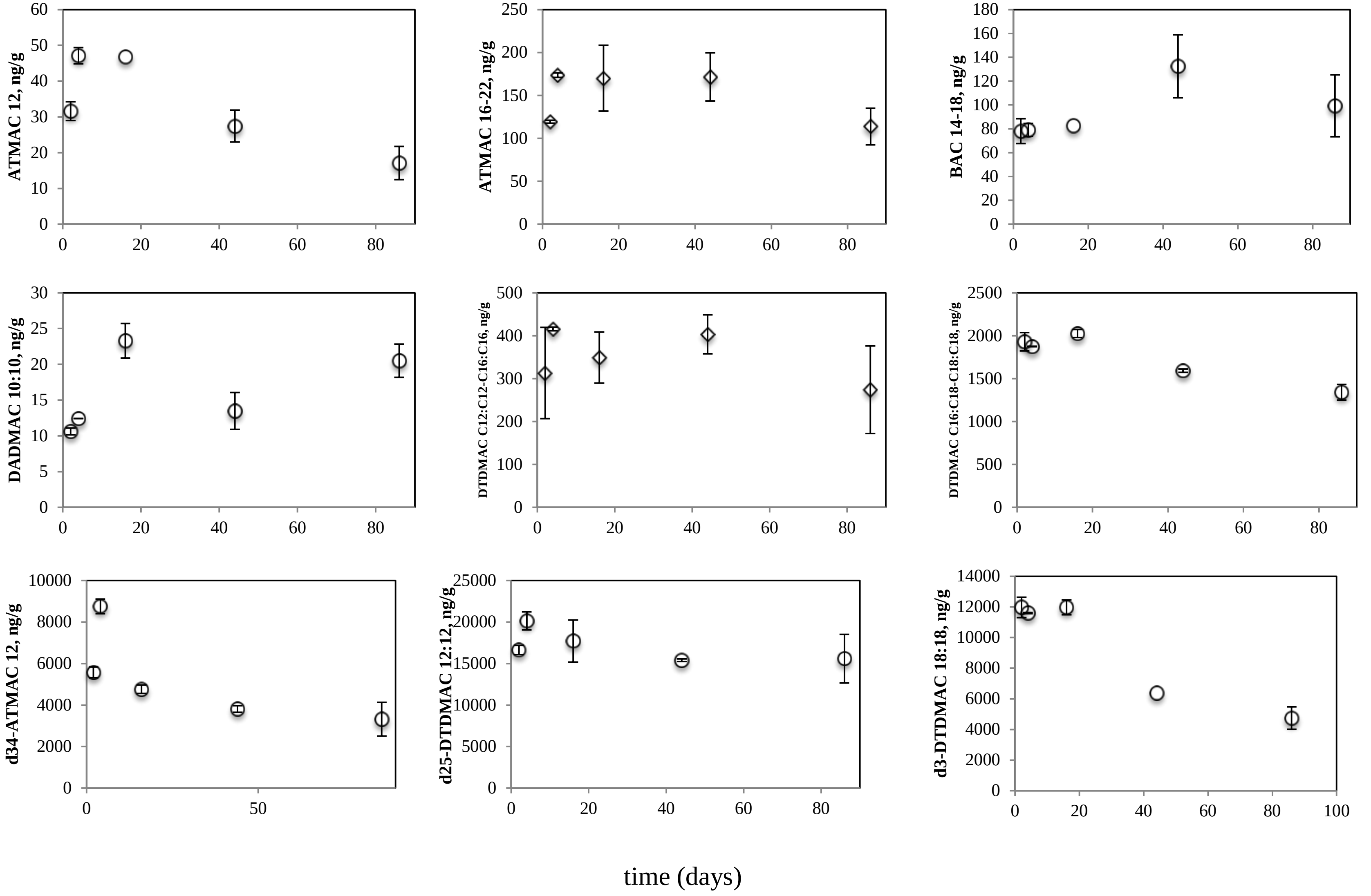


Figure A2.2. The ratio of deuterated to native compounds for ATMAC 12, DTDMAC 12:12 and DTDMAC 18:18.

