Quaternary ammonium compounds (QACs) in marine sediments: detection, occurrence, and application as geochemical tracer

A Dissertation Presented

By

Xiaolin Li

to

The Graduate School

In Partial Fulfillment of the Requirements

for the Degree of

Doctor of Philosophy

in

Marine and Atmospheric Science

Stony Brook University

May 2009

Stony Brook University

The Graduate School

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Abstract of the dissertation

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2009

Quaternary ammonium compounds (QACs) are a major class of cationic surfactants and have been wildly used in commercial products. However, there is very little knowledge of their environmental sources and fates. This thesis mainly focused on developing robust methods to detect QACs in marine sediments, then studying their occurrence, fate, and application as wastewater-specific tracers of other contaminants in estuarine systems. The study area included large regions of the lower Hudson Basin, especially the highly urbanized and sewage affected New York/New Jersey Harbor complex.

A robust analytical method was developed using HPLC-MS detection with electrospray (ESI) and Time-of Flight (ToF) detection. Analytical methods were developed with superior extraction efficiency, analyte recoveries and sensitivity than prior approaches. The HPLC-ESI-ToF-MS method was sensitive for all targeted QACs, which included dialkyldimethylammonium compounds (DADMACs), benzalkonium compounds (BACs), and alkyltrimethylammonium compounds (ATMACs). A number of QACs were detected for the first time in environmental samples (e.g., DADMAC C8:C8 and C8:C10), and other high concentration QACs that have not been reported in the scientific literature to date (ATMAC 20 and 22). The specificity of alkylammonium ion detection proved to be surprisingly great. A unique positive mass defect of quaternary ammonium ions was discovered and provides significant resolving power when utilizing ToF or other higher resolution mass spectrometers.

This thesis provides the first extensive study of major QACs in any sedimentary environments. QACs are found to be ubiquitous in the NY/NJ Harbor complex with extraordinary high level in the sediments impacted mainly by the wastewater from municipal wastewater treatment plants (WWTP) and combined sewer overflows (CSO). Ditallowdimethylammonium compounds (DTDMAC) are DADMACs with longer alkylchains (C14-C18), and are consistently seen to be the most important QACs in sediments of the lower Hudson Basin. However, more soluble QACs are found to be more abundant in the samples impacted by less treated wastewaters coming from CSOs. Further evidence shows that the extent of biodegradation of QACs during treatment in WWTP positively correlates with the solubility of the compounds, but multiple lines of evidence suggest that all of the QACs studied are preserved well in muddy sediments after they are discharged into the environment.

The geochronology of QACs was determined in dated sediment cores and time series surface sediments collected from WWTP-affected areas of the Harbor complex.

Preservation of all major QACs was further indicated by comparison of matched sediment cores collected 8 years apart. Different classes of QACs, including ATMAC16-18, ATMAC22, DADMAC C8:C8 to C10:C10, BAC 12-18, and DTDMAC, were characterized by different time histories, which generally agreed well among sites and were in agreement with what little is known about the history of sales and uses of these chemicals. ATMAC22 is reported here for the first time with exponential increases in concentrations over the last 30 years. The potential application of the ATMAC22/ATMAC18 ratio as a highly time-sensitive marker of sewage affected sediment age was demonstrated, providing a good prediction of the time of sewage sludge dumping in sediments collected from the former deep water sewage sludge disposal site, 106 miles off the shore of New Jersey

DTDMAC was applied as sewagesource-specific tracer for the source and fate study of three major endocrine disrupting compounds – PCB, PBDE, and NPEO metabolites. Uncharacterized industrial sources for PBDE from upstream Hudson River and Passaic River are separated from the sewage inputs at lower Hudson River by the PBDE congener composition and confirmed by the relationship between sediment concentrations of PBDEs and DTDMAC. A comparison between DTDMAC and different PCB homolog series indicates that the relative importance of upper River sources of PCBs to New York Harbor have continued to decline since the mid 1970s, when serious contamination from two General Electric factories was greatly reduced. While upstream Hudson River sources of lower chlorinated PCBs are still seen in sediments collected in the lower Hudson River between 1998 and 2005, the distributions of all PCB homologs, especially higher chlorinated congeners, has become dominated by urban harbor sources. Throughout the lower Hudson Basin, there was strong correlation between NPEO and DTDMAC levels in sediments collected in the highly depositional sedimentary environment, indicating a common sewage derived source well preserved at those sites. However, in Jamaica Bay sediments, relative depletion of NPEOs and steroid estrogens were observed due to less association of these compounds with suspended particles and sediments that may result in preferential solubilization or microbial degradation.

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LIST OF ABBREVIATIONS

AP	Alkylphenol
ATMAC	Alkyltrimethylammonium compound
BAC	Benzalkonium compound Benzylalkyldimethylammonium compound
BOD	Biochemical oxygen demand
CID	Collision-induced dissociation
CNPEC	Carboxynonylphenol ethoxycarboxylate
CSO	Combined sewer overflow
DADMAC	Dialkyldimethylammonium compound
DEEDMAC	Diethylesterdimethylammonium compound
DEQ	Diesterquaternary
DTDMAC	Ditallowdimethylammonium compound
E1	Estrone
E2	Estradio
ESI	Electrospray ionization
FID	Flame ionization detector
GC	Gas chromatography
HPLC	High-performance liquid chromatogrphy
LC-MS	Liquid chromatography-mass spectrometry
MDL	Method detection limit
MGD	Million gallon daily
ND	Not detected
NP	Nonylphenol
NPEC	Nonylphenol ethoxycarboxylate
NPEO	Nonylphenol ethoxylate
PAH	Polycyclic aromatic hydrocarbon
PBDE	Polybrominated diphenyl ester
PCA	Principle components analysis
REMAP	Regional estuarine monitoring and assessment program
SPE	Solid phase extraction
STP	Sewage treatment plant
TAM	Trialkylamine
TAMAC	Trialkylmethylammonium compound
TCC	Triclocarbon
TCS	Triclosan
TOC	Total organic carbon
ToF	Time of flight mass spectrometer
TPH	Total petroleum hydrocaron
USITC	United States International Trade Commission
WWTP	Wastewater treatment plant

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ACKNOWLEDGEMENTS

I am still not exactly sure what made me came to U.S. six years ago. I think I was trying to follow the steps of some good friends I knew in China studying modern oceanography on the other side of Pacific Ocean. It has been such an interesting journey. I have gotten to know so many wonderful people and have learned a different culture and life here. Most importantly, I am going to get my doctoral degree. At this point, I would like to thank all my friends, family and colleagues for supporting me throughout the last six years.

This work would be absolutely impossible without my advisor, Bruce Brownawell. Bruce helped me train to be an analytical chemist, oceanographer, and mass spectrometry expert. I would never have imagined that we could get so much great data for my thesis, mostly in the last 3 years. I want to thank Bruce for his guidance, great scientific insight, and support for all my experiments and education. Thank you for always being so passionate and giving me endless ideas that pushed my research forward.

I want to thank all my thesis committee members. Robert Cerrato gave me valuable suggestions about the statistical analysis that I included in my thesis . Kirk Cochran provided very helpful comments and suggestions for my thesis that made my research work better. Special thanks to Lee Ferguson for all of his help during method development as well as comments on the paper and thesis drafts. Richard Bopp gave me essential help for the thesis, there would be no Chapter 4 and 5 for this thesis without samples, data and advice from Richard.

I would like to thank all professor and staff from SoMAS for helping me with my study and research. Especially Robert Aller, Josephine Aller, Cindy Lee, Mary Scranton, Nick Fisher, Qingzhi Zhu, Dorothy Tsang, Shelagh Palma and Joseph Ruggieri for all your help during classes and advice on my research.

I want thank all my friends at SoMAS who give me support and a lot of fun in my life here. In particular for some great friends, Zhanfei, Jianhong, Xuejue (my roommate in China), Weijun, and Yanluan for helping me start the new life here when I first arrived U.S. Shawn, Anne Cooper, Pablo, Mark, Sharanya and Haifei, it was really nice to work with you guys in the Brownawell lab; Fanghua, Jianhua, Yan, Yuan, Zhengrui, Xiaona, Xi, Jindong, Tiantian, Jin, Jing, thank you all for your support and making me not forget how to speak Chinese. And other friends including my officemates Keith, John, Santiago, and all my softball teammates. There are too many names to list here but I will remember you all for my best time at SoMAS.

There are some other people I want to thank, Kai, Chunyi, and Lihong, thank you all for always supporting me to make it through.

I want to give a sincere thanks to my parents who always give me support and made me feel better faraway from home.

The last acknowledgement goes to my wife, Ying. I could not have done all of this without her support. Thank you!

This research was supported by the NIEHS/EPA Superfund Basic Research Program and the Hudson River Foundation.

CHAPTER ONE: INTRODUCTION

Municipal wastewaters are recognized as an important source of many chemical contaminants to surface waters and sediments that receive those wastes, especially in highly urbanized settings. Not only, has a small fraction of the high-volume chemicals entering municipal sewage systems been identified, but most are not regulated, and for many wastewater derived chemicals known to occur at high levels, there has been a paucity of work on not just their occurrence in the environment, but on developing an understanding of their fate and transport in the environment. Such understanding is needed to better characterize potential risks associated with these compounds, as well as to determine whether, and how, wastewater derived chemicals might be applied as tracers of the sources or fate of co-occurring chemicals of environmental concern (Eganhouse 1997; Benotti and Brownawell 2007). This thesis set out to characterize the occurrence of Quaternary ammonium compounds (QACs) as highly sorbed sediment contaminants and assess their utility as tracers of contaminants sources, transport, and differential fate in estuarine and coastal waters. QACs studied here are cationic surfactants that have received essentially no research, despite some of them being recognized as among the highest concentrated contaminants in sewage sludges and affected sediments. Those studies have turned out to be more exciting than even imagined, and form the primary basis for the work presented here. I have also been concerned with nonylphenolethoxylates (NPEOs), a better studied class of nonionic surfactants and their relatively persistent metabolites, including nonylphenol (NP), which is a chemical of ecotoxicological concern. It was hypothesized from earlier work that the composition of NPEOs and their metabolites could provide powerful information about the sources (e.g., the efficacy and extent of sewage treatment) of NPEOs and other contaminants, and that metabolite patterns in sediments could be useful to understand sedimentary redox conditions that control the fate of not only NPEOs, but also other organic contaminants of interest.

Results presented here are primarily aimed at new research in QACs that includes better methods for analysis and discovery of new compounds, understanding the distributions, preservation, and histories of input, and the utility of using the most persistent QACs as tracers to better characterize the relative sources of other sediment contaminants, including NPEOs, that may have multiple sources into a large area of the lower Hudson Basin. Also presented are less developed research on the power of using NPEO and NPEO metabolites as tracers of sources, in-situ degradation, and indicators of sediment properties most correlated with sediment toxicity.

The following background sections serve as an introduction to what is known and not known about the chemicals and some of the processes important for this research.

1.1 What are QACs?

QACs are classified as high production volume (HPV) chemicals by both the U.S. Environmental Protection Agency (EPA) and the Organization for Economic Cooperation and Developed (OECD), and comprise a large fraction of cationic surfactant production world wide (United States International Trade Commission. and United States Tariff Commission.). Cationic surfactants are considered to be amphililic, and are characterized by a more hydrophilic ammonium head (containing one to three covalently bonded methyl groups) and at least one hydrophobic tail that make up the more lipophilic portion of the molecules. The hydrophobic part of the molecule typically consists of n-alkyl chains, and may contain aromatic functional groups as well. Figure 1.1 shows the molecular structures of different major classes of QAC, each of which contains homologous series compounds with different alkyl chain lengths. The most important classes of QACs studied here consist of three major structural classes:

- dialkyldimethylammonium compounds (DADMAC) can actually be separated into two classes: those containing longer alkyl chains (C12:C12-C18:C18), which are used as fabric softeners and also conditioners in hair care products; this group of QACs was historically referred to as ditallowdimethylammonium compounds (DTDMAC), a term retained here despite the fact that there are an increasing number of feedstocks other than animal fat that serve as the source of longer chain DADMACs; a second group of DADMACs are those with shorter alkylchains

(C8:C8 to C10:C10) used as potent and later generation QAC-based disinfectants; throughout this thesis, the use of DADMAC is primarily restricted to this more soluble group of C8 – C10 homologs;

- alkyltrimethylammonium compounds (ATMAC 12-22)
- benzylakyldimethylammonium compounds also called benzalkonium compounds (BAC 12-18)

Other QACs detected, some for the first time in this research (but not considered in the thesis) include: trialkylmethylammonium compounds (TAMAC), diethylester dimethylammonium compounds (DEEDMAC), diesterquaternary (DEQ), and dimethyl ethylbenzylammonium compounds (Ethyl-BAC). Also shown in Figure 1.1 are the tertiary trialkylamines (TAM), which are known as impurities in DADMAC and TAMAC that have previously been used as persistent tracers of sewage derived traces in coastal and open waters (Valls et al. 1989). The mouthwash ingredient cetylpyridinium has also been detected at trace level quantities in sediments of the lower Hudson Basin.

To my knowledge, DADMAC, BAC and ATMAC still represent the largest classes of QAC surfactants in present use (Boethling and Lynch 1992; Boethling 1994). This assessment is complicated by the fact that reporting of QAC sales and production data is no longer required to be presented in a form that is available in a useful way. Pure QACs, which are not dissociated in solution, exist and are sold as salts (for example, for most reports of DTDMAC, ATMAC, and BAC compounds the C stands for chloride, despite the fact that they are sold as other salts depending on application, with common anions being mostly chloride as shown in Figure 1.1.), bromide, and methosulfate. QACs have numerous different common names and trade names, and when the salts are different or the homolog compositions of QAC mixtures are different, they often carry different IUPAC numbers. Thus, gathering information in the published and unpublished literature on these compounds is very difficult. Unfortunately, the same situation often holds for many other classes of surfactants, especially those never previously studied. These factors contribute to the lack of a general understanding of the industrial ecology of this group of diverse compounds, their sources to wastewaters, and difficulty in accessing literature related to their environmental behavior.

QACs are used in greatest quantities as active agents in detergent formulations and fabric softener products, but they also fulfill many other important uses as microbicides, algaecides, preservatives, antistatic agents, anticorrosives, in drilling fluids, a variety of industrial processes, and especially in many thousands of personal care products, especially hair care products (Boethling and Lynch 1992; Boethling 1994). Sometimes, QACs are sold as organo-clay complexes, especially with bentonite – the most important applications of organo-clays are less well known, but include uses as lubricants and are found in a variety of personal care products as well (http://www.cosmeticsdatabase.com).

DTDMAC was the most widely used ingredient in fabric softteners since its introduction in the 1950's (Levinson 1999), and has been the most widely studied for many years. However, its uses have been restricted or reduced in some countries due to persistence, build up of extremely high concentrations in European sewage sludges, and lack of biodegradability (Giolando et al. 1995; Levinson 1999). In portions of Europe there was a voluntary phase-out of DTDMAC in the early 1990s, with replacement by more biodegradable esterquats – DEEDMAC and DEQ (Gerike et al. 1994; Fernandez et al. 1996; Radke et al. 1999). It appears that DTDMAC use was then reduced but to a much lesser extent in the U.S. in the 1990's and has since leveled off (Levinson 1999). DTDMAC is also extensively used in applications including fabric softeners and hair care products in non-European countries, but current production for those applications is not well known. There appears to be increased use of plant oil-based stock material for the production of longer alkyl chain DADMACs (supported by very recently collected data on sewage sludge samples not reported here), resulting in high proportions of shorter alkyl chains (more C12, C14 alkylchains), so that the term DTDMAC is less appropriate than it used to be.

More water soluble QACs are used as disinfectants and preservatives, and many personal care products. In the 1940s, BAC was used as the first generation of quaternary ammonium disinfectants. Less alkylated BAC 12-16 are used as disinfectants, and BAC 18 is used as algaecides (e.g., in pools) and in hair care products. Ethyl-BAC has been used since 1955 as a second generation of QAC disinfectants with improving tolerance to environmental conditions. Twin chain QACs, the DADMACs with lower alkyl chain lengths (C8:C8-C10:C10), were introduced into the most recent generation of QAC disinfectants in 1965 (www.antrixgroup.com). ATMACs are applied in many industrial applications and personal care products as softeners, antistatic agents, and also have antimicrobial and algaecidal properties. They are the main ingredient of hair conditioners, imparting softness, manageability, and antistatic properties to hair (Ding and Tsai 2003). It is notable that docosanyltrimethylammonium (ATMAC 22, the most common names being behentrimonium chloride or methosulfates) was previously unreported in the environment matrix and is preferred in hair care and other personnel care products, in part due to lower skin irritancy, which then has allowed much higher levels to be incorporated in personal care products. Most of this new work on behentrimonium is reported in a related study (Lara-Martin et al. 2009), but the sediment geochronologies of this compound are presented. In the latest analyses behentrimonium has become one of the two most concentrated chemicals found in recently collected surficial sediments and sewage sludge samples.

1.2 Occurrence of QACs in WWTP and aquatic ecosystems

Occurrence of QACs, especially for DTDMAC, has been better studied in the wastewater and sludge derived from wastewater treatment plants (WWTP), although most of that work was published before the mid-1990's. Concentrations of DTDMAC in sewage sludge from European countries were found to be extraordinary high (maximum concentration reported of 9200 μg/g).(Hellmann 1989; Gerike et al. 1994; Breen et al. 1996; Fernandez et al. 1996; Merino et al. 2003; Martinez-Carballo et al. 2007) DTDMAC concentrations varied from 3600-8000 μg/g for sludge samples collected from different treatment steps from WWTPs in Germany (Gerike et al. 1994). Fernandez and coworkers (1996) reported that levels of DTDMAC in anaerobically stabilized sewage sludge from Switzerland decreased from 2570 – 5870 μg/g in 1991 to 150-300μg/g in 1994, as a result of the voluntary phase-out of DTDMAC in European countries, and the replacement with more biodegradable esterquats. Important esterquats include DEEDMAC and DEQ, which have been shown to be effectively biodegraded during biological wastewater treatments (Matthijs et al. 1995; Radke et al. 1999).

There are very few reports about QACs in aquatic ecosystems, especially in the U.S. In this country, concentrations of BAC (C12-C16) were found in the sewage impacted riverine sediments (22-206 ng/g) (Ferrer and Furlong 2002) and in surface water samples (1.2 to 36.6 μg/L) downstream of WWTPs (Ferrer and Furlong 2001). ATMAC (C12-C18) was only found in the river water sample from Taiwan (up to 1.24 μg/L), which directly received untreated municipal wastewaters (Ding and Tsai 2003). Martinez-Carballo et al. (2007) determined selected QAC homologues in wastewater and riverine sediment samples in Austria in the most comprehensive study of QACs, including DADMAC (C10:C10-C18:C18); BAC (C12-C18); and ATMAC (C12-C16). The one report of DTDMAC levels in U.S sediments found concentrations between 3-67 μg/g in river sediments in South Dakota (Lewis and Wee 1983).

1.3 Aquatic toxicity of QACs

Recent research on the aquatic toxicity for QAC and other surfactants is summarized by Ying (2005) and Kreuzinger (2007). Utsunomiya and co-workers (1997) compared toxic effects of ATMAC (mixture C16-C18), BAC (mixture C12-C14), DTDMAC (mixture C16-C18) and LAS on unicellar green alga *Dunaliella sp.* by determination of ^{13}C-glycerol after exposure to different surfactants. For the 24 hours median effective concentrations (EC50-24h) ATMAC had the lowest effective concentration of 0.79mg/L, as comparing to BAC at 1.3 mg/L, LAS at 3.5 mg/L and DTDMAC at 18 mg/L, which is not surprising considering that ATMAC and BAC are also widely used as disinfectants to kill bacteria and biocides to kill algae when applied as additives in large-scale industrial water systems to minimize undesired biological growth.

DTDMAC (with dominant homologs being C16:16 C16:18, and C18:C18) and replacement esterquat compunds are not particularly toxic in most studies, perhaps owing to poor biovailabily as are superhydrophobic cation exchangers, and likely unmeasurably low aqueous solubility. Twenty-one days growth on observable effects of concentration (NOEC) values on *D. magna* showed less toxicity of DEEDMAC (1.0mg/L) (Giolando et al. 1995) than DTDMAC (0.38mg/L) (Lewis and Wee 1983). Singh et al. (2002) evaluated toxicity on six freshwater microbes (assessing immobility EC50-48h) among cationic surfactants (ATMAC16, DTDMAC C16-18), anionic surfactants (LAS C12, AS C12) and nonionic surfactants (C12EO6, OPEO6), and reported that cationic surfactants were more toxic than anionic and nonionic surfactants.

Further toxicity tests of more soluble BACs and DADMACs showed a much lower range of EC values than previously reported (Kreuzinger et al. 2007). BAC and DADMAC showed similar EC levels for the most sensitive algae (*P. subcapitata*, 72-h EC50: 41μg/L BAC; 21 μg/g DADMAC), daphnids (*D. magna* 48-h IC50: 41μg/L BAC; 23 μg/L DADMAC), and the rotifers (*B. calyciflorus*, 48-h EC: 125μg/L BAC; 25 μg/L DADMAC). Kreuzinger and co-workers (2007) also reported that the lowest actual ecotoxicological effective concentrations determined, exceeding the highest concentrations measured in surface water (BAC C12 1.9 μg/L; DADMAC C10:C10 0.15 μg/L) and effluents (C12 4.1 μg/L; DADMAC C10:C10 0.85 μg/L), are not much greater than concentrations that can affect phytoplankton. It was concluded that environmental risks associated with QACs in receiving waters could not be excluded in the evaluation of BAC and DADMAC.

Besides the fragmentary ecotoxicology research described above, little has been done to assess the long term effects of QAC on reproduction, development and growth of aquatic organisms. It is noteworthy that some QACs have been used as disinfectants for more than 60 years. One potential negative environmental impact of QACs is the selection for enhancement of bacterial resistance and many well characterized QAC genes. Gaze and co-workers (2005) found that a selection of QAC resistance genes in the natural environment has the potential to co-select for antibiotic resistance genes. (Gaze et al. 2005).

1.4 Behavior and fate of QACs in the environment

Environmental fate and behavior of QACs are influenced by many processes like sorption, micro-biodegradation, and transport, especially of suspended particles and sediment. Sorption onto particles controls the distribution of QACs in different environmental compartments (sediment and water) as well as bioavailability and microbial-degradation. As hydrophobic cation exchangers, QAC sorb strongly onto soil and sediments, with sorption energies controlled both by hydrophobic effects of increasing alkyl chain length and favorable electrostatic interactions that lead to relatively pH insensitive cation exchange (Brownawell et al. 1990; Brownawell et al. 1991). Sorption coefficient (K_d) of ATMAC (C18) and DEEDMAC on activated sludge were found significantly higher than some other anionic and nonionic surfactants (Games et al. 1982; Giolando et al. 1995; Ying 2006). Brownawell et al. (1991) found that for similar alkylchain length compounds that cationic surfactants sorbed to sediments and soils to a much greater extent than nonionic surfactants, which sorbed more than anionic surfactants (Brownawell et al. 1991). Sorption of BACs was seen to be affected greatly by increasing the alkyl chain length of QAC homologous series and was associated with slower biodegradation controlled by less bioavailability to microbes (Garcia et al. 2006).

The literature is very inconsistent when it comes to the biodegradability of QACs in wastewater treatment plants and receiving water. The extent to which QACs are biodegraded before and after release into receiving waters has implications for their suitability as sewage tracers. Much of the literature on biodegradation of QACs in environmental settings has been reviewed (Boethling 1984; Ying 2006). Estimates of QAC degradation range between 0 and 100% in laboratory tests where QACs are spiked, most often at very high levels where the extent of sorption can be greatly reduced, and selection of bacteria that can be grown on QACs is favored. It is clear that under aerobic conditions, even the most hydrophobic DTDMACs can be biodegraded when introduced at high concentrations (Sullivan 1983), although most studies do not use radiolabeled compounds, which makes recovery of undegraded DTDMAC extremely difficult (Chapter 2). Microbial transformation under anaerobic conditions is not observed for DTDMAC, and is greatly reduced for other QACs (Garcia et al. 1999). Microbial degradation of QACs is more favored for more soluble and lower chain length QACs (Sullivan 1983; Garcia et al. 1999; Garcia et al. 2000; Garcia et al. 2001; Garcia et al. 2006).

Measurements of QAC degradation under actual field or treatment plant conditions are difficult to conduct, but estimates of the role of biodegradation of QACs have been estimated through mass balance considerations in sewage treatments plants. By comparing different classes of QACs and their alkylchain homolog distributions, Kreuzinger and co-workers (2007) separated the importance of removal of QACs in wastewater treatment plants (WWTPs) in Austria from removal and preservation in sludge and/or biodegradation. More soluble QACs like BAC, DADMAC, and ATMAC were removed (80-99%) by biotransformation, although the amount that was preserved in sediments increased with alkyl chain length for the BACs and ATMACs studied. However, the fate of much more hydrophobic DTDMAC homologs could be fully accounted for by removal to sludge and a smaller percentage releases in effluents (Kreuzinger et al. 2007). The fraction of relatively soluble DADMAC C10:C10 preserved in sludge was relatively low. As a class of QACs, greater biodegradation loss of ATMACs was seen than for BACs, presumably due to the increase in hydrophobicily of BACs when the a methyl group of ATMAC is replaced by a larger benzyl group in BACs. For both classes the fraction removed to a preserved in sludge increased with alkyl chain length(Kreuzinger et al. 2007).

An important underlying hypothesis in this work is the hypothesized that at least DTDMAC is essentially conservative in WWTPs, and especially resistant and particle reactive in marine sediments after entering the environment. Evidence has been showed in my thesis that is consistent with this hypothesis, and that other QACs are highly persistent once they leave WWTPs, at least under some sedimentary conditions. The assumption that DTDMAC is persistent is based on a combination of evidence:

1. As reviewed above, DTDMAC has been found at very high levels in sewage sludges and digested sewage sludges in the past (Hellmann 1989; Gerike et al. 1994; Breen et al. 1996; Fernandez et al. 1996; Merino et al. 2003; Martinez-Carballo et al. 2007), and in sludges composted or treated for agricultural applications. Amazingly it is not lost even after 12 weeks of partially aerobic vermicomposting with high densities of earth worms (the latter preliminary data part of a related study and not presented here).
2. In addition to the recent mass balance study discussed above (Clara et al. 2007), simple watershed and WWTP mass balance modeling was able to predict both the influent concentrations of DTDMAC, and the high concentrations in sewage sludge by assuming no degradation (Denijs and Degreef 1992; Vanleeuwen et al. 1992).
3. In discussing the reasons for replacing DTDMAC with biodegradable esterquats as replacements in fabric softeners, scientists from Proctor and Gamble (Giolando et al. 1995) state that "DTDMAC is not significantly biodegraded in EC and OECD screening tests". Thus, it appears that at least in some experiments with important management implications, DTDMAC was found to be stable in WWTPs or sludge, matrices that should be more acclimated and active in the degradation of DTDMAC than that which might be expected in sediments.
4. As mentioned there are literatures that show that under conditions of very high loadings of DTDMAC that they can be degraded when spiked to suspensions of sludge or even sediment, but the adsorbed surface concentrations may exceed essentially mono-layer coverage, as opposed to the situation that exists in receiving waters or even sewage treatment plants. The highest levels of QACs determined in surficial and subsurface sediments in the lower Hudson Basin are seen in this thesis to be on the order of 100 – 500 μg/g (approximately 0.2 -1 μmol/g); generally concentrations are much lower. The extent of QAC adsorption can be expected to decrease greatly with increasing concentration, even at sub nM levels, but especially as the surface coverage of sorbed QAC approaches or exceeds the cation exchange capacity of the sediment or soil (Brownawell et al. 1990; Brownawell et al. 1991). The highest surface concentrations on sediments

are much lower (less than a fraction of a percent) than cation-exchange capacities (CEC) of fine grain coastal sediments (on the order of 100-200 μequiv/g). Thus, it seems unlikely that any appreciable fraction of ultra-hydrophobic cation exchangers like DTDMAC would be in the dissolved phase under environmental conditions.

As the other QACs studied in this work are also extremely particle reactive, it is also expected that once in receiving waters they should also be strongly sorbed to sediments, especially muds with high surface area and CEC.

5. TAMs have been shown to be highly persistent particle tracers in coastal and even off-shore marine settings. TAMs are impurities of DTDMAC and are tertiary amines with the same structures of DTDMAC without one methyl group (Figure 1.1). At seawater pH they are positively charged and likely interact with particles in a way similar to DTDMAC. This provides further evidence that DTMAC should be highly stable in coastal receiving waters.
6. QACs, are extremely hard to extract from sediments during analysis (Fernandez et al. 1996), consistent with the expected particle reactivity and persistence that is expected.

The hypothesis that DTMAC can be a conservative source-specific tracer needs further assessment, and this issue is addressed, in part, in the work that follows.

1.5 Organic contaminants as molecular tracers in environmental geochemistry

During the last century, numerous organic chemicals have been produced either intentionally or inadvertently through industrial activities. While these organic chemicals contribute to economic development and enhance our daily lives, there is increasing concern about various environmental problems caused by organic wastes. Usually, organic wastes from factories and residential houses are collected in wastewater and transported to WWTP as sewage influent. Many organic wastes can be removed and decomposed in WWTP before they are released to natural waters. However, there are still significant quantities of organic contaminants and their metabolites discharged to surface water through WWTP outlets, especially in highly urbanized and industrialized areas. Municipal waste water and urban run-off can enter directly into the environment without any treatment through combined sewer overflows (CSOs); sanitary sewer overflows (SSOs); storm sewer outlets, and other non-point sources. There is a need for better tools to understand organic contaminants sources and their ultimate fates in the urbanized estuary.

Hydrophobic organic contaminants from various sources tend to associate with suspended particles in the water and are eventually deposited in bottom sediments which can act as short or long term reservoirs for these compounds. Sediments are a major repository of many organic and metal contaminants, especially in shallow coastal and estuarine ecosystems which receive waste water. Particularly in urban harbors and coastal embayments, contaminated sediments are prevalent, potentially causing problems for ecosystem health, for human consumption of seafood, and for management of dredged materials. Disposal of sediments containing toxic levels of contaminants is both more difficult and costly than disposal of uncontaminated sediments, creating problems for effective harbor management.

Sediment toxicity remains a challenging problem for coastal managers. We need to know more about sources of contaminants in sediments, their pathways to the environment, and their ultimate fates and toxicity to effectively address these issues. In recent decades, contaminant tracers have been utilized to provide information on the sources and fates of organic contaminants, providing information on preservation, bioaccumulation, and biodecomposition. Interpreting the distribution of organic contaminants in sediments would be improved if we had better source specific tracers of contaminants and improved understanding of processes that regulate the accumulation and preservation in sediments of potentially toxic contaminants and tracers.

What are the qualities of useful organic contaminants tracer in sediments? Contaminant tracers for determining sources should exhibit conservative behavior. They need to be relatively refractory throughout the processes of concern (e.g. transportation, deposition, degradation) so that we can use them as tracers to evaluate origination, transportation and degradation of specific contaminants. However, for example in the case of the production and persistence of NPEO metabolites, if we knew enough about a tracer's biodegradation pathway and its metabolites we may also use them to indicate the extend of biodegradation process and different sources they could come from.

Chemicals used as tracers should also have source specificity. Molecular structures of many organic materials synthesized for industrial and/or human activities have specific chemical characteristics associated with their purpose or uses. Advances in environmental analytical chemistry during the past 40 years utilizing gas and liquid chromatography connected with mass detector-GC/MS and LC-MS to selectively identify molecular structure and levels in trace amounts (parts per billion (ppb) or parts per trillion (ppt)) levels of anthropogenic organic tracers in complex environmental samples has facilitated the development of new tracer molecules. Finally, good tracers of sediments or sediment-associated chemicals must be very particle reactive on their own.

There have been many examples of waste water-derived organic chemicals being applied as potential molecular tracers in the environment (Eganhouse 1997). Of interest here are the trialkylamines (Figure 1.1.), which are formed during the synthesis of DTDMAC and present as trace impurities in fabric softeners used in household applications. Previous reports showed that TAM is ubiquitous in river waters (Chalaux et al. 1995), coastal sediments (Valls et al. 1989; Valls et al. 1990; Chalaux et al. 1995; Maldonado et al. 2000) sewage sludge (Valls et al. 1989) and wastewater (Fernandez et al. 1991). Valls et. al. (1989) compared TAM with another domestic surfactant, long-chain alkylbenzenes (LABs), and proposed that TAM may serve as a more conservative indicator of urban sewage contamination of coastal areas. Maldonado and co-workers (1999) showed the occurrence and distribution of TAMs and the fecal steroid coprostanol (COP), which is a tracer for fecal matter sources such as sewage effluent, in the open seawaters from the western Mediterranean and the northwestern Black Sea and TAM was used as a molecular marker to assess the long-range transport of domestic pollution into the open sea (Maldonado et al. 1999). Research work at San Pedro Shelf in U.S. showed that the TAM/COP ratio was larger in sediments (0.3-11.2) than in the effluent (0.07), indicating a relatively higher stability of TAM than COP in sediments under prevailing oxic conditions (Maldonado et al. 2000). Lamoureux and Brownawell (1999) provided evidence that hydrophobic linear alkylbenzenes were largely degraded after reaching sediments at the Deep Water Disposal Site for sewage sludge that was 106 miles off the New Jersey Coast (Lamoureux and Brownawell 1999). Thus, prior to this work, it was apparent that not all hydrophobic sewage tracers were persistent in sediments, and TAM might be a superior tracer even as minor impurities in DTDMAC mixtures.

The homologous series of QAC showed an excellent match among all criteria as a powerful tracer in the urbanized estuarine sediments. In addition to the special physiochemical properties of QAC, the analytical method developed in this thesis gained extra point for this tracer study. Our ultra-sensitive detection method by LC-MS with fewer sample amounts needed provides a large dynamic range for quantitive study, which will be discussed in Chapter 2. Decreased sample size makes this method very practical for a variety of particle samples ranging from suspended particles in the estuary to sewage sludges. Chapter 4 focuses on application of DTDMAC as tracers to study the source and fate of some other organic contaminants known as endocrine disrupting compounds (EDCs).

1.6 Analysis of QACs in sediments and sewage sludges

One reason that QACs have been so little studied is that they can be difficult to analyze in environmental matrices, and there has been a little effort placed on developing robust and sensitive method for QACs analysis, especially the analysis of multiple classes and homologs of QACs. The development and testing of a more robust method to measure DTDMAC and a range of other QACs has been a large part of what I've worked on and present in the thesis.

1.6.1 Separation and identification of QAC homologues

Waters and Kupfer reported the colormetric disulfine blue active substances (DBAS) method which measured the absorbance of QACs-disulfine blue ion-pairs that partition into chloroform out of water with concentrations estimated by spectroscopic absorption at 628 nm (Waters and Kupfer 1976). That method eliminates the interference of anionic surfactants and other anionic components from natural matrix, making it the first realistic method for determination of cationic surfactant (0.1-10 mg l^{-1}) in wastewater and contaminated surface water samples (Waters and Kupfer 1976). It was further modified and used as a standard method to measure total organic cations in wastewater and sludge in Europe (HMSO 1981). DBAS is a non-specific method for all compounds in the sample extract that can form ion-pairs with disulfine blue regent. However, large discrepancies were found in the sludge and sediment samples between DBAS and other specific methods (Gerike et al. 1994), especially when QAC concentrations were not exceptionally high and the extracted matrix was complex.

Several analytical methods for DTDMAC or QAC analysis have been reported since the DBAS method was developed for determination in environmental matrixes: isocratic HPLC method coupled with conductometric detection for sewage sludge and river sediments from the United States and Germany (Wee and Kennedy 1982; Gerike et al. 1994); gradient HPLC method applying postcolumn ion-pair formation coupled with UV/vis or fluorescence detection for sewage sludge and marine sediment from Switzerland and Spain (Deruiter et al. 1987; Fernandez et al. 1996); and potential of Fast Atom Bombardment (FAB) mass spectrometry (MS) to identify the trace levels of DTDMAC in sewage influent and effluent samples in United States (Simms et al. 1988). For ATMAC and BAC, numerous analytical methods have been developed in the fields of food, pharmaceutical, water treatment, and environment sciences. Capillary electrophoresis (CE) separataion methods have been coupled with indirect UV detector (Heinig et al. 1997), direct UV detector (Lin et al. 1996; Heinig et al. 1997), and tandem MS detector (Norton et al. 2006). A gas chromatography (GC) method was applied to determine BAC and ATMAC in environmental samples after derivatization and determined by MS detection (Ding and Liao 2001; Ding and Tsai 2003). HPLC-based separation often allows for excellent detection, with less adsorption on column, and is relatively easy to use for QAC analysis.

Most recently, for QAC analysis in environmental matrices, HPLC coupled with electropspray ionization MS detection (HPLC-ESI-MS) has found wider use for the analysis of DTDMAC and C10:C10 DADMAC (Martinez-Carballo et al. 2007; Martinez-Carballo et al. 2007); BAC (Ferrer and Furlong 2001; Ferrer and Furlong 2002; Martinez-Carballo et al. 2007; Martinez-Carballo et al. 2007); and ATMAC (Martinez-Carballo et al. 2007; Martinez-Carballo et al. 2007). However, there has been little work addressing the identification of alkyl homologs of multiple classes of QACs in any sediment. HPLC-MS methods have not been applied to measurements of QACs in marine or estuarine sediments, nor has time-of-flight mass spectrometry (ToF-MS) ever been used to measure QACs in any complex matrix. Additional work is necessary to better characterize concentrations and compositions of these compounds in environmental matrices.

1.6.2 Extraction methods for QACs

Part of the problems associated with analysis of QACs relates to extraction techniques. Different extraction and matrix cleanup methods for sludge and sediment sample have been used in previous studies: acidic methanol extraction in steam bath with further matrix cleanup by anion exchange resin (Waters and Kupfer 1976; Gerike et al. 1994); accelerated solvent extraction (ACE) was applied for BAC measurement which is less hydrophobic compared to DTDMAC (Ferrer and Furlong 2002) ; supercritical fluid extraction (SFE) was reported with no need of matrix cleanup and gained 30-40% more DTDMAC than acidic methanol extraction in marine sediments (Fernandez et al. 1996); and most recently, Soxhlet extraction using acidic methanol for analysis of QAC homologues in sewage sludge samples (Martinez-Carballo et al. 2007). Potential problems existed in previous reports that may affect the effiency of extraction, ability to conduct trace level analysis, or recover highly surface active QACs during sample preparation. Glassware used in analysis has often been pre-treated with QACs (especially for super-hydrophobic DTDMACs) to minimize loss of DTDMACs by adsorption to active sites (Gerike et al. 1994; Fernandez et al. 1996). There has been little effort to determine the efficiency of QAC extraction from sediments or other environmental matrices. Tests of extraction efficiencies have often relied upon recovery of QAC recently spiked to sediments, water, or sludge,(Gerike et al. 1994; Ferrer and Furlong 2002; Martinez-Carballo et al. 2007) rather than compare the ability of different methods to extract field aged QACs that may be more tightly sorbed (Fernandez et al. 1996). A systematic analysis of extraction methodology is needed.

1.7 QACs as tracers of the relative sources and fate of other particle reactive contaminants of concern in the lower Hudson Basin

DTDMAC has been applied as a potential tracer to study the relative importance of municipal wastewater and other sources as contols on the distribution of three classes of particle reactive contaminants in the lower Hudson Basin: PCBs, PBDEs, and neutral NPEO metabolites. The following sections review the context of the source tracking studes on PCBs and PBDEs, and the section on NPEOs reflects background related to work with DTDMAC to characterize other potential sources and differential fate, as well as some background to the work on NPEO and metabolite compositions to probe other questions raised in this work.

PCBs and PBDEs are two classes of organic contaminants of concern that have accumulated in sediments of the lower Hudson Basin. There are many modes of toxicity of these different halogenated hydrocarbons and their metabolites (Brouwer et al. 1999; Darnerud 2008; Legler 2008), including disruption of endocrine function. PCBs belong to a class of organic compounds with 1-10 chlorine atoms attached to biphenyl (see Figure 1.2). PCBs were mainly used as dielectric fluids in transformers and capacitors, coolants, lubricants, flame retardants, sealants and some other industrial materials. Major chemical and physical properties of PCBs include low vapor pressure, solubility and chemical reactivity, high Kow coefficients. PCBs can have a strong affinity to natural particles for these properties and become ubiquitous environmental contaminants for their widespread use and improper disposal. The toxic effects of PCBs to humans and/or animals include chlorane, liver and thyroid damage, reduced birth weight, reproductive toxicity and cancer (Silberhorn et al. 1990). PCBs have been shown to be capable of disrupting reproductive and endocrine function in fish, birds, and mammals, including humans, particularly during development (Bergeron et al. 1994). Mono-hydroxylated metabolites of PCBs are also considered as a class of EDCs because they can disrupt endocrine systems by a combination of direct mechanisms including strong competitive binding with thyroid transport proteins, interference with enzymes responsible for conjugation, and as strong estrogen agonists and antagonists (Campbell et al. 2003; Sandala et al. 2004).

Characterizing the sources and fate of PCBs in the Hudson Basin has been a high priority given the high concentrations in sediments and biota, and because the main exposure pathway of PCBs to the human population is the ingestion of contaminated food (e.g. contaminated fish) (Benedict 2007). The NY/NJ harbor complex and Hudson River is a unique area for the study of PCB sources and fates, and well studied because of the high concentrations of PCBs that contaminate the system. There are two major sources for PCB in the tidal portions of the Hudson River, and upper NY Harbor: improper disposal by General Electric Company (GE) capacitor manufacturing plants in the Upper Hudson River and effluent from WWTPs located in the Lower Hudson River and metropolitan harbor area (Benedict 2007). Between 1947 and 1977 GE released up to 1,300,000 pounds (590,000 kg) of PCBs into the Hudson River, and in 1976 New York State Department of Environmental Conservation (DEC) banned all fishing in Upper Hudson River, as well as commercial fishing of striped bass and several other species in the Lower Hudson River (EPA 1984). In 1984 approximately 200 miles of the Hudson River (from Hudson Falls to the Battery in New York City) was designated as a Superfund site. Attempts at remediation began in 1977-1978 when 180,000 cubic yards (140,000 m3) of sediment was removed near Fort Edward. Several additional remediation programs started in 1991, and in 2002, the EPA announced a further 2,650,000 cubic yards (2,030,000 m^3) of contaminated sediments in the Upper Hudson River would be removed (EPA 1984). There are also clearly important inputs of PCBs to the lower Hudson Estuary that are derived from the large inputs of municipal wastewater.

Several investigations have argued that the dominant source of PCBs to the lower Hudson River and NY/NJ Harbor sediments has shifted over the past 20 years, from a much more important downstream transport of upper Hudson sediments and PCBs derived from inputs from the GE plants to a combination of sources including STP effluent, atmospheric deposition, and poorly characterized industrial sources (Bopp et al. 1981; Bopp et al. 1993; Yan et al. 2005; Yan et al. 2006; Benedict 2007). Farley (2005) estimated approximately equal contributions of PCBs reaching the tidal portion of the Hudson Basin coming from GE-derived sources coming over the Troy dam, and contributions of wastewater sources in the lower estuary. Emphasis has been placed on reducing inputs of PCBs to the lower Hudson Basin as well as allocating the damages due to PCBs exposure from different sources. Predicting how the system will respond to different dredging scenarios or source reduction strategies is highly dependent on knowing the loadings of PCBs from different sources.

PBDEs are mainly used as an additive flame retardant in a variety of commercial products which have emerged as a new class of environmental contaminants of concern recently since their first production in the early 1970s. PBDEs have “PCB like” molecular structures with bromide atoms attached to the diphenyl ether as opposed a biphenyl backbone in the case of PCBs (Figure 1.2.). Replacement of chloride with bromide and the addition of “O bridge” (ether group) make the molecules larger and more hydrophobic than PCBs with similar number of chlorines. The larger size then contributes to their overall lower vapor pressures and aqueous solubilities (Hardy 2002).

Toxic effects of PBDE on biota include thyroid, liver, kidney and neurobehavioral alterations, teratogenicity, endocrine system disruptions, and possible carcinogenic effects (Eriksson et al. 2001; Darnerud et al. 2006). Concern about PBDEs has been fueled by reports demonstrating their ubiquitous presence in humans with exponentially increasing concentrations in sediments and biota from many areas (Hites 2004; She et al. 2007; Tsydenova et al. 2007) (Rayne et al. 2003; North 2004; Rule et al. 2006; Song et al. 2006). PBDEs have increased by a factor of ~100 in humans over the last 30 years (Benedict 2007). .

Another important exposure pathway of PBDE is through consumption of contaminated seafood (Wilford et al. 2005; Harrad et al. 2006). In coastal waters water, discharge of WWTP effluent can be the largest source for PBDE. PBDE concentrations have been detected in effluent and sludge up to 0.9 μg/L and 1440 μg/g respectively in U.S. (North 2004; Rule et al. 2006). PBDE congeners are separated by the location and amount of bromine substitution on the phenyl rings (Figure 1.2). Hites, (2004) reported that PBDE congener composition varies greatly among commercial products, biota samples and sediment samples. Large differences in PBDE congener composition were also found between in sewage effluent and sediment (North 2004).

Benedict (2007) showed the first report of 49 PBDE congeners in sediment samples from Upper Hudson River and NY/NJ Harbor area. In the most recent surface sediment samples (2001-2005), total PBDE levels varied from 40-490 ng/g. It was concluded that variations in PBDE congener composition were associated with different sources: WWTP effluent from the Lower Hudson River basin and potential industrial sources from Upper Hudson River and Passaic River sources.

1.8 Nonylphenol polyethoxylates (NPEOs) and their neutral metabolites: applications as biogeochemical tracers, and sources and fate in the lower Hudson Basin

Nonylphenol ethoxylates (NPEO) are important non-ionic surfactants used in industrial cleaning products, household cleaners, car cleaners and aircraft deicer and antiicer fluids. The surface activity of NPEOs comes from their specific amphiphilic molar structures - the hydrophilic part is the polyethoxylate chain and the hydrophobic part is the nonylphenol group (Figure 1.2.). A typical NPEO surfactant formulation is comprised of an average of ~10 and a range of 1-20 ethoxy units. The fact that NPEOs and their relatively persistent metabolites can survive wastewater treatment and be detected ubiquitously in the aquatic environment (Giger et al. 1981; Stephanou and Giger 1982; Giger et al. 1984) attracted attention to these compounds. Water quality regulations for NPEOs and metabolites are generally based on the acute toxicity risks associated with high concentrations of the metabolites like nonylphenol (NP) in wastewater effluent. However, more scientific interest has been generated as NP and other metabolites have

have also been shown to cause endocrine disruption in aquatic organisms (Jobling et al. 1996; Laws et al. 2000).

Simlar to comparisons with PCBs and PBDEs, this thesis employed DTDMAC as an additional test of the sources of NPEOs in the lower Hudson Basin. Municipal wastewater is known to be a major source of NPEOs and their metabolites into receiving waters, but specific industries also have used large quantities of NPEOs and might provide additional inputs that might be important near those sources. Some of those high use industries are pulp and paper mills, textile manufactures, and leather tanneries. Brownawell et al. (Brownawell et al. 2005) analyzed samples in the lower Hudson Basin below sources from these industries relatively unaffected by WWTP inputs. They concluded that in recent years the textile industry on the Passaic River above the Dundee Dam is the most likely example of a non-sewage related source of NPEOs in this region. NPEOs are also less particle reactive and more labile than PCBs and PBDEs, and comparisons with DTDMAC may provide information about differential fate, when the sources of the two compound classes are the same.

The composition of NPEO metabolites can provide information about the local sources of NPEOs or processes occurring during sewage treatment or after NPEOs reach the sediments reservoir. Microbial transformations produce NPEO metabolites such as short chain NPnEO (n=1-3), NP, nonylphenol polyethoxycarboxylates (NPECs) and carboxyalkylphenol polyethoxycarboxylates (CAPECs) are produced through biodegradation and concentrated in sewage effluent and sludge (Ahel et al. 1994; Di Corcia et al. 2000). The formation of NP and de-ethoxylated NPEOs is favored under anaerobic condition while the NPEC and CAPEC oxidation products are favored under more aerobic condition (Ahel et al. 1994; Di Corcia et al. 2000; Ferguson and Brownawell 2003; Jonkers et al. 2003).

Most research on NPEO distributions in the environment has focused on more toxic, less ethoxylated NPEO metabolites. There have been a few studies of the distributions of higher ethoxymers of NPEO in natural sediments (Shang et al. 1999;

Ferguson et al. 2001; Ferguson et al. 2001; Ferguson et al. 2003; Jonkers et al. 2005). Where sewage receives effective biological treatment, the proportion of higher ethoxylated NPEOs in effluents and sediments is low, but polyethoxylated NPEOs can be persistent and very abundant when there is only primary sewage treatment (Shang et al. 1999), where there may be direct discharges of NPEOs from non-sewage sources (Jonkers et al. 2005), and when sewage treatment is less than modern secondary treatment (Ferguson et al. 2003). Ferguson and co-workers were able to relate the proportion of polyethoxylated NPEOs (NP(4-15)EO/NP(0-3)EO found in a dated sediment core in Jamaica Bay, New York, to the time history of sewage treatment upgrades at the local WWTP plant.

The most abundant neutral NPEO metabolites found in biologically treated sewage effluent and local sediments are NP and NP(1-3)EO (Giger et al. 1981; Giger et al. 1984; Di Corcia et al. 2000; Ferguson et al. 2001; Ferguson et al. 2001). However, it is relatively clear that the relative persistence of these metabolites and potential interconversions are affected by microbial processes that are likely dependent on the redox conditions of sediments or surface waters. NP can be a product of NPEO degradation under reducing conditions, e.g., in sewage sludge (Giger et al. 1984); and Ferguson et al., 2003 provided good evidence from analysis of sediment core profiles for the conversion of NP1EO to NP under highly reducing sediment conditions. However, NP was not found as a metabolite under the aerobic experimental conditions (Jonkers et al. 2001). In earlier work (Brownawell et al. 2005), it was found that there was a lot of variability in the proportions of individual NP, NP1EO, NP2EO, and NP3EO in sediments through the lower Hudson Basin. A better understanding of the ifluence of redox conditions on the preservation of NPEO metabolites is needed to resolve their utilitiy as tracers of sewage treatment processing.

1.9 Study Area: sediments from the lower Hudson Basin

The Hudson River and NY/NJ Harbor complex presented an excellent location on which to base a study on tracers of organic contaminants. This thesis examines samples collected from the Hudson River main stem up to the Thompson Island Pool (TIP) to more urbanized areas of the lower Hudson River basin, including the lower Hudson Estuary, NY Harbor, Jamaica Bay; Raritan Bay; Newark Bay and its surrounding waterways, and western Long Island Sound. This area has been heavily impacted by anthropogenic activities for over 100 years. It includes a watershed that encompasses over 42,000 km^2, portions of 5 states and a population of over 20 million people (Adams and Benyi 2003). NY/NJ Harbor is an incredibly complex estuary in which the fresh water flows of the Hudson, Passaic, Raritan and Hackensack Rivers (as well as several smaller rivers) mix with tidal currents in the Harbor's multiple bays, straights and channels. In total, the Harbor discharges a mean flow of nearly 16,000 million gallons per day (MGD) of fresh water including 2,300 MGD from WWTP, storm drains, and combined sewer overflows (CSOs). (Figure 3) (DEP report). With respect to municipal sewage inputs, the Passaic River and Newark Bay receive little or no significant direct WWTP-derived effluent; thus Passaic River sediments are likely more impacted by CSO inputs concentrated there, and Newark Bay sediments reflect mixtures of WWTP inputs from the Hackensack River and from outside the Bay, as well as local and upstream CSO inputs.

Jamaica Bay was emphasized as a study area in this work, because of the extent of municipal wastewater impacts and for comparisons with prior studies on the fate of wastewater-derived contaminants (Ferguson et al. 2001; Ferguson et al. 2001; Ferguson and Brownawell 2003; Reddy et al. 2005; Benotti and Brownawell 2007; Miller et al. 2008). There is somewhat limited flushing of Jamaica Bay with the ocean, and the natural freshwater flow into Jamaica Bay is small in comparison to the discharge from four WWTPs and CSO outfalls along the bay (Swanson and West-Valle 1992; Bopp et al. 1993). The hydrology and bathymetry of Jamaica Bay have been affected by morphological alterations including one biggest dredging event for the construction of John F. Kennedy International Airport (JFK) in the early 1940s which changed a shallow marsh (Grassy Bay) to a deep basin. (Swanson and West-Valle 1992; Ferguson 2002). Grassy Bay has become a highly depositional, stagnant sediment catchment (Swanson and West-Valle 1992; Bopp et al. 1993; Ferguson 2002).

1.10 Objectives and outline of the thesis

There are three general objectives in the present study of this thesis:

- Develop analytical methods for major classes of QACs and their alkyl homologs that are robust and provide high analytical sensitivity and resolving power in marine sediments.
- Explore the occurrence and fate of QAC homologs in a highly urbanized estuary
- Test DTDMAC and perhaps other QACs as molecular tracer for separating the sources of other particle reactive contaminants, and to provide insight into the transport and fate of other wastewater contaminants.
- Determine the historical inputs of QAC reflected in the well dated sediment cores

An additional set of objectives at the beginning of my thesis involved the use of NPEO compositional patterns as indicators of the extent of local sewage treatment and to explore whether they may be useful for understanding more average redox conditions in estuarine sediments that would be important for the preservation of other organic contaminants. Due to the exciting results from my work on DTDMAC and less clear results from the NPEO composition work, the majority of my thesis fconernes the new work on QACs in estuarine sediments.

The objectives of my thesis are addressed in the following chapters:

- Chapter 1 introduces and reviews significant background studies and illustrates the significance and need for this study.
- Chapter 2 describes work developing better tested and improved methods for analyzing QACs in sediments; it also provides some new insights into mass spectrometric analyses of compounds and ions that consist of combinations of elements with high mass defects.
- Chapter 3 describes analyses documenting the occurrence of QACs in sediments from the NY/NJ Harbor complex, the relationship of between levels of sediment QACs and TOC, and the different compositions of a range of QACs in areas affected by more and less treated sewage inputs.

- Chapter 4 examinins the ability of DTDMAC to provide information about the relative importance of inputs of three classes of particle reactive contaminants (PCBs, PBDEs, and NPEO metabolites) in the lower Hudson Basin
- Chapter 5 presents the results from a combination of dated sediment cores and time series of surface sediments at the same sites to assess the geochronologies of QAC analytes depositied in the Harbor complex; further explored in this Chapter is the use of ratios of selected QACs that are apparently persistent enough to provide valuable dating tools and assess the relative persistence of more soluble QACs in deep continental slope sediments.
- Chapter 6 presents the results from several studies related to my work on NPEO and NPEO metabolite compositions as tools to: 1) determine whether the relative importance of less treated sewage could be traced by the abundance of polyethoxylated NPEOs; 2) look at the correlation of redox-sensitive NPEO metabolite rations in comparison to two redox sensitive metals (Cd and Mn); and 3) to utilize the new data that might be related to sediment redox chemistry, as well as QACs as wastewater sources, to test for possible correlations between many sediment variables and observed sediment toxicity defined by an acute amphipod toxicity test.
- Chapter 7 contains a summary of the most important findings in my thesis, highlights their significance and presents recommendations for future study.

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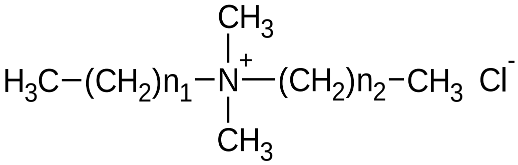
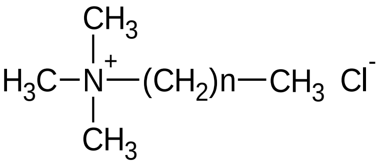
Figure 1.1. Molecular structures of different homologous series of QACs.



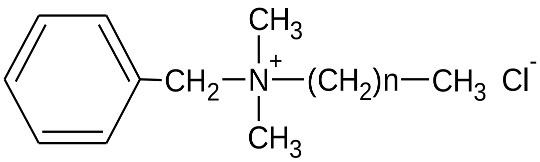
$H_3C-(CH_2)n_1-\overset{CH_3}{\underset{CH_3}{\overset{+}{N}}}-(CH_2)n_2-CH_3\ Cl^-$

DTDMAC
n1,n2=11,13,15,17;

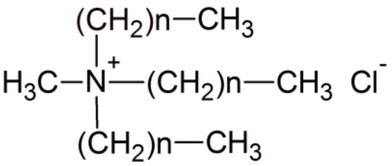


$H_3C-\overset{CH_3}{\underset{CH_3}{\overset{+}{N}}}-(CH_2)n-CH_3\ Cl^-$

ATMAC

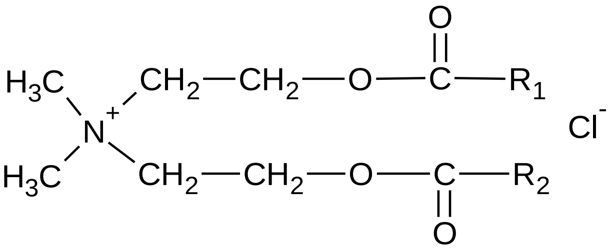


BAC

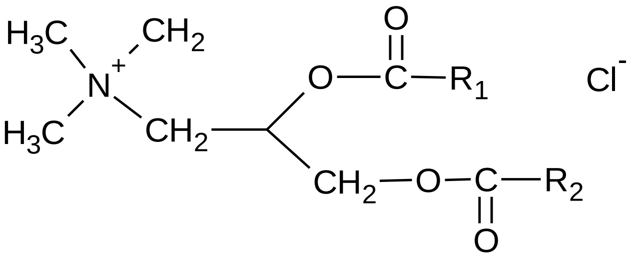


$H_3C-\overset{(CH_2)n-CH_3}{\underset{(CH_2)n-CH_3}{\overset{+}{N}}}-(CH_2)n-CH_3\ Cl^-$

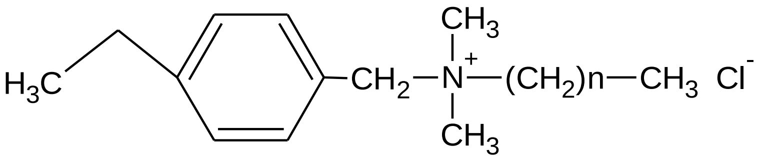
TAMAC



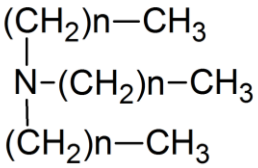
DEEDMAC



DEOMAC



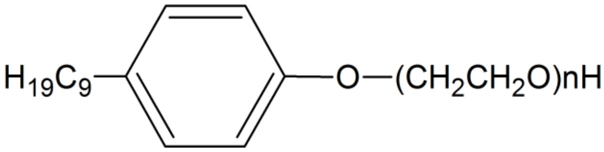
Ethvl-BAC



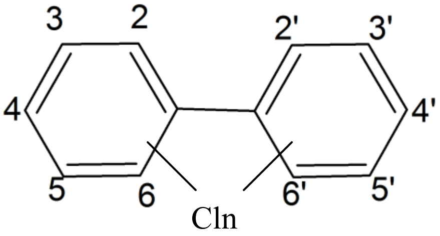
$\overset{(CH_2)n-CH_3}{\underset{(CH_2)n-CH_3}{N}}-(CH_2)n-CH_3$

TAM n=13.15. 17

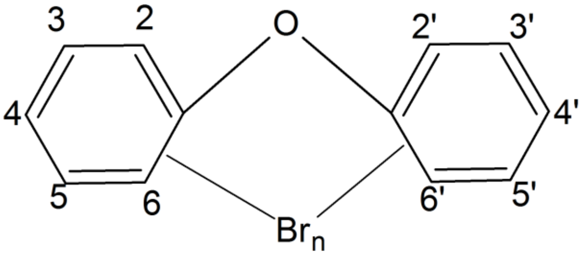
Figure1.2. Molecular structures of NPEO, PBDE, PCB.



NPEO n=0-20

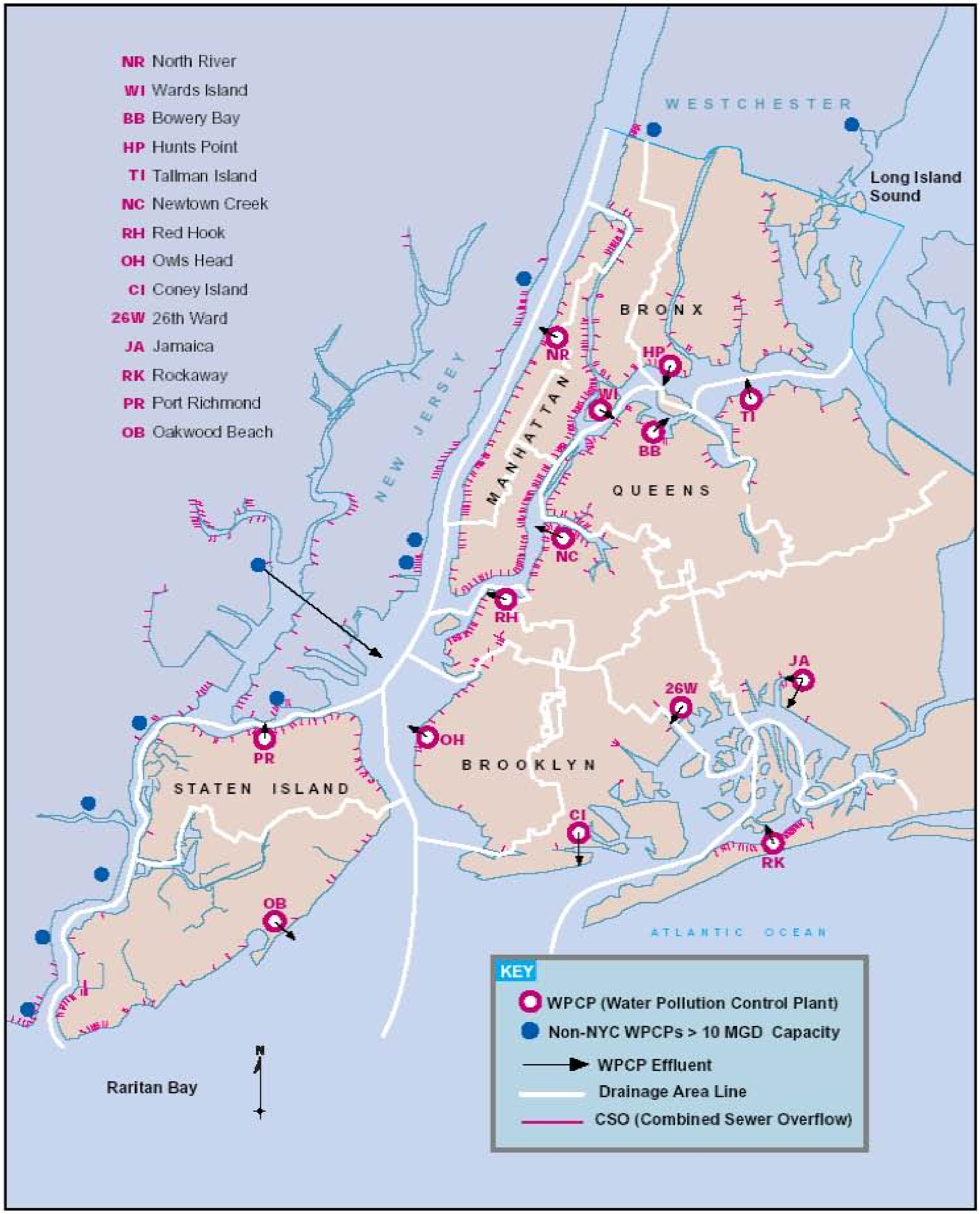


PCB $C_{12}Cl_nH_{(10-n)}$



PBDE $C_{12}Br_nH_{(10-n)}O$

Figure 1.3. Locations of major WWTPs and CSO outlets in NY/NJ Harbor complex



CHAPTER TWO: ANALYSIS OF QUATERNARY AMMONIUM COMPOUNDS IN ESTUARINE SEDIMENTS BY LC-TOF-MS: VERY HIGH POSITIVE MASS DEFECTS OF ALKYLAMINE IONS PROVIDE POWERFUL DIAGNOSTIC TOOLS FOR IDENTIFICATION AND STRUCTURAL ELUCIDATION

2.1 Abstract

A sensitive and robust method of analysis of quaternary ammonium compounds (QACs) in marine sediments is presented. Methods for the extraction, sample purification, and HPLC-Time-of-Flight (ToF)-MS were optimized for small sample sizes and provide solutions to some of the difficulties identified with the analysis of QACs. An ultrasonically-assisted acidic methanol extraction approach proved more efficient than two previously reported methods. Total concentrations of targeted QACs (up to 74 µg/g) in sewage-impacted estuarine sediments were higher than concentrations of other classes of organic contaminants measured in the same or nearby samples, suggesting that QACs have been largely ignored as environmental contaminants that merit additional study. Of equal or greater significance is the recognition of the exceptionally high positive mass defects associated with alkylamine and alkylammonium ions produced during electrospray ionization. For alkylammonium ions with 0 – 2 sites of unsaturation, no alternative, chemically-viable elemental formulas exist within 25.2 mDa, effectively allowing facile discrimination of this compound class in complex mixtures using ToF-MS. The uniqueness of alkylammonium ion masses continue to exist with a further increase in double bond equivalents. This analysis suggests that there are many applications for high resolution mass spectrometry in the analysis of diverse aliphatic amines and ammonium in complex mixtures.

2.2 Introduction

Quaternary ammonium surfactants are high-production volume chemicals that comprise a large fraction of the cationic surfactant market.(United States International Trade Commission. and United States Tariff Commission. 1955-1994) The salts of quaternary ammonium compounds (QAC) are used as active agents in detergent formulations, fabric softener products, microbicides, personal care products, and they find application in a variety of industrial processes.(Boethling and Lynch 1992; Boethling 1994) As hydrophobic cation-exchangers, QACs sorb strongly to soils and sediments,(Brownawell et al. 1990) and many tetra-alkylammonium QACs, including benzylalkyldimethylammonium compounds (BAC), alkyltrimethylammonium compounds (ATMAC), and dialkyldimethylammonium compound (DADMAC), are persistent enough to be found at appreciable concentrations in wastewaters,(Ferrer and Furlong 2001; Clara et al. 2007; Kreuzinger et al. 2007; Martinez-Carballo et al. 2007) , sewage sludges,(Hellmann 1989; Gerike et al. 1994; Breen et al. 1996; Fernandez et al. 1996; Merino et al. 2003; Martinez-Carballo et al. 2007) receiving waters,(Wee and Kennedy 1982; Lewis and Wee 1983; Ding and Liao 2001; Ferrer and Furlong 2001; Ding and Tsai 2003) and sediments.(Lewis and Wee 1983; Gerike et al. 1994; Fernandez et al. 1996; Ferrer and Furlong 2002; Kreuzinger et al. 2007; Martinez-Carballo et al. 2007)

Early work on the analysis of QACs in the environment focused primarily on DADMACs with n-alkyl chain lengths of C14, C16, and C18. Although these relatively high molecular weight DADMAC homologs are produced from a number of oleochemical feedstocks, technical mixtures have commonly been referred to as ditallowdimethylammonium chlorides (DTDMAC). DTDMAC has primarily been used in fabric softeners and was voluntarily phased out in the early 1990's in some European countries when concentrations in sewage sludges were found to be extraordinary high (maximum concentration reported of 9200 μg/g).(Hellmann 1989; Gerike et al. 1994; Breen et al. 1996; Fernandez et al. 1996; Merino et al. 2003; Martinez-Carballo et al. 2007) DTDMAC concentrations in sludges from Switzerland were observed to decrease sharply after the phase-out,(Gerike et al. 1994) although use has continued in other regions of the world. In the same study, DTDMAC concentrations (42.3-1140 μg/g) in two sediments near Barcelona were reported and these remain the only reports of DTDMAC in marine or estuarine sediments. A recent ecotoxicological risk assessment that compares toxicological endpoints to measured levels in wastewater effluents suggests that QACs are environmental contaminants deserving more attention.(Kreuzinger et al. 2007) Future studies on their occurrence and fate in the aquatic environment will require well tested and robust analytical methods of analysis.

QACs, as amphiphilic organic cations, are especially amenable to sensitive and selective detection using HPLC-ESI-MS, yet relatively few studies have taken advantage of such approaches for specific, isomer-specific detection in environmental samples.(Ferrer and Furlong 2001; Ferrer and Furlong 2002; Martinez-Carballo et al. 2007; Martinez-Carballo et al. 2007) Just as significantly, there has been a paucity of research addressing problems related to sample preparation prior to HPLC-ESI-MS analysis of QAC compounds in the environment. First, there has been little effort to optimize methods for extracting QACs from sediments or other solid environmental phases. Fernandez et al.(Fernandez et al. 1996) reported that supercritical fluid extraction (SFE) resulted in 30-40% higher DTDMAC concentrations in two marine sediment samples relative to those determined using a steaming acidic (1 M HCl) methanol method(Waters and Kupfer 1976; Gerike et al. 1994) was used. In other studies, tests of extraction efficiency have often relied upon recovery of QAC spiked to sediments, water, or sludge immediately prior to extraction,(Gerike et al. 1994; Ferrer and Furlong 2002; Martinez-Carballo et al. 2007) Such techniques may overestimate extraction efficiency QACs from field-aged soil or sediment, in which the QAC compounds may be more tightly sorbed.(Fernandez et al. 1996) A second problem that has confounded trace level analysis of QACs in environmental samples is adsorptive losses of these compounds to surfaces present in extraction, purification, and separation (e.g adsorption of more hydrophobic QACs to glass capillary columns).(Heinig et al. 1997) Glassware used in QAC analysis has often been pre-treated with specific QACs (especially in analysis of the super-hydrophobic DTDMACs) in order to minimize loss of analytes by adsorption to active sites (Gerike et al. 1994; Fernandez et al. 1996). A third limitation encountered has been ubiquitous instrumental contamination by more hydrophobic DTDMAC homologs during the LC-ESI-MS analysis of QACs and peptides, an important problem observed here and by others.(Suter ; Manier et al. 2008)

The aims of this study were to address these analytical problems systematically in order to realize an optimized and holistic method for the extraction and analysis of QACs in estuarine and marine sediments. The methods reported have been developed for analysis of smaller sediment sample size (0.1 g), in order to minimize co-extracted matrix, sample size requirements, increase speed of analysis, and to minimize materials used. Reducing the amount of co-extracted organic matter is advantageous as this can mitigate ionization suppression effects in ESI-MS analysis of amphiphilic compounds.(Ferguson et al. 2000) Special attention was paid to the efficiency of extraction methods, and an ultrasonically-assisted extraction method is described, which leads to improved extraction of QACs when compared to two other previously-reported methods.(Gerike et al. 1994; Martinez-Carballo et al. 2007) Ultrasonically-assisted extraction was found in an earlier study to significantly increase extraction of other amphiphilic sediment contaminants during development of a high temperature continuous-flow sonication extraction method.(Ferguson et al. 2000)

It became apparent over the course of this work that the accurate mass determination provided by ToF provides a remarkably powerful diagnostic tool for confirmation of the elemental formulas of alkylammonium ions ($C_nH_{(2n+2x)}N^+$). The differences in m/z values of even-electron ions formed from aliphatic amines and aliphatic ammonium ions in ESI-MS are so distinct that virtually all possible isobaric interferences can be eliminated during LC-ToF-MS analysis of environmental samples, even with moderate mass resolution used in this work (6000-6500). Nitrogen and especially hydrogen are the only elements that commonly occur in high-production volume chemicals with mass defect values greater than 0. As a result, ions formed from protonated aliphatic amines and quaternary ammonium compounds in ESI-MS have higher net positive molecular mass defects than do any other singly charged ions that are commonly detected in positive-ion ESI-MS. This is especially true for alkyl amine ions with low numbers of sites of unsaturation or double bond equivalents (DBE), We show that the separation in monoisotopic masses between aliphatic amines and all other probable elemental formulas is exceptionally large for ions with DBE <5 and especially when DBE = 0, 1, or 2, a fact which opens up new opportunities for structural confirmation, elucidation, and resolution from interfering isobaric interferences.

The ability to readily resolve saturated hydrocarbons with high mass defects using higher resolution mass spectrometry has been illustrated before,(Hughey et al. 2001; Gross 2004) albeit with less mass resolution. Analogously, there has been increased interest in taking advantage of the negative mass defects of heavy element to provide more selective determination of phosphorylated peptides(Bruce et al. 2006) and other peptides through the use other related approaches such as element-coded affinity tags (Whetstone et al. 2004) and fragment ion mass defect labeling.(Yao et al. 2008) In the present work, the concept of using distinctive highly positive mass defects of alkylamine ions for identifying QACs in complex environmental samples is more developed, and the use of precursor and fragment ions to separate, identify and confirm the identity of non-target QAC analytes is illustrated in the case of C8:C8 and C8:C10 DADMAC, two biocides previously unreported in environmental samples.

2.3 Experimental section

2.3.1 Standards.

Individual standards of the dialkyldimethylammonium bromides: didecyldimethylammonium bromide (C10:C10), didodecyldimethylammonium bromide (C12:C12), ditetradecylammonium bromide (C14:C14), dihexadecyldimethylammonium bromide (C16:C16), and dioctadecylammonium bromide (C18:C18) were purchased from Sigma-Aldrich (Milwaukee, WI). Benzyltetradecyldimethylammonium chloride (BAC 14). Benzylhexadecyldimethylammonium chloride (BAC 16) was purchased from Pfaltz & Bauer Inc. (Waterbury, CT), and the tertiary amine tridodecylamine was purchased from Acros Organics (NJ). A commercial mixture of DTDMAC (C14:C14 to C18:C18) was purchased from Chem Service (West Chester, PA). A commercial mixture of Benzalkonium chloride mixture (BAC12 ~ 60%; BAC14 ~ 40%; traces of BAC 16 and 18) was purchased from Sigma-Aldrich (Milwaukee, WI).

2.3.2 Sediment samples.

Surface sediments from four estuarine locations were collected and used for method development in this study. The samples were characterized by a range of measured QAC concentrations and organic matter contents. Sediment samples included: organic-rich sediments (0-5 cm) from sewage-impacted Jamaica Bay (JB) collected in 1998,(Ferguson et al. 2001) a sample from Bowery Bay (BB), collected in 2004 proximate to LaGuardia International Airport, NY and impacted by local inputs of sewage; a surficial fine-grain sediment from a central Long Island (LIS) site located approximately 85 km east of BB; and two samples from a 2006-collected sediment core in the Forge River (FR), located on the north shore of Moriches Bay, Suffolk County, NY. Samples from the former site included a recently-deposited sediment from the upper 15 cm (FR-S); and a sample from deeper within the core (50-67 cm, FR-D) found to be old enough to be devoid of QACs. This sample was used in method blank and spike recovery experiments.

2.3.3 Sediment extraction and purification.

Extraction. Sequential extraction approaches were utilized to test the efficiency of different extraction methods. Method objectives were met with two significant modifications of the Gericke et al. method which employed multiple extractions with steaming acidic methanol(Gerike et al. 1994): 1) addition of low-power ultrasonic energy was found to increase extraction efficiency; and 2) the volumes and size of materials were greatly reduced in accordance with the smaller sediment samples (100 mg) analyzed in the present study. An additional difference between the present method and that reported previously(Gerike et al. 1994) was the use of a single glass test tube throughout extract collection and multiple subsequent purification steps. This approach was found to greatly mitigate loss of more hydrophobic DADMACs by strong sorption to glassware(Gerike et al. 1994; Fernandez et al. 1996) or to residual sample matrix accumulating on glassware.

Frozen sediment samples were freeze-dried, ground and homogenized with mortar and pestle. 30 mL glass centrifuge tubes were used for extractions. DADMAC C12:C12 (10-300 ng) was added as a surrogate standard at concentrations high compared to the native analyte, which does exist in relatively low abundance (well under 1%), compared to total QACs in the samples analyzed or commercial formulations of DTDMAC. All glassware was combusted at 450°C for 8 hours before use. Sediment samples were extracted (1 hr) in a 60°C ultrasonic bath (Model 75HT, VWR) three times with 10mL acidic (1 M HCl) methanol. Following centrifugation, combined extracts were collected in separate 30mL test tube, and solvent evaporated to dryness under nitrogen flow.

The efficiency of this ultrasonic assisted extraction method was tested by using sequential extraction approaches to determine if additional, modified extraction conditions resulted in further extraction of native compounds. Tests conducted included the effects of solvent polarity (1 M HCL in 1:1 methanol:dichloromethane, DCM), the number and length of time of sonic bath extractions, the energy of ultrasonication (Cole Parmer, 4700 Series, 600 W ultrasonic probe), and addition of a strong cation exchanger (0.1 M CsCl in methanol)(Sposito 1989; Palomo and Pintauro 2003) that competes with quaternary ammonium compounds for strong cation exchange sites.(Bors et al. 1997; Palomo and Pintauro 2003) BB and LIS sediments (1 g) were used for these extractions and the sequences and details of extractions are provided in Table 2.1.

Sequential extraction approaches were also used to test whether this method provided improved recovery when compared to the Gerike method(Gerike et al. 1994), and to the Soxhlet extraction method for QACs in sediments and sludge recently reported by Martinez-Carballo et al.(Martinez-Carballo et al. 2007) The latter method also differs by employing a lower (0.1 M) HCl concentrations. Five grams of sample was first extracted following the published methods,(Gerike et al. 1994; Martinez-Carballo et al. 2007) and efficacy of extraction was tested with a sequential extraction of sediment using the currently developed method. Tests were conducted with two sediments: high QAC, high organic carbon content JB sediment and low QAC, lower organic carbon content LIS sediment. Following either the Soxhlet or steaming acidic methanol extraction, the remaining sediments were dried and 1 g portions further processed by the extraction method developed here (described above). The total extract from the second extraction and an equivalent amount (20%) of extract from the first extraction were then purified and analyzed with identical methods.

Sample purification. Modifications of prior methods utilizing liquid-liquid extraction and anion exchange chromatography(Gerike et al. 1994) were employed to minimize the effects of co-extracted organic matter and nonvolatile salts in samples for HPLC-ESI-MS analysis of QACs. Samples were transferred into 60 mL separatory funnels for liquid-liquid extraction with 4 sequential washes with 5 mL of water, each time sonicating and vortexing to suspend dried sample matrix prior to transfer. The water was extracted with 10 mL chloroform three times, and the chloroform was collected back into the original test tube. Linear alkylbenzene sulfonate (LAS) has been added during liquid-liquid extraction to facilitate extraction of QACs into chloroform.(Waters and Kupfer 1976; Gerike et al. 1994; Fernandez et al. 1996) It was determined that in this method that the addition of LAS was not necessary for recovery of QACs. The combined chloroform extract was brought to dryness under nitrogen.

Anion exchange(Gerike et al. 1994) was then used to further reduce the organic matrix remaining in the extract(Waters and Kupfer 1976; Gerike et al. 1994; Fernandez et al. 1996). Anion exchange resin **(**AG 1-X2 resin**,** BIO-RAD, Hercules, CA) was conditioned overnight in methanol and ~3g of the resin was loaded into 6 mL glass SPE columns, held with Teflon frits (Supelco, Bellefonte, PA). The SPE columns were preconditioned with 50 mL of methanol. Extracts were reconstituted in methanol and QACs were eluted with methanol at 3 mL/min to 15 mL volume, and collected again in the same test tube.

2.3.4 Chromatographic separation.

HPLC-ToF-MS separation and analysis of QACs employed a Waters Alliance 2695 LC and LCT mass spectrometer with a Z-spray ESI source (Micromass, Manchester, UK) described elsewhere.(Benotti et al. 2003) The 15 mL volume of methanol was adjusted by concentration (1 mL under nitrogen gas flow) or further dilution, as necessary (as high as 300 mL), to account for expected concentration ranges and the dynamic range of the ToF analyzer. An internal standard, tridodecylamine, was then added at a concentration of 5 ng/mL prior to 10 μL sample injection.

Trace level analysis of more hydrophobic DADMACs (C16:C16, C16:C18; C18:C18) by reverse phase HPLC-MS is complicated by small and reproducible instrument blanks(Manier et al. 2008) that are magnified when mobile phase gradients are used. These broader peaks are especially important if initial HPLC mobile phase conditions contain a high fraction of aqueous buffer. The instrument blank is present when either a new or well used HPLC column is used. The cause of this blank is as yet unknown, but it can become significant when injected DTDMAC masses are less than 2-10 pg. It is noteworthy that a similar problem was encountered in the analysis of surface active perfluorinated ocatanoic acid, in which case blank problems were overcome with an isocratic HPLC-MS method.(Dinglasan et al. 2004) Two different HPLC methods were employed in this study. HPLC separation of QACs was initially modeled after the method reported by Martinez-Carballo et al.,(Martinez-Carballo et al. 2007) utilizing a Luna C18 column (Phenomenex; 150x2.00 mm, 5 μm). The first (Method 1) was utilized to retain and provide good chromatographic separation of more soluble DADMACs. To greatly reduce DADMAC blanks, HPLC gradient Method 2 employed a shallower solvent gradient that allowed for much lower DADMAC blank levels that still allows for retention and resolution for later eluting BACs and more highly alkylated DADMACs. Despite the broader peak shapes afforded by Method 2 (and the much smaller 100 mg sample size extracted in this work), the method detection limits for QACs using Method 2, reported below, are as low, or lower than, those reported with other methods published to date.(Martinez-Carballo et al. 2007)

Method 1 most closely resembles protocols reported elsewhere. (Martinez-Carballo et al. 2007) A gradient separation was achieved with three solvents: solvent A, 20:80 acetonitrile:water with1% acetic acid; solvent B, 95:5 acetonitrile:water with 10 mM ammonium accetate; and solvent C, Isoproponol with 0.1% formic acid. Gradient conditions were initiated at 100% A maintained for 2 minutes; linear gradient changed to 20% A and 80% C in 0.1 minute and held for 5 minutes; changed to 100% B in 2 minutes; changed to 90%B and 10% C in 0.1 minute and held for 6 minutes; then changed to 50% B and 50% C in 2 minutes, and maintained for 18 minutes before the column was re-equilibrated to initial conditions for 4 minutes.

Method 2 overcame the DADMAC instrument blank. A gradient separation utilized two solvents: solvent A, 95:5 acetonitrile:water with10 mM ammonium acetate and solvent B, Isoproponal with 0.1% formic acid. In this case, gradient conditions were initiated at 90% A and 10% B for 6.2 minutes, changed to 50% A and 50% B in 2 minutes, held for 12 minutes and changed back to 90% A and 10% B in 1 minute, then held for 4 minutes to re-equilibrate the column. Column oven temperature was held at 45 ^{o}C in both methods.

2.3.5 Mass spectrometry.

ESI in positive ionization mode was conducted with capillary and cone voltages of 2800 V and 55 V, respectively. The daily instrument calibrations and utilization of co-infused mass calibrant, accurate mass estimation methods are provided elsewhere.(Benotti et al. 2003) Identification relied upon measurement of molecular ions (M^+ or $M+H^+$ in the case of the tridodecyl amine internal stanard, although collision-induced dissociation (CID) ions corresponding to dealkylation reactions (M-CnH2n) were also diagnostic for DADMACs. Mass resolution of the ToF-MS was generally between 6000 and 6500; instrument manufacturer specifications for mass accuracy is 5 ppm, and limited to +/- 2 mDa at m/z < 500 amu, consistent with realized performance**.**

2.3.6 Quantification.

A six-point calibration series (typically 0.1-20 ng/mL in methanol) was analyzed daily, and the raw data files were processed using the all-file accurate mass measure (AFAMM) function in MassLynx.(Benotti and Brownawell 2007) Analyte responses were normalized to the internal standard for quantification. The ESI-MS response of different DADMACs, and the internal standard trioctadecylamine, were within 20% of each other, whereas the response was less for more soluble BACs and decreased with decreasing BAC alkyl chain length. Concentrations of C14:C16 and C16:C18 DADMAC were estimated by interpolating very similar response factors of the most closely eluting DADMAC homologs, and the concentrations of BAC 12 and 18 were calculated assuming the response factors of BAC 14 and 16, respectively. Nontargeted C8:C8 and C8:C10 DADMACs were estimated from the response factor of DADMAC C10:C10.

2.3.7 Sediment analysis of QACs with the disulfine blue method.

The disulfine blue active substances (DBAS) method has long been a standard method for detection of cationic surfactants in environmental samples. Utilization of the DBAS method(HMSO 1981) as a useful screening tool for QAC levels in marine sediments was tested here by comparing it with HPLC-MS quantification for two dissimilar sediments, BB and LIS. Absorbance (628 nm) of disulfine blue that partitioned into the chloroform extract was measured and the response calibrated to the mixed standard of DTDMAC.

2.4 Results and Discussion

2.4.1 HPLC-ToF-MS separation and identification of target and nontarget QAC analytes.

The DADMAC and BAC homologues in the sediment sample extract were well separated by HPLC Method 2 (Figure 2.1). Selected ion chromatograms (mass window of 0.05 Da) of targeted analytes in samples were in excellent agreement with retention times and peak shapes of pure standards, or to the mixed BAC and DTDMAC standards in the cases of BAC 12 and DADMAC C14:C16 and C16:C18. The identification of BAC 18 was confirmed by accurate mass and predicted retention time. The average mass discrepancy between the actual and estimated accurate masses for the 11 DADMAC and BAC analytes shown in Figure 2.1 was 2.6 ± 1.6 mDa.