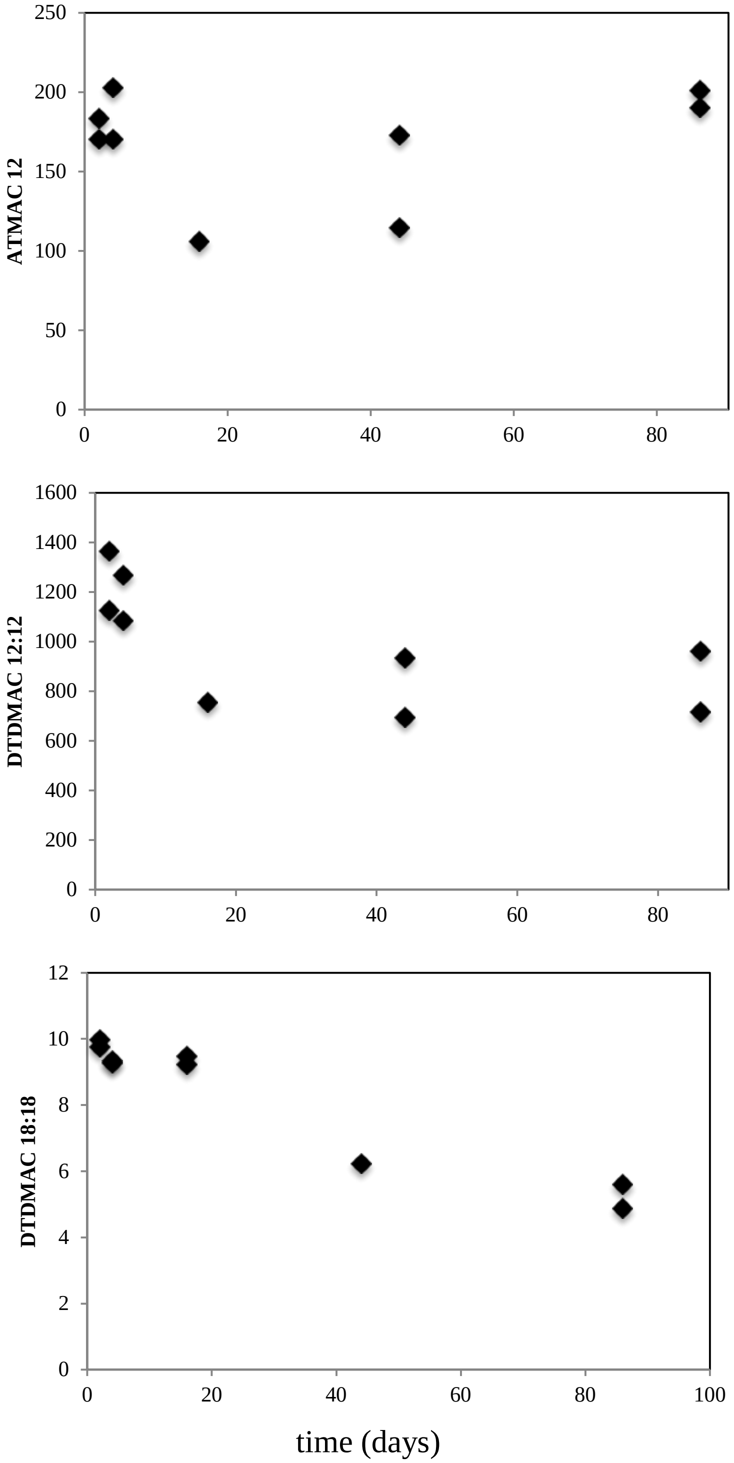
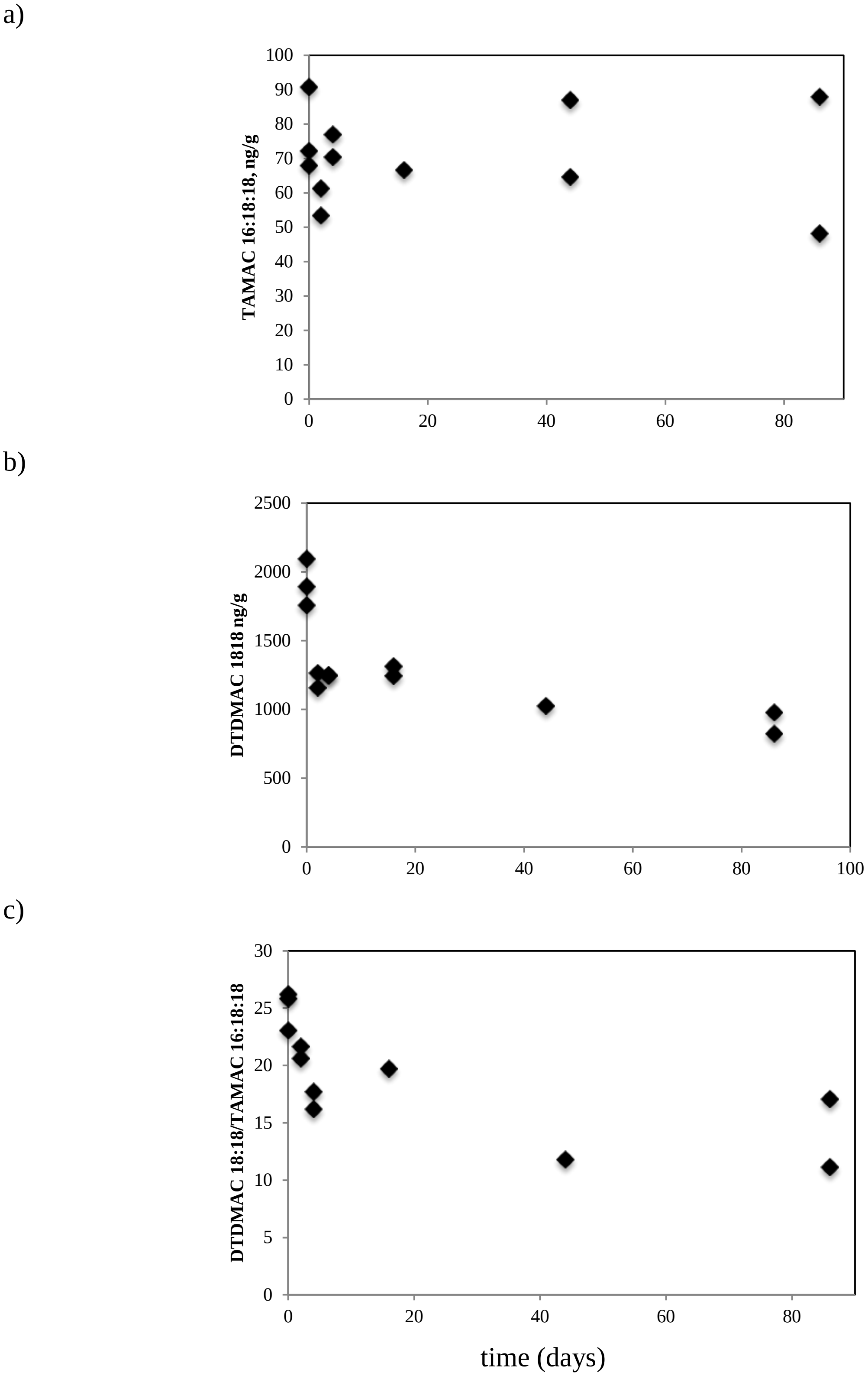


Figure A2.3. a) TAMAC 16:18:18 concentrations (ng/g), b) DTDMAC 18:18 concentrations (ng/g) and c) DTDMAC normalized to TAMAC 16:18:18 in the East Bay oxic incubation.



APPENDIX 3: X-radiographs of Hempstead Bay cores.

Figure A3.1: X-radiographs of top portions of the Hempstead Bay cores a) HB Core 1, b) HB Core 2, c) HB Core 3 and d) HP Core 11.