The utility of LC-ToF-MS to screen for previously unreported QAC analytes is illustrated in Figure 2.2. Given the ease of detection of C10:C10 DADMAC, the presence of C8:C8 and C8:C10 DADMAC was also assayed. DADMAC C8:C8, C8:C10, and

C10:C10 are used in current-generation mixtures of disinfectants and have been detected in personal care products,(Morrow et al. 2001) but only DADMAC C10:C10 has been measured in the environment.(Kreuzinger et al. 2007; Martinez-Carballo et al. 2007) The relative retention times of the putative DADMACs (Figure 2.2) are consistent with those of the DADMAC C10:C10 standard. Furthermore, the even mass parity of the even-electron ions detected for these compounds after electrospray ionization is indicative of an odd number of nitrogens in the formulas, according to the nitrogen rule.(McLafferty and Turecek 1993) In this sample, the accurate mass measurements of peaks associated with putative 8:8 and 8:10 DADMAC homologs differed from theoretical values by 1.9 and 2.4 mDa, respectively – within the performance characteristics of the ToF-MS. Narrowing the m/z window from 0.5 to 0.05 Da largely eliminates isobaric interference and allows for the identification and confirmation of the lower abundance C8:C8 and C8:C10 homologs. Several of the interferences eliminated by narrowing the mass window were indentified to be the "M+1", predominately ^{13}C isotope peaks from compounds having molecular ion m/z one nominal mass unit lower. The measured accurate mass of a large isobaric interference with a base peak of 270.2438 was 72.3 mDa less than the theoretical mass of DADMAC C8:C8; the most likely elemental formula for that ion is $C_{12}H_{32}NO_2$.

2.4.2 Unique positive mass defects of alkylammonium ions and implications for mass spectral analyses of aliphatic ammonium species.

Elemental mass defects, the numeric difference between monisotopic mass and integer mass, generally decrease with increasing atomic number due to a corresponding decrease in the strong nuclear forces, as these small mass deviations are a direct consequence of the equality of mass and energy (Figure 2.3A). The monoisotopic formulae of aliphatic amines and ammonium ions possess only isotopes having zero (^{12}C) or positive (^{1}H and ^{14}N) mass defects, making them unique among common heteroatomic organic molecules leading to heavier masses when compared to ion masses of alternate elemental formulas with same nominal mass. Indeed, the extent to which even-electron, singly-charged positive ions of the general formula $C_nH_{(2n+x)}N^+$ can be separated from other nominally isobaric organic ions using high accuracy MS is remarkable large. ESI-

MS is especially useful for resolution of masses of other formulas because even electron, singly charged ions are primarily formed during electrospray ionization of small molecules Figure 2.3A shows the mass defects of elements that are most likely to be encountered in ions of naturally occurring organic compounds by electrospray ionization in positive mode; Na and K are included as potentially important adduct forming elements. The overall highly positive mass defects of alkylammonium ions are dominated by the fraction of the mass made up by high mass defect hydrogen atoms. As seen in Figure 2.3A, inclusion of only the elements C and N also favor a high positive ion mass defect. Thus, important factors that decrease the magnitude of positive mass defects of $C_nH_{(2n+2x)}N^+$ ions include an increase in DBE (a decrease in x), and replacements of C or H with heteroatoms of greater monoisotopic mass. The number of possible elemental formulas is further limited for even nominal mass ions that must contain an odd number of N atoms and even electron ions; in fact, the nearest nominal-mass elemental formulas to that of $C_nH_{(2n+2x)}N^+$ are often aliphatic ammonium species with 3 or 5 N atoms.

Figure 2.3B illustrates the large separation in mass of alkylammonium ions from other nominally isobaric ions with reasonable elemental formulas, as well as elemental composition controls on the magnitude and uniqueness of the resulting mass differences. The elemental formula calculator provided in MassLynx 3.5 software was utilized to determine elemental formulas with nearest mass to the selected $C_nH_{(2n+2x)}N^+$ alkyl amine ions, as well as for caffeine, an example of a smaller molecule that does not include elements with large negative mass defects. Because of the use of electrospray to generate ions in the present work, only even electron ions were considered. Very few parameter restrictions on elemental formula composition were specified in order to test the veracity of the results. The number of atoms of each element was allowed to range up to 5 for N, O, S, Si, P, F, Cl, and Br. A single Na, or K, atom was considered in this analysis, as adduction of more than one alkali metal adduct in a small and singly charged ion is unlikely; only three possible formulas (found in calculations for DBE = 3-5 only) were discarded in preparing Figure 2.3B, and each alternative formula contained a Na with only N heteroatoms. Not shown in the calculations illustrated in Figure 2.3B was that inclusion of additional mono isotopes, corresponding to 13C, 37Cl, and 82Br atoms, into the calculation did not affect any of the closest elemental formula matches.

The positive mass defect of alkylamine ions, when compared to masses of other elemental formulas calculated here increases are exceptionally high when the numbers of DBE are relatively low. The example formulas provided (Figure 2.3B) correspond to those of DADMAC C18:C18; DADMAC C10:C10, and the latter with increasing number of DBE. The results for the BAC homologs, were essentially the same as those shown for DADMAC C10:C10: with 4 DBE. Most striking was that there were no alternative formulas within 25.2 mDa (replacement of C2H4 with N2) for $C_nH_{(2n+x)}N^+$ when DBE = 0, 1, or 2; and the next closest masses being 36.6 and 50.2 mDa lighter when DBE = 0 – 1 (replacements of CH4 or C4H8, with O or N4 respectively). An additional elemental formula exists for DBE = 2 that is 38.8 mDa lighter (replacement of C3H3 with NaO). With respect to the very closest elemental formula matches, it is of great interest to note that increasing number of carbons (n) between DADMACs C10:C10 and C18:C18 does not affect the closest elemental formula matches. Constant offsets in ion masses from nearest elemental formula as a function of alkyl chain length have been shown in examples that considered a smaller range of possible elemental substitutions.(refs 26,39)

The effect of increasing the degree of unsaturation of aliphatic ammonium ions increases the numbers of alternate formulas within a given difference in mass. For DBE = 3 (Figure 2.3B) additional formulas, containing F atoms, that are 12.8 – 24.0 mDa lighter appear. When DBE = 4, there are three possible alternative formulas that are now heavier in mass than the nominally isobaric alkylammonium ion. Each of those alternative formulas are characterized by zero DBE (higher proportion of H) and contain one either F or N_5O element substitutions. Even in the example calculation for which DBE =4 there is only one other elemental formula ($C_{19}H_{41}NOF$) with a mass difference of 1.1 mDa, that is within 12.7 ppm (4.0 mDa) of the alkyl ammonium ion of interest. Thus even when DBE = 4, there is a reasonable chance that accurate mass estimation by ToF can provide elemental formula with high confidence.

The results for the analysis of possible formulae corresponding to the nominal m/z of the [caffeine+H]$^+$ ion illustrate a not uncommon problem encountered by the analytical chemist conducting trace analyses of polar molecules within highly complex sample matrices. There are a much larger number of candidate elemental formulas within very close proximity on the m/z scale to the "correct" value corresponding to the elemental formula for caffeine. Unlike alkylammonium species, caffeine does not contain an abundance of elements with a significant negative mass defect, thus it is relatively unremarkable and poorly discriminated from other chemically-viable organic molecules with regard to mass. In sharp contrast to the resolving power provided by high mass defect alkylammonium ions, this example illustrates the difficulty in using accurate mass as a tool to provide unambiguous elemental formula confirmation for heterogeneous molecules such as caffeine.

The use of accurate mass to determine elemental formula identification of alkylammonium ions provides additional structural information and unambiquous formula confirmation not only for molecular ions, but also for CID fragments of these molecules (Figure 2.4). CID fragments produced in the ionization of putative C8:C10 DADMAC were observed to be characterized by the highly diagnostic accurate mass analysis. In this case, the fragment ions serve to further confirm parent ion identification, and similar approaches could be employed profitably in tandem MS applications for either structural elucidation or for selective screening of small molecules using parent ion scans.

2.4.3 Comparison of sediment extraction methods.

The surrogate standard DADMAC C12:C12 was well recovered by the currently developed method. Average recoveries that include all baked sand (n=3), blank solvent (n=3), LIS (n=3), and JB and BB sediment samples was 99±10% (n=11). No appreciable additional amounts of QACs in BB and LIS field collected samples were measured in a variety of different or more rigorous sequential extractions (Table 2.1). These results provide a much higher level of confidence in the ability of ultrasonic assisted extraction to efficiently extract QACs from marine sediments.

Sequential extraction of sediments using the method developed in the present work demonstrates that the efficacy of the Soxhlet method(Martinez-Carballo et al. 2007) for the extraction of QACs is not always complete and is dependent upon sample, as well as analyte (Table 2.2). Results suggest that similar conclusions can be drawn for the standard acidic methanol extraction,(Gerike et al. 1994) although the extraction efficiency of that method appears to be better than that observed with the Soxhlet method. In this limited comparison, it was observed that that the previously published methods were relatively more efficient in recovery of the high QAC, high total organic carbon JB sediment (Table 2.2 and 2.3), The percent of additional individual QACs found during a sequential re-extraction of Soxhlet extracted JB sediment varied between 4.0 and 20% of amount measured during the initial analysis, representing a modest improvement that is still much greater than the amount of QACs determined (about 1% additional recovery) in more rigorous sequential extraction experiments that tested the method developed here (Table 2.1). More troubling is the inefficiency of Soxhlet extraction method when it was applied to the lower QAC and TOC LIS sample (Tables 2.2 and 2.3), where an additional 33 to 130% of Soxhlet extracted QAC concentrations were recovered upon re-extraction with the ultrasonic assisted acidic methanol method. The difficulty of efficient extraction of "field aged" sediment-sorbed QACs is most likely due to less reversible of QACs, following aging.(Wagner et al. 1994) More resistance to extraction observed with the lower QAC and TOC LIS sediment, when compared to the JB sample could be attributed to a combination of high sorption energies at lower concentrations (strongly nonlinear sorption isotherms),(Brownawell et al. 1990) or more access to a greater fraction of stronger or less accessible binding sites;(Fernandez et al. 1991) perhaps related to differences in clay mineralogy or structure, or the affect of organic matter on access to mineral binding sites. It is notable that when an optimized SFE extraction method(Fernandez et al. 1996) was compared to the standard acidic methanol extraction method of Gericke (Gerike et al. 1994) there was no difference found between methods with matrix-rich digested sewage sludge samples, but the SFE method led to an apparent 30-40% increase in extraction of DTDMAC from two marine sediments that were much more mineral and clay-rich than the sludge samples.

2.4.4 Method validation.

QACs were quantified in estuarine sediments from two sewage-impacted urban harbor sites (BB and JB) and sites (LIS and FR) less impacted by sewage (Table 2.3). The LIS sample was extracted in triplicate. This was the lowest-concentration sample analyzed and yet, the precision of analysis (Table 2.3) was good (4% relative standard deviation for total QAC), although it was not as good for BAC 12 (20% RSD), which was found in very low abundance. As stated above, recovery of the surrogate standard was uniformly excellent. There was no detection of QACs in the deeply buried FR-D sediment, and it was also analyzed in triplicate after spiking DADMACs C10:C10, C12:C12, C14:C14, C16:C16, and C18:C18 at small nominal concentrations (equivalent to 10 ng/g of spiked sediment). The recoveries from these organic matrix-rich samples (TOC = 4.0 %) were uniformly good (98-104%), except for C10:C10 (118%), with RSD between 5 and 8%.

The sensitivity of this method is excellent given the small sample size extracted. Table 2.3 shows the calculated limits of quantification (LOQ; S/N = 10). LOQ for the C10 – C18 DADMACs (0.1 – 2.0 ng/g) and BAC 14 and 16 (2 -2.6 ng/g) were determined by spiked addition to FR-D, but at lower nominal concentrations (1 ng/g) than above. With injection of only 10 uL out of 1 mL extract, these LOQs are dramatically lower than those reported in earlier analysis of marine sediments that did not incorporate ESI-MS,(Fernandez et al. 1996) and similar to or lower than the LOQ values reported by Martinez-Carballo et. al.(Martinez-Carballo et al. 2007) (0.6-3 ng/g for much larger 5 g of sediment samples). In comparison much less sample clean-up is employed in that method that utilizes HPLC-MS-MS.(Ferrer and Furlong 2002; Martinez-Carballo et al. 2007) Ferrer and Furlong(Ferrer and Furlong 2002) reported similar method detection limits for BAC 12 and BAC 14 (0.5 and 0.6 ng/g when corrected for the same S/N), again based on much larger mass of extracted sediment (10 g wet wt.).

2.4.5 Analysis of QACs with the DBAS method.

The DBAS method proved to be inadequate for even screening of total QACs in estuarine sediment samples. The same extracts of sediments (LIS and BB) were quantified by DBAS and HPLC-ToF-MS. DBAS – based QAC concentrations of LIS and BB sediments were 60 and 300 μg/g, whereas HPLC-MS quantification results were 1.8 and 74 μg/g respectively. Comparisons of DBAS and relatively non-selective HPLC methods for determining QACs were much better when applied to extracts of wastewaters or sludges,(Gerike et al. 1994) the latter characterized by DTDMAC concentrations often in excess of 1000 μg/g;(Gerike et al. 1994; Breen et al. 1996) Gerike et al.(Gerike et al. 1994) also compare DBAS and HPLC methods for quantification of DTDMAC in Belgian river sediments and agricultural soils found greater discrepancies between methods in samples with low DTDMAC. The use of DBAS as even a screening tool for levels of QACs in sediments or soil should be avoided or viewed with skepticism.

2.4.6 Occurrence of QACs in estuarine sediments.

The total QAC concentrations determined in these 4 estuarine sediments extends much higher (1800 – 74000 ng/g) than those recently measured in freshwater sediments from Austria (12 –5100 ng/g, n=21(Martinez-Carballo et al. 2007)). The difference is largely the result of much greater concentrations of DADMAC C16:C16, C16:C18, and C18:C18 (DTDMAC) in this work, likely attributed to the historically extended use of DADMACs as fabric softeners in the U.S. It is also surely do the location of our samples stations, two of which are located in more sewage affected areas of the highly urbanized New York Harbor complex. There have been very few reports of QACs in any sediments or sludges collected in the U.S., none of which were collected from marine or highly urbanized settings. The concentrations of BACs measured in this work (121 to 21,000 ng/g) were generally higher than those reported in another study (Ferrer and Furlong 2002) of four U.S. river sediments (78 – 571 ng/g), again most likely reflecting the concentrated sewage inputs of the highly populated New York metropolitan area.(Ferguson et al. 2001) Finally, the concentrations of DTDMAC (1700 – 52,000 ng) determined here, can be compared to measurements of DTDMAC in two estuarine sediments close to sewage discharge from Spain (42.3and 1140 μg/g).(Fernandez et al.

1996) and to HPLC measurements of DTDMAC in sewage affected Rapid Creek (South Dakota, USA) sediments (3000 – 67,000 ng/g).(Lewis and Wee 1983)

The concentrations of QACs reported in sewage affected JB and BB sediments are high compared to those of other more frequently monitored organic contaminants of concern. Total QAC levels in JB sediment are greater than the sum of neutral metabolites of alkylphenol ethoxylates(Ferguson et al. 2001) and much higher than that of the combined sum of PCBs, DDT residues, and PAHs all measured in splits of the same JB sample.(Adams and Benyi 2003) Finally, concentrations of the levels of total BAC and C10:C10 DADMAC disinfectants are greater than that of triclocarbon (low levels) and triclocarban (approximately 2000 ng/g) reported in surficial sediments from a Jamaica Bay site in very close proximity.(Miller et al. 2008)

2.5 Conclusions

A sensitive and highly selective method is presented for the determination of a range of QACs in sediments. Progress has been reported in developing a method that provides more complete and well tested sample extraction of QACs and provides solutions for problems associated with loss of DTMAC to surfaces and instrumental blank problems. HPLC-ESI-ToF-MS has proved to be especially powerful in the analysis of both target QAC analytes and in the discovery based determination of other saturated alkylamines. Illustrated here are the identifications of two non-targeted DADMACs that occur at trace levels. The concentrations of QACs are higher than those of organic contaminants measured in the same or other nearby urban estuarine sediments suggests that their study will require more attention.

The extraordinarily high positive mass defects associated with alkylammonium ions allows for the selective and sensitive HPLC-ToF-MS based measurement of the QACs studied in this work. The large positive defects of alkylammonium ions as function of molecular weight and DBEs has been explored here. This analysis suggests that there are many applications for high resolution mass spectrometry in the analysis of diverse range of alkylamines and analytes with alkylamine fragment ions.

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Figure 2.1 Extracted ion chromatograms of targeted QACs obtained from sewage impacted estuarine sediment (BB). HPLC method 1 was employed. Note that only 10 µL out of 300 mL extract was injected, illustrating the high sensitivities that can be achieved in analysis of QACs in sediments. The elution pattern of the DADMAC homologues series as a function of alkyl chain length is explained by variable HPLC mobile phase gradients employed. The internal standard (IS) is tridocecylamine.

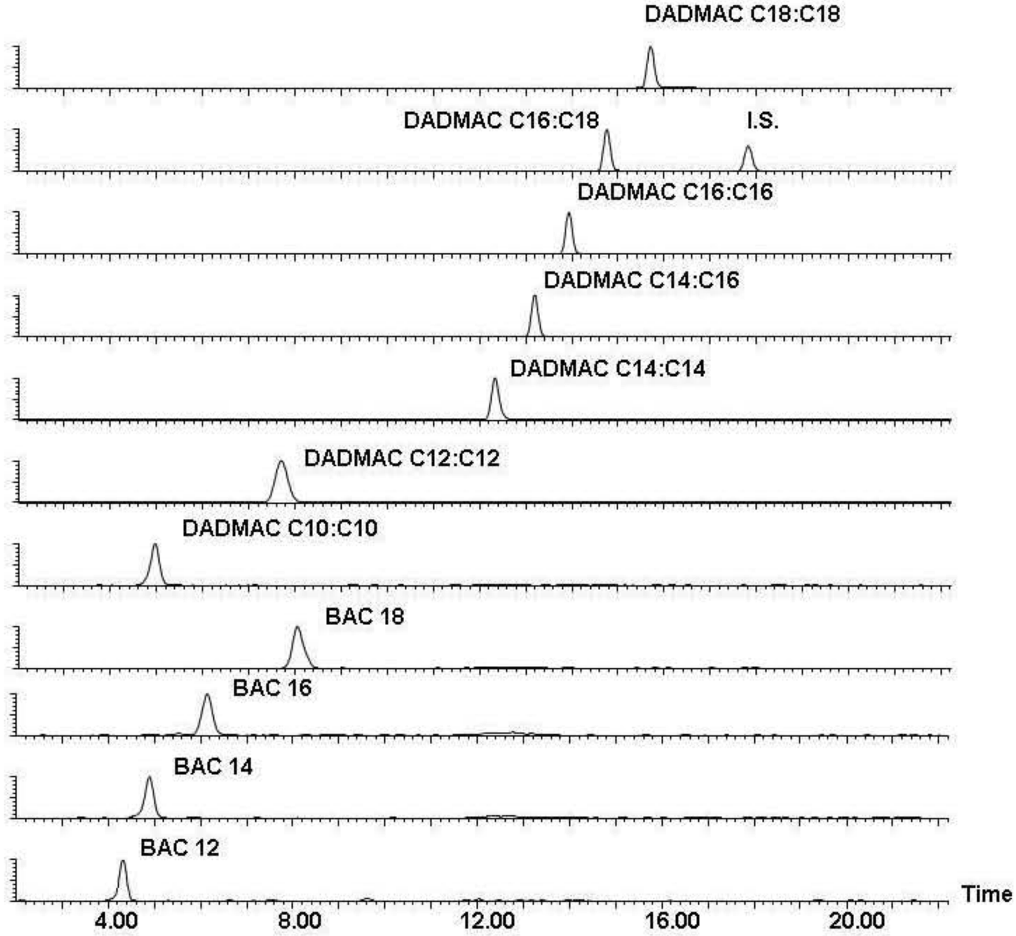

Figure 2.2 HPLC-ToF-MS ion chromatograms of DADMACs (C8:C8, C8:C10, and C10:C10) in BB sediment with mass widows of 0.5 Da (A); and 0.05 Da (B). HPLC method 2 was utilized. 10 μl out of 15 mL extract was injected. Nominally isobaric interferences appararent with the larger mass window (A) are from 13C isotopes of compounds with M-1 base peaks (†), or an ion with likely elemental formula of $C_{12}H_{32}NO_2$ (††).

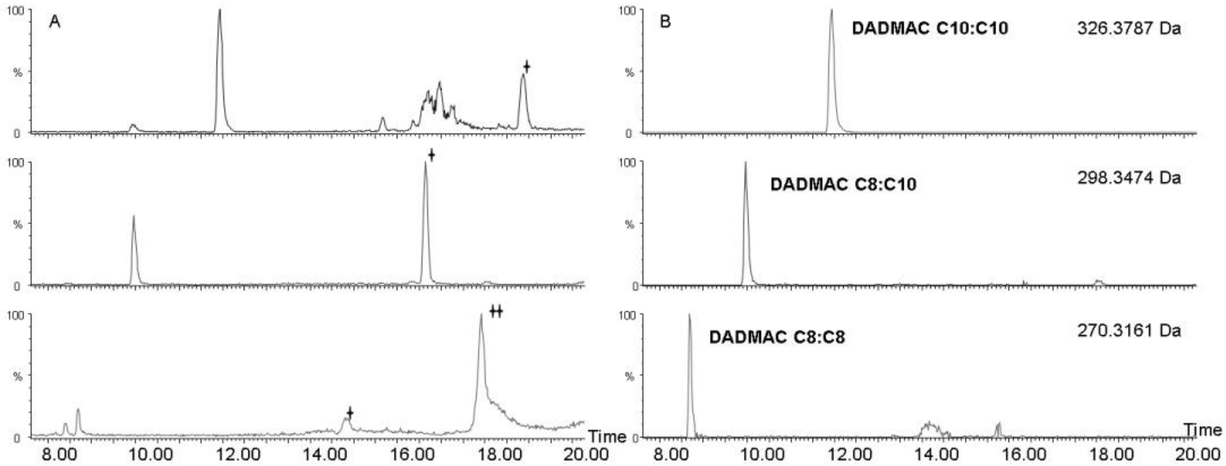

Figure 2.3 A) an illustration of the change in mass defect with increasing atomic number for elements most commonly encountered in electrospray ionization of organic compounds in positive ionization mode. B) the difference in mass between selected target ions and masses of nominally isobaric ions with alternate elemental formulas, illustrated for caffaine and DADMACs with different DBE (0-5).

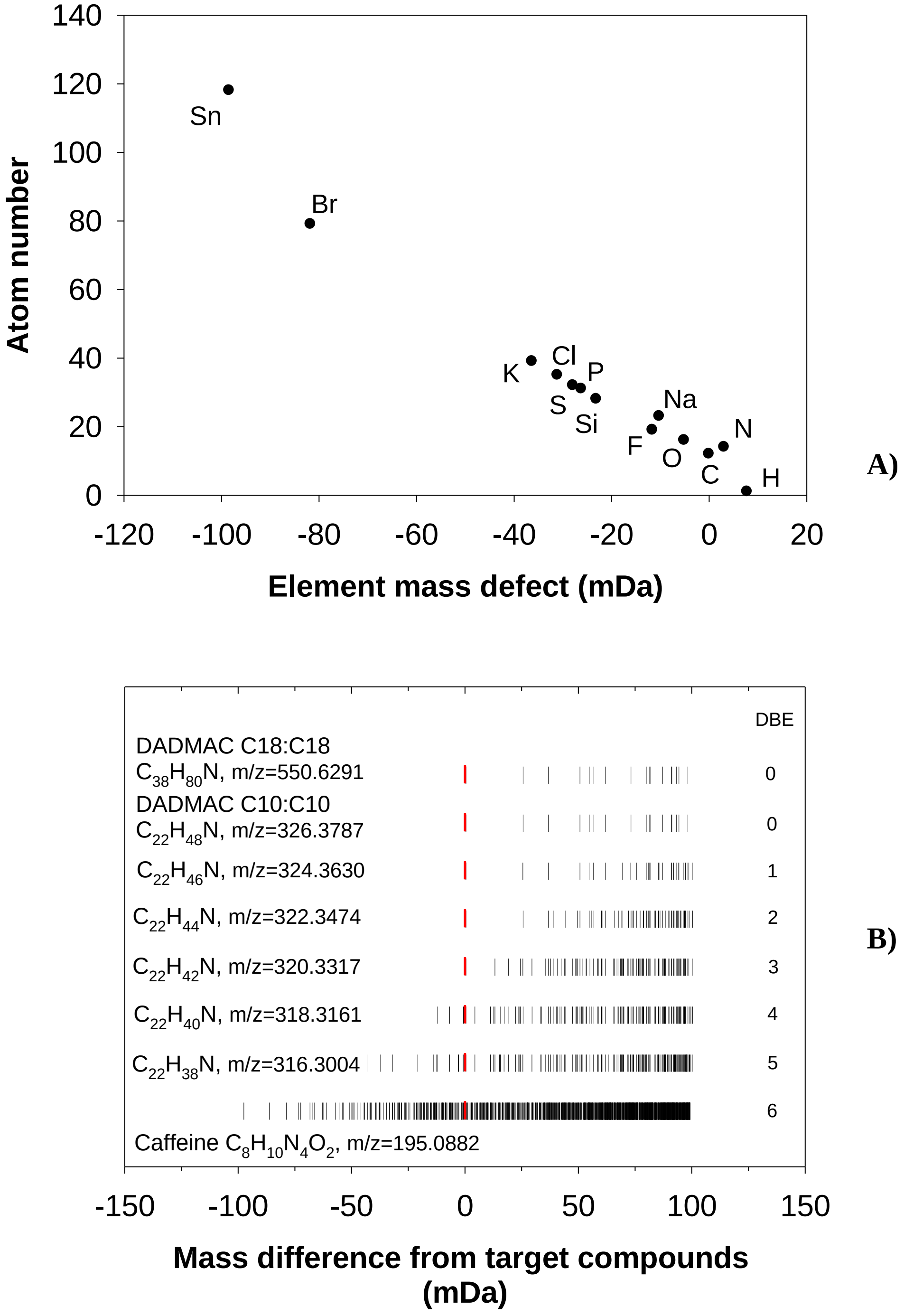

Figure 2.4. Mass spectrum of putative peak for DADMAC C8:C10 in sediment extract (Figure 2.2). Proposed CID fragment ions (m/z = 185.1919 and 186.2221) are also found in mass spectra of DADMAC C8:C8 and C10:C10, respectively (data not shown). The estimated accurate masses of the CID fragments are within 2.0 mDa.

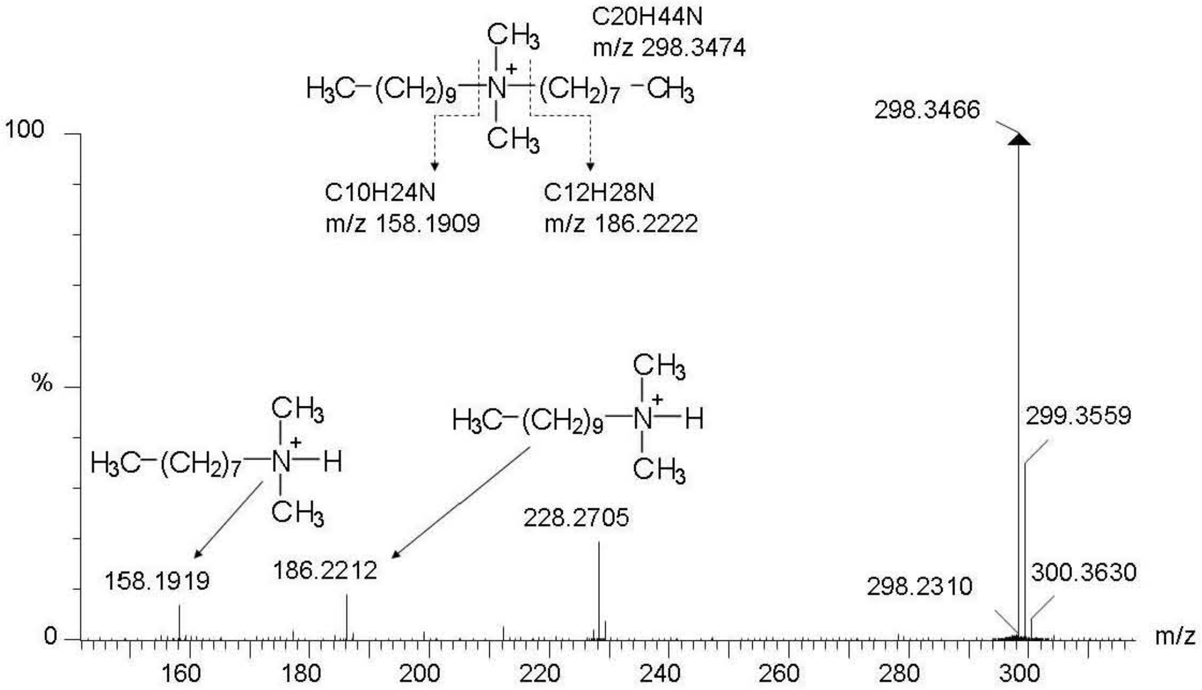

Table 2.1. Sequential extraction conditions and results. Indicated are the percentages of the sum all native QACs measured during sequential extraction of either BB or LIS sediments.

Sediment	Percentage of each extraction (%)		
BB	base extraction [a]	CsCl in methanol [b]	1:1 methanol:DCM [c]
	99.4	0.4	0.2
BB	base extraction [a]	8 hrs sonicate bath [d]	CsCl in methanol [b]
	98.8	1.0	0.2
LIS	base extraction [a]	8 hrs sonicate bath [d]	Sonic probe [e]
	97.7	1.3	1.0

Note: a. extraction method used in this paper. b. sample was extracted with 10 mL methanol with 0.1 M CsCl for one hour in ultrasonic bath. c. sample was extracted with 10 mL acidic 1:1 methanol:DCM for one hour in ultrasonic bath. d. sample was extracted with 10 mL acidic methanol for eight hours in ultrasonic bath. e. sample was extracted with 10mL acidic methanol for 5 min sonication by ultrasonic probe.

Table 2.2 Enhanced extraction of QACs from sediments by sequential extraction with the ultrasonically assisted acidic methanol method following Soxhlet extraction(Martinez-Carballo et al. 2007) and acidic methanol steam extraction (Gerike et al. 1994)

	% additional QAC extracted following soxhlet extraction (%)									
	BAC				DADMAC					
	C12	C14	C16	C18	10:10	14:14	14:16	16:16	16:18	18:18
LIS	n.d.[a]	33	n.d.	64	110	130	92	61	67	45
JB	6.2	10	6.4	7.9	20	8.1	6.6	4.8	4.0	4.3
	% additional QAC extracted following acidic methanol steam extraction (%)									
LIS	n.d.	n.d.	n.d.	21	8.4	22	23	23	27	26
JB	n.d.	5.0	7.4	8.4	14	5.2	6.3	4.7	6.1	6.8

a. not detected

Table 2.3. Concentrations (ng/g) of BAC and DADMAC in estuarine sediments (RSD%) [a]

	TOC	BAC				DADMAC								Total
	(%)	C12	C14	C16	C18	8:8	8:10	10:10	14:14	14:16	16:16	16:18	18:18	
LIS	1.6	6.2 (20)	19 (5)	23 (7)	73 (5)	n.d.[b]	n.d.	6.0 (2)	11 (4)	31 (7)	110 (8)	620 (6)	930 (2)	1800(4)
JB	5.1	64	210	420	590	5.4	14	130	300	440	3300	12000	18000	35000
BB	6.7	3700	7200	5900	4500	24	120	780	760	860	5100	19000	26000	74000
FR-S	7.9	17	60	84	57	n.d.	n.d.	7.4	28	87	470	1400	2700	4900
FR-D	4.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
LOQ	-	-	2.0	2.6	-	-	-	0.2	0.1	0.1	0.2	0.3	2.0	-

a. Based on triplicate samples measurement. RSDs given in percent. b. not detected.

CHAPTER THREE: QUATERNARY AMMONIUM COMPOUNDS IN URBAN ESTUARINE SEDIMENT ENVIRONMENTS – A CLASS OF CONTAMINANTS TOO LONG UNDER THE RADAR?

3.1. Introduction

Quaternary ammonium compound (QAC) represents an important class of cationic surfactants that are widely used in a host of products and applications, including fabric softeners, detergents, disinfectants or preservatives, and various personal care products, especially hair care products.(United States International Trade Commission. and United States Tariff Commission. ; Boethling 1984; Boethling and Lynch 1992; Levinson 1999; Ying 2006). As hydrophobic cation-exchangers, QACs sorb strongly to soils and sediments (Brownawell et al. 1990), and tetra-alkylammonium QACs are generally persistent enough to be present at high levels, in sewage sludge(Gerike et al. 1994; Breen et al. 1996; Fernandez et al. 1996; Merino et al. 2003; Martinez-Carballo et al. 2007), wastewaters (Ferrer and Furlong 2001; Clara et al. 2007; Kreuzinger et al. 2007; Martinez-Carballo et al. 2007), receiving waters (Wee and Kennedy 1982; Lewis and Wee 1983; Ding and Liao 2001; Ferrer and Furlong 2001; Ding and Tsai 2003) and sediments (Lewis and Wee 1983; Gerike et al. 1994; Fernandez et al. 1996; Ferrer and Furlong 2002; Kreuzinger et al. 2007; Martinez-Carballo et al. 2007).

Three important classes of QACs have received the preponderance of study and are also the focus of this report. They include: dialkyldimethylammonium compounds (DADMAC), most with even carbon n-alkyl chain lengths varying between C8 and C18; alkyltrimethylammonium compounds (ATMAC) possessing even carbon n-alkyl chain between C12-C18; and benzylalkyldimethylammonium compounds (BAC) possessing similar n-alkyl chain lengths (C12-C18). Early studies of QAC occurrence and fate in the environment focused almost entirely on DADMAC, with alkyl chain lengths primarily consisting of C14, C16, and C18 (Gerike et al. 1994; Fernandez et al. 1996). As the major source of the lipid stocks used to produce these compounds was hydrogenated animal fat, they were most commonly known as ditallowdimethylammonium chloride compounds (DTDMAC), a term retained here to refer to these more hydrophobic and persistent QACs (Fernandez et al. 1996).

It is not clear if there is cause for toxicological concern for QACs, despite the high levels that have been measured in sediments and other environmental compartments. The potential for acute toxicity of QACs to metazoans is thought to be relatively low in aquatic ecosystems (Ying 2006; Kreuzinger et al. 2007). However, many QACs are used as microbicides, antimicrobials, and algaecides (Levinson 1999), such that risks associated with phytotoxicity in sewage contaminated surface waters (Kreuzinger et al. 2007) and their potential roles in the selection and spread of resistance genes (Plante et al. 2008) may be of greater concern. Gaze and co-workers (2005) found that a selection of QAC resistance genes in the natural environment has the potential to co-select for antibiotic resistance genes. (Gaze et al. 2005).

The recalcitrance of DTDMAC to microbial degradation is illustrated by the concentrations that have been reported in sewage sludge plants collected from European plants prior to the early 1990s, often exceeding 2000 μg/g and reaching as high as 9200 μg/g (Hellmann 1989; Gerike et al. 1994; Breen et al. 1996; Fernandez et al. 1996; Merino et al. 2003; Martinez-Carballo et al. 2007). DTDMAC was the major ingredient in fabric softeners; its use was voluntarily phased out in many European countries during the early 1990s and replaced by classes of much more biodegradable compounds referred to as esterquats (Gerike et al. 1994). Fernandez and coworkers (1996) reported that levels of DTDMAC in anaerobically stabilized sewage sludge from Switzerland decreased from 2570-5870 μg/g in 1991 to 150-300 μg/g (Fernandez et al. 1996). Clara and co-workers (2007) concluded that the fate of DTDMAC in sewage treatment plants may be explained only by sorption and accumulation in settled sludge, and biodegradation can be important but incomplete for less hydrophobic QACs: DADMAC C10:C10, ATMAC 12–16, and BAC 12-18, which are still accumulated in sludge at significant concentrations (Clara et al. 2007). Strong sorption of QACs protects them from biodegradation, the rates of which increase within homologous series of QACs with shorter alkyl chain lengths (Nishiyama et al. 1995; Garcia et al. 1999; Clara et al. 2007).

In contrast, replacement chemicals in fabric softeners, including esterquats such as diethylester dimethylammonium chloride (DEEDMAC) and diesterquaternary (DEQ), have been shown to be effectively biodegraded during wastewater treatments (Matthijs et al. 1995; Radke et al. 1999). However, DTDMAC continued to find extensive use in the U.S. and other regions of the world after the European phase-out (Levinson 1999), and there have not been studies since the European phase-out to determine the levels at which DTDMAC exist in U.S. sludges or sediments. In fact, there have been a very limited number of measurements of QACs in surface sediments since the early measurements of high DTDMAC in the 1980's and early 1990's. This lack of research focus is surprising in light of the maximum concentrations of total QACs determined in each of five separate studies ranging between 67 and 1140 μg/g (Table 3.1).

The accumulation of QACs in surface sediments will be controlled by inputs, the strong sorption of these organic cations to sediment, the deposition and transport of contaminated sediments, and the susceptibility of QACs to biodegradation under field conditions. Literature on the microbial degradation of QACs is largely based on lab studies and the results and conclusions have been very inconsistent. In Chapter 1, many lines of evidence, including mass balance approaches, point to DTDMAC being especially resistant to degradation, which leads to the hypothesis that DTDMAC, and maybe other QACs, could be very useful as sediment-associated, source-specific tracers in estuarine and marine settings.

The few studies on QACs to date have primarily focused on their detection, and little has been done to assess their distribution, transport or fate in receiving waters or sediments. This is especially true in comparison to a much larger body of literature on the occurrence and fate of major classes of nonionic and anionic surfactants and their metabolites (Ying 2006). Further, many of the reports on occurrence of QACs in the environment have either employed non-specific analytical methods, or ignored QACs other than DTDMAC. In this study, a newly developed analytical method (Chapter 2) was used to determine the concentrations of a broad range of QACs, including some previously unreported homologs. QACs are shown to be persistent, and the compositions found in sediments are related to the degree of local inputs of less treated municipal sewage. Finally, the concentrations of QACs are compared to those of other organic contaminants that have been analyzed in most of the same samples.

In a related study, the identification of a previously unrecognized C22 ATMAC (behentrimonium) is reported (Lara-Martin et al. 2009). It is shown that the concentrations of this compound have exponentially increased over the past three decades; they have quickly reached surprisingly high levels in the environment (Lara-Martin et al. 2009), and the changes in the ratios of behentrimonium to the products it replaced is assessed in the sediment geochronology studies reported in Chapter 4.

3.2. Experimental section

3.2.1. Study Area and Sediment.

The NY/NJ Harbor complex (Figure 3.1) located in the lower Hudson River is one of the most urbanized estuaries in the U.S. The watershed has a population of over 20 million people (Adams and Benyi 2003) that discharges 2.3 billion gallons of wastewater per day into the study area from wastewater treatment plants, storm drains, and combined sewer overflows (CSOs) (Adams and Benyi 2003). The primary sources of sewage-derived contaminants in the regions are effluents from municipal wastewater water treatment plants (WWTP); however, the Passaic River receives no significant direct WWTP-derived effluent and is likely more impacted by CSO inputs concentrated there, and Newark Bay sediments reflect mixtures of CSO inputs and WWTP discharges from the Hackensack River and from outside the Bay. Semi-enclosed Jamaica Bay is highly impacted by wastewater inputs, and the distributions and fate of a variety of wastewater-derived contaminants have been studied extensively there (Bopp et al. 1993; Ferguson et al. 2001; Reddy et al. 2005; Benotti and Brownawell 2007; Miller et al. 2008).

Locations of sediment grab samples are shown in Figure 1, with more detailed site information provided in the Appendices. (Table A1). The preponderance of analyzed sediment samples (n=45) were collected as part of an EPA sponsored Regional Environmental Monitoring and Assessment Program (REMAP) conducted in 1998, which was a detailed study of sediment toxicity and contamination by metal and organic contaminants on splits of the same samples sediments (Ferguson et al. 2001; Adams and Benyi 2003). Selection of this set of samples was based on availability of analytical data for a wide range of other contaminants, as well as corresponding sediment toxicity data (Adams and Benyi 2003; Brownawell et al. 2005; Brownawell et al. 2007). Sediment sampling (0-5 cm grab samples) and storage conditions are described in those reports. The samples selected for analysis of QACs were based on geographical and sediment type considerations; an emphasis was placed on muddier samples that had also been analyzed for other wastewater contaminants (Ferguson et al. 2003; Brownawell et al. 2005) and characterized by high total organic carbon (TOC) and Al contents (Adams and Benyi 2003). Four additional sediment samples were derived from a sampling trip conducted in August, 2004. Two of those samples were collected within 200 m of CSO outfalls, and two from Flushing Bay, another area affected by a mixture of CSO and treated WWTP discharges

3.2.2. Sample collection, extraction and analysis

The development of methods for the analyses of DADMACs and BACs in estuarine sediments is reported in Chapter 2 and briefly summarized here. ATMAC 12, 14, 16, 18 were also determined in this study with the same analytical method. Authentic standards of the ATMACs were purchased from TCI America (Portland, OR).

Frozen sediments were freeze-dried. An ultrasonic assisted extraction of 0.1 g sediment aliquots with 10 mL acidic methanol (1M HCl at 60^{o}C for one hour) was repeated three times and resulted in improved recovery of native QACs when compared with other extraction methods. The same test tube was used throughout subsequent purification steps to minimize loss of more hydrophobic DTDMACs. Samples were purified by a combination of liquid-liquid extraction with chloroform and anion exchange chromatography. Final extracts were brought up in 15 mL of methanol; in this work, QAC concentrations were great enough that no further concentration of extract was necessary. Further dilution of extracts (as great as 300 mL) was required for samples with higher DTDMAC concentrations, in order to keep analyte signal within the linear range of detector response. DADMAC C12:C12 was used as a surrogate standard and spiked in high amounts (15-300 ng) compared to the native analyte. Surrogate spike recoveries are 104±19% for all detected samples.

QACs were analyzed by HPLC-ToF-MS. Two different HPLC separation methods were used and detail of HPLC methods provided in Chapter 2. Method 1 was used for the analysis of DTDMAC and employed a higher initial fraction of non-aqueous solvent in the mobile phase during gradient elution. This method greatly reduced trace instrumental backgrounds of DTDMAC C16:C16, C16:C18 and C18:C18. A second HPLC method with a longer mobile phase gradient was used for analyses of ATMACs, BACs and less alkylated DADMACs. Tridodecylamine was used as an internal standard. HPLC-ToF-MS separation and analysis of QACs employed a Waters Alliance 2695 LC and LCT mass spectrometer with a Z-spray ESI source (Micromass, Manchester, UK). Luna C18 reverse phase column (Phenomenex; 150x2.00 mm, 5 μm) was applied for HPLC separation. ESI in positive ionization mode was conducted with capillary and cone voltages of 2800 V and 55 V, respectively. The surrogate standard DADMAC C12:C12 was well recovered by the method developed. Limits of quantification (LOQ at S/N = 10) were determined by spiked addition to a deeper QAC-free sediment core sample. When the final volume of sample extract is 1.0 mL, the LOQs are reported in Chapter 2 as C10 – C18 DADMACs (0.1 – 2.0 ng/g), BAC C14 and C16 (2 -2.6 ng/g) and ATMAC C16 and C18 (0.25 and 0.15 ng/g). In this work, the final sample volume was 15 – 300 mL and method detection limits were higher by approximately that sample-dependent difference in volume. Concentrations of C14:C16 and C16:C18 DADMAC were estimated by interpolating very similar response factors of the most closely eluting DADMAC homologs, and the concentrations of DADMAC C8:C10, BAC 12 and 18 were calculated assuming the response factors of DADMAC C10:C10, BAC 14, and BAC 16, respectively.

3.3. Results and discussion

3.3.1. Occurrence and distributions of QACs in NY/NJ Harbor complex sediments

The HPLC-ToF-MS method utilized for this study was highly sensitive (Chapter 2), such that all, or nearly all, targeted QACs were easily measured in every sediment sample. The ease of detection is remarkable, given the small mass of sample (0.1 g) extracted and the minute fraction of the extract loaded onto the HPLC-MS; 10 uL injections represented the equivalent of an extraction of 3 – 65 μg of sediment in this study. Table 1 summarizes concentration medians and ranges of targeted compounds measured in this study, and compares them to those measured in other studies of QACs in sediments. Total concentrations of QACs in this study of surface sediments in the New York/New Jersey Harbor complex range between 0.98 and 114 ug/g (n = 49), with a median concentration of 32 μg/g. Total QAC in these samples is dominated by DTDMACs (median level of 26 μg/g), primarily consisting of DADMAC C16:C16, and especially C16:C18, and C18:18. This homolog distribution is expected for DTDMAC (Fernandez et al. 1996) and the lipid composition of hydrogenated animal fat. The distribution of total QAC concentrations is better illustrated in Figure 3.2, which is further discussed below. It is noted here that the concentrations of all QACs measured in this study of the NY/NJ Harbor complex are much greater than those reported in areas more remote from intense inputs of municipal wastewaters in central Long Island Sound and the Forge River (Chapter 2).

DTDMAC. The concentrations of DTDMAC found in surficial sediments bracket (or overlap in the case of the two highly contaminated estuarine sediments taken off of Barcelona) (Fernandez et al. 1996) the concentrations found in studies where sediments were collected before the phase-out of DTDMAC in the early 1990s. To my knowledge, the analyses of DTDMAC in the two Spanish sediments represent the only prior reported measurements of QAC in estuarine sediments. The median concentration of DTDMAC measured in this work is 120 times higher than those determined recently in river sediments collected in Austria (Table 3.1). This large difference is likely due to three factors: 1) the greater reduction of DTDMAC use in parts of Europe than in the U.S., where, the sediment core and surface sediment samples indicate that maximum concentrations in sediments were about four to five times greater than they are presently (Chapter 4); 2) in the Austrian study (Martinez-Carballo et al. 2007), the concentrations of DADMAC C16:C18 were not estimated; correcting for this would increase total DTDMAC concentrations by approximately 50%; and 3) the highly urbanized metropolitan harbor complex investigated in this study can be expected to be more significantly impacted by municipal wastewater than sediments collected in Austrian rivers; evidence for this explanation includes not only differences in population density, but also the comparatively lower concentrations measured for DADMAC C10:C10 and the lower alkyl chain BAC homologs in the Austrian samples (Table 3.1).

BACs. Benzalkonium compounds, including BAC 12, 14, 16, and 18, are the second most abundant class of QACs measured in this work, with median concentrations of 140, 450, 320, and 490 ng/g, respectively (Table 3.1). The concentration ranges and median values for individual BACs are again higher, and sometimes much higher, than those measured in two other studies of riverine sediments (Ferrer and Furlong 2002; Martinez-Carballo et al. 2007). What is surprising is the compositions of the BAC mixtures determined in this work, notably the much higher levels of BAC 16 and 18 reported, when compared to prior work (Ferrer and Furlong 2002; Martinez-Carballo et al. 2007). The primary components of BAC mixtures used in disinfectant products are BAC 12, 14, sometimes 16, and may contain very low levels of BAC 18 (Schaeufele 1984). The higher levels of BAC 16 reported here could be due to factors including: 1) fractionation of BACs during WWTP treatment, in which the more soluble, lower chain length BACs are preferentially removed by biodegradation; 2) other product formulation not intended for disinfection containing BAC 16; and 3) possible differences in extraction efficiency between this work and prior studies. Most striking is the high levels of BAC 18 estimated here. It is likely that the concentrations of BAC 18 are somewhat overestimated because they were calculated assuming the same instrumental response of BAC 16, while we have seen that for this particular homologous series of QACsm, sensitivity increases (less than a factor of two) when alkyl chain length increases

(Chapter 2). Despite that possibility, the relative proportions of BAC 18 measured here are much higher than estimated in the two prior studies. Biocidal activity of BACs and skin irritancy of QACs generally decrease with alkyl chain lengths of the compound classes considered in this work. A survey of marketing information, MSDS sheets, and product formulations found in searches of the internet, indicates that BAC 18 (http://www.cosmeticsdatabase.com/) is sold for uses in personal care products and as algaecides in pool cleaners. Further work is required to more accurately determine the concentrations of BAC 18 and the primary uses of BAC homologs that result in wastewaters.

ATMACs. Alkyl trimethyl ammonium compounds were the next most abundant class of QACs found in this study (a median concentration of for the sum of these compounds was 520 ng/g. ATMAC 16 and 18 are the primary compounds in cetrimonium and formulations used in applications such as hair care products. ATMAC C14 was only found in trace levels in some samples and is not reported here. ATMAC 16 and 18 were not measured in sediments by Martinez and coworkers (2007), who reported levels of ATMAC 16 in sewage sludge. Given the antimicrobial properties of ATMAC 16 and 18 and their application as preservatives (Boethling 1994), they may be environmental contaminants worthy of further study. It will be seen in Chapter 4 that the composition of ATMACs in sediments may be an exceptionally powerful tracer for dating purposes.

Recent work on sewage sludge and bio-solid samples indicates significant levels of ATMAC 12, which was not targeted in the present study. After this work was completed, this lab discovered that there are very high concentrations in recent sediments of previously unrecognized ATMAC 22 (docosammium or behentrimonium), with lower relative amounts of ATMAC 20, as seen in commercial products. The concentrations of these compounds in sediments have increased exponentially over the past 30 years (Lara-Martin et al. 2009). Behentrimonium chloride or methosulfate has become a favored ingredient in well over 1500 hair care products (http://www.cosmeticsdatabase.com) and has likely replaced other active ingredients, such as ATMAC 16 and 18, over time (European Commission 2007).

DADMAC Disinfectants. Formulations of DADMACs (with and without BACs) are more recent generation disinfectant (Schaeufele 1984). DADMAC disinfectants can contain variable mixtures of DADMAC C8:C8, C8:C10, and C10:C10. The presence of DADMAC C10:C10 in environmental samples was recently reported for the first time in work conducted in Austria (Clara et al. 2007; Kreuzinger et al. 2007; Martinez-Carballo et al. 2007). In Chapter 2, the presence of lower-abundance DADMAC C8:C8 and C8:C10 were confirmed, with the latter found in greater abundance in sediments. In this survey, we have found lower abundances of the C8:C10 homolog (median concentration of 10 ng/g) in comparison to the C10:C10 (median concentration of 190 ng/g). DADMAC C10:C10 was also found at higher levels here compared with those determined in Austrian sediments (median concentration of 21 ng/g); at the dilutions used in this study, only trace or non-detectable levels of DAC8:C8 were measured, and their concentrations are not reported here.

3.3.2. Relationship of QACs with sediment total organic carbon (TOC).

Concentrations of total QACs are high throughout the Harbor complex, tending to increase directly with sediment TOC on a Harbor complex-wide basis. There is a stronger relationship between these two properties (r^2=0.80) when only muddy sediments (defined as samples with Si/Al ratios < 10), and not proximate to CSO inputs, are considered. Other outliers, not included in the correlation, were a few samples from highly eutrophied far western Long Island Sound. The higher proportions of TOC in CSO samples may be the result of relatively greater removal of more labile organic matter during treatment in WWTPs, when compared to more recalcitrant QACs, especially DTDMAC. That explanation is perhaps better supported by much higher enrichment of nonylphenol ethoxylate metabolites relative to DTDMAC in the same CSO samples (Chapter 5). It is clear that NPEO is much better degraded in WWTPs than is DTDMAC.

It is hypothesized here that the correlation observed between total QACs (dominated by more persistent and particle reactive DTDMAC) and TOC is due to QACs serving as source-specific tracers of sewage derived organic matter; its persistence in sediments is reflected by higher TOC values. Among the more likely alternative explanations is that the QAC levels are correlated with sediment organic matter that either acts as a controlling sorbent phase for QACs or that both TOC and QACs are co-correlated with sediment grain size, While the hypothesis provided is speculative, it is supported by several observations and considerations:

1. There exists a positive intercept in which QAC-free sediments correspond to TOC = 1.73%; this TOC value is consistent with that found in muddy sediments from less contaminated areas of Central Long Island Sound (Mayer 1994) or from middle and upper Hudson River that are estimated to be little impacted by sewage (Olsen et al. 1978);
2. Olsen and coworkers (1978) also concluded that excess sediment organic matter in the NY/NJ Harbor complex was due to sewage inputs. TOC in the NY/NJ Harbor complex may be less affected by local primary productivity than in Long Island Sound due to light limitation from high turbidity from sediment resuspension that characterizes these shallow, highly energetic areas;
3. The fact that the correlation near zero QACs indicates a positive intercept with TOC provides evidence that TOC is not the only sediment property controlling the adsorption of QACs on particles;
4. Neither TOC nor QACs are correlated with aluminum, generally considered an excellent tracer of clay content and sediment surface area (Figure 3.3). It can then be argued that both TOC and QACs are controlled by factors other than grain size, which might overwise be expected.
5. Extrapolation of the linear regression to TOC values between 25 and 40%, values characteristic of sewage sludges and stabilized sludges, predict QAC concentrations of 127 – 202 μg/g; close to QAC concentrations of 175 – 500 ug/g recently measured in 9 treated sludges collected in 2003 (preliminary unpublished data).

Whether or not the relationship between TOC and QACs indicates relatively conservative behavior for more persistent QACs or both QACs and bulk TOC. Additional evidence for persistence of QACs and especially DTDMAC is presented in Chapters 4 and 5. A study of the relationship between TOC, QACs and other measures of organic matter source inputs (including multiple elemental and isotope ratios that include S) would likely shed additional light on whether excess TOC in this area is controlled by sewage derived inputs of carbon, rather than eutrophication.

3.3.3. Compositions of QACs in sediments – insights into sources and differential preservation.

The average compositions of the QACs measured in each sample are illustrated in Figure 3.4, which divides the samples into four defined areas. Only samples from Jamaica Bay (n= 16) and CSO samples (n=4) are precisely defined; the division of samples followed the designations given by EPA (Adams and Benyi 2003): Newark Bay (n = 17); includes samples within the Bay and those in the Arthur Kill and Kill van Kull that define the waterways at its mouth. The rest of the samples have been grouped into the Upper Harbor, which includes all other sites (n = 12) that are found on Figure 3.1.

Figure 3.4 more clearly illustrates those DTMAC homologs C16:C16, C16:C18, and C18:C18 are the major contributor to total QAC levels. Integrating the average compositions of individual samples, DTMAC averages between 84 and 94% of total QACs in less CSO affected sediments from different regions of the sampling area, and 67% in the four CSO impacted samples. The small relative standard deviations in the DTDMAC composition, suggests that the DTDMAC mixtures used in different sewersheds in the region are similar, and the lack of differences in compositions between sites for different homologs would be consistent with their persistence and possible use as conservative sediment tracers.

The contribution and composition of ATMACs are generally consistent with between different groups of samples. However, there are generally lower relatively abundances of BACs and DADMAC disinfectants in Jamaica Bay when compared with other samples measured. It is not known whether this is related to a different pattern of uses of disinfectants or DTDMAC in the sewershed of Jamaica Bay, serving an estimated 2.05 million people (Benotti and Brownawell 2007), or if there are significant differences in the extent of biodegradation in WWTPs or within Jamaica Bay compared to other areas of the Harbor. Given the similarity in compositions within BAC homologs between Jamaica Bay and other non-CSO impacted samples, one might argue against large differences between the degradation or transport of BACs in Jamaica Bay, but more focused study would be required to understand these differences

The difference in compositions for individual homologs of DADMACs, BACs, and ATMACs between CSO and less CSO affected samples are illustrated in a different way in Figure 3.5, where concentrations of all targeted QACs are plotted against DTDMAC, the latter is assumed here to be much more conservative (with respect to microbial degradation and transport on particles) during sewage treatment as well as in sediments. These plots suggest both similarities and pronounced differences between the distributions and likely fate of the different classes and homologs of QACs studied.

Each QAC increases directly with DTDMAC, which would be consistent with a hypothesis that many of these QACs being relatively persistent particle tracers once they reach receiving waters. The linearity of the relationships between DTDMAC and ATMAC 16 and ATMAC 18 are the most obvious. However, much of the scatter associated with the relationships for BACs and DADMAC homologs can be explained by lower levels of these contaminants in Jamaica Bay (not plotted separately for simplicity). Perhaps more interesting is that all of the QACs are enriched relative to DTDMAC in the CSO samples. This enrichment varies greatly between and within classes of QACs. It is especially noteworthy that there is always less enrichment of QACs in CSO samples as alkyl chain length increases with a given class of QACs particularly within a class of QACs as a function of alkyl chain length. It is hypothesized that this is largely controlled by the greater rates and extents of biodegradation of more soluble, shorter alkyl chain length QACs within biological treatment used in WWTPs in the region, as was observed elsewhere (Clara et al. 2007).

The extent of biodegradation has been observed to depend on the extent of QAC sorption onto suspended particles or sediments which then controls bioavailability. The extent of sorption of surfactants (Brownawell et al. 1991) is known to increase predictably with increasing alkyl chain length, consistent with less biodegradation of less soluble homologs within a class of QACs (Garcia et al. 2001; Clara et al. 2007; Kreuzinger et al. 2007). As a further test of the hypothesis that degradation of QACs, measures of relative biodegradability and hydrophobicity of QACs were estimated from the data collected in this study. An indicator of biodegradability is estimated here as differences in the slopes between CSO (CSO) and other sediments from Hudson River complex (HC) from linear regressions (y = ax, where y is the concentration of an individual QAC(i) and x is the DTDMAC concentration) plotted in Figure 3.6. The greater the difference in slopes (lower a_{HC}/a_{CSO}) relates to greater depletion of a given QAC relative to DTDMAC in sediments relative to CSO samples and the hypothesized extent of biodegradation that occurs primarily during sewage treatment. An estimate of the relative hydrophobicities and implied biovailability of QACs is estimated from the retention times of each analyte during our reverse-phase HPLC elution of QACs, an approach that is well established (Schwarzenbach et al. 2003). The result of the relationship between indicators of biodegradation and tendency to sorb to particles is shown in Figure 3.6. This analysis supports the idea that biodegradation of all of these QACs may be related to particle reactivity that decreases bioavailability and that the class of QACs or base structure makes less difference with respect to liability.

3.3.4. QAC concentrations in comparison to other organic contaminants of concern.

Total concentrations of QACs are much greater than summed concentrations of chlorinated pesticides (not shown), and total PAHs measured in the same EPA collected samples (Table 3.2; n = 45). It is seen that QACs are also much higher than PCB levels found by EPA in a similar 1993 sampling effort at many of the same sites; the 1998 PCB analyses were not released. The median ratio of QACs to total PAHs (based on 18 of the major PAHs) is 25; The concentrations of nonylphenol and nonylphenolethoxylate metabolites with one to three ethoxylates (together referred to as NPEOs in Table 2) were also measured in these same samples (Brownawell et al. 2005); Chapter 6), and the median QAC/NPEO ratio is 2.1. The only class of organic contaminants in these sediments that is greater than that of total QACs are defined as total petroleum hydrocarbons (TPH), characterized as unresolved complex mixtures, often consistent with the composition of used motor (Brownawell et al. 2007).

It is not clear which class of QACs might be most important to further assess for ecotoxicological risk. DTDMAC comprises most of the QACs measured in this work, but owing to its high particle reactivity may be of less potential concern with respect to any toxicological risks, than for some of the more soluble BACs that have antimicrobial and algaecidal properties. To put the concentrations of other QACs in perspective, the median concentrations of total BACs, DADMACs, and ATMACs are 1.5, 0.18, and 0.47 μg/g, with maximum values much higher (Table 3.1). The concentrations of these three classes of QACs can be again compared to median total PAH concentrations (2.1 μg/g). BACs, ATMACs, and DADMAC all possess antimicrobial properties. A recent study has reported the concentrations of antimicrobials triclosan (< LOQ) and triclocarbon (~2.5 μg/g) measured in the surface section of a 1996 collected sediment core obtained in Jamaica Bay (ref). Those concentrations can be compared to the concentrations total BAC (3.4-3.7 μg/g), ATMAC (1.2-1.3 μg/g), and DADMAC (0.35-0.37 μg/g) measured in this study, and much higher levels of the same QACs have measured in other areas of QACs in the Harbor Complex (Table 3.1).

3.4. Summary and conclusions

This study represents the most comprehensive study of important classes of QACs in any sedimentary system to date, and the first reports of QACs, other than DTDMAC (Fernandez et al. 1996) in marine or estuarine sediments. The total QAC concentrations are dominated by persistent and superhydrophobic DTDMACs, which appears not to be the case in one European study conducted years after a voluntary phase-out of those compounds in fabric softeners in the early 1990's. It is shown that DTDMAC represents the most abundant single class of organic contaminants in the highly urbanized New York/New Jersey Harbor complex, as might have been expected based on work conducted many years earlier. Evidence is presented that DTDMAC may be acting as tracer of sewage derived sediment organic matter in the highly sewage impacted system, but more study would be needed to test this hypothesis. The concentrations of more soluble QACs are higher in proportion to DTDMAC in sediments proximate to less treated sewage sources, and is interpreted as an indication of selective biodegradation of more soluble and bioavailable QACs during biological treatment in WWTPs, after which they may be relatively well preserved in the sediment deposits studied here.

The concentrations of BACs, ATMACs, and DADMACs, some homologs reported in sediments for the first time, are also at high abundance in comparison to other organic contaminants of concern, including PAHs, various chlorinated hydrocarbons, NPEO metabolites, and the recently measured antimicrobials triclosan and triclocarban. Given the exceptionally high concentrations of many classes of QACs, many possessing antimicrobial properties, it is argued that the study of these chemicals has gone under the radar for far too long.

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Figure 3.1. **Surface sediment sample locations in the NY/NJ Harbor Complex. Blue squares indicates samples collected from Flushing Bay; red triangle indicates samples collected near CSO outlets or CSO impacted Passaic River; black dots indicate locations of all other sample collection sites.**

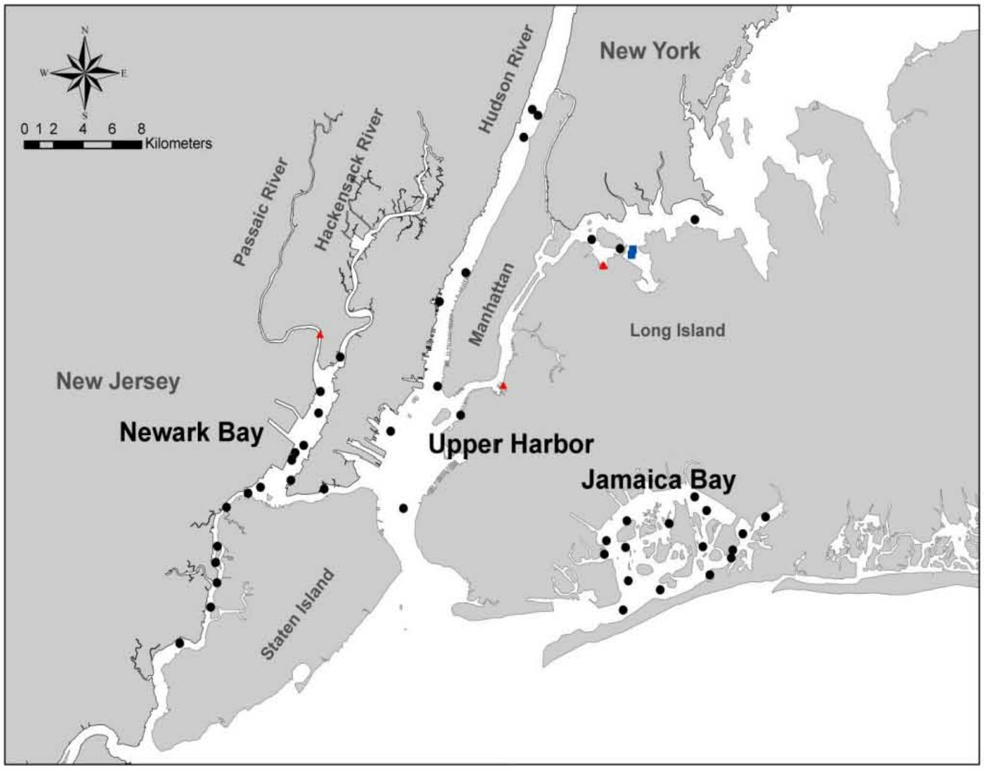
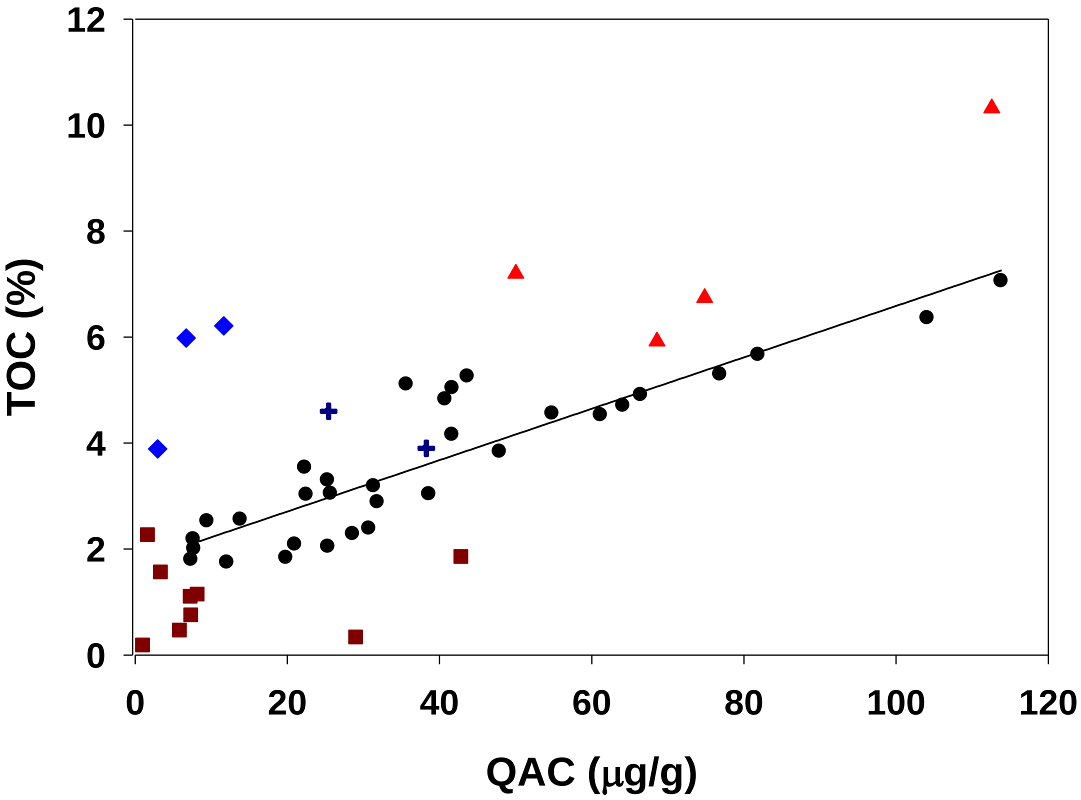


Figure 3.2. Relationship between sediment TOC and and total QAC concentratrions in all samples. Red triangles represent CSO influenced samples; dark blue crosses represent two samples from Flushing Bay; brown squares represent sandier sediments (defined by Al/Si > 10), blue diamonds represent samples from far western Long Island Sound, and black dot indicate all other sample sites. The linear regression plotted is only calculated based on samples indicated with black dots (y=0.05x+1.73, r^2=0.80).



Figue 3.3. The relationships between total QAC vs. Al and TOC vs Al is illustrated for REMAP samples suggests that sediment grain size or surface area explains little of the variability in QACs or TOC.

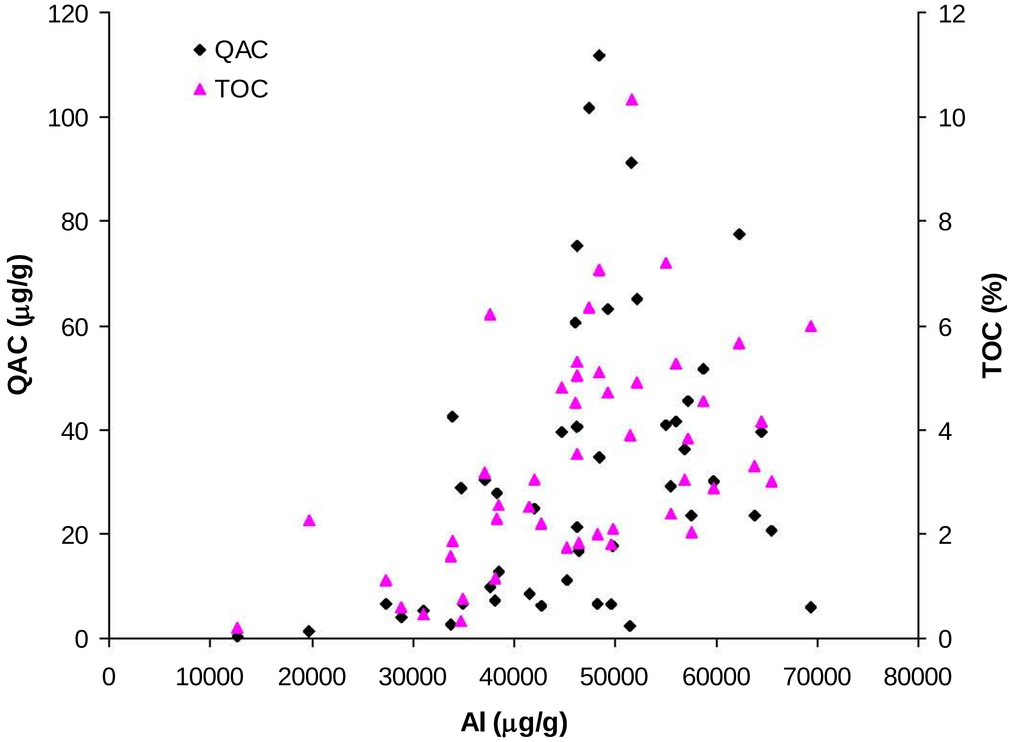


Figure 3.4. Average compositions of detected QAC in the samples from Jamaica Bay (n=16); Newark Bay (n=17); Upper Harbor (n=12) and CSO influenced samples (n=4); error bars represent one deviation.

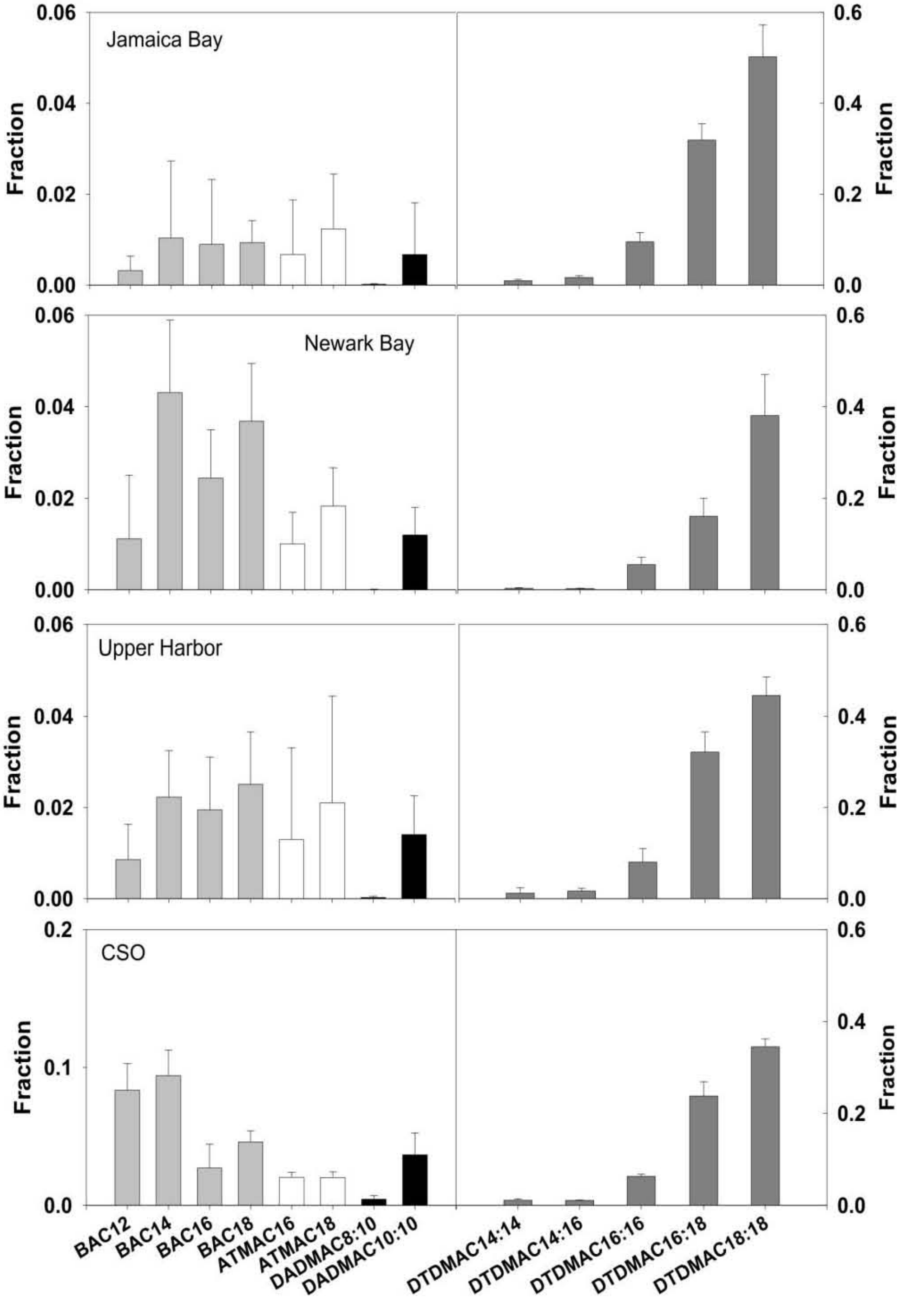


Figure 3.5. Relationships between sediment concentrations of different homologs of DADMACs, BACs, and ATMACs with DTMAC indicate higher levels of more soluble QACs in sediments affected most by CSO inputs (red triangles). The two samples from Flushing Bay, which also receive significant CSO inputs are depicted by blue squares. Linear regression results (y = ax) are calculated for CSO and non-CSO affected samples as indicated by the solid lines.

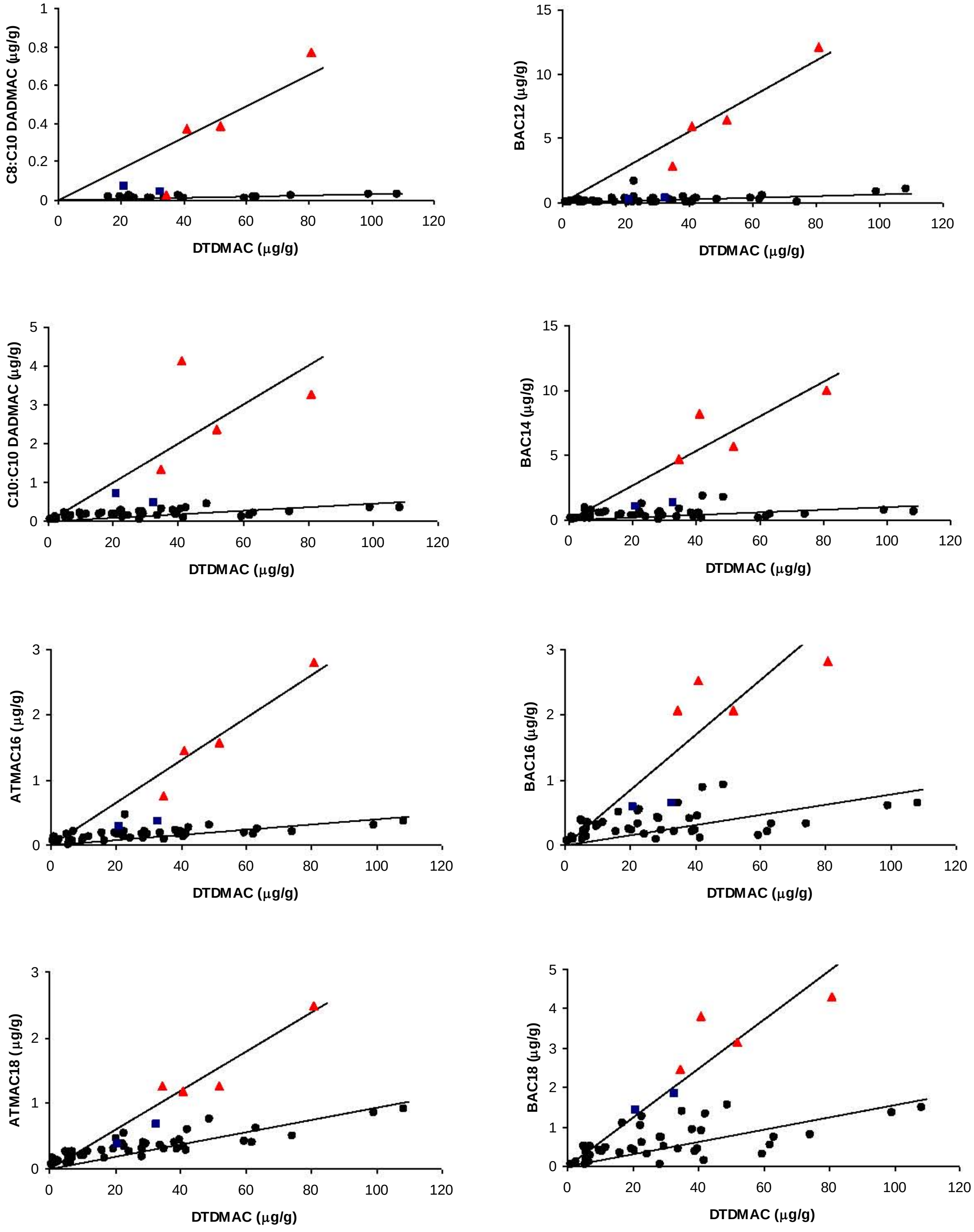


Figure 3.6. An indicator of relative biodegradation of QACs (ratio; see text for details) is plotted as a function of QAC retention time in the reverse phase HPLC method used. The latter is an indicator of the relative hydrophobicity of the each QAC.

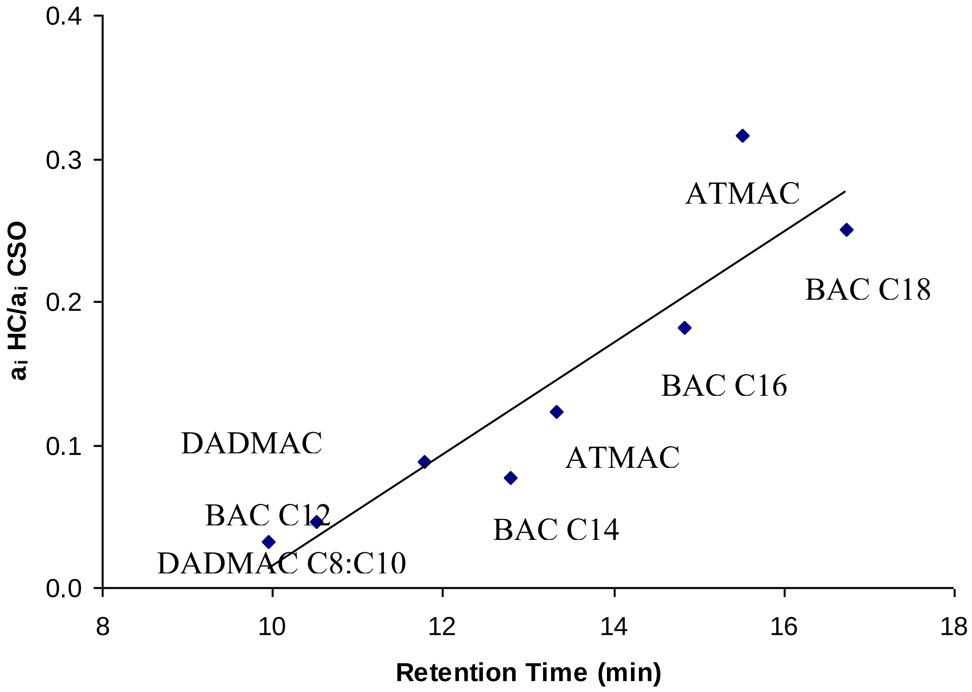


Table 3.1. Comparison of QAC concentrations in surficial sediments determined in this and prior studies; median concentrations are indicated in parentheses where complete data is available.

Sample type	DTDMAC (ng/g)	DADMAC (ng/g)		ATMAC (ng/g)		BAC (ng/g)				Total QAC (μg/g)
	C12:C12-C18:C18	C8:C10	C10:C10	C10-C14	C16-C18	C12	C14	C16	C18	
Marine sediments (n=51) NY, NJ, U.S. [a]	690-110,000 (26,000)	n.d.-767 (10)	n.d.-4,100 (190)	-	8.6-5,300 (520)	40-11,000 (140)	60-8,900 (450)	n.d.-3,800 (320)	n.d.-4,000 (490)	0.98-114 (29)
Remote Marine sediments (n=2) NY, U.S. [b]	1700-4700	n.d.	6.0-7.4	-	-	6.2-17	19-60	23-84	57-73	1.8-4.9
Riverine sediments (n=21) Austria [c]	5-2700 (140)	-	n.d.-510 (21)	n.d.-127 (6.8)	-	3.4-3600 (60)	n.d.-1,600 (23)	1-510 (10)	n.d.-290 (7)	0.06-6.8 (0.88)
Marine sediments (n=2) Barcelona, Spain [d]	42,300-1,140,000	-	-	-	-	-	-	-	-	42.3-1140
Riverine sediment SD, U.S. [e]	3,000-67,000	-	-	-	-	-	-	-	-	3.0-67
Riverine sediment Japan [f]	6,000-69,000	-	-	-	-	-	-	-	-	6.0-69
Riverine sediments (n=3) Belgium [g]	11,000-67,000	-	-	-	-	-	-	-	-	11-67
Riverine sediments (n=4) KS, MO, CO, U.S. [h]	-	-	-	-	-	23-105	22-206	21-260	-	0.066-0.571

a. this research; b. (Li and Brownawell 2009); c. (Martinez-Carballo et al. 2007); d. (Fernandez et al. 1996); e. (Lewis and Wee 1983); f. (Boethling 1994); g. (Gerike et al. 1994); h. (Ferrer and Furlong 2002);

Table 3.2. Comparison of the concentrations of total QACs and other organic contaminants determined in 1998 NY/NJ REMAP Sediments (n=45)

	TOC (%)	TPH (mg/g)	PAH[a] (µg/g)	PCB[b] (µg/g)	NPEO (µg/g)	QACs (µg/g)	QAC/PAH	QAC/NPEO
Minimum	0.19	0.024	n.d.	n.d.	0.030	0.98	0.13	1.0
Maximum	10	13	91	2.5	78	110	1300	130
Mean	3.5	2.2	5.7	0.15	6.1	34	65	16
Median	3.0	1.4	2.2	0.043	2.4	27	11	9.3

a. including 25 PAH homologues; b. data was calculated from 1993 REMAP samples (n=168) that including 20 PCB homologues;

CHAPTER FOUR: BIOGEOCHEMISTRY OF QUATERNARY AMMONIUM COMPOUNDS IN URBAN ESTUARINE SEDIMENTS: HISTORY OF INPUTS PRESERVED IN THE SEDIMENTARY RECORD

4.1 Introduction

Quaternary ammonium compounds (QAC) are a major group of cationic surfactants that have been mainly used in fabric softeners, disinfectants and a wide range of personal care products. There has been little attention paid to QACs as environmental contaminants, and there have been few measurements of QAC in sediments (Chapters 1 – 3). For example, the only previous report of QACs in estuarine or marine sediments (Fernandez et al. 1996) determined concentrations of ditallowdimethylammonium compounds (DTDMAC) in two sewage-impacted sediment samples (42.3 and 1140 μg/g) collected in areas proximal to Barcelona. Those measurements, and other prior studies that showed high concentrations in surface sediments and sewage sludges (reviewed in Chapters 1 and 3), clearly illustrate the high levels of input and relative persistence that are possible for some QACs in urban sediments environments. In Chapters 2 and 3, relatively significant concentrations of DTDMAC and other QACs have been found in surface sediments throughout the highly urbanized New York/New Jersey metropolitan Harbor complex. While literature reports on the biodegradability of QACs provide conflicting conclusions (Chapters 1 and 3), evidence is presented that DTDMAC homologs are stable in wastewater treatment plants (WWTPs) and receiving waters (Clara et al. 2007). More soluble classes of QACs are more clearly degraded in WWTPs, but appear to persist to a significant extent in surface sediments following wastewater discharge into the Harbor complex (Chapter 1 and 3). Greater understanding of inputs and biogeochemical controls on the distribution and fate of QACs is needed for ecotoxicological risk assessment (Ying 2006; Kreuzinger et al. 2007), and determination of QACs' effectiveness as tracers of the sources and transport of sediments and contaminants. QACs may also serve as potential probes for understanding the processes affecting other contaminants in natural waters. In this Chapter, a study of time-dated sediments provides information about the history of QAC inputs and persistence of major classes of QACs in sewage-impacted depositional environments found in areas of the NY/NJ Harbor complex.

Most prior field measurements and initial research studies on the environmental chemistry and toxicology of DTDMAC have been associated with a mixture of longer alkyl chain length (C12-C20) dialkyldimethylammonium compounds (DADMACs) possessing primarily 16 and 18 carbon chain lengths that provide the best fabric softening performance (Levinson 1999). DTDMAC were (and may still be outside of Europe) the most abundant cationic surfactants produced for many years (United States International Trade Commission. and United States Tariff Commission. ; Levinson 1999). However, the same DTDMAC alkyl homologs (mixtures or as single compounds), produced and sold as different salts in addition to chlorides (bromide, sulfate, methosulfate and others) are derived from different alkyl chain sources, including vegetable oils and are used as organo-clay products. Retained here is the acronym DTDMAC (ditallowdimethylammonium compound rather than cloride), that distinguishes these still important chemicals from other DADMACs (C8 and C10 alkyl chain lengths) used as disinfectants. The problems concerning nomenclature, multiple chemical abstract numbers for the same quaternary ammonium compounds, and a myriad of common and trade names confound research efforts on each of the classes of QAC studied here. Not unique to QACs, these problems complicate satisfactory review of the published and unpublished literature and just as important to this work, is the associated difficulty in obtaining or distilling data that may be reported about the historical production of QAC.

This study is concerned with QACs, divided here into four classes: DTDMAC, DADMAC, benzylalkyltrimethylammonium compounds (BACs); and alkyltrimethylammonium compounds (ATMACs). In this Chapter, the scope of work is broadened to consider previously unreported ATMAC C22, which belongs to a higher molecular weight class of ATMACs that is extensively used in hair care products (Lara-

Martin et al. 2009) at rates that have been exponentially increasing over the past three decades.

The primary inputs of QACs in the study areas are sewage-derived. Presently, there are no geochronological studies of QACs in sediments, nor any detailed time series data in any environmental matrix that would provide information about the time histories of inputs to the environment. In turn, better understanding of QAC distributions in dated sediment samples requires information about the history of their production, and other factors that affect their release to the environment. Unfortunately, there is also a paucity of published data about the history and trends in use of QACs. Levinson (1999) provided a review on the history of cationic surfactants used in fabric softeners, which supplements the work here on DTMAC use in the United States. Cationic surfactants were first used in the textile industry in the 1930s, and household fabric softeners did not appear until the 1950s. DTDMAC became the primary fabric softener, and came to comprise a large part of the market for cationic surfactants (Boethling 1984). Later, as concentrations of DTDMAC in sewage sludges and effluents were seen to be high, and due to concerns about biodegradability, there was a voluntary phase out of DTDMAC from fabric softeners in European countries in the early 1990s. Over that time, DTDMAC was replaced by classes of biodegradable esterquats (Gerike et al. 1994; Fernandez et al. 1996; Radke et al. 1999). The effect of this phase-out was seen in the dramatic reduction in sewage sludge concentrations measured in Switzerland between 1991 (2570 – 5870 μg/g) and 1994 (150-300 μg/g) (Fernandez et al. 1996). Recent measurements of DTDMAC compounds in sewage sludges from Austrian wastewater treatment plants (WWTPs) are even lower (Chapter 3), consistent with a continued decline of DTDMAC usage in Europe (Martinez-Carballo et al. 2007). The U.S. and other countries have not been as concerned about meeting European biodegradability standards; consequently, use of DTDMAC has not dropped to the same extent in this country (Levinson 1999), as supported by data from United States International Trade Commission (Figure 4.1). USITC data that has been reviewed to date indicates an appreciable increase in DTDMAC use between 1970 and maximal production in 1990 (38000 metric tons), followed by a more modest decrease until 1994 (27000 metric tons), after which production and sales reporting by the USITC were no long required. It is not clear the extent to which the U.S. DTMAC production data is comprehensive (Figure 4.1); plant seed oil-based formulations, and products listed as different salts of DTDMAC (e.g. sulfate), are not consistently listed. As production volumes of those listings are relatively small, they are not included in Figure 4.1. In addition, apparently not reflected in the USITC data is a large amount of additional DTDMAC used in drilling fluids (Boethling 1984), likely as organo-clay complexes. Given the complete absence of environmental measurements and the lack of production data available for DTDMAC in the U.S over recent years, the trends of DTDMAC release to the environment in the United States and many other parts of the world are unknown.

Other classes of QACs have antimicrobial properties, some serving as an important class of disinfectants for approximately 60 years. BAC was the first QAC disinfectant and its improved disinfectant properties were reported in 1935 (Schaeufele 1984). It appears that the first products based on BACs were likely available in the late 1940s (a partial history of U.S. production is seen in Figure 4.1). Considered as first-generation QAC disinfectants, BACs are still widely used, often in combination with other BACs. In addition, some BAC homologs (notably benzyloctadecylammonium, BAC 18) are also found in personal care products and even as algaecides. DADMACs, including pure C10:C10 or C8 to C10 mixes, represent later-generation QAC disinfectants that are used alone, or in combination with other compounds like BACs (Schaeufele 1984). DADMACs were introduced in the 1960's, and only recently were the first detections of DADMACs reported in the environment (Martinez-Carballo et al. 2007; Li and Brownawell 2009). Production data for these compounds have not appeared in the USITC reports reviewed to date.

Less is known about the history of use and production of the ATMAC compounds. ATMAC 16 and 18 were the targeted analytes in much of this study, with only trace amounts of ATMAC 12 and 14 detected. ATMACs with 14, 16 and 18 carbons also have many names and CAS numbers (Lara-Martin et al. 2009), but the mixture in which they are commonly found has often been referred to as cetrimide or cetrimonium. A search of the Web of Science of these terms reveals the first references to research on cetrimide skin sensitivity and as cetrimide shampoos in 1949 and 1951, resepectively (Cruickshank and Squire 1949; Hodges 1951).

After cessation of the USITC data reporting after 1994, other potential sources of data have been even more limited. For example, the production volume data are often reported within very large range. Recent production estimates are used to screen for chemicals of potential environmental concern in the U.S., and are discussed by Muir and Howard (2006) (Muir and Howard 2006). Not including polymers and other classes of chemicals, the U.S. High Production Volume (HPV) Chemical List includes over 2800 products manufactured or imported in amounts greater than 454 metric tons/year, and thousands more listed as Low Production Volume (LPV) Chemicals, with sales greater than 4.5 tons/year. The QACs targeted in this study would fall under both lists. In fact, one of the QACs with the highest concentrations, ATMAC 22, has reported production based on HPV data for 2002, which is just below the cut-off for inclusion in the HPV list (Lara-Martin et al. 2009), questioning the use of the current cut-off as a means to screen chemicals of potential concern and identify them as needing additional research.

From this introduction, it is seen that for many of the targeted QACs, there is information about the times that they might first appear in the sedimentological record. For a subset of these QACs, there is also information about U.S. production in sales between the mid-1950s and 1994. It is seen that the interpretation of different types of production estimate data are extremely complex, even when such data are required or even available. If QACs are well preserved under at least some sedimentary conditions, it is likely that studies of the sediment record will prove more meaningful in understanding which QACs have been used in greatest quantities, and which ones may be of increasing concern.

In this Chapter, the geochronologies of QACs are presented for sediment cores from WWTP-affected areas of Jamaica Bay and Hackensack River sites, and similarly in time series of surface sediment samples collected from a site in Newtown Creek and seven sites in Jamaica Bay, re-sampled in 1998, 2003, and 2008. The normalized time history profiles of different classes of QACs are compared at each site. Normalized concentrations profiles are used to provide information about the time history of QACs release in different areas. A pair of well studied and dated sediment cores (Bopp et al. 1993; Ferguson et al. 2003; Miller et al. 2008), collected eight years apart in a highly depositional area of Jamaica Bay, were also analyzed to test preservation of QACs, using a "matched core" approach that proved successful for demonstrating the persistence of wastewater-derived nonylphenol ethoxylates in the same samples (Ferguson et al. 2003). Finally, the possibility of using time-dependent ratios and profiles of QACs as new particle-reactive tracers to date the time of sediment deposition is considered.

4.2 Experimental section

4.2.1 Description of study sites and sample collection

Sediment core and surface sediment samples analyzed in this study were primarily collected from three sites in the NY/NJ Harbor complex including Jamaica Bay, the Hackensack River, and Newtown Creek, which receives effluent from the Newtown Creek WWTP (Figure 4.2). The Harbor complex has been heavily impacted by anthropogenic activities for over 100 years. It includes a watershed that encompasses over 42,000 km^2, portions of 5 states and a population of over 20 million people (Adams and Benyi 2003). In total, the Harbor discharges a mean flow of nearly 16,000 million gallons per day (MGD) of fresh water including 2,300 MGD from wastewater treatment plants, storm drains, and combined sewer overflows (CSOs) (Adams and Benyi 2003); in combination the three study areas are directly influenced by over 4 million people, integrating the influence from a large cross section of urban populations across different sewersheds.

4.2.1.1. Jamaica Bay sediments.

Jamaica Bay is an extensively urbanized estuary surrounded by the boroughs of Queens and Brooklyn in New York City. Jamaica Bay receives most of its fresh water as effluents from four major WWTPs (see Figure 1.3) that discharge more than 300 MGD wastewater into the Bay (Swanson and West-Valle 1992). Numerous studies have been conducted in Jamaica Bay to examine the distribution of fate of sewage derived organic contaminants. The current study relied upon two separate approaches to look at the time histories of QAC inputs and their post-depositional in-situ diagenetic alteration. Samples from two dated gravity cores (Bopp et al. 1993; Ferguson et al. 2003; Miller et al. 2008) were collected from the same sampling site eight years apart (1986 JB13 and 1994 JB16) in Grassy Bay. This location and a nearby sediment grab sample station (Figure 4.2) are situated in a locally deep basin characterized by high sediment deposition rate, located proximate to John F. Kennedy International Airport and direct sewage inputs to Grassy Bay come from the Jamaica WWTP. Full description of the cores, sampling methods, and dating are provided in Ferguson et al., (2003) who used the same set of samples to study the processes affecting the input and preservation of nonylphenolethoxylates (NPEO) and their metabolites at this site. The time histories of NPEO concentrations and compositions of parent and metabolite compounds were compared to known production and sales data. Their metabolites, could be related to two upgrades (in 1963 and 1978) in the history of sewage treatment at the Jamaica (Ferguson et al. 2003). Utilized again in this work, analysis of core samples, dated to be of the same age, were compared to examine differences in concentrations and compositions of NPEOs that may be diagnostic of in-situ transformations of target chemicals over the 8 year period between the two cores were obtained. This concept has been developed and more fully discussed elsewhere (Bopp et al. 1993; Ferguson et al. 2003).

QACs were also analyzed in a time series of surface grab samples (0-5 cm intervals) collected at seven Jamaica Bay stations, characterized as muddy high organic contaminant locations. Splits of samples from 1998 and 2003 samples were provided by an EPA sponsored Regional Environmental Monitoring and Assessment Program (REMAP) in 1998 (Adams and Benyi 2003). In August, 2008 surface grab samples were again obtained from the same locations by this group, utilizing the GPS data provided from the 2003 study.

4.2.1.2. Hackensack River sediment cores samples.

A geochronology of contaminant deposition at a depositional site in the upper tidal portion of the Hackensack River was constructed from a ^{7}Be and ^{137}Cs-dated gravity cores collected in 1995 (Hack 14B), as well as a 0-2 cm ^{7}Be bearing sample from the same location collected in 2003 (Hack 14F). This site is approximately 3 miles downstream of the Bergen county WWTP which was placed in service in 1951 and provided secondary treatment with a design capacity of 20MGD. There were several upgrades of the treatment capacity to match the increasing population on the sewershed in 1964 (50MGD), 1977, (62.5 MGD) and present (109 MGD). Today, the WWTP serve a population of about 536,000 in 46 municipalities.

4.2.1.3. Newtown Creek surface sediments.

^{7}Be bearing sediments samples (0-2 cm) were obtained from gravity cores collected every couple of years between 1987 and 2001 (provided courtesy of Richard Bopp). These samples provide dates of surface sediment contamination in a depositional area that receives effluent from one of the largest WWTPs in the U.S. with 310 MGD. The plant was built in 1967 and used a high-rate activated sludge process without primary sedimentation. Unlike other WWTPs in the Harbor complex, effluents do not meet regulatory requirements for treatment. The plant removes around 65% BOD_5 and 75% TSS. The upgrade of Newtown Creek WWTP aiming at 85% BOD_5 removal by 2013 involves the construction of a series of new grit, aeration and sedimentation tanks.

4.2.1.4. Surficial sediments from the former DWD-106 site.

To compare the compositions of QACs determined at shallow water sites proximate to municipal waste water influence, two sediment samples were analyzed from the former 106-mile deep water disposal site (DWD-106) off New Jersey. Those samples were from sites in approximately 2600 m of water, and collected in August, 1991, approximately a month after sewage sludge disposal (1986-1991) ceased at the 106 mile site. Samples collection and site description is provided in previous reference (Lamoereux thesis, 1996) and results presented for the two samples also containing the highest levels of sewage tracers Ag and linear alkyl benzene (LAB).

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4.2.2. Sample analysis

The methods for analysis of QACs are detailed in Chapters 2 and 3. In this chapter, concentrations of ATMAC 22 (calculated based on the response factor for ATMAC 18) have also been estimated. The average recovery of the surrogate standard DADMAC C12:C12 was 105±15% (n = 51). The sediment geochronologies of different classes of QACs are compared to that of nonylphenol ethoxylate metabolites, and antimicrobial compounds triclosan and triclocarban that have been measured in the same samples and reported elsewhere (Ferguson et al. 2003; Miller et al. 2008).

4.3 Result and Discussion

4.3.1. QACs profiles in sediment cores from Jamaica Bay

The concentrations of different classes of QACs in cores in Jamaica Bay are shown in Figure 4.3 as a function of estimated age of the sediment samples. These results are compared to results from analysis of the same samples for NPEO metabolites (Ferguson et al. 2003), with data modified here to include only NP, and NP(1-3)EO to allow for better comparison with data from the other data presented in this Chapter The JB16 core was sampled in 1996. In order to examine changes in sediment concentrations to more recent times, the profiles depicted for each class of QACs includes results from more recently collected surfacial (0-5 cm) grab samples from a site very nearby and well within the depositional area Grassy Bay (Figure 4.2). Those samples collected in 1998, 2003, and 2008. Based on analysis of ATMAC 22/18 ratios (discussed below and calculation showed in Apendix Figure A1 and Table A3), estimates of the approximated average ages of the 1998 and 2003 grab samples were 1999.3 and 2002.8, respectively. That analysis is based on the linear regression of log ATMAC 22/18 using a large data base formatted ^{7}Be bearing sediments from a number of sites in the lower Hudson Basin, which were sampled between 1978 and 2005. This analysis provides more confidence for including the more recent grab sample to extend the gechronologies established for JB13 and JB16 cores

There are many features of the data shown that are noteworthy. The surface and peak concentrations of each class of QAC follow the same order that was found in the

Harbor-wide survey of surface samples presented in Chapter 3; i.e., the concentrations of DTDMAC > BAC > ATMAC > DADMAC. Importantly, as was also observed for individual and total NPEOs (Ferguson et al. 2003), the concentrations of each class of QACs are very similar in three depth intervals analyzed in the 1996 collected core that directly correspond with the samples in the 1988 collected core that share the same estimated date of deposition (Figure 4.3). These results are consistent with the preservation of QACs in sedimentary environments over the 8 year period between collections of the two cores. We note that this preservation occurs in a highly depositional sediment regime that likely is suboxic to anoxic.

There are at least two lines of evidence that suggest that the depth profiles of QACs are controlled by sediment burial rather than physical or biological mixing. First, the sediment profiles of the different classes of QACs differ greatly from each other. Secondly, the there are sharp concentration gradients for several of the QACs over the upper 2 to 16 cm of the JB16 core. Those concentration gradients, range from a sharp decline in ATMAC 22 with depth, to subsurface maxima in other QAC profiles. Thus, the differences in profiles of three very particle reactive contaminants are largely controlled by differences in their inputs over time, and likely most importantly from the Jamaica WWTP, proximal to the sites.

4.3.1.1. DTDMAC.

As seen earlier, DTDMAC is the most abundant chemical at this site. A subsurface maximum in DTDMAC concentrations (510 μg/g) corresponds to an estimated 1987 date in the vertical midpoint of that sample, consistent with the push in Europe during that time to remove DTDMAC from fabric softeners and the complete voluntary phase-out of DTDMAC in some European countries of such products in the early 1990’s. The concentrations of DTDMAC in surface sediments has leveled off at concentrations (~100 μg/g) from 1995 to 2008. Current levels of DTDMAC are then approximately 20% of that found at the maximum deeper in the core, probably mostly the result of a shift of fabric softener ingredients to much more biodegradable (Gerike et al. 1994; Fernandez et al. 1996; Radke et al. 1999) classes of “esterquats”, or possibly other classes of compounds also used as fabric softeners (Levinson 1999). However, very high levels of DTDMAC continue to be present in Jamaica Bay and other sewage affected estuarine surface sediments. The drop in DTDMAC concentration observed in the U.S. sediments is likely much smaller than the reduction that would be found in European coastal waters, given the sharp decrease in DTDMAC use in Europe that occurred over a short time. As mentioned above, there was an approximate 20-fold drop in DTDMAC seen in sewage sludge samples from Switzerland between 1991 (2570 – 5870 μg/g) and 1994 (150-300 μg/g) (Fernandez et al. 1996). An additional more than order of magnitude drop is seen when one compares concentrations in the 1994 Swiss sludges and those collected in 2004 from Austrian WWTPs. The smaller drop in DTDMAC inputs in the U.S. is very much consistent with both modest drops in U.S. production data between 1990 and 1994 (Figure 4.1), and the with the statements found in Levinson (1999) stating that use of DTDMAC in the U.S. had fallen less sharply in comparison to Europe, and was leveling off at the time of his paper.

The times of first appearance of DTDMACs and other QACs analyzed can not be precisely given, but the data in Figure 4.3 is consistent with the advent of important uses of DTDMAC in fabric softeners starting around the mid to late 1950s (Levinson 1999). Further research studies of additional high resolution dated sediment cores and a review of the earlier USITC production data reports, should constrain such estimates. One feature of the sediment records of DTDMAC, BAC, and ATMAC (all with the longest history of use) that is not yet understood well is the presence of higher relative levels of DTDMAC is buried sediments during the time period between 1960 and 1975. If per capita use of DTDMAC and the efficiency of sewage treatment were constant in this area, the production data provided in Figure 4.1 suggests that DTDMAC should be observed to increase to a much greater degree between the early 1960s and peak levels around 1990; a similar argument could also be made for BACs during the time period between 1970 and 1990. Ferguson et al. (2003), explained similar bumps in NPEO concentrations around this time as being related to a combination of increased NPEO production and upgrades in WWTP treatment that occurred in 1963 (higher flow capacity) and 1978 (a higher level of secondary treatment) that may have discharged more untreated NPEOs and its metabolites (Ferguson et al. 2003). Detailed analysis of the data argues against this being the only reason for the trends observed, but should wait until QAC production data is obtained.

4.2.1.2. BACs.

BACs have until recently been the most important class of QACs with respect to total concentrations in sediments. The first appearance of BAC in this core is close to 1950, again consistent with the production history (Schaeufele 1984), and is followed by a dramatic rise concentrations into the mid-1960's, and then remains at high levels till the early 1980s.

Since that time the levels of BACs are observed to have leveled off. As mentioned above the absence of significant increase in BACs from 1970 and 1990 does not match the estimate of increased production shown in Figure 4.1. A likely explanation for this is there have been two upgrades in sewage treatment at the plant during this time period, and that the expected increase is offset by increased removal during that time period. Possible interpretation should wait until there is more of the USITC production and sales data gathered, and a closer examination of what is known about the time history of uses of different BAC mixtures that have been sold over time. For example, it is suggested that even the composition of BAC 12, 14, and 16 changed markedly through different generations and formulations of more common disinfectants. More limited data provided by the USITC reports hints at the higher relative use of more persistent BAC 18 going back in time before 1990, which would be consistent with sediment core results from the Hackensack core (dicussed below).

BAC concentrations are much lower than those for DTDMAC in Jamaica Bay and elsewhere, yet the annual production is much closer (Figure 4.1). A simple analysis of that data has been conducted to examine this relationship further for only three sediment intervals that are dated more recently than the last upgrade at the Jamaica WWTP and where there are sales data. BAC is greatly depleted relative to DTDMAC in these sediments to where 4.7 – 7.6% of the expected ratio based on production. In many respects this depletion is consistent with mass balance- based estimates of biodegradation of BACs estimated for WWTPs in Austria (Clara et al. 2007), and the great depletion of BACs relative to DTDMAC in surficial sediment samples collected near and away from CSOs where the extent of sewage treatment varies tremendously.

4.2.1.3 DADMACs.

DADMACs are a newer generation of disinfectants that can be used as different homolog mixtures (DADMAC C8:C10, C8:C8, C10:C10), or as purer products, such as didecyldimethylamonium. DADMACs are often sold both with BAC and on their own (Clara et al. 2007). Sometimes referred to as "Twin chain QACs" , DADMAC disinfectants were introduced in 1965, in agreement with estimated first appearance in the Jamaica Bay core. General but not continuous increase in DADMAC levels has been observed since then. The drop in DADMAC concentrations throughout the 1990s is not, however, reflected in geochronologies established at the Hackensack and Newtown Creek samples discussed below. Unfortunately, the interpretation of DADMAC trends is complicated by a near absence of production and sales data in the USITC reports. DADMACs disinfectant mixtures are generally more effective than BAC when the latter are used alone (www.antrixgroup.com). Thus, given these uncertain factors and the controls on the vertical profiles in BACs, if is not possible at this time to determine how much of the drop in absolute concentrations of BACs over time can be explained by the smaller increase (in absolute concentration) of DADMAC in this core and related data presented below.

4.3.1.4. ATMACs.

The profiles of ATMAC 14-18 (dominated by ATMAC 16 and 18) largely mirrors that of DTDMAC, although the first appearance (around 1950) of ATMAC is earlier (approximately in agreement with the estimated time period of first appearance and the first literature reports of it being in personal care products or applications in 1949 and 1951 (Cruickshank and Squire 1949; Hodges 1951). There are inconsistent reports of the production of ATMAC 16 and ATMAC 16 and 18 (trimethyl(tallow)ammonium chloride) in the USITC reports. However, as shown elsewhere, within the more recent

HPV data collected by the EPA, there are 13 product lines listed that contain significant portions of ATMAC 16 and 18; without information from industry sources, it does not seem prudent to interpret the USITC sales data at this time.

The sediment profile of ATMAC 22 is plotted for comparative purposes in Figure 4.3, and illustrates what is an exponential increase in concentrations of this compound over the last 30 years, with a doubling time of approximately 4 years (Lara-Martin et al. 2009). The discovery, confirmation, and detailed interpretation of ATMAC 22 are described in a related report (Lara-Martin et al. 2009). ATMAC 22 is the primary homolog (lesser amounts of ATMAC 20) in formulations commonly referred to as behentrimonium chloride or behentrimonium methosulfate. It has become a product of choice in many personal care products and a recent and ever-expanding database lists it as an ingredient in over 1500 over the counter products (http://www.cosmeticsdatabase.com), most of which are hair care products. It appears that behentrimonium is replacing ATMAC 16 and 18 in personal care products not only because of its characteristics related to hair (e.g., volumizing; combability), but because with a longer alkyl chain length it is less irritating to skin, and has been approved for use at concentrations four times higher than for ATMAC 16 and 18 in personal care products that have significant skin contact times (European Commission 2007). Hence, it appears that this is a case of product replacement that has not been recognized until now. Below it is argued that there appears to be powerful information found in the relative proportions of ATMAC 22 and other more persistent QACs as geochemical tracers.

4.3.1.5. NPEO metabolites.

The profiles and biogeochemistry of NPEOs in these cores is described at length elsewhere (Ferguson et al. 2003), and the general features of the profile for NP(0-3)EO shown in Figure 4.3 are largely the same as that shown earlier for the sum of NPEOs with up to 15 ethoxymers. The first appearance of NPEO again (approximately 1950) is very similar to that found in the USITC (calculated from the USITC data in by Ferguson and coworkers, 2003). The concentrations of NPEO is quite high in these sediments (for the sum of all NPEOs peaking at approximately 40 μg/g), but still small in comparison to

DTMAC levels at the time period about 1990 (510 μg/g). However, an analogous calculation to that provided for BAC above, estimates that NPEO levels are found at 1.7 – 2.9% of the expected ratio, given assumptions that include the same ratio of use in the Jamaica Bay sewershed as produced nationwide and that the same fraction enters the municipal wastewater stream. The large apparent loss of NPEOs is not inconsistent with the high fractions of NPEOs that are lost to microbial degradation during sewage treatment and that only about 20% of relatively more soluble NPEO metabolites are found to be in the suspended particle phase in surface waters of Jamaica Bay (Ferguson et al. 2001).

4.3.2. Newtown Creek surface sediments and Hackensack River core results.

The estimated time histories of QACs obtained from the highly depositional sediments from Newtown Creek (Figure 4.4) and the Hackensack River (Figure 4.5) sites are consistent, in many ways, with each other and with the results discussed above for the Jamaica Bay core. The record of QAC concentrations in surface sediments at Newtown Creek sediments only dates back to 1987, and the sediment record in the sewage impacted Hackensack sediment core site are not dated, at this time, with the same detail as they are in the case of the Jamaica Bay site. The most notable differences observed at the Newtown Creek site are the much higher concentrations observed for BACs, DADMACs, and C14-C18 ATMACs at Newtown Creek, in contrast to very similar concentrations observed between the two sites for DTDMAC and ATMAC 22; the most particle reactive and persistent class of QACs. The explanation for the higher concentrations of all BACs, DADMACs and ATMAC 14-18 in Newtown Creek sediments could be due lower inputs of these contaminants from the Jamaica Bay sewershed in comparison to the rest of the metropolitan Harbor complex (Chapter 3), the close proximity to adjacent WWTP at the more confined Newtown Creek site or to lower levels of biological treatment that exist at the Newtown Creek Plant. This very large WWTP provides the least efficient sewage treatment in the regions and does not meet requirements of the Clean Water for removal of biological oxygen demand, as do the other WWTPs in the region. The latter explanation would be consistent with these compounds being the most readily biodegradable QACs considered here (Chapter 3).

The profiles of QACs at the Hackensack site are qualitatively similar to that seen in Jamaica Bay. Times of first appearance and peak concentrations, and relative compositions of QACs in upper portions of the cores are very similar; this is best illustrated in the normalized concentration profiles that are overlain in Figure 4.6. One notable difference in the profiles at the two sites include the more gradual increase in ATMAC and DTDMAC concentrations between the 1950s and samples dated to the 1960s and 1970s. It is of interest to point out that evidence exists that the population served by the Bergen County WWTP appears to have increased faster over the past several decades than it has for the area served by the Jamaica WWTPs; population demographic changes need to be gathered to test this hypothesis. However, it is known that Bergen County WWTP, upstream of the Hackensack site, was constructed with full secondary treatment in 1951 with a capacity of 20 MGD but increased needs from a growing population and the number of municipalities served increased rapidly over time (http://www.bcua.org). The first upgrade in plant capacity occurred 1964 to 50 MGD. Additional plant expansion has continued in several phases since then and presently has a treatment capacity of 109 MGD. In contrast the Jamaica WWTP, constructed in 1939 has required only one upgrade in capacity, from 60 to 100 MGD in 1963 (Ferguson et al. 2003).

A second major difference seen in the sediment geochronologies at the two sites include is the high levels of total BACs that exist in deeper sections of the Hackensack Core. The two deep samples corresponding to the mid 1950s and 1960s are dominated by BAC 18 (80 – 82% of total BACs). In other sediment samples from the same core BAC 18 only averages 38% of total BACs; similary BAC 18 is 47-51% of total BACs in the JB16 core samples from the same time period. Thus, much of the BAC observed is due to a higher relative input of BAC 18 that may be specific to this area of the Hackensack River. BAC 18 is not sold as a disinfectant and has other uses that currently include use in personal care products and algaecides for pools. However, the major uses of BAC 18, and how they may have changed over time, require further investigation. It is possible that they were once highly used in industries that existed in the Bergen County area.

4.3.3 Variation of QAC concentrations and compositions in Jamaica Bay surface sediments over the past decade.

Data presented above indicate that a range of QACs are well preserved in the cores collected in Grassy Bay, a high sedimentation rate, where sediments are highly reducing and significant populations of benthic infauna have not been detected (Adams and Benyi 2003). But are QACs persistent in a wider range of sedimentary environments? Insight into this question is provided in comparisons in QAC concentrations measured in seven sites collected on three different dates throughout muddy portions of the Bay in 1998, 2003 and again in 2008 (Figure 4.7) Generally there is close agreement between the changes in QAC concentrations seen at all these sites and those estimated from the Grassy Bay core. Concentrations of QACs at the different sites are remarkably similar to each other with only Grassy Bay site (proximate to the Jamaica WWTP) having much higher levels of QACs. There is no explanation for the much lower level of DTDMAC, BACs and DADMAC in one of the 21 samples compared in this analysis (the JB15 site collected in 2003). The sample was re-analyzed for DTDMAC with and the same result was obtained. The biggest difference between that site and the other six collected at the same time is that it occurs in very shallow water. However, the similarity in the ATMAC 16 and 18 concentrations measured in the same sample, to the concentrations determined for 1998 and 2008 samples remains a mystery.

The observations that QAC concentrations are relatively similar between sites that likely have very different depositional and biogeochemical properties and vary with time in a manner consistent with the sediment core record provides a measure of confidence that QACs are quite persistent after incorporation into sediment beds at a range of sites that are relatively muddy. It is argued below that the surface grab samples analyzed at the seven stations are likely highly depositional areas, based upon the measured time-sensitive ratios of ATMAC C22/18.

4.3.4 Application of QAC homologs as geochorological tracer in the sediments from NY/NJ Harbor complex

The possibility for obtaining chronological information from sediment cores from QAC profiles is well illustrated in Figure 4.6 and discussed above are apparent. Such tools could include times of first appearance for DTDMACs and DADMACs, and the very pronounced first appearance of ATMAC 22 in around the 1980. The subsurface maximum and well understood timing of drops in DTDMAC levels in the early 1990s, can also provide useful geochemical information in some applications. Here we examine the changes in ratio of various classes of QAC homologs to determine the sensitivity of such ratios as either time markers or tools to determine relative transport or persistence of different classes of compounds.

Figure 4.8 illustrates the changes in ratios of different classes of QACs normalized to DTDMAC as a function of time and contrasts those ratios at the different sites studied here. In the case of BACs, DADMACs, and ATMAC 14-18, there are distinct differences in the ratios that are apparent between sites, and the utility of using such ratios is likely to be specific to sediments that are near to each other or are affected only by one source of QACs. Those possible applications are not considered further here.

The results for normalized ratios for ATMAC 22/DTDMAC (Figure 4.8) and especially for ATMAC22/ATMAC18 (Figure 4.9) are of much greater interest. The difference in these ratios over the past 30 years is seen to vary in a consistent manner at all sites, increasing approximately 1000-fold over time. The actual ratios are seen to be much more similar between sites than those that occur for other analytes, perhaps due to their greater persistence or widespread use in many consumer products. It is also interesting to note that relationships observed at different sites appears less variable when ATMAC 22 is normalized to ATMAC 18 (Figure 4.9) rather than when normalized to DTDMAC (Figure 4.8). This may to related to ATMAC 22 acting as a replacement for ATMAC 14-18 in many products

Also plotted are the QAC/DTDMAC (Figure 4.8) and ATMAC 22/ATMAC 18 (Figure 4.9) ratios determined in two surface samples collected at the former 106 mile Deep Water Dumpsite. The timing of the sludge dumping is restricted to 1996-2001. The ratios of some QACs (e.g., of more soluble total BACs and DADMAC) are on the low end of those measured in sediment samples from the Harbor complex, that are primarily obtained at high sediment accumulation sites; the variability of the ratios seen for those QACs makes hardly any conclusions from those data, although the compositions of individual QAC homologs of different hydrophobicites should be examined. More interestingly is the similarity ratios at the DWD site to the age predicted from the inshore sewage affected sites. The fact that this analysis was conducted when the concentrations of ATMAC C22 were much lower than they are recently (combined with the very low amount of sediment and extract analyzed) is reason to further test the utility of ATMAC 22 and composition of the most particle reactive QACs as tracers of sediment transport and sediment burial/mixing in sediments far removed from coastal settings.

The relationship betweenATMAC 22/18 and sediment age has been analyzed further in Appendix Figure A1 and Table A3. A larger data base of data from ^{7}Be sediment samples (including both the data shown in Figure 4.9 and another 45 surface sediment samples collected in 1998-2005 (Chapter 5). From the linear correlation from these high deposition sediment environments, a predicted average age of surface grab samples (those from the seven Jamaica Bay sites here, and the other 38 REMAP surface samples from 1998 described in Chapter 3).

Finally, the persistence of many QACs in surface sediment at the 106 mile site is impressive and provides another useful test of the persistence of this class of compounds in sediments that are more oxidized, more reworked by benthic infauna and where desorption during transport is much more likely. In contrast, compelling evidence was provided elsewhere that other very hydrophobic sewage sludge derived tracers such as linear alkylbenzenes were degraded (over 90% relative to excess silver) or otherwise lost after their deposition to sediments (comparisons of compositions to sludge as well as deep sediment trap samples).

In conclusion this study provides multiple lines of evidence that QACs can not only be analyzed with amazing sensitivity, but that they may be very conservative particle tracers that are specific to sources that are sewage derived. With respect to cross margin transport or deposition in offshore marine sediments (e.g., as test of sediment burial rates, as opposed to mixing processes), the limited evidence provided here suggests that there are potential applications that should be explored further in future studies.

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Figure 4.1. Production history of DTDMAC and BAC in United States (1960-1994)

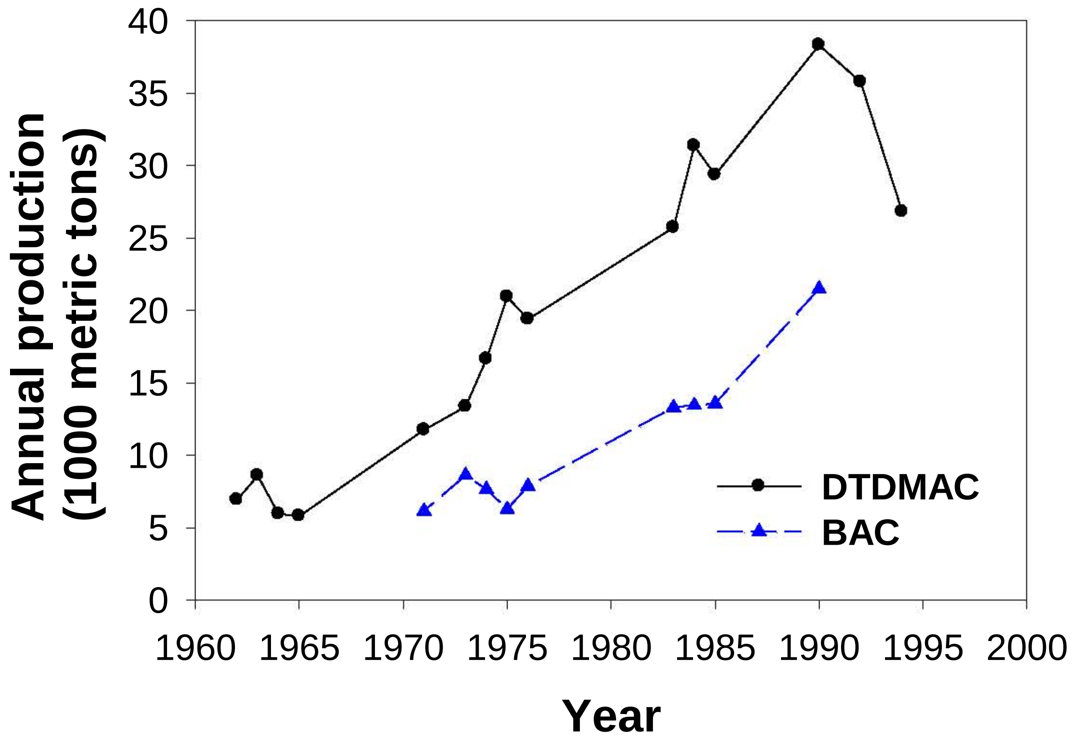


Figure 4.2. Map of sample sites for this chapter. Red circles correspond to sediment core sites in Jamaica Bay and the Hackensack River; the blue circle is location of the Newtown Creek; and the Jamaica Bay surface grab samples indicated by the black squares.

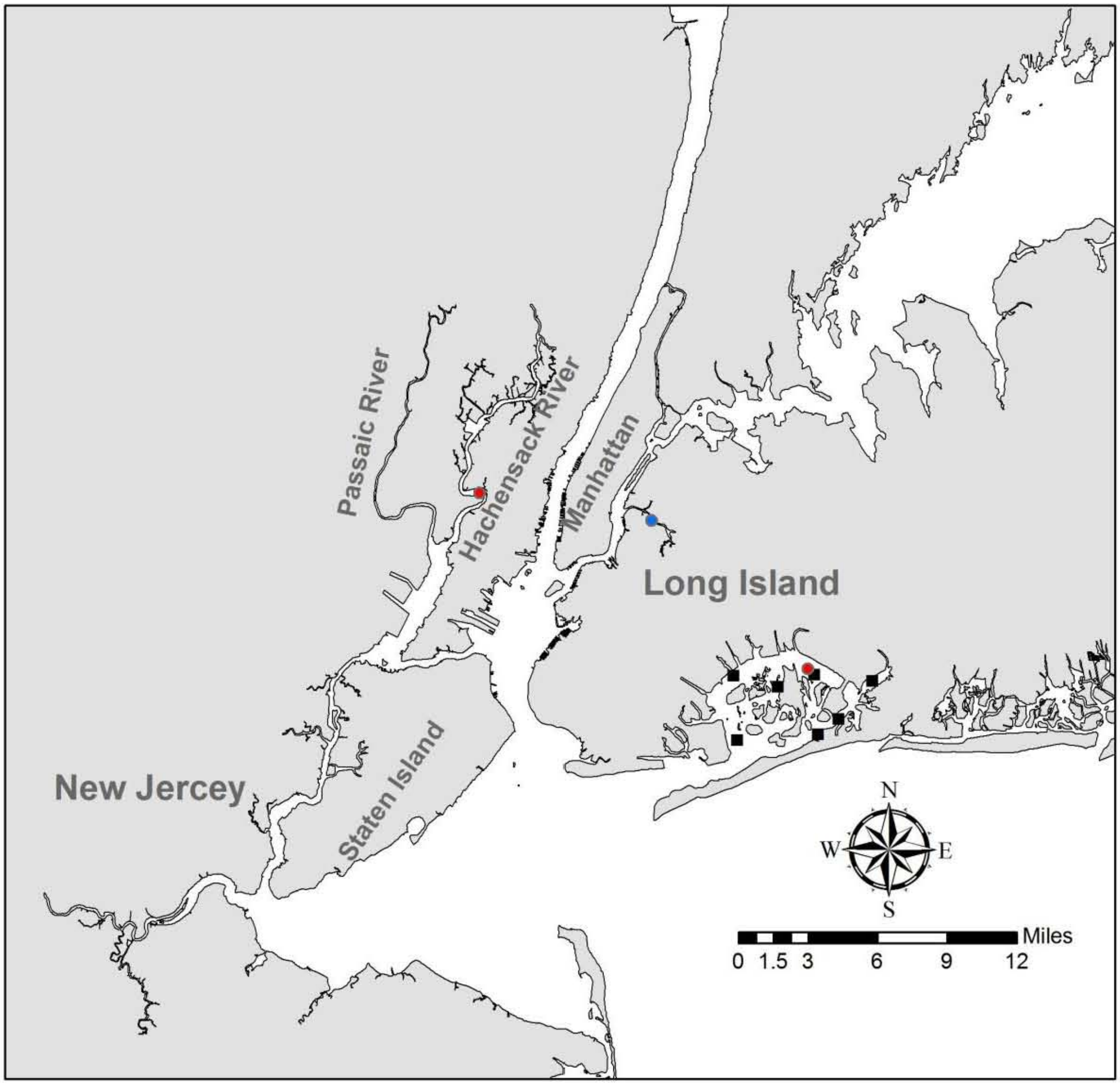


Figure 4.3. Vertical profiles of different classes of total QACs in the dated sediment core from Jamaica Bay collected in 1996 (JB16) (black bar) and matched core collected in 1988 (JB13) (red bar). Profiles for QACs are extended with data from surficial (0-5 cm) sediment samples obtained in 1998, 2003, and 2008 from a station nearby to the sediment core site (black square). For comparison the NPEO metabolite profile from the JB13 core is shown; the data plotted is modified from Ferguson et al., (2003) to include only nonylphenol, and the NP(1-3)EO metabolites.

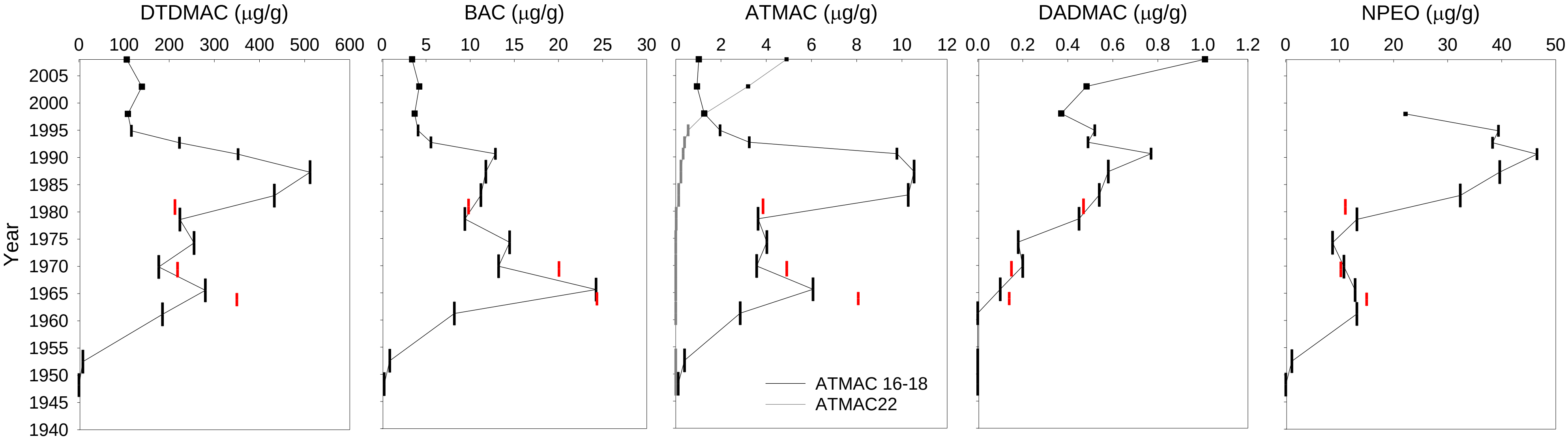


Figure 4.4. Concentration of total concentrations of different classes of QACs and NP(1-3)EO plotted vs the time of sampling surficial sediments (0-2 cm) at a site next to the Newtown Creek WWTP.

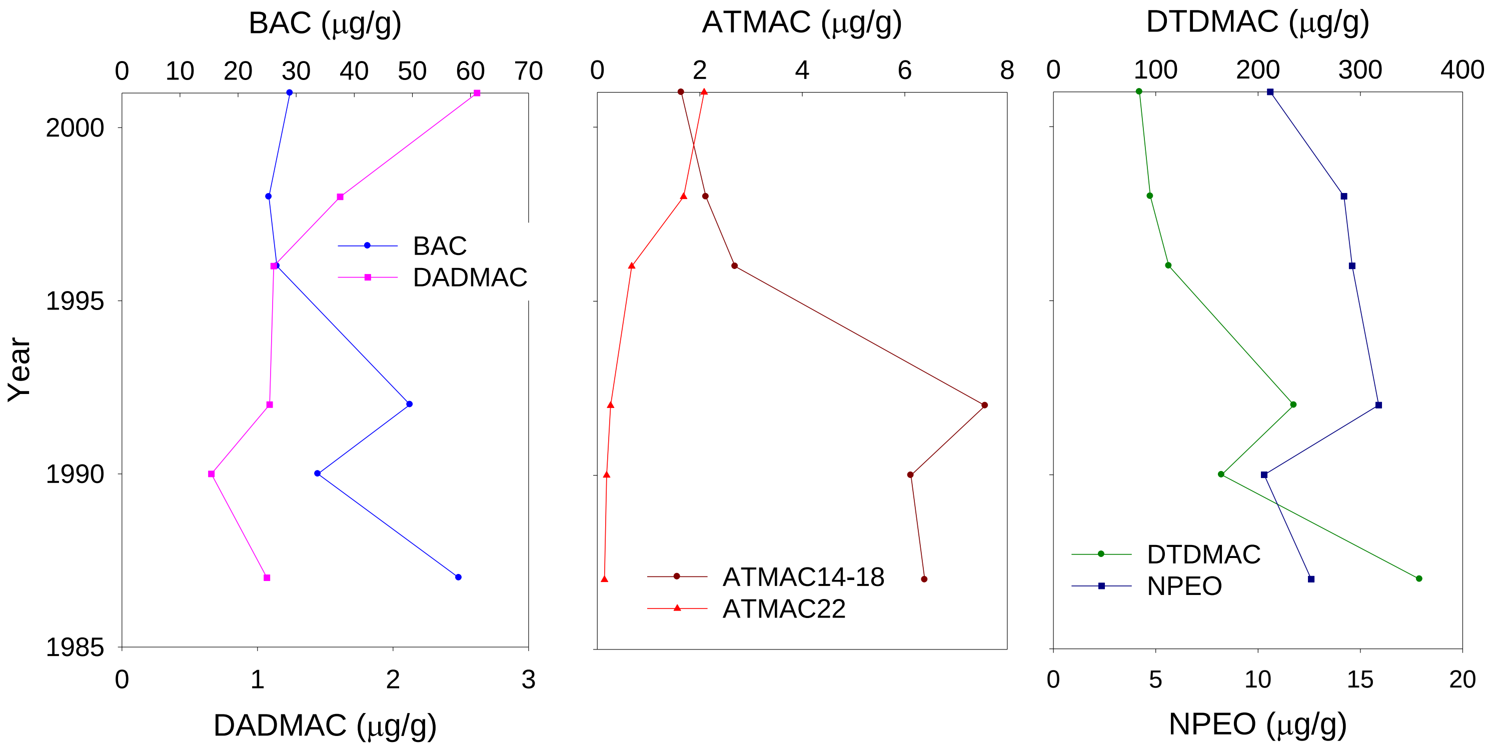


Figure 4.5. Concentration profiles of QACs and NPEO metabolites as a function of estimated average date from a sediment core samples from a Hackensack River core collected in 1995, combined with results of analysis of a surficial sediment sample from another core at the site obtained in 2003; the depth profiles of 137Cs and the same analytes are provided in Appendix Figure A2.

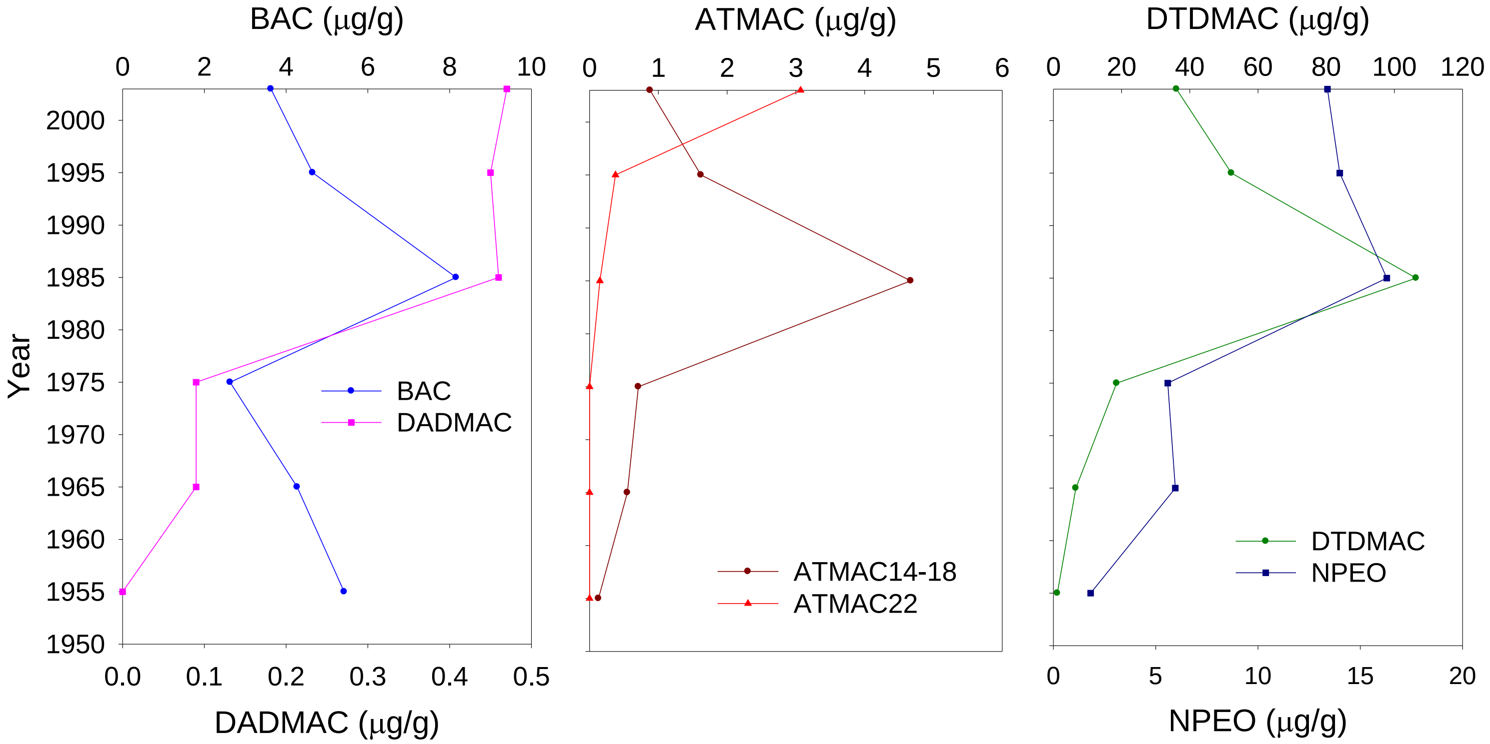


Figure 4.6. Comparison of normalized profiles of DTDMAC, BAC, ATMAC, DADMAC, and NPEO from Jamaica Bay, Newtown Creek, and Hackensack River. Each profile is normalized to the concentration measured that most closely approximated 1987.

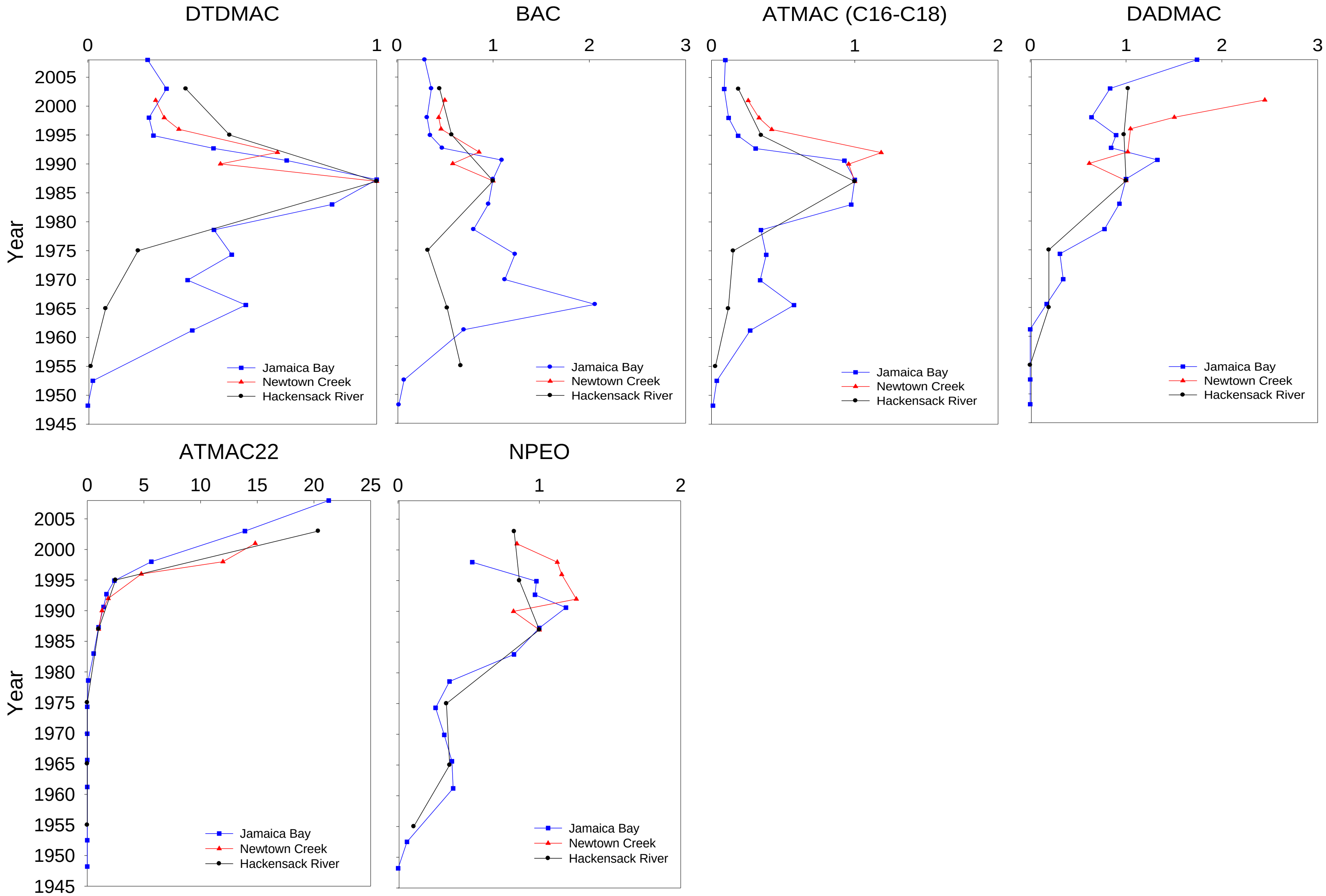


Figure 4.7. Variation of DTDMAC, BAC, ATMAC and DADMAC in surficial sediment (0-5 cm) samples collected over a ten year time frame at each of seven stations in Jamaica Bay

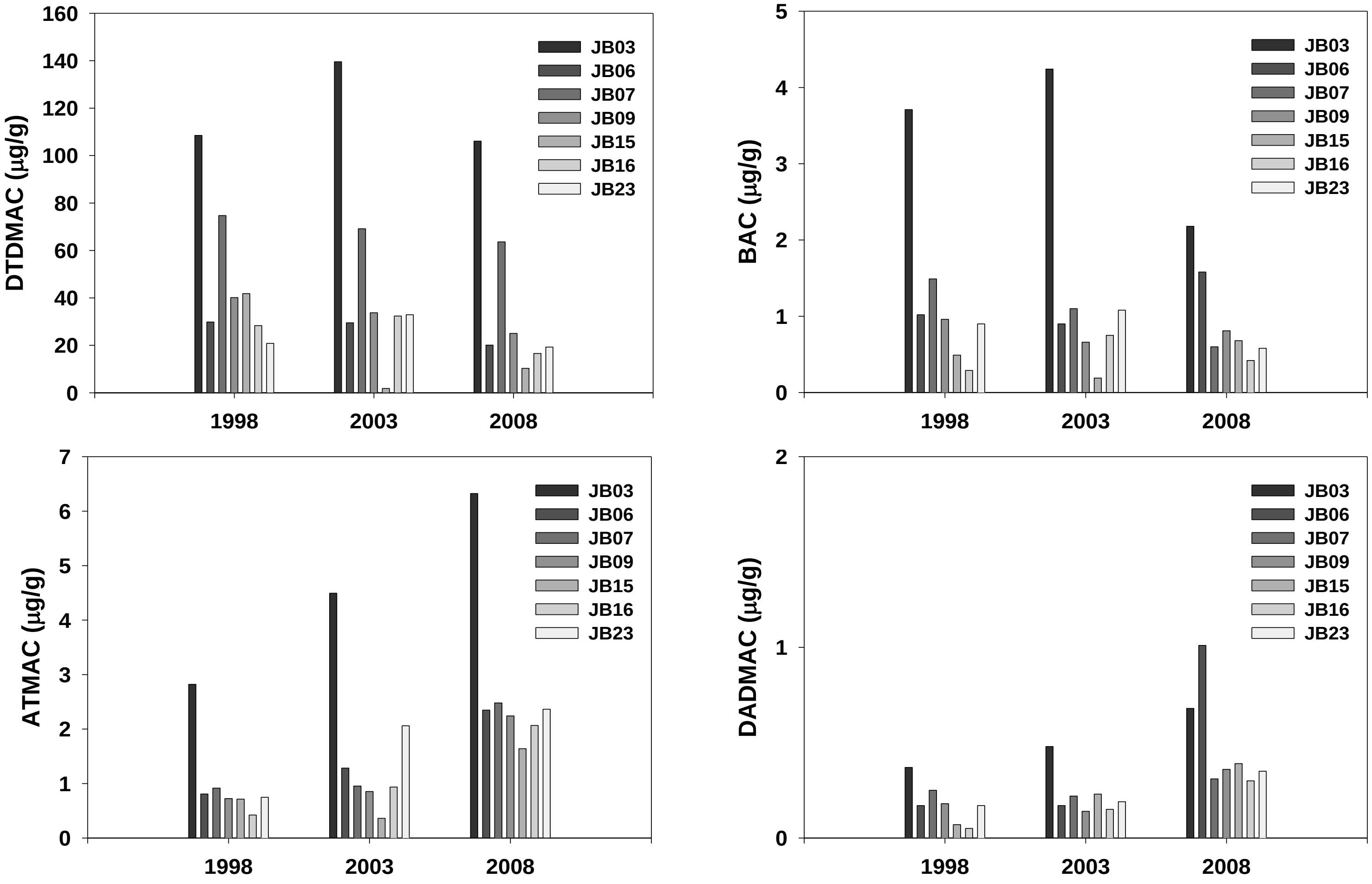


Figure 4.8. Historical changes in compositions of different classes of QACs normalized to DTDMAC measured in sediment core sites from the Jamaica Bay and the Hackensack River; time series measurements of surficial sediments at Newtown Creek and seven Jamaica Bay sites; and similar ratios obtained in two surface sediments analyzed from the former 106 Mile Deep Water Sewage Disposal Site, which represents the signal from dumping sewage sludge from the NY/NJ metropolitan area between 1986 and 1991.

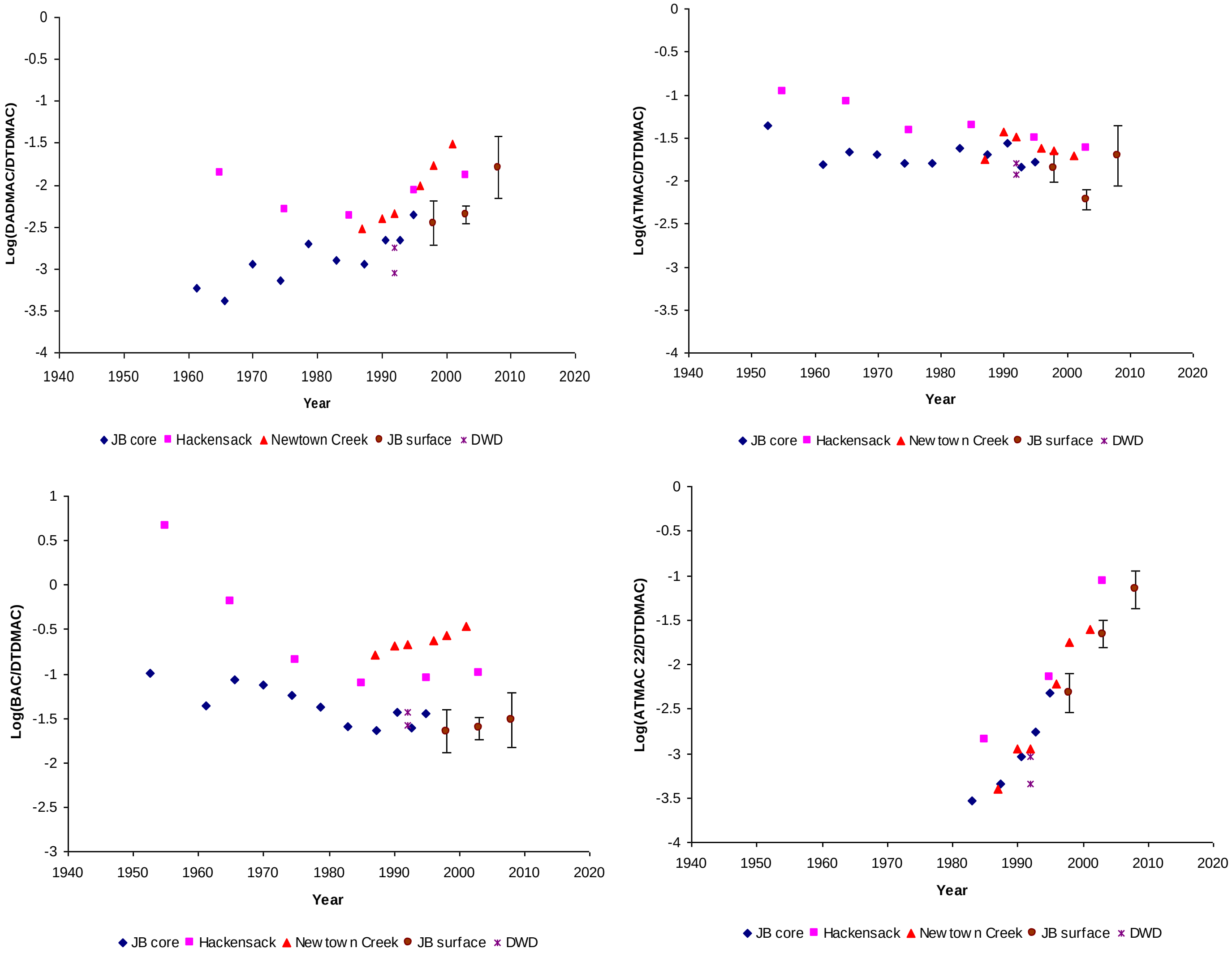
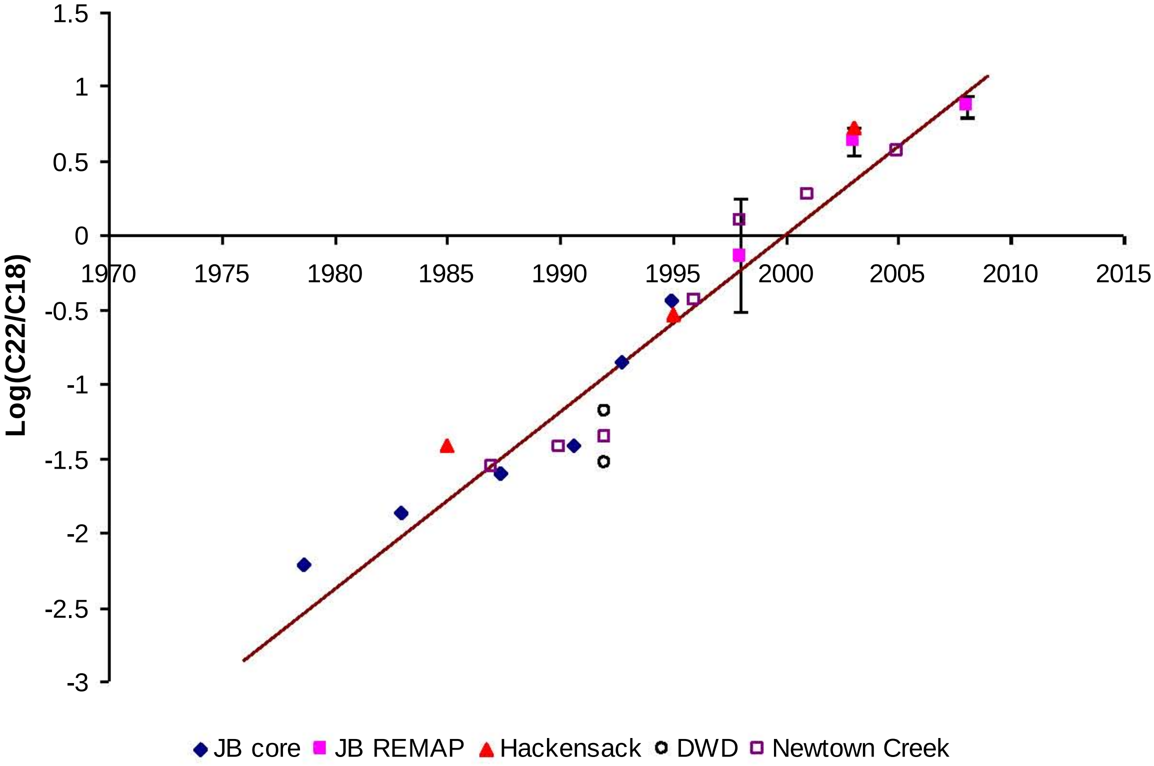


Figure 4.9. Historical changes in the concentration of ATMAC 22 normalized to ATMAC 18 for different data sets, as seen in Figure 4.8. The solid line represents the linear regression of all data, using the means of the seven Jamaica Bay ATMAC 22/ATMAC 18 value



CHAPTER FIVE: APPLICATION OF DTDMAC AS A TRACER FOR THE SOURCES AND DIFFERENTIAL FATE OF ENDOCRINE DISRUPTING COMPOUNDS (EDCS) IN SEDIMENTS OF THE LOWER HUDSON BASIN

4.1 Introduction

Large-scale production of numerous synthetic organic chemicals and global consumption of fossil fuels have risen sharply since early last century. Unfortunately, most of the chemicals can find their way to the natural environment through a combination of point and non-point sources and threaten the health of humans and wildlife. We are often challenged by our limited knowledge of the sources and pathways of these chemicals to the environment, as well as their ultimate fates. From the perspective of finding management solutions, or the allocation of sources of natural resource damages, identification of contaminant source is essential for establishing contaminant control and remediation policies. For the study of anthropogenic contaminants in the natural environment, the use of molecular tracers, which can provide information about sources and geochemical processes affecting the distributions of chemicals can be a powerful tool (Eganhouse 1997). Tracers of processes that affect the occurrence and persistence of contaminants in sediments are especially useful for many particle-reactive contaminants, where sediments act as a major reservoir and long-term source back to the ecosystem. New tracers that can be measured with greater sensitivity, without natural sources native to the environment, and are highly persistent would be useful additions to those already in use or proposed in prior work (Eganhouse 1997). There are many examples of sediment contaminants in the Hudson Basin that are known to have multiple sources (Bopp et al. 1981; Mueller et al. 1982; Bopp and Simpson 1989; Bopp et al. 1993; Feng et al. 1998; Feng et al. 2002; Chillrud et al. 2003; Yan et al. 2005; Baker et al. 2006; Levinton and Waldman 2006; Yan et al. 2006; Benedict 2007). Due to the shear volume of municipal wastewater that enters the metropolitan regions of the lower Hudson Basin (2300 MGD), sewage is often a significant contributor to overall contaminant sources within the NY/NJ Harbor complex and throughout the saline portions of the lower Hudson Estuary. In this Chapter, sewage source-specific DTDMAC is used to test or develop an informed understanding of the relative importance of sewage derived sources and sediment associated organic contaminants in the lower Hudson basin. In earlier chapters, it has been argued that DTDMAC has many properties that suggest its applicability as a valuable tracer to address such questions.

The classes of contaminants considered in this Chapter are polychlorinated biphenyls (PCB), polybrominated diphenyl ethers (PBDE) and the neutral metabolites of nonylphenyl polyethoxylates (NPEOs), which include nonylphenol (NP) and NPEOs possessing 1 to 3 ethoxy groups (NP(1-3)EO) (chemical structures shown in Chapter 1, and in this Chapter we use the term "NPEOs" for total NP(0-3)EO). All three classes of contaminants have been utilized in multiple applications over many years, and are of concern given their potential toxicity. From a human health perspective, PCBs and PBDEs are especially persistent because they can bioaccumulate in aquatic food webs, such that seafood can potentially become a significant source of exposure to humans and terrestrial wildlife. All three classes of contaminants have multiple mechanisms for toxic effects, and each can act as endocrine disrupters (Colborn et al. 1993; Bergeron et al. 1994; Jobling et al. 1996; Brouwer et al. 1999), an issue of increasing concern over the past two decades.

PCBs and PBDEs share several common properties. As classes of hydrophobic chemicals with very low solubilities, they are highly sorbed to sediments where most often they are very persistent. Their transport in estuarine settings is controlled by sediment transport, especially for the more halogenated components of these mixtures.

PCBs were utilized in a very large number of applications, and due to their dielectric properties and low flammibility were used extensively as dielectric fluids in transformers and capacitors. They were first produced in the late 1920s; but due to raising health concerns about their ubiquitous levels in the environment and biota, (Brouwer et al. 1999; Darnerud et al. 2006; Darnerud 2008; Legler 2008), they were banned for most applications in 1977. PBDEs, being "PCB like" chemicals, due to very similar structures (ten aromatic carbons that can be occupied either by H, Cl or Br, and have similarities in their physical properties, chemical stability), have been primarily used as flame retardants in a wide array of products since 1970s (Hites 2004). As a consequency of their persistence and expanded use, PBDE levels in human milk, blood and tissue samples have exponentially increased by a factor of ~100 during the last 30 years, and PBDE concentrations detected in fish and human samples from the U.S. is 10-18 times higher than those found in Europe (Hites 2004). In 2002, the two product mixtures of PBDE congeners that are most bioavailable, pentaBDE and octaBDE, were banned by the European Union. At the end of 2005, production of those products was also voluntarily ceased by the one major production company in the U.S. (USEPA report, http://www.epa.gov/oppt/pbde/).

PCBs and PBDEs were both sold as different mixtures of congeners (halogen number ranging from one (mono-) to ten (deca) halogen substitutions. In total, there are 209 different possible PCB or PBDE congeners, with commercial mixtures containing different complex mixtures of congeners varying in average number of halogens and molecular weight. PBDEs, and to a much lesser extent PCBs, were also sold as primarily single decahalogenated compounds As a result of widely varying compositions of congeners in the products used, the congener distributions of PCBs and PBDEs can greatly differ among different sources to the environment. In the absence of sufficiently large congener-specific changes in composition during transport caused by differential transport or biodegradation, the potential exists for utilizing source-specific differences in PCBs (Bopp and Simpson 1989) and PBDEs (Benedict 2007) to distinguish the relative importance of different sources of these contaminants to receiving waters and sediments.

Awareness and concern about PBDE contamination has been relatively recent; to date, there have been only two reports of PBDE measurements in the Hudson River and NY/NJ Harbor complex (Litten et al. 2003; Benedict 2007), with the work by Benedict far more comprehensive. As discussed below, high levels of total PBDEs were found in most of the tidal portion of the Hudson Basin, as well as in sediments from tributaries that act as sources to the estuarine basin in both the upper Hudson and Passaic Rivers. Benedict argued effectively that PBDE sources to the lower Hudson Basin must include spatially varying contributions from urban wastewater-derived sources concentrated in the NY/NJ Harbor complex, as well as other, likely industrial sources.

The lower Hudson Basin has experienced a very high degree of PCB contamination traced to two General Electric capacitor manufacturing plants located on the upper Hudson River, which have directly discharged at least several hundred tons of PCBs into the river between 1950 and 1976 (DEC report 1975). Some of the historical context, and many of the scientific issues associated with recent management of contaminated sediments at the upriver Superfund site, has been recently reviewed by Baker et al. (Baker et al. 2006). Bopp and coworkers have conducted numerous sediment studies of PCB deposition and compositions over a three-decade period (Bopp et al. 1981; Bopp and Simpson 1989; Bopp et al. 1993; Bopp et al. 1998). They have shown that the transport of PCBs and contaminated sediments over the Troy Dam to the tidal river has led to Hudson River-wide PCB contamination, important even in the highly urbanized NY/NJ Harbor area (Bopp et al. 1981; Bopp and Simpson 1989; Bopp et al. 1993). Some of these studies have estimated, from PCB congener composition data, the relative proportion of urban sources of PCBs (primarily sewage) relative to upriver sources, finding that the relative proportion of urban sources in the area of NY Harbor has increased in importance (Bopp et al. 1981; Bopp and Simpson 1989). Similar conclusions, with respect to loadings of PCBs above and below the Troy Dam, have been made elsewhere (Farley et al. 2006).

Also described in this study are comparisons between major NPEOs and DTDMAC on sediments of the lower Hudson Estuary. The toxicological properties of NPEOs, including their environmental chemistry and potential role as estrogen mimics in exposed fish (Jobling et al. 1996), are well reviewed elsewhere (Sonnenschein and Soto 1998; Ying et al. 2002). Much of the work conducted on the distributions of NPEOs in the lower Hudson Basin has been previously reported (Ferguson 2002; Ferguson et al.

2003; Brownawell et al. 2005), and also in Chapters 4 and 6 of this thesis. An important difference between NPEOs and PCBs and PDBEs, is that the former are less particle reactive, can be extensively degraded in sewage treatment plants (Ahel et al. 1994; Ahel et al. 1994; Ferguson et al. 2001), and can be subject to further microbial transformation reactions within estuarine surface waters (Ferguson et al. 2001) and sediments (Ferguson et al. 2003; Ferguson and Brownawell 2003).

It is well recognized that municipal waste waters are a very large source of NPEOs to receiving waters (Ahel et al. 1994; Ferguson et al. 2001), but other potentially significant sources of NPEOs also exist (Jonkers et al. 2003; Brownawell et al. 2005). European and Canadian risk assessments (Commission 1999) have indicated that pulp and paper mill operations, the textile industry, and leather tanneries may use NPEOs in large enough quantities to warrant their role as significant sources of NPEOs to the environment:

In this work, we have [tested some of the hypothesis from research on PCB, PBDE, and APEO metabolite sources, by comparing their distributions with highly particle reactive and sewage-source specific DTDMAC (Chapters 1, 3, and 4). Splits of archived samples, previously analyzed for PCBs, PBDEs, and APEOs were analyzed for DTDMAC along with surficial samples from gravity cores taken at locations characterized as depositionalt, based on the presence of naturally derived 7Be, and most often with evidence of long-term sediment burial based initially on the presence of bomb derived ^{137}Cs. For the NPEOs comparisons, similar analyses were performed on a larger array of surface sediments (Chapter 3) that encompass a wider range of sedimentary regimes, some of which may not be as favorable to preservation of more labile contaminants such as NPEOs.

5.2 Experimental design and analysis

5.2.1 Sample collection and storage

Two sources and types of surficial sediment samples were obtained and analyzed for this work. Our emphasis was to measure DTDMAC on sediments that had already been analyzed for PBDEs and PCBs (Benedict 2007) or NPEOs (Brownawell et al. 2005). The locations were chosen to provide a better understanding of potential sources and transport of those contaminants throughout the lower Hudson Basin. Surficial sediment samples (0-2 cm) from known depositional areas were collected by Richard Bopp's research group between 1984 and 2005 (Figure 5.1). The samples all possessed sufficient amounts of atmospherically derived ^{7}Be ($t_{1/2}$ = 53 days) to indicate that there had been significant, recent deposition of fine grain sediments at the site (Bopp et al. 1993); many of the samples came from cores where 137Cs dating also indicates high net sediment deposition rates. Station locations are often indicated as mile points (mp) of the stations referring to statute miles upriver from Battery Park at the southern tip of Manhattan. Many of these sites are revisited every few years as part of sediment quality monitoring for PAH, PCB, PBDE, APEO, PCDD/F, and heavy metals in the harbor areas (Bopp et al. 1982; Bopp et al. 1998; Chillrud et al. 1999; Chillrud et al. 2003; Ferguson et al. 2003; Brownawell et al. 2005; Yan et al. 2005; Yan et al. 2006; Benedict 2007). Surface samples (0-2 cm) were collected sediment cores collected by gravity, push, piston, or vibra coring techniques (Benedict 2007). Sediment sections were dried in an oven at 35^{o}C, under a flow of air filtered through Florisil (magnesium silicate) to minimize contamination from laboratory air. Dried samples were ground with a mortar and pestle, and then stored in pre-baked glass vials with Teflon-lined screw caps for further analysis of APEO and DTDMAC in our lab. An additional set of 47 surface grab samples (Chapter 3; Figure 3.1) were analyzed for NPEOs and compared to DTDMAC levels. Those samples (0-5 cm) were collected in 1998 as part of EPA's New York/New Jersey Harbor wide monitoring study funded under the REMAP program (Chapter 3).

5.2.2 Chemical analysis of sediments.

The PCB and PBDE data for these samples along with details of sample analysis have been reported previously (Benedict 2007). The analytical method for PCBs was based on EPA method 1668. Dry, homogenized sediment samples were spiked with ^{13}C-labeled PCB congener surrogate compounds and extracted into dichloromethane using a Soxhlet continuous extraction apparatus. Extracts were treated with HCl-activated copper to remove elemental sulfur; run on a Florisil column to remove interfering co-extractants, and again treated with activated copper. Finally, the extracts were spiked with a second group of ^{13}C-labeled PCB congener recovery standards, and analyzed on a capillary column gas chromatograph with selected ion monitoring mass spectrometry (GC-SIM-MS).

The measurement of PBDE was based on EPA method 1614 and up to 49 congeners (single and coeluting) were analyzed. Sediment samples were spiked with ^{13}C-labeled PBDE congeners and extracted with toluene using a Soxhlet apparatus. After being spiked with a ^{13}C labeled standard and concentrated, extracts were subjected to gel permeation chromatography to remove high molecular weight interferences, and silica and alumina, and finally Florisil chromatography to eliminate non-polar and polar interferences respectively. ^{13}C- labeled mixture was added as internal standard prior to analysis by high-resolution gas chromatograph, coupled to a high-resolution mass spectrometer (HRGC/HRMS), to quantify PBDE congeners.

NPEOs concentrations for 67 surface sediments are reported in this Chapter. That data was generated from two sets of analyses. 51 samples were analyzed according to the method of Ferguson et al. (Ferguson et al. 2000) and reported in Brownawell et al., 2005; 22 samples were analyzed by a modification of Ferguson et al., (Ferguson et al. 2001), the details of which are presented in Chapter 6.

DTDMAC was determined according to the method developed in this work (Chapter 2). Included in this Chapter are results from analysis of 27 surficial sediment samples for which PBDEs and PCBs have been analyzed. DTDMAC results from another 47 samples (Chapter 3) are compared here to analyses of NPEOs in the same samples. For all samples, the average recovery of surrogate standard DADMAC C12:C12 was 105±15%.

5.3 Results and discussion

5.3.1. Distribution of DTDMAC in depositional surface sediments of the lower Hudson Basin.

The concentrations of DTDMAC in 25 surficial sediments collected between 1998 and 2005 are shown in Table 5.1. Measurements made at two of the sites in the mid 1980s are also given for comparison. Distributions of DTDMAC in the Lower Hudson Basin follow an expected trend. Extremely high concentrations (84.1 and 98.1 ug/g) were measured at the Newtown Creek site sampled in 1998 and 2001, respectively. An even higher concentration of DTDMAC was measured in a 2005 sample (Table 5.1); however, the concentrations and compositions of a wide range of QACs, PBDE's, and PCBs measured in this sample were very much outside the range of other samples analyzed in these studies (Chapters 3, and 4; Benedict, 2007). Therefore the data from that sample are not included in later data analyses. High concentrations were also found throughout the highly urbanized New York/New Jersey Metropolitan Harbor complex. DTDMAC levels were 21 – 54 μg/g in 13 samples collected in the upper New York Harbor (mp -1.7 to mp 6.4), Newark Bay, Hackensack River, Kill van Kull, and Arthur Kill sites. The concentration in the upper Hudson River and Mohawk River sites were much lower, ranging between 1.8 and 5.7 μg/g. These lower concentrations are consistent with diminished sewage effluent discharges to these less urban areas. DTDMAC concentrations were also low in, Central Park Lake (CPK, 1.2 μg/g) and upper Passaic River (3.4 μg/g) sites, the latter consistent with little direct discharge of sewage into the upper Passaic. The reason for the detection of relatively low, yet easily measured, DTDMAC in Central Park Lake is unknown. DTDMAC is not volatile, and while there is a finite amount that is aerolized during sewage treatment or discharge of raw sewage in a storm, there are likely other unknown small sources of DTDMAC from activities in or near the Lake.

5.3.2 DTDMAC as a tracer of PBDE sources to the lower Hudson Basin.

Total PBDE concentrations in all samples ranged from 40 to 490 ng/g (Table 5.1). This range of PBDE sediment concentrations is significant higher than levels found in most river and marine sediments that have been sampled in Europe and U.S. (Hites 2004; Benedict 2007). The highest level was found in the Upper Passaic River (486 ng/g) which has very little direct sewage wastewater input upstream of the site (Benedict 2007). Other samples that contained elevated PBDE levels and not influenced by sewage sources were from the mp157 and mp87 sites from the upper Hudson River (250 and 390 ng/g, respectively). The lowest concentrations of PBDEs (40 ng/g) were found in the Mohawk River, a tributary of the upper reaches of tidal Hudson. These data are, consistent with a PBDE source specific to the main stem of the upper Hudson above the Troy Dam. The other samples with the highest PBDE levels (410 – 430 ng/g) came from the Newton Creek site which is proximate to one of the biggest WWTP in U.S. which treats up to 300 MGD of wastewater. Finally, the concentration of the CPK sample was 65 ng/g. The latter measurement was attributed to atmospheric deposition (Benedict 2007). CPK is a closed system and concentrations should be more closely tied to sedimentation rates and only minimally affected by lateral transport prior to deposition as compared to the other sedimentary environments considered. Thus, concentration comparison between CPK and lower Hudson River Basin may be less comparable to those in river and estuarine sediments; better comparisons of fluxes or inventories would be more appropriate, as sedimentation rates are not only different but lateral transport of sediment contaminants from multiple sources is surely less important in CPK than in the other regions studied.

The composition of major PBDE congeners was observed to vary in consistent ways within different areas of the Hudson Basin. Based on the distribution of concentrations and congener compositions, Benedict concluded that that important sources from WWTPs and likely industrial inputs could be distinguished (Benedict 2007). The percentage of $\sum_{\text{tri-hexa}}$BDE were consistently higher (> 12%) in samples from Newtown Creek collected in different years, and also in sample from Hackensack River collected downstream of the WWTP. That range of compositions agreed with what were found in sewage effluents and surface sediment samples close to WWTP in previous studies (North 2004; Oros et al. 2005). In contrast, lower percentages of $\sum_{\text{tri-hexa}}$BDE were found in the upstream Passaic River and Hudson River sediments where unidentified industrial inputs most likely dominated sources of total PBDEs.

Figure 5.2 (modified from Benidict, 2007) shows the percentage of $\sum_{\text{tri-hexa}}$BDE out of total PBDEs along the Hudson River stem and in the NY/NJ Harbor complex. The samples were separated into three categories, depending on a range of the $\sum_{\text{tri-hexa}}$BDE percentage of total PBDEs (Figure 5.2 and 5.3). The sites with higher $\sum_{\text{tri-hexa}}$BDE percentage (> 12%, indicated by black dots) are primarily found in the lower Hudson River Basin at sites proximal to areas of high sewage discharge (upper New York Harbor and the Hackensack River). The Mohawk River site is also characterized by a high $\sum_{\text{tri-hexa}}$BDE percentage, consistent with it being isolated from the upper Hudson source. Among the six sites characterized by the lowest $\sum_{\text{tri-hexa}}$BDE percentage (< 5% and indicated as red dots on Figures 5.2 and 5.3), the lowest (1.8 - 2.6%) percentages correspond to sites from the upper Passaic and the freshwater reaches of the upper and lower Hudson River (mp 54 - 157). Newark Bay and Kill van Kull sites also show low (4.8 - 4.9%) percentages. Newark Bay does not receive direct discharge from WWTPs, but is affected by sewage inputs from large municipal sewage inputs from the Hackensack, the Arthur Kill, and New York Harbor. The sources of PBDEs at those sites are expected to be affected to some extent by mixed sources. The three other sites (Arthur Kill; upper New York Harbor, mp -1.7; and Hastings, mp 21.6) are characterized by higher, yet still intermediate $\sum_{\text{tri-hexa}}$BDE percentages (averaging between 7.1 and 9.8%, Blue squares in Figure 5.2 and 5.3). Given the locations of these sites, they can also be expected to be impacted by a combination of sewage and either Passaic or Upper Hudson sources.

The relationship between total PBDE and DTDMAC concentrations is consistent with the conclusions of Benedict (2007) and the above discussion (Figure 5.3). The data at the sites in the lower Hudson Estuary that are expected to be most influenced by sewage sources (including the Newtown Creek sewage source end-member samples) are well described by the linear correlation between total PBDE (ng/g; y) and DTDMAC (ug/g; x) concentrations ($y=4.2x+27$, $r^2=0.91$). As predicted, the upper Passaic River and upper Hudson River samples with the clearest difference in PBDE compositions ($\sum_{\text{tri-hexa}}$BDE percentages of 1.8 - 2.6%) have PBDE levels far above the sewage source correlation, providing clear support for a non-sewage source of those PBDEs. The other two sites characterized by low $\sum_{\text{tri-hexa}}$BDE percentages (Newark Bay and Kill van Kull) are also seen to have PBDE levels that are approximately double the levels corresponding to the linear correlation between DTDMAC and PBDE concentrations, hypothesized to come from sewage sources. These higher PBDE levels are consistent with a mixed source of PBDEs and the somewhat greater $\sum_{\text{tri-hexa}}$BDE percentages (4.8-4.9%). Concentration data from two of the sites with less distinct intermediate compositions ($\sum_{\text{tri-hexa}}$BDE percentages of 7.1 - average of 9.8%) fall close to the line relating PBDEs to the sewage tracer (Arthur Kill and Hastings on the Hudson sites; mp 21.6). However, at the upper New York Harbor site (mp -1.7 WE), the PBDE levels measured in 2001 and 2005 samples are also nearly double that expected from sewage derived sources, while the PBDE level in the 1998 sample was closer to that predicted from sewage derived source relationship.. It may be that this site is affected by both upper Passaic River and urban harbor sewage sources may give the proximity of the site to the sewage outfall transporting effluent from the Passaic River Authority to the upper NY Harbor by sewage sources.

5.3.2 Source evaluation for different fractions of PCB congeners

Total PCB concentrations in riverine and estuarine sediments varied between 0.33 and 11.5 μg/g (n=19 for surficial sediments collected between 1998 and 2005). Concentrations were highest, 11.5 μg/g, above the Troy Dam, (the Thompson Island source area), much lower, 0.68 μg/g (mp 157) in the main stem of the Hudson River, and even lower, 0.33 μg/g, in the Mohawk River that does not receive PCBs from the upper Hudson source area. The highest concentrations in the tidal portion of the lower Hudson Basin were found in highly sewage affected Newtown Creek and Hackensack River samples (1.55 μg/g). The range of total PCBs in the rest of the lower Hudson Basin does not vary in a remarkable nor spatially systematic way (0.49 – 1.20 μg/g). These concentration data contrasts with those observed during, and following the time that PCBs loadings from General Electric plants were much greater, when large differences in concentrations between upriver source areas and the mouth of the Hudson Estuary were observed. It has been estimated that the PCBs released directly from the GE plants into the Hudson decreased from 2700-16,000 kg/yr between the 1940's and 1977, to no more than 30 kg/year of PCBs in the late 1990s (Baker et al. 2006)..

The concentrations of PCBs (Benedict 2007) are a small fraction of maximum levels measured in sediments corresponding to the mid-1970s (Bopp et al. 1982). The sharp declines in PCBs over time throughout the area were due to many factors: GE stopping the use of PCBs in1976; reduction of PCBs concentrations in surface sediments due to a combination of new inputs of cleaner sediments, and loss of PCBs from the sediment bed to the water column; reductions in municipal WWTP inputs, and decreases in direct and indirect atmospheric deposition following the bans on most uses of PCBs, that also occurred during the 1970s.

The reservoirs of PCBs residing in surface sediments have continued to act as an important source of PCBs to the upper to the tidal Hudson River sediments (Achman et al. 1996; Bopp et al. 1998), but those inputs have also decreased over time. Farley (2006) estimated that by 2002 the load of PCBs coming over the Troy Dam had decreased to 180 kg/day, and had become less important than the primarily sewage-derived inputs into the urbanized area of the lower Hudson Estuary. In the past, the upper Hudson River source of PCBs was easily observed in sediments all the way down to the NY Harbor. In the period between 1971 and 1976, Bopp and coworkers (Bopp et al. 1981; Bopp and Simpson 1989) estimated that upriver sources of PCBs accounted for approximately 70-85% of PCBs deposited in NY Harbor sediments. However, the sediment record indicates that loadings of PCBs from the upper Hudson have decreased faster than inputs into the urban estuary. The sources of PCBs to the lower Hudson Estuary appear to be dominated by WWTP discharges (Farley et al. 2006). Bopp and coworkers have estimated that by the mid-1980s the proportion of PCBs loadings to NY Harbor from local sources had increased to $\geq$ 50 %(Bopp and Simpson 1989; Bopp et al. 1998) .

The PCBs congener compositions reported here vary markedly along the main stem of the Hudson River, consistent with previously reported large differences in PCB congener distributions between up-river and urban Harbor sediments (Bopp et al. 1981; Bopp et al. 1982; Bopp and Simpson 1989; Benedict 2007). The primary PCBs products used at the GE plants before 1971 were Aroclor 1242, after which Aroclor 1016 was the major product used in the plants. Both technical mixtures were dominated by di- through tetrachlorobiphenyl congeners (see Figure 5.4). Upper Hudson River sources of PCBs can also be affected by the presence of some mono- and di-chlorinated PCBs congeners which are produced by microbial dehalogenation reactions that occur in sediments in areas of the upper Hudson River (Benedict 2007). In contrast, PCB congener compositions in NY Harbor sediments are more similar to technical mixtures of PCBs like Aroclor 1254, which consist primarily of penta- and hexa-chlorinated, and lesser amounts of hepta-chorinated congeners (Figure 5.4). NY Harbor sediments also contain higher abundances of octa-, nona- and dechlorinated congeners (Bopp and Simpson 1989; Bopp et al. 1993; Bopp et al. 1998). One way that Bopp and coworkers (Bopp and Simpson 1989; Bopp et al. 1993; Bopp et al. 1998) distinguished the relative contributions of upriver and Harbor sources of PCBs was to compare the distributions and compositions of PCBs. However, such interpretation can be potentially complicated by differential transport and fate of PCBs as a function of the physical chemical properties of individual congeners which depend on the degree of chlorination.

The concentrations of DTDMAC are compared to different components of the PCB residues in sediments representative of different sources in Figure 5.5: a) the sum of mono- through tetra-PCBs, most characteristic of up River Hudson River sources; b) penta- and hexa-PCBs, which are more likely to be affected by both upper River and urban Harbor sources; and c) hepta through deca-PCBs that have been interpreted in prior work to be most diagnostic of sewage-derived PCBs sources in the Hudson Estuary (Bopp and Simpson 1989; Bopp et al. 1993; Bopp et al. 1998). The relationship between DTDMAC and total PCBs is shown in Figure 5.5D.

The lower chlorinated PCBs are seen to correspond directly with sewage-derived DTDMAC in the sediment samples from the urban NY/NJ Harbor complex. The linear correlation ($y=8.1x+195$, $r^2=0.82$) that describes these data is consistent with an important contribution of lower chlorinated PCBs from sewage derived sources in Harbor complex, that is well predicted by the Newtown Creek sewage source end member (Figure 5.5A). The positive intercept (190 ng/g) may be related to some continued upstream or other local point or non-point sources. However, more data would be required to support further interpretation. Concentrations of the same PCBs in upper Hudson River and the fresh water reaches of the lower Hudson River (mp 54) are dramatically enriched relative to DTDMAC, consistent with a common source of these PCB congeners in the upper parts of the Hudson River between Foundry Cove (mp 54)_and Thompson Island Pool (TIP) (mp 189). Furthermore PCB concentrations measured in the TIP sediment are in great excess of any measured down river. More information would be required to determine how much of the decrease in concentration of these more soluble PCBs along the axis of the river has been the result of dilution with additional PCB-clean sediment, or due to solubilization and possible volatilization during transport. The ratio of these PCBs congeners to DTDMAC in the samples from Hastings (mp 21.6) are intermediate between the up-river and harbor end members. As further seen below the concentrations and composition of PCBs that are observed at the Hastings site are anomalous, and may be the result of a local industrial source of PCBs near that location (Richard Bopp, personal communication).

The relationships between the sum of penta and hexa-PCBs and DTDMAC concentrations for sediments from New York Harbor are also well correlated (Figure 5.5b), but in this case the PCB concentration corresponding to zero DTDMAC is near the origin (y=6.3x+9.5, r2=0.85). The Hackensack River sample has a higher of these PCB congeners in comparison to DTDMAC, for reasons which are unclear. The data for the other urban Harbor complex sites are well described by a single sewage source term, again consistent with Newtown Creek sewage end-member samples. Note that the concentration of these PCBs homologs at the TIP site is now only a factor two greater than it is at the Newtown Creek site, and the concentrations at the other freshwater Hudson sites are now similar to or lower than the concentrations seen in NY Harbor. The potential for the upper Hudson PCB source of these congeners to contribute to the concentrations measured in NY Harbor has thus become small over time.

The concentrations of hepta-deca PCB homologs in sediments from the NY Harbor are again well described (with the exception again of the Hackensack River sediment) by the linear regression with DTDMAC ($y=1.6x+9.0$, $r^2=0.79$) and the

Newtown Creek sewage-source end member (Figure 5.5c). For sites in the freshwater reaches of the upper Hudson River (mp 54-189), the levels of higher chlorinated PCBs congeners are very low, with the exception of the TIP site. Once again, in samples collected at Hastings, the ratio of PCB congeners to DTDMAC is intermediate between the upper Hudson source (as defined primarily by the TIP sample) and the NY Harbor source. Figure 5.5c now illustrates clearly that concentrations of higher chlorinated PCBs congeners in sediments along the fresh water reaches of the Hudson River are not nearly high enough to contribute in a meaningful way to more recent levels of higher chlorinated PCBs found in the Harbor complex.

Total PCB concentrations as a function of DTDMAC concentrations are shown in Figure 5.5d ($y=16x+213$, $r^2=0.92$). Neglecting the Hackensack River sample, total PCB concentrations in NY Harbor sediments are consistent with a primary sewage-derived source. This conclusion that urban source is primarily from sewage inputs, rather than other inputs into the Harbor complex, relies in part on assuming that a single Newtown Creek sample is characteristic of sewage-derived end member composition. When compared to DTDMAC concentrations, the PCB levels in freshwater Hudson River sites (mp 54, 87, 157, and 189) are generally consistent with a continued upper Hudson PCB source.

The relationship between PCBs and DTDMAC are consistent with a very large fraction of the total PCBs in NY Harbor being derived from local sewage derived sources during the 1998-2005 time periods. In fact there is little indication of an upstream input of penta- through decachlorinated homologs, although there is seemingly potential for upper Hudson River Sources to be a source of di- through tetrachlorinated PCBs. With respect to total PCB loadings to the upper NY Harbor, this analysis, as illustrated in Figure 5.5d, suggests that local source, dominated by sewage inputs, are likely the largest source of PCBs during the 1998-2005 time period. These results support the temporal decline in the estimates of the relative importance of upper Hudson River PCB sources to NY Harbor. As discussed above., 70 – 85% of total PCB loading to NY Harbor where estimated to have derived from Hudson River sources in the mid-1970's, as compared to similar estimated of 40-50% in the mid-1980s (Bopp et al. 1981; Bopp and Simpson 1989; Bopp et al. 1998).

5.3.4 DTDMAC as a tracer for NPEOs source and transformation in surficial sediments from the lower Hudson Basin.

DTDMAC and NPEO concentrations are generally well correlated in the 19 surface samples collected between 1998 and 2005 (Table 5.1; Figure 5.6a). NP(0-3)EO concentrations ranged between barely detectable levels (0.05 μg/g) at the mp 87 sample at Kingston on the upper tidal Hudson, to a high of 14.2 μg/g in one of the Newtown Creek samples. With the exception of the Hackensack River sample, NPEOs track the particle reactive DTDMAC sewage tracer amazingly well. The high ratio of NPEOs to DTDMAC measured at the Hackensack River site is an exception to the pattern, an observation that would most easily be explained if the upstream WWTP discharged a higher proportion of NPEOs. It is of interest to note that in dated sediment samples between 1995 and 2002, the NPEO/DTMAC ratio in Hackensack samples is consistently about twice the ratio found in Newtown Creek or Jamaica Bay samples (Chapter 4).

There is no clear evidence in the data (Table 5.1; Figure 5.6a) to support a significantly large upstream input of NPEOs from pulp and paper mill plants which operated above the mp 187 site and on the Batten Kill tributary further down river but above the Troy Damn (Figure 5.1). Concentrations of NPEOs were only 0.08-0.09 μg/g in two samples from a station downstream of pulp and paper mill sources on the Batten Kill (Brownawell et al. 2005). Furthermore, the relatively low NPEO concentrations on the Mohawk provide evidence against a large source of these contaminants from the leather tannery farther upstream.

The possibility that textile manufacturing or other industrial inputs of NPEOs have acted as a significant source of NPEOs to the upper Passaic River would be worthy of further investigation. Unfortunately, the comparison between NPEO metabolites shown in Figure 5.6 is complicated by the fact that DTDMAC have not been determined in the same sample (Table 5.1). The high ratio of NPEOs/DTDMAC might suggest a non-sewage source to the area; and the upper Passaic River receives little sewage input. However, it is known that DTDMAC inputs have decreased markedly since approximately 1990. Geochronologies of both compound classes on the same samples would be useful to determine the extent of any non-sewage sources of NPEOs to the upper Passaic and how such inputs have varied in the past.

There is an input of NPEOs to Central Park Lake as observed in a surface sediment sample (Figure 5.6a), consistent with a sediment core profile for NPEOs from the same site. A partial sediment geochronology completed for at Central Park suggests that the levels of NPEO metabolites are representative of longer term inputs. As is the case for DTDMAC, the possible source of NPEOs to Central Park is unknown. It is doubtful that this input is primarily atmospherically derived, and NPEOs are used in pesticide formulations, and many cleaning solutions and personal care products that may come in contact with the Lake or its small watershed.

Unlike highly particle reactive and persistent DTDMAC, NPEOs and their metabolites are likely to be differentially transported due to greater solubility, and degraded to a much greater extent, at least under more oxidizing conditions (Ferguson and Brownawell 2003). Thus, the correlation between NPEOs and DTDMAC (Figure 5.6a), is not only consistent with these two classes of contaminants sharing the same wastewater derived sources, but also suggests that NPEOs are persistent and well preserved in highly depositional sediment regimes that were sampled.

The relationships between NPEO metabolites and DTDMAC in 49 grab samples (0-5 cm as described in Chapter 3) are shown in Figures 5.6b-d. The patterns of NPEOs and DTDMAC in sediments are much more variable than seen in Figure 5.6a. NPEOs are especially high in four samples at sites close to CSO sources (Chapter 3) and two samples from Grassy Bay, a relatively deep and poorly flushed area of Jamaica Bay, that is both proximate to a WWTP effluent source and characterized by high sediment burial rates (Ferguson et al., 2003; Chapter 4). In Chapter 3, much higher concentrations of more soluble and biodegradable QACs were found in the same CSO samples, which was attributed to less efficient removal prior to release to the environment and relatively high subsequent preservation of the more labile compounds in the muddy, organic rich sediments characterizing the CSO affected sites. Such mechanisms could also explain the higher ratios of NPEOs in those four samples. The explanation for the high concentrations of NPEOs relative to DTDMAC in the two Grassy Bay sediment samples (24 – 37 μg/g), is as yet unknown, but many explanations are possible. The high NPEO/DTDMAC ratios in two Jamaica Bay sites could be related to close proximity to source, very high levels of total organic carbon that could favor greater scavenging (Ferguson et al. 2001), or as speculated for the Hackensack River sediment above, a different source ratio of NPEOs/DTDMAC entering from the Jamaica WWTP.

Figure 5.6c shows all samples collected by EPA-REMAP from New York Harbor and Newark Bay compared to the linear regression of samples characterized as being sampled in depositional sediment environments by 7Be (Figure 5.6a). Figure 5.6d shows all samples collected by EPA-REMAP from Jamaica Bay. The concentrations of natural estrogens (E1and E2) measured in subsamples of selected Jamaica Bay samples (Reddy et al. 2005) is also provided. In both figures it is seen that for a large number of samples, NPEOs are much lower than predicted from analysis of the data from depositional sites (Figure 5a). This is especially true in Jamaica Bay. Interestingly, the same relative trend is seen in the data for the steroid estrogens E1 and E2. In contrast, only the two Jamaica Bay sites in Grassy Bay have NPEOs that are above that predicted. Relative depletion of more degradable and less particle reactive NPEOs and steroid estrogens could be due to a number of factors: differential transport in the water column, as more soluble compounds become less associated with suspended particles due to time of transport or dilution with cleaner water; microbial transformations that occur in the water column (Ferguson et al. 2001); post depositional microbial degradation or alteration by benthic infauna; and finally that these surface grab samples have not been characterized as being depositonal (e.g., from 7Be or sediment core depositon rate estimates). However, in Chapter 4 (showed in Apendix Figure A1 and Table A3), a dating estimation tool (the time-sensitive ratio of alkyltrimethylammoniums with 22 and 18 carbon chain lengths) suggests that the preponderance of these surface grab samples are have particle reactive contaminant signatures that are relatively young compared to the dates that the grab samples where collected (primarily 1998).

5.4 Summary

DTDMAC have properties as particle- reactive, persistent, and sewage source-specific organic contaminants that should allow their use as tracers of the sources of other particle reactive organic and metal contaminants. In Chapter 3, it was hypothesized that DTDMAC may provide information about the source of sediment organic matter in urban estuarine settings where sewage derived organic matter can be important. Analysis of distributions of DTDMAC and other very particle reactive and persistent PBDEs and PCBs provides a complementary tool for source allocation that was shown to be consistent with independent analyses that have been done. The comparisons between DTDMAC and more soluble and labile NPEOs provides insights into how one class of sewage-derived class of contaminants might be used to determine the relative transport or liability of other classes of wastewater contaminants. In this study, it was hypothesized that NPEOs are transported and relatively well preserved in depositional sediment environments, and in other environments are seen to be greatly depleted. This work could not distinguish the reasons for NPEOs (or estrogen) losses, but future work could be done to test different hypotheses.

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Figure 5.1 Surface sample sites in Upstream Hudson River and NY/NJ Harbor complex that have characterized for 7 Be and 137. All samples were measured for DTDMAC and PBDE. As labeled, not every sample is measured for PCB or/and NPEO (Table 5.1).

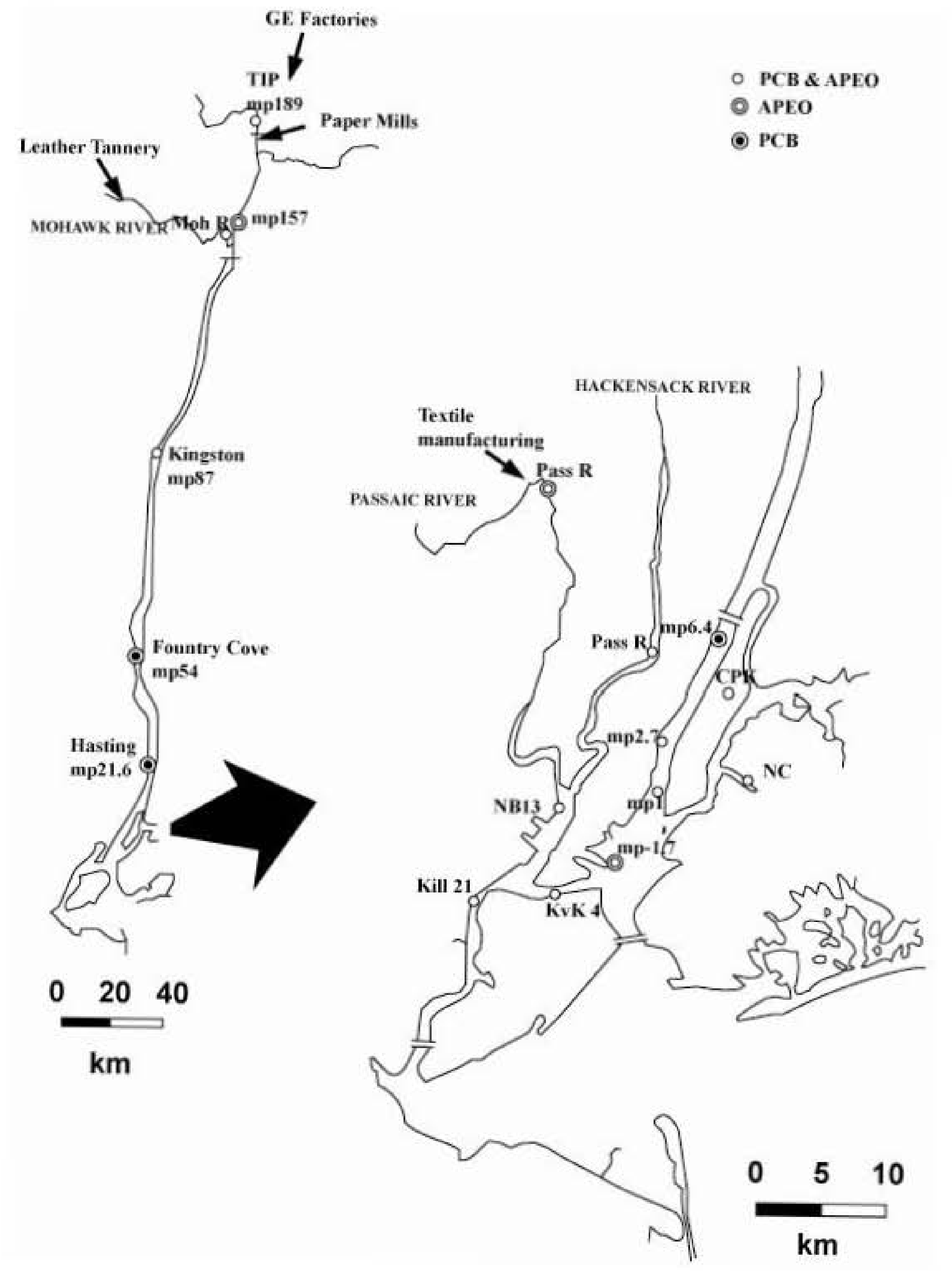

Figure 5.2 Percentage of $\sum_{\text{tri-hexa}}$BDE out of total PBDEs in sediment samples collected between 1998 and 2005. Three different categories were separated by different range of the percentage: lower than 5% (red squares); average percentages between 7%-9.8% (blue squares); and average values bigger than 12% (black dots). (modified from Bendict's thesis 2007)

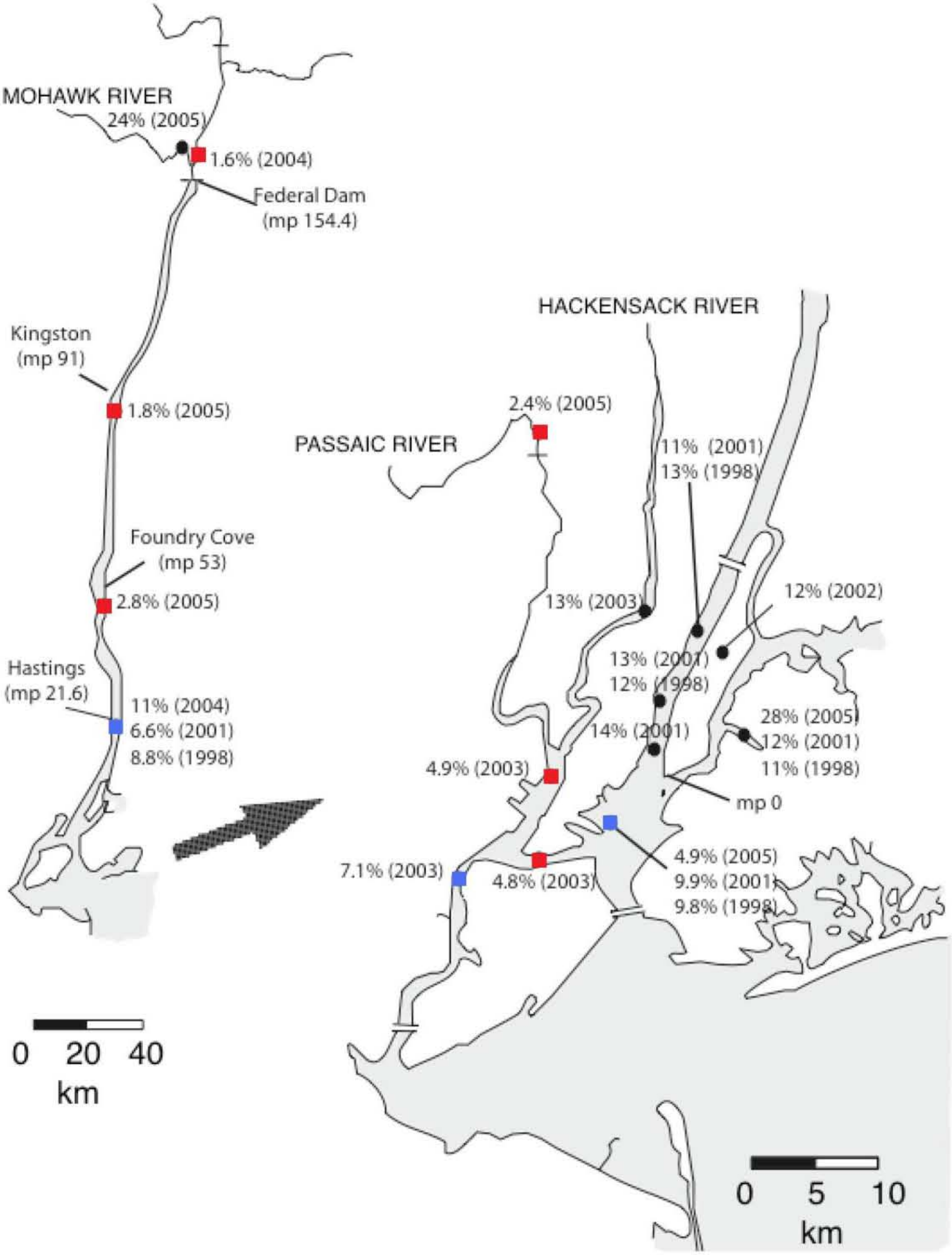

Figure 5.3 Sources separation of PBDE by the DTDMAC and congener compositions. Samples were also separated by the PBDE congener's composition pattern as in Figure 5.2 (note the percentage ranges need to be changed to be consistent with Fig. 5.2).

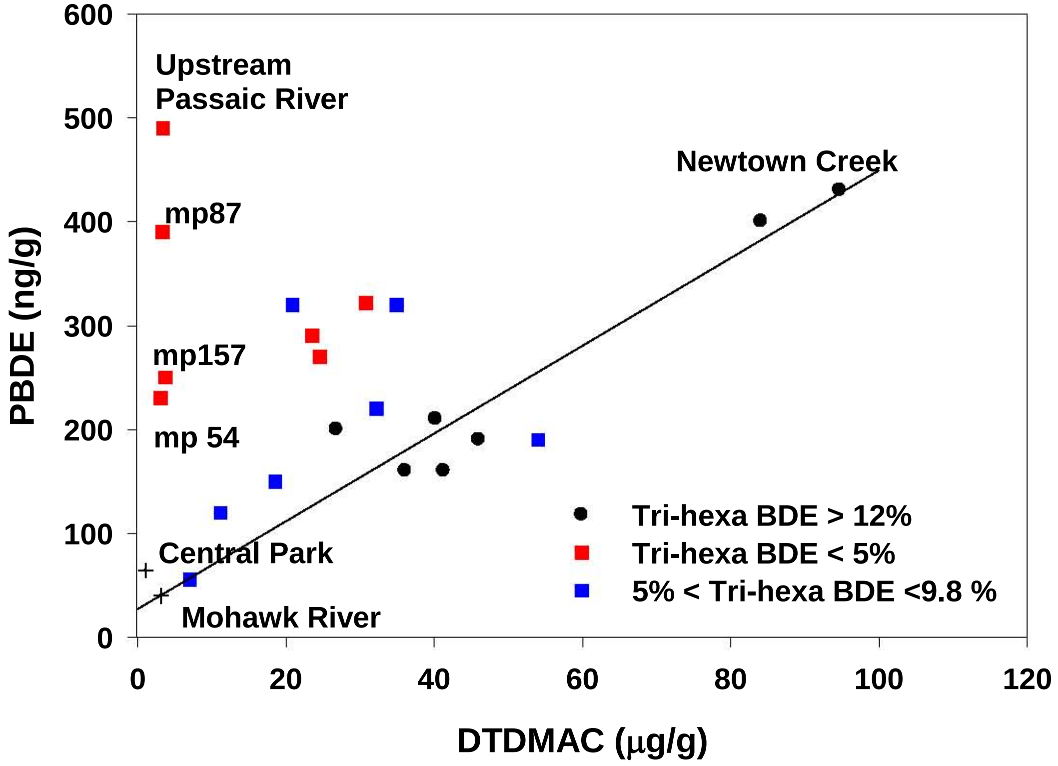

Figure 5.4 PCB homolog compositions of important major commercial PCB products: Aroclor 1016, 1242, and 1254. (ATSDR, 2000; Benedict, 2007)

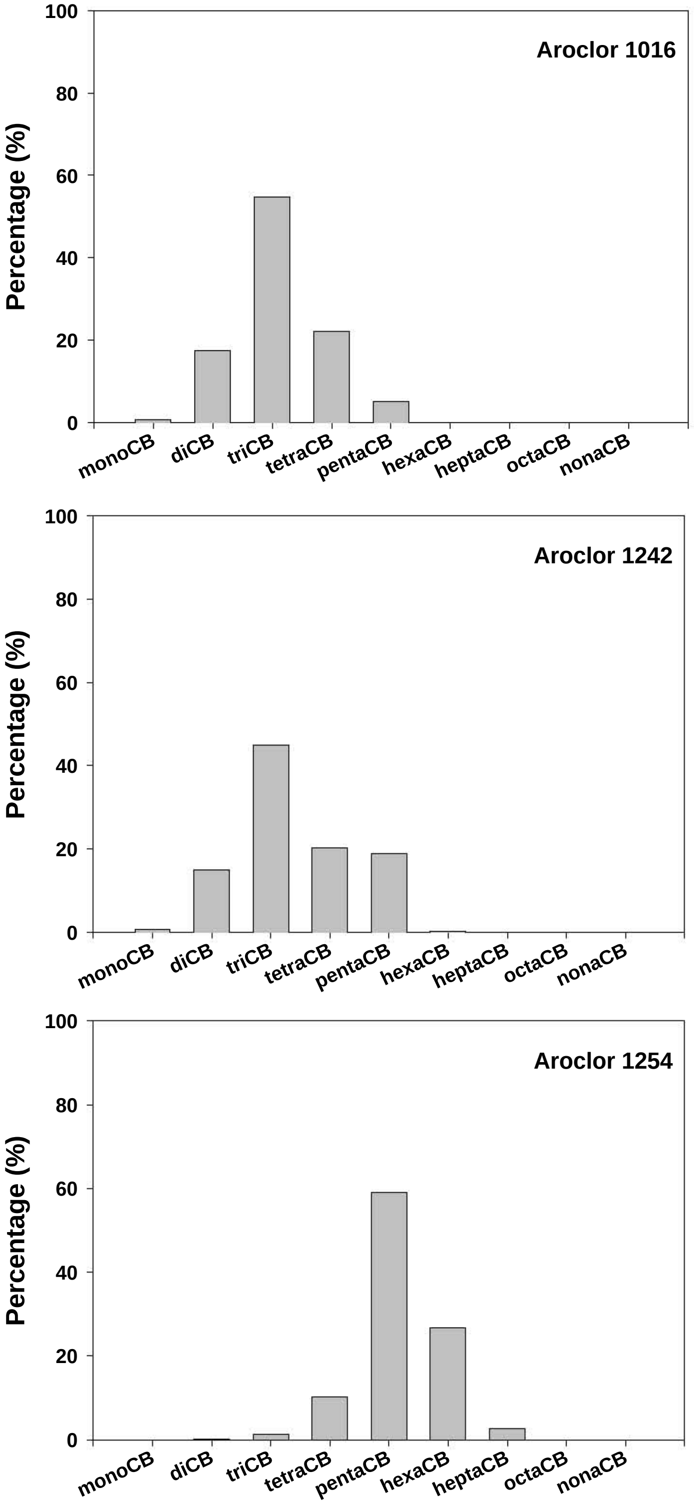

Figure 5.5 Source separations of total and different fractions of PCB congeners by the sewage tracer DTDMAC. (A) mono-tetraCB; (B) penta-hexaCB; (C)hepta-decaCB; and (D) total PCB. The solid line represents that linear regression (of form y = ax+b) determined from the data most likely affected by sewage sources (black dots).

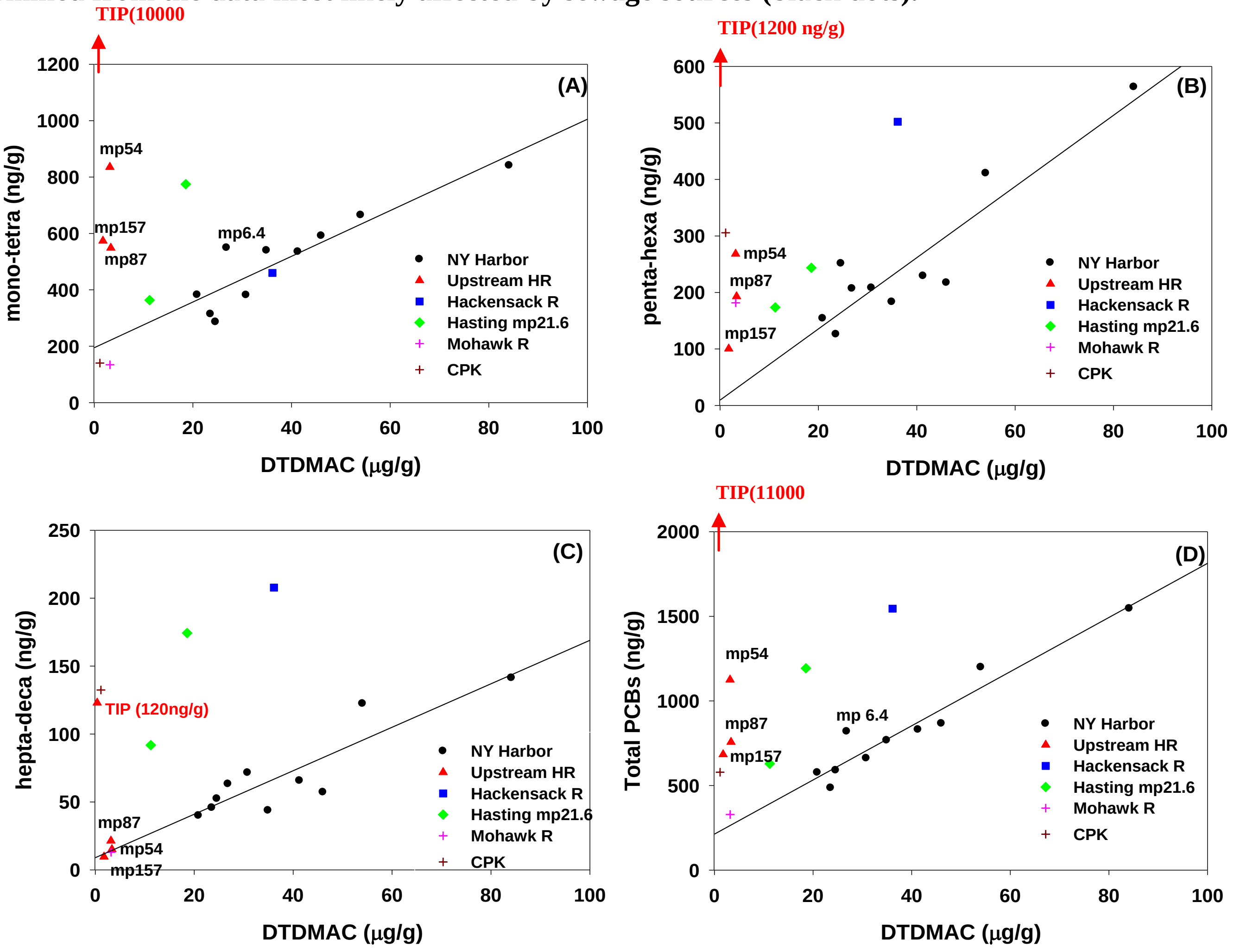

Figure 5.6 Total concentration of NPEOs vs. DTDMAC in (A) Sediment samples collected by Bopp's Lab from NY/NJ Harbor complex; (B) All sediment samples collected by REMAP 1998 (C) REMAP samples from NY/NJ Harbor (D) REMAP samples from Jamaica Bay only (plus steroid hormone data) (y=0.14x, r^2=0.91). The same regression like determined in panel A is compared to the data presented in panels C and D.

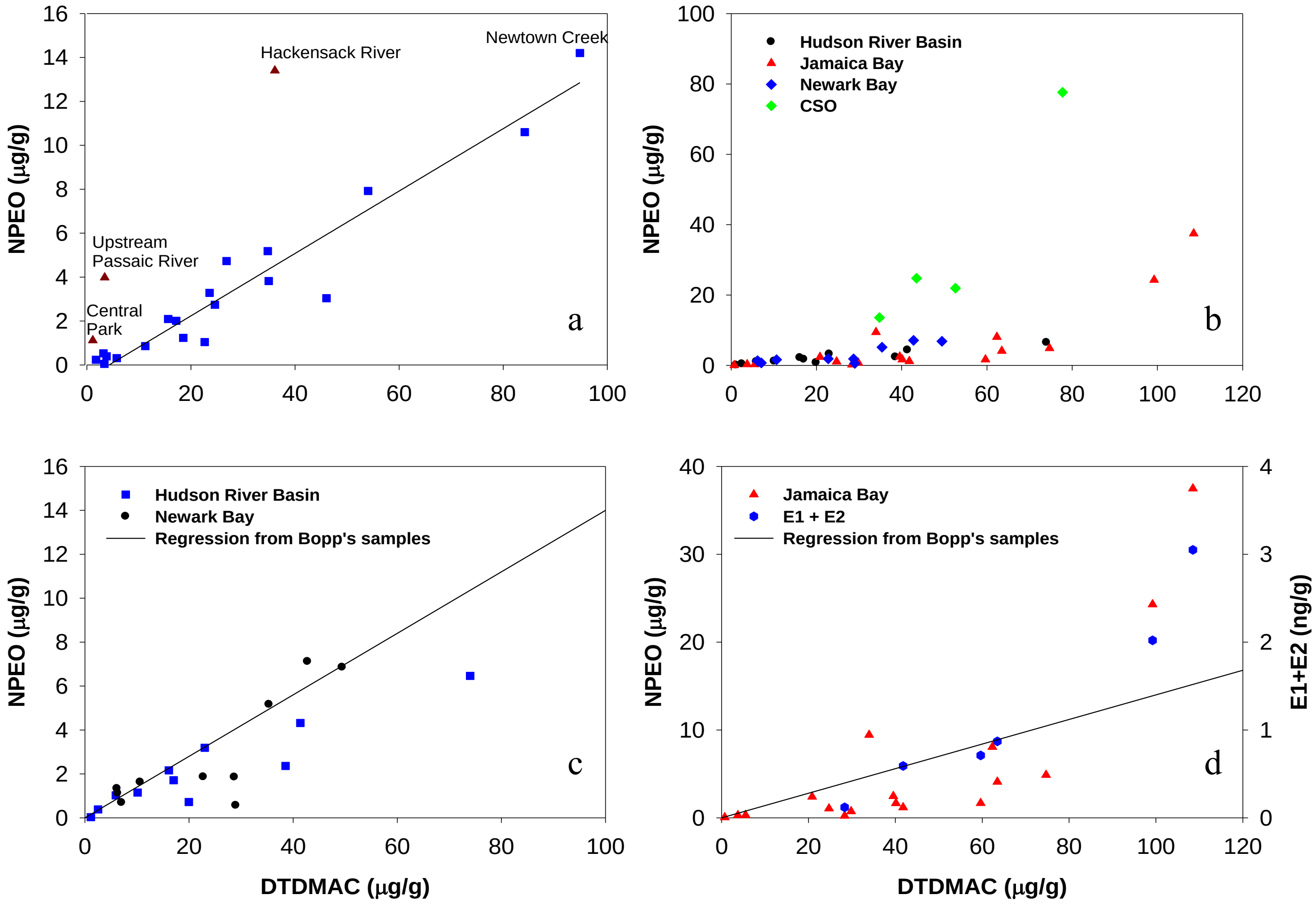

Table 5.1 Concentrations of DTDMAC, PBDE, PCBs and NPEOs metabolites in surficial sediment (0-2cm) from NY/NJ harbor complex and upstream Hudson River. The data utilized in this Chapter is limited to samples collected between 1998

Sample ID	Year	Location	DTDMAC (μg/g)	NPEOs (μg/g)	PBDE (ng/g)	PCBs (μg/g)
R1436	2002	Thompson Island mp189	5.74	0.31	n.d.	11.50
R1558A	2005	Mohawk river	3.19	0.53	40	0.33
R1521A	2004	mp157	1.76	0.39	250	0.68
R1535A	2005	Kingston mp87	3.36	0.05	390	0.76
R1537A	2005	Foundry Cove mp54	3.16	n.d.	230	1.13
R1498A	2004	Hast 04 Hasting mp21.6	7.04	n.d.	56	n.d.
CN2296A	2001	Hast 2 Hasting mp21.6	18.57	n.d.	150	1.19
R1242A	1998	Hasting mp21.6	11.22	0.86	120	0.63
R1393A	2001	mp6.4	26.84	4.73	200	0.82
R1222A	1998	mp6.4W	41.31	n.d.	160	0.83
R1223A	1998	mp2.77E	40.24	1.42	210	n.d.
R1394A	2001	mp2.77ED	46.04	3.04	190	0.87
R1227A	1998	NC10 Newtown Creek	94.75	14.20	430	n.d.
R1397A	2001	NC11 Newtown Creek	84.14	10.60	400	1.55
R1548A[a]	2005	NC12E Newtown Creek	142.70	n.d.	410	0.90
R1427A	2001	CPK	1.15	1.50*	65	0.58
CN1923A[a]	1984	mp-1.7	58.72	7.91	260	n.d.
R1225A	1998	mp-1.7C	32.21	n.d.	220	n.d.
R1396A	2001	mp-1.7WE	34.95	3.82	320	0.77
R1545A	2003	mp-1.7WE	20.88	n.d.	320	0.58
R1490A	2003	NB 13F Newark Bay	24.61	2.74	270	0.59
CN1964A[a]	1983	NB13 Newark Bay	34.77	5.18	170	n.d.
R1226A	1998	KvK4	30.81	1.74	322	0.66
R1488A	2003	KvK4F Kill van Kull	23.59	3.28	290	0.49
R1489A	2003	Kill 4F Arthur Kill	54.05	7.92	190	1.20
R1531A	2005	Pass8B Passaic River	3.42	3.98[b]	490	n.d.
R1487A	2003	Hackensack14F	36.13	13.40	160	1.55

a. Sample was not included in the data analysis in this chapter.

b. The analysis of NPEOs at the Passaic River site are from a sample collected in 1986.

CHAPTER SIX: FURTHER ANALYSIS OF OF NONYLPHENOL POLYETHOXYLATES AND THEIR METABOLITES IN SEDIMENTS OF NY/NJ HARBOR COMPLEX: POTENTIAL APPLICATIONS AS TRACERS FOR REDOX CONDITION WASTEWATER SOURCE, AND AS INDICATORS OF SEDIMENT TOXICITY

6.1 Introduction

6.1.1. Context of the research in this Chapter.

Nonylphenol ethoxylates (NPEO) are important non-ionic surfactants used in both industrial and domestic detergent and emulsifier formulations, with an average of about 10 and a range of 1-20 ethoxy units. The finding that NPEOs and their metabolites survive wastewater treatment and can be detected ubiquitously in the aquatic environment (Giger et al. 1981; Stephanou and Giger 1982; Giger et al. 1984) has raised environmental concern about these compounds. Water quality regulations for NPEOs and metabolites are generally based on the acute toxicity risks associated with high concentrations of the metabolites like nonyphenol (NP) in wastewater effluent. However, more recent scientific interest in NP and other NPEO metabolites is associated with their potential to cause endocrine disruption in aquatic organisms (Jobling et al. 1996; Laws et al. 2000). Therefore, there is concern about NPEOs and their preservation in sediments that is of environmental interest.

This Chapter discusses the results of three related studies of the use of NPEO to understand their sources found in sediments; whether the compositions are characteristic of integrated redox state of surficial sediments that likely control persistence of NPEO metabolites; and whether any insights into the causes of sediment toxicity observed in sediments from the New York/New Jersey Harbor complex can be informed by the NPEO concentrations and compositions determined in this work.

The composition of NPEOs and it metabolites measured in receiving waters and sediments can depend upon several factors: the extent NPEOs are microbially degraded in wastewater treatment plants, as operating conditions can affect pathways that control the concentrations and compositions of sediments, the amount of sorption to suspended particle that settle to sediments and differential sorption of NPEOs as a function of ethoxylate chain length are expected (Brownawell et al. 1997; Ferguson et al. 2001), how much NPEOs and their metabolites are desorbed during transport to cleaner waters or continued resuspension over time; and the extent of degradation that occurs in the water column and in sediment bed following deposition (Giger et al. 1981; Giger et al. 1984; Ferguson et al. 2001; Ferguson et al. 2001; Ferguson et al. 2003; Ferguson and Brownawell 2003). In Chapter 5 it was shown that that NP and NP(1-3)EO in highly depositional sediments was correlated well with the particle reactive sewage tracer DTDMAC in sediments, but lower metabolite levels were found in many other sediments that had not been characterized as being depositional. Further evidence for the persistence of more highly ethoxylated NPEOs is found in the work of Shang et al. (Shang et al. 1999), who estimated the half life of these compounds at 60 yr in a sediment core from Canada, where sewage had only been subjected to primary (non-biological) treatment. Ferguson et al. (Ferguson et al. 2003) found that NPEO concentrations and compositions of NPEOs and their neutral metabolites were well preserved in high deposition rate and anoxic/disoxic sediment cores collected eight years apart at the same location in Jamaica Bay, NY (Ferguson et al. 2003). Also significant to this work, the latter study argued that the composition of NPEOs in the dated sediment cores closely tracked the history of sewage treatment at the local Jamaica plant. This was consistent with the work of Shang et al. (Shang et al. 1999), more highly ethoxylated, less degraded, NPEOs were found at much higher relative abundance at times when NPEO treatment was less. Thus NPEO compositions looked more like sewage influent when there was less biological treatment, and the mixture was more like sewage effluent (Ferguson et al. 2001) when the degree of biologically treatment was greater. It should be pointed out here however, that there was evidence of extensive in-situ loss NP1EO in surface sediments of those cores that corresponded with an increase in NP. This de-ethoxylation is consistent with reactions that occur under anaerobic conditions. In this thesis, I tested the hypothesis that the relative amount of less degraded nonylphenol polyethoxylates could provide valuable information about the relative source inputs of NPEOs to urban estuarine sediments that might come from biologically treated sewage effluents vs. inputs from combined sewer overflows (CSOs) or other direct discharges of NPEOs. Another reason to quantify higher ethoxylate chain NPEO homologs could underestimate total delivery of NPEOs to sediments, and obscure potentially important interpretations of the degree of sewage treatment applied prior to discharge.

In earlier work (Brownawell et al. 2005), data was presented that showed a relationship between the ratios of NP(1-3)EO/NP to the abundances of redox sensitive metals Cd and Mn. As discussed above, the composition of the smaller NPEO metabolites can be indicative of sediment conditions that lead to losses of NPEOs (oxidizing) or conversion of NPEOs to NP (reducing). If these metal and relatively persistent metabolites of NPEO could be shown to be useful indicators of more time integrated sediment redox conditions, such relationships could provide useful information about longer term processes that affect oxygenation and supply of organic matter to sedimentary environments, as well as aiding in the interpretation of the abundance of both organic contaminants that are microbially transformed differently under different redox conditions, or metals that may be scavenged or preserved, especially under high reducing conditions. I have extended the prior data set, to provide a more complete picture of this relationship.

In earlier work (Brownawell et al. 2005) there was a possible relationship found between NPEO metabolite compositions in sediments and the frequency of amphipod toxicity observed in standard lab testing; the sediments with indicators of possibly more reducing conditions were more toxic. It is not clear why this might be so; possibly the chemical form and rapid release of certain sulfide associated metals, or that more reducing sediment are correlated with stress associated with more ammonia or sulfide that amphipods might be exposed to. In this study, I have statistically analyzed further possible correlations between a wide variety of chemical parameters measured in the same 45 sediments that I have measured quaternary ammonium compounds for, and NPEO metabolite compositions have been determined.

In the following in sections are brief additional background on NPEO degradation; redox sensitive metals; and sediment toxicity in urban harbor sediments in the region.

6.1.2 Microbial degradation of NPEOs.

NPEOs and their metabolites during sewage treatment in WWTPs and the natural environment have been extensively studied (Ahel et al. 1994; Di Corcia et al. 2000; Ferguson and Brownawell 2003; Jonkers et al. 2003). Generally degradation of NPEOs during sewage treatment results in the shortening of the ethoxylate chain, leading to the formation of NP (Giger et al. 1984; Ahel et al. 1994; Ferguson and Brownawell 2003). NPEO composition patterns in sewage influent were dominated by higher ethoxymers (10-15), while the composition of sewage effluent was dominated by lower ehoxymers (0-3), with sewage impacted sediments containing the highest concentrations of NP (White et al. 1994; Ferguson et al. 2001). In sediments samples, most of the study focused on NP and NP(1-3)EO due to their high levels and their relative potentency as estrogen mimics (White et al. 1994) . In contrast, there is relatively little known about the distribution of higher ethoxymers of NPEO in aquatic sediments (Shang et al. 1999; Ferguson et al. 2001; Jonkers et al. 2005) despite that fact that these higher ethoxymers can be well preserved in the sediment, particularly under reducing conditions.

Degradation pathways of NPEOs are significantly different under aerobic and anaerobic conditions. Jonkers and co-workers (Jonkers et al. 2001) reported that under aerobic conditions NPEO biodegradation is initiated by the carboxylation of the individual ethoxylate chains forming nonylphenol ethoxy-carboxylates (NPECs), with further degradation shortening the NPEC chain length. NP was not found as a metabolite under aerobic conditions (Jonkers et al. 2001). In contrast, under reducing conditions, accumulation of NP was found in the sewage sludge (Giger et al. 1984). As mentioned above, Ferguson and co-workers (Ferguson et al. 2001; Ferguson et al. 2003) in a nearshore highly reducing sediments, and a non-steady state diagenetic model developed to fit their data indicated that conversion of NP1EO to NP was much faster than the degradation of NP. In Chapter 3, and earlier work (Brownawell et al. 2005) found that NP(0-3)EO are ubiquitous contaminants in the NY/NJ Harbor complex, and very high concentrations of NP and other sewage derived estrogenic chemicals are found to be associated with highly reducing sediments in other areas of the lower Hudson Basin.

6.1.3 The distribution of redox-sensitive metals in coastal estuarine sediment.

REMAP samples were collected in 1993/4 and 1998 lower Hudson Basin wide sediment and characterized for a very large range of sediment, metal, organic contaminant properties. The samples or sites were also characterized for sediment toxicity and benthic community analysis. Cadmium and manganese are two redox sensitive metals that were analyzed in all of the monitoring study. While Cd is likely enriched in areas of the harbor with intense pollution inputs, it is also known to be enriched in marine and estuarine sediments, when there is low oxygen in water columns or sediments, likely due to interactions with sulfides or metal sulfides. Cd is one of a few redox-sensitive metals in sediments that are relatively soluble in seawater and can be enriched or depleted in sediment depending on the oxygenation of sediments/bottom waters. Metals that have been shown to be highly enriched in sediments under low oxygen conditions include uranium (Barnes and Cochran 1993), molybdenum, rhenium , cadmium (because of strong chloride complex that makes it less likely to be sorbed to particles in seawater) and vanadium. Relatively particle reactive copper (Cu) has also been observed to be enriched in sulfide rich sediments (Morford and Emerson 1999; Nameroff et al. 2002; Morford et al. 2005). Most of the work has been conducted in offshore or deep seas in anoxic estuarine fiords (Murray et al. 1989). However, recent work shows Cd (and even more Mo) enrichement in the most hypoxic/anoxic areas of the highly polluted Forge River, a tidal inlet on the South Shore of Long Island (Brownawell 2009).

Another redox sensitive metal is manganese (Mn). Mn is preferentially mobilized from sediments relative to otherwise geochemically similar iron (Fe) under reduced sedimentary conditions due to the precipitation of Fe with sulfide (Morford et al.

2005), and the Mn/Fe ratio has been recognized as an indicator of sediment reducing conditions in LIS (Varekamp et al. 2003) and the median concentration of ratios of Mn/Fe in "depositional" LIS surface sediments are modestly (about 30%) greater than those in otherwise very similar LIS sediments that are classified as more "unsorted and reworked" (Mecray and ten Brink 2000); the former sediments might be expected to be more reducing than the latter population of sediments. In this Chapter findings on relating NPEO metabolite compositions to aluminum normalized levels of Cd and Mn are reported. Planned work on the less pollution affected Mo is planned, but not yet conducted for these and other sediments.

6.1.4 Background on sediment toxicity in the NY/NJ Harbor complex.

The regional environmental mapping and assessment program (REMAP) conducted by the U.S. EPA in 1993, 1998, and 2003 in the NY/NJ Harbor Complex provides a wealth of data on levels of organic and inorganic contaminants in sediments, sediment properties and sediment toxicity(Adams and Benyi 2003). Several investigators have attempts to discern potential causes of sediment toxicity by correlative analysis of toxicity against various chemical parameters of the sediments in these and previous large scale assessments conducted by the National Oceanic and Atmospheric Administrations (Long et al. 1995; Brownawell et al. 2005). Long et al. (1995) found significant correlations between levels of polycyclical aromatic hydrocarbons in sediments during their harbor-wide assessment in 1991, whereas sampling in 1993 focused on Newark Bay and the Passaic River found significant associations between chlorinated hydrocarbons and toxicity. In a re-analysis of the 1993 and 1998 REMAP data, related research is presented in a discussion of the results below. Brownawell and co-workers found that there was no obvious relationship between sediment toxicity and Ag which has been used as sewage indicator, however, sediment toxicity is positively correlated with indicators of sediment reducing conditions as indicated by redox sensitive tracers such as Cd/Al and NP(1-3)/NP) ratios (Brownawell et al. 2005). A more holistic approach was employed here that applied principle components analysis (PCA) to discern patterns between groups of sediments chemicals or indices of sediment properties and toxicity.

6.2 Experimental methods.

6.2.1 Sample collection and analysis

Forty-five REMAP samples collected in 1998 discussed in Chapter 3 (Figure 3.1) were included in this chapter. Thirty of them were analyzed by Yin (2007) for NP(0-3)EO and 15 were analyzed in this chapter (Table 6.2) by a different modified method for NP(0-15)EO (Ferguson, 2001). An additional 11 samples collected in 2004 from CSO and WWTP affected Bowery Bay and Flushing Bay sites in western Long Island Sound were analyzed along with another sample collected feet away from a large CSO outfall near the Williamsburg Bridge off the East River. These were also analyzed for the full range of NPEO homologs (Figure 6.1). Finally 2 samples collected in 1995 and 2003 from same Hackensack River sites (from Chapter 4, Figure 4.2) were analyzed for NP(0-15)EO by the same method in this chapter (Table 6.2). In total 29 samples have been analyzed for the NP(0-15)EO, and 45 for NP(0-3)EO; 15 of those samples overlap.

Much larger data sets for samples collected by REMAP in 1993/4 (n=168) (Figure 6.2) and 1998 (n=112) (Figure 6.3) were included in the principle component analysis (PCA) in the chapter. In both sets of samples a variety of geochemical factors and contaminants were measured by EPA including total organic carbon (TOC), acid volatile sulfide (AVS), silt/clay (SICL, %), metals (Ag, Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se, Sn, Tl, Zn), PAHs. Detail information of sediment analysis was included elsewhere (Adams and Benyi 2003). Sediment toxicity was also tested involving the exposure of amphipod, *Ampelisca abdita*, to sediments in a laboratory setting. Sediments at a station were considered toxic using the *Ampelisca abdita* toxicity test if percent survival was less than 80% compared to controls. Detail about the projection information, sample collection and analysis were included in the previous report (Adams and Benyi 2003).

6.2.2 Detection of NPEO and metabolites

A major effort in this work was to modify the previously developed method of Ferguson et al. (Ferguson et al. 2001) to utilize liquid chromatography electrospray ionization, time of flight mass spectroscopy (LC-ESI-ToF-MS) to quantify NPEOs and metabolites and apply it to a wide range of sediments from throughout the NY/NJ Harbor complex. The analytical methods developed here were modified from those previously published by Ferguson et al. (Ferguson et al. 2001). Freeze dried sediments (0.1-0.5g) were packed in a stainless steel column (Alltech Chromatography, Deerfield, IL), spiked with 1.6 μg of [$^{13}C_6$]-labeled surrogate standards, and then extracted in an ultrasonic water bath at 60°C with methanol pumped through the column at 0.5mL/min for 14 minutes. Extracts were collected and evaporated to dryness under gentle flow of nitrogen gas, and then reconstituted in 400 μl methanol and filtered through a 0.45 μm membrane filter (Millipore Utrafree-MC). Extracts were then cleaned up by injecting 100 μl into a Hewlett Packard HPLC system with UV detector (HP series 1050) using a reverse phase C18 column XTerra prep column (Waters, 7.8X100 mm) by isocratic methanol elution at a flow of 2mL/min. Retention time of NPEOs was determined based on the peak of a NPEO standard mix at 273 nm (Figure 6.3a). The fraction of sample extracts eluting within the time window of the NPEO standard mix (1.5-3.0 min, Figure 6.3b) were collected and evaporated to dryness again, and reconstituted in 1 ml of 50% methanol in water. Internal standards were added directly into the injection valve right before detection on HPLC-ESI-ToF-MS.

Analysis of NP and NPEOs was conducted using a Waters 2695 LC equipped with a Shodex (Japan) gel filtration column (MSpak GF-310 4D), coupled to a ESI-ToF-MS. NPEOs were measured using positive ionization and NP measured using negative ionization of of ESI-MS. Under positive mode mobile phase A was 10 μM sodium acetate in water; mobile phase B was 10 μM sodium acetate in methanol. Under negative mode pure water and pure methanol were used as mobile phase A and B respectively. The cone voltage and capillary voltage for positive mode were 25V and 2800V which was optimized for NP1EO ionization with slightly sacrificed sensitivity of long-chain NPEOs. The cone voltage and capillary voltage for negative mode were set to -45V and -2500V. Cone gas was set at 50 L/h for both positive and negative mode. Otherwise analysis conditions were the same for both positive and negative ionization modes. Initial solvent composition was 50:50 (A:B) and changed to 0:100 (A:B) with a linear gradient over 23 min, the gradient held for 10 min, changed to 100:0 (A:B) and held for 2 min, changed back to 50:50 5 min and finally held for 10 min. Flow rate of mobile phase was 0.2ml/min. Calibration standards were made in 50% methanol in water and included a mixture of NEPOs, [$^{13}C_6$]NPEOs (including NP), and internal standards (n-NP and n-NP3EO). Recovery was calculated by the signal of [$^{13}C_6$]NPEOs relative to the internal standard.

6.2.3 Principal component analysis (PCA)

PCA is mathematically defined as an orthogonal linear transformation that transforms the data to a new coordinate system such that the greatest variance by any projection of the data comes to lie on the first, and the second greatest variance on the second axes (called the first and second principal components). Higher order projections can also be assessed. PCA is the simplest of the true eigenvector-based, descriptive multivariate analyses. Generally PCA can be thought of as revealing the internal structure of the data in a way which best explains the variance in the data. By projecting all variables on two or three dimensional components, PCA allows one to evaluate relationships between variables.

Sediment property parameters, termed chemical species, of individual samples were evaluated by PCA using statistical software (Canoco 4.5). To compensate for differences in the magnitude of each species, all data were centered and normalized among species which means only the relative extent of variability of each species (not the absolute value) is evaluated by the PCA. The PCA results are reported as loadings and scores projected on coordinates of the greatest two components (PC1 and PC2). Loading and score figures can be plotted on species score as vectors and sample scores as points respectively. Both sample and species can be plotted together in a biplot figure. The smaller the angle between any two vectors the stronger positive correlation between the two species. If the angle equals 90^{o}, the two variables are independent to each other, and an angle of 180^{o} indicates a strong negative correlation. Evaluting the PCA scores is a simple means by which samples with a similar suite of species can be grouped by how well they cluster on the two dimensional projection of PC1 and PC2. Plotting sample scores and species scores on the same figure allows identification of how each sample compares to the rest with respect to a selected species. For example a more positive score when projecting a sample onto a vector implies that the sample had a value greater than the average value for the selected species.

6.3 Results and discussion

6.3.1 Method validation

This work utilizes a modification of the Ferguson et al. (Ferguson et al. 2001) quadrupole method to analyze NPEOs using ESI-ToF-MS. In addition to the potential for additional confirmatory data, the ToF method provides similar or significantly better MDLs for almost all NPEO metabolites. Matrix cleanup prior to ESI-ToF-MS has been found to be essential to reduce the ion suppression during the ionization of target compounds (Ferguson et al. 2000). ^{13}C labeled NPEOs provide an excellent surrogate standards as almost identical mimics to the analytes of interest for assessment of losses during the sample treatment and ion suppression effects influencing detection. All surrogate standards showed excellent recovery in the 29 sediments analyzed. Recovery for NP to NP15EO ranged 71-112% (Table 6.1). The method detection limit (MDL) of this method (0.61-8.29 ng/g) is slightly lower than that reported for the method utilizing the quadrupole mass detector (Table 6.1). Both techniques reported the highest MDL for NP and NP1EO, which may due to the same separation and ionization conditions used in both methods.

6.3.2 Occurrence of composition of NPEOs in NY/NJ Harbor complex

In this study NP(0-15)EOs were analyzed using an LC-ESI-ToF-MS method on 29 sediment samples throughout the NY/NJ Harbor complex, including some previously analyzed by Yin (2007). NPEOs were found to be ubiquitous in the NY/NJ Harbor complex being detected in all 29 sediments analyzed at concentrations varying from 0.07 to 90 μg/g with a median value of 10 μg/g (Table 6.2).

The composition of NPEO homologs varied significantly in different samples (raw data on compositions and illustrative figures in Appendices 6.1 and 6.2. The concentrations of NP(0-15)EOs varied between 0.07 and 90 μg/g in the 29 samples analyzed here for polyethoxylates. Most of the samples chosen for these analysis were affected by sewage or CSO inputs to same extent, and 18 of 29 samples had NPEO concentrations between 9.4 and 90 μg/g, and all of these sites are near areas of sewage inputs or proximate to CSOs or CSO source areas. Six sites are thought to be most impacted by CSOs (BB1, BB2, BB3, UH206, NB205, and WB), where NPEO levels were exceptionally high (18 – 90 μg/g). The only other two samples with NPEO levels within that range are from Grassy Bay sites within Jamaica Bay (JB008 and JB203 with concentrations of 26 and 39 ug/g respectively).

It was hypothesized that the samples closest to CSO sites would have a higher proportion of polyethoxylated compounds that are degraded during biological treatment in WWTPs. Two indicators of the degree of ethoxylation are shown in Table 6.2 are average ethoxymer (EO) chain length, and the ratio NP(4-15)EO/NP(0-3)EO (as in Ferguson et al., 2003). The average EO chain lengths varied widely from 0.49-8.65 with median value around 3.78. However, contrary to expections many of the lowest values were found for the CSO samples (0.49 – 3.23). The other four samples with the lowest average EO chain length (1.06 -2.0) corresponded to the sites likely most affected by sewage (the two Grassy Bay samples and two samples from the Hackensack River site).

The distribution of the ratio NP(4-15)EO/NP(0-3)EO within the 29 samples was also much different than what might be predicted from Ferguson et al. (2003). The median NP(4-15)EO/NP(0-3)EO is 0.46 indicating that about 30% of total NPEOs would be under estimated if only NP(0-3)EO were quantified, as in Chapter 5. Again, the ten samples with the lowest ratios are the 6 CSO affected samples (0.04 – 0.31) and the four Grassy Bay and Hackensack River samples that are greatly affected by local treated sewage inputs (0.05 – 0.15). For the other 19 sites, only two (JB018 and 213) have NP(4-15)EO/NP(0-3)EO ratios that fall within this range (Table 6.2). It unclear why there is so little polyethoxylates at these sites. It is expected that there has been large inputs of NP(4-15)EO at the CSO sites, suggesting that the microbial communities at the sites that receive untreated sewage are better able to degrade NPEOs (likely be de-ethoxylation due to the high concentrations of lower ethoxylates and the anaerobic conditions in the sediments. Clearly much more work would be required to understand not only why polyethoxylated NPEOs were so low at CSO sites. It is also not really clear why the NP(4-15)EO/NP(0-3)EO ratio is lower at sites proximate to sewage treatment plants than away from them. Whether this is due to differences in microbial degradation, physical chemical fractionation during transport, or some other factor, is unknown

6.2.3 Separating NPEO sources or compositions in sediments through statistical analysis.

The results presented above do not support the hypothesis that higher relative abundances of NPEO ethoxymers are characteristic of sources more affected by less treated CSO inputs. However, there may be associations of widely varying NPEO compositions that may be useful for understanding conditions (e.g., source type or area, differences in distance from NPEO sources, or depositional environments) that control those compositions. The principal component analysis described above was used to determine whether the NPEO composition could be used to determine sources and fate processes that may vary with location or potential properties of the sedimentary environment.

The PCA analysis (see methods above) included 13 species: NP(4-15)EO/NP(0-3)EO; and the concentrations of each NPEO ethoxymer in the NP(4-15)EO range. All sediment samples were separated into three groups on the PCA scores figure of PC1(36.5%) and PC2(25.2%) (Figure 6.5). Examination of the groupings yields little correlation with the the magnitude of the NP(4-15)EO/NP(0-3)EO. However, 5 of the 6 CSO sample fall into the lower portion of group X; the sixth CSO sample is WB which is found in Group Z. Interestingly, Group X that contains most of the CSO samples does correspond to an ethoxymer composition within NP(4-15)EO that is most enriched in higher ethoxymers peaking at NP13EO, but it is not clear what the most likely mechanism for this fractionation (e.g., greater adsorption of higher ethoxymers) might be. It is also pointed out that none of these samples fall along the NP(4-15)EO/NP(0-3)EO vector, presumably because this is only one of the thirteen species considered in the PCA.

Interestingly, all samples from group Y are located proximate to WWTPs (Jamaica Bay (100MGD), North River (170MGD), Hackensack River (109MGD) WWTPs). Samples from group X are mostly collected by the CSO outlets (Bowery Bay and Jamaica Bay samples) and in the Passaic River where no direct sewage is discharged. The average ethoxymer distribution pattern of group Y (Figure 6.6) is perhaps closest to what Ferguson et al. (Ferguson et al. 2003) observed in surficial sediment samples collected in surficial sediments in the Grassy Bay core. It is harder to make any generalizations concerning commonalities that are apparent among samples that are found in group Z (Figures 6.5 and 6.6).

6.3.4 Application of NP(1-3)EO/NP ratio as a redox sensitive tracer in the sediments

A relationship has been found between NP(1-3)EO/NP and the ratios of Cd/Al, and to a lesser extent between NP(1-3)EO/NP and Mn/Al. The hypothesis was formed that these relationships are coupled mechanistically, and reflect a measure of some time averaged redox condition in the sediments. There are other possible mechanisms for all of these measures to vary (e.g., local Cd contamination), but the hypothesis was based upon known behavioral patters of redox sensitive metals, the accumulation of NP in areas that are highly reducing; the importance of de-ethoxylation reactions under reducing conditions, and the in-situ transformation of NP1EO to NP found in a Grassy Bay sediment core (Ferguson et al. 2003). I include here and expanded data set comparing these ratios adding additional new data from this Chapter. The results are shown in Figure 6.7, where it is seen that there is an inverse relationship between NP(1-3)EO/NP ratios and Cd/Al. NP(1-3)EO/NP is positively related to Mn/Al, althought there is more scatter in that relationship. This work has not been further developed in this thesis, and future measurements of molybdenum are planned to test this idea further Sediment redox conditions may control preservation, concentration, bioavailability, and mineral associations of other organic contaminants and heavy metals in sediments. These processes would not only affect contaminant distributions and fate, but may affect the results of sediment toxicity tests as well.

6.3.5 Relationships among toxicity, inorganic and organic chemicals, and other geochemical factors in REMAP sediments

This investigation used previously collected REMAP data (Adams and Benyi 2003) on survival of the amphipod, *Ampelisca abdita*, to indicate sediment toxicity. Sediments at a station were considered toxic using the *Ampelisca abdita* toxicity test if percent survival was less than 80% compared to controls. Toxicity data shown in the following discussion is presented as mortality of the amphipod from the test. The toxicity test provides a direct indication of the effects of sediment contaminants which is a complex mixture of chemicals, including chemicals that are not measured. The frequency and spatial intensity of amphipod toxicity test were similar in both 1993/4 and 1998 results (Table 6.3). Sediments from Newark Bay showed higher toxicity (46-50% toxic) than the rest of the Harbor complex - Jamaica Bay (25-32% toxic) and Upper Harbor (14-18% toxic); while Long Island Sound, New York Bight and Raritan Bay showed the lowest toxicity level (Table 6.3). In order to evaluate the relative associations between a large suite of geochemical factors measured as part of the 1993/1994 and 1998 REMAP studies and the additional measurement made as part of this present study, PCA was utilized.

PCA species scores for the 1993/1994 and the 1998 data are shown in Figure 6.8a and 6.8b, and represent the inter-correlation of all variables projected on the first and second principal components. Scores from both sample sets show a similar pattern of correlation between geochemical factors and sediment toxicology. Si shows straight negative correlation with all size indicating variables: Fe, Al and SICL indicating a natural distribution of sediment size from sandy (bigger size with more Si and less Fe, Al) to muddy (smaller size with more Fe and Al and less Si) sediments. The PCA score shown in Figure 6.9 indicate that most of Jamaica Bay, Raritan Bay, NY Bight apex (only collected in 1993) and Long Island Sound (only collected in 1993) samples are separated along the trend of sediment grain size as indicated by Si versus Fe and Al. Other variables like TOC and to a lesser extent, Ag which may be more sewage derived, also have a relatively strong positive correlation with Al and Fe. The contribution from municipal sewage wastewater input may be one end member of this particle size distribution mixing with the other end member of more sandy sediments.

A number of interesting variables plot perpendicular to the sediment size relationship, indicating a lack of correlation. Sediment toxicity (indicated as mortality in the Figure 6.8) has no obvious relationship with the mixing trend (perpendicular to the toxicity vector) between fine sediments and sewage input versus natural sandy sediment. This agrees with the previous report by Brownawell (Brownawell et al. 2005) that showed no relationship between sediment toxicity and sewage tracers like Ag and total NP(0-3)EOs. Plotting along the same general direction as mortality are PAHs and several heavy metals (Sn, Sb, Hg, Cu, Cd, Pb), indicating strong correlations between these variables and toxicity. Brownawell et al. (2005) suggested that the toxicity related to sediment redox condition indicated by the NP(1-3)EO/NP ratio could be related to the ability of reducing sediments to preferentially trap organic contaminants and heavy metals or releasing of ammonium from more reducing sediment during the toxicity test (Brownawell, 2005). Figure 6.9 indicates that most samples from Newark Bay and some samples from Upper Harbor are distributed along the positive mortality vector.

To test this hypothesis, a second PCA was done on a smaller set of the 1998 REMAP samples with the NP(1-3)EO/NP ratio (indicated as NP ratio on the plot) was added as redox tracer, and DTDMAC and total NP(0-3)EO (indicated as NPEO on the plot) were added as sewage input tracers (Figure 6.10). Very similar results were found in Figure 6.10 as compared to the data shown in Figures 6.8 and 6.9. Jamaica Bay samples are separated along the particle size mixing trend and DTDMAC and total NP(0-3)EO as sewage tracers also plot near this trend. Some samples from Upper Harbor and Newark Bay project near mortality along with heavy metals (Sn, Hg, Sb, Cu, Pb, Cd, As) and PAHs. The NP(1-3)EO/NP ratio redox tracer strongly correlates with the heavy metals and mortality providing some support for the hypothesis that reducing environments could to some extend contribute to higher toxicity in the sediments.

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Figure 6.1. Sediment sample sites collected from Bowery Bay and Flushing Bay in 2004

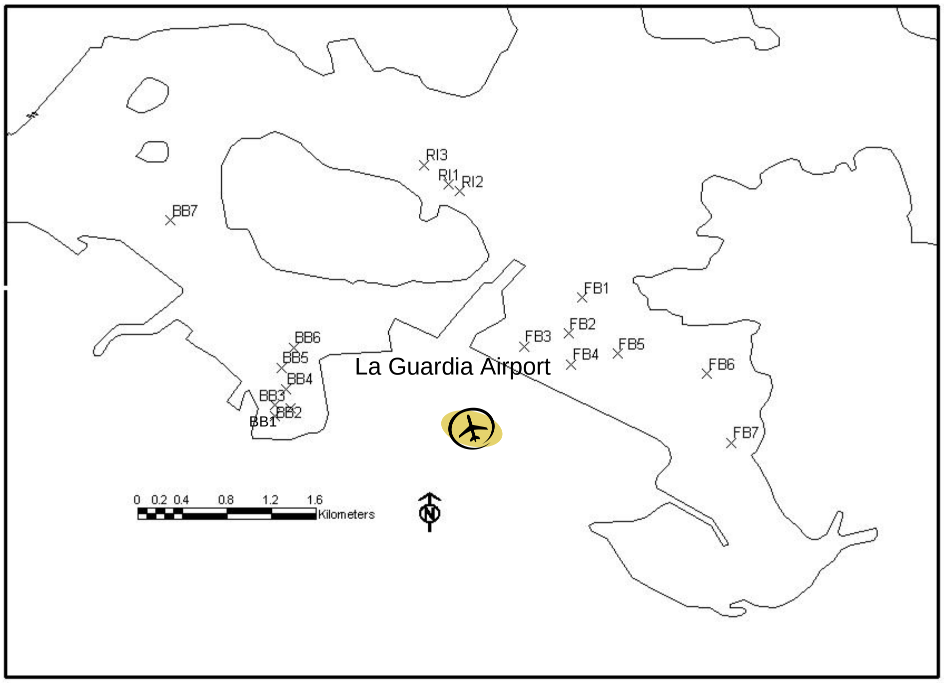


Figure 6.2

R–EMAP SUMMER 1993 AND 1994 SAMPLING LOCATIONS, NY/NJ HARBOR

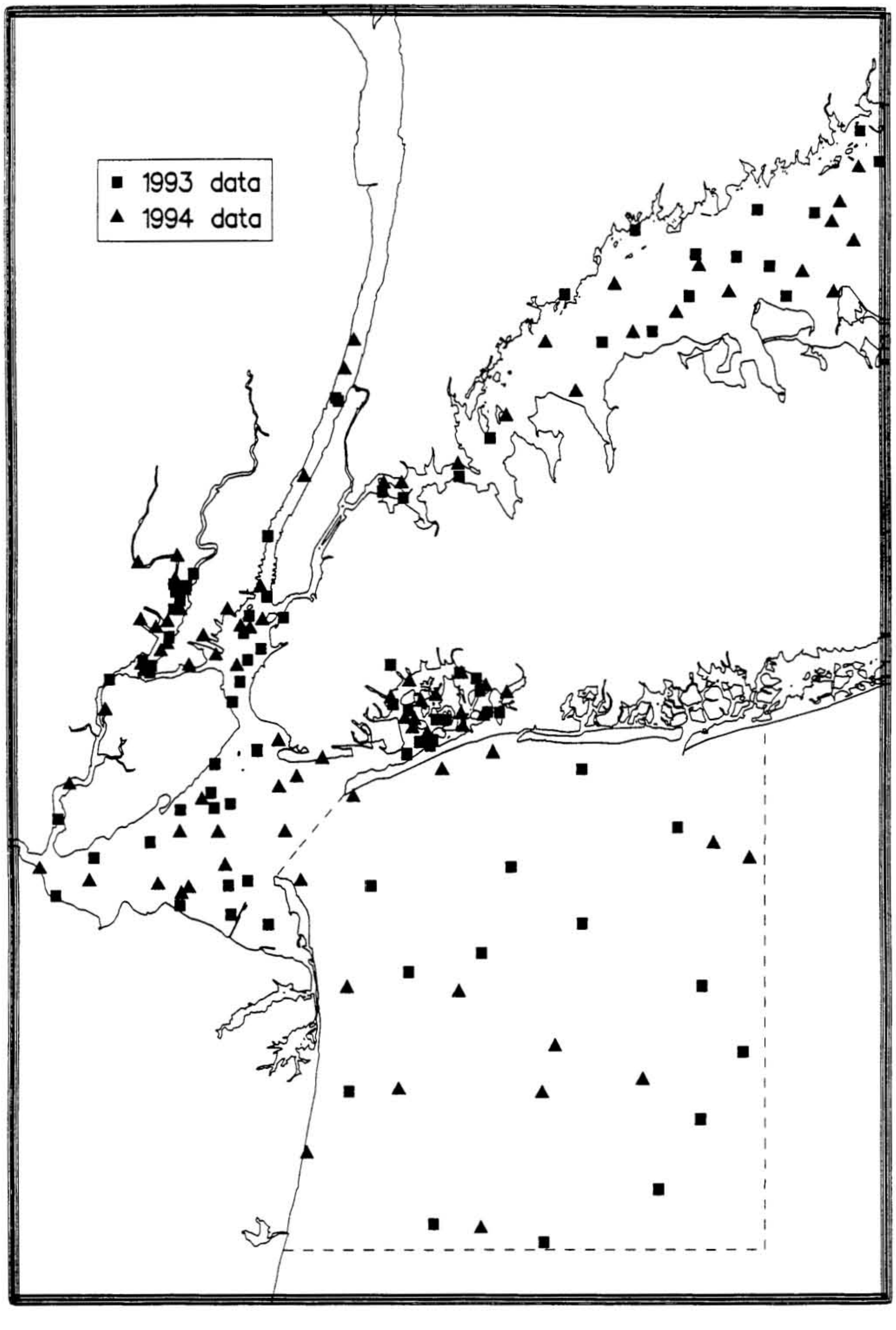


Figure 6.3. REMAP 1998 sediment sample sites in NY/NJ Harbor complex

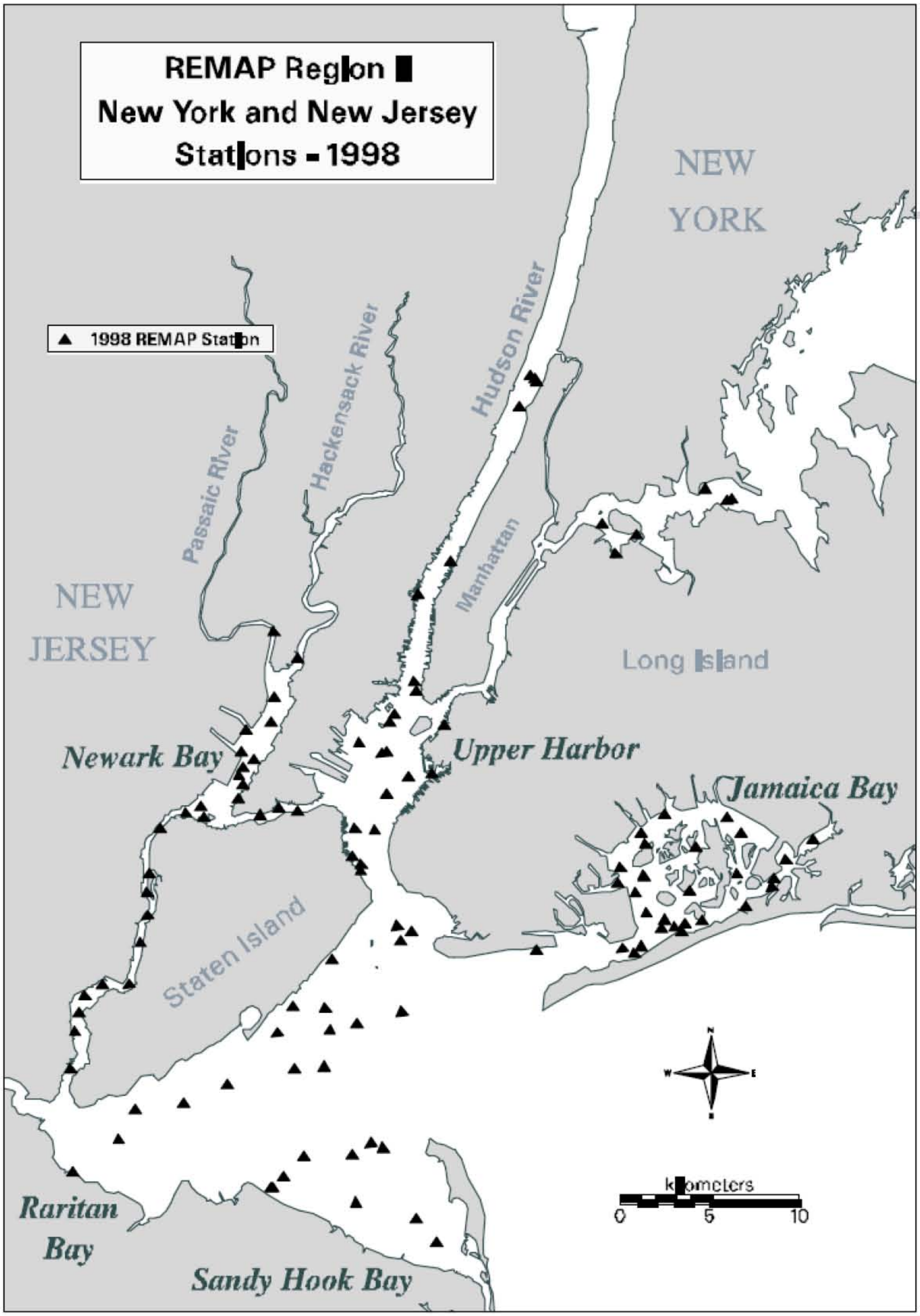
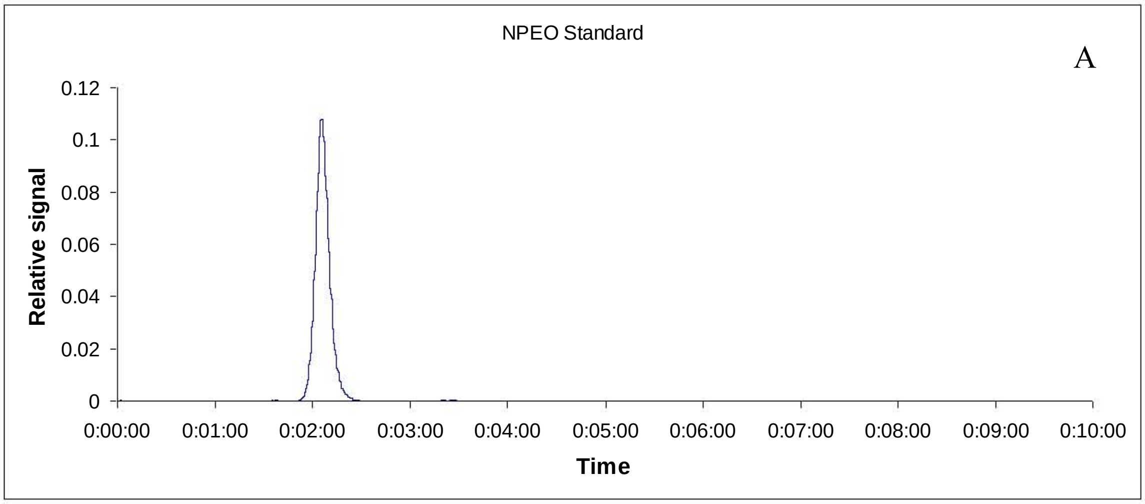


Figure 6.4. Chromatograms of NPEOs standard (A) and real sediment extracts (B) from the matrix cleanup step. 100 μL out of 400 μL sample extract is injected on the a reverse phase C18 column (Waters XTerra prep column, 7.8X100 mm) coupled with UV detector (n=273nm). Fraction was collected within 1.5-3.0 min (gray box in B) for sediment extracts.



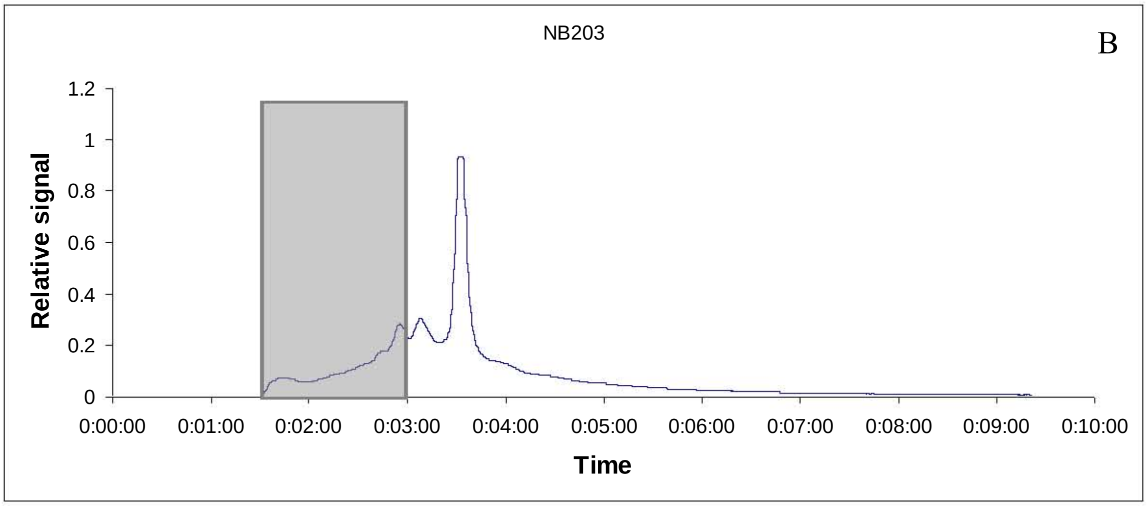


Figure 6.5. Source separation of NPEOs by PCA of higher ethoxymers and sewage treatment tracer (NP(4-15)EO/NP(0-3)EO). Loading (A) and scores (B).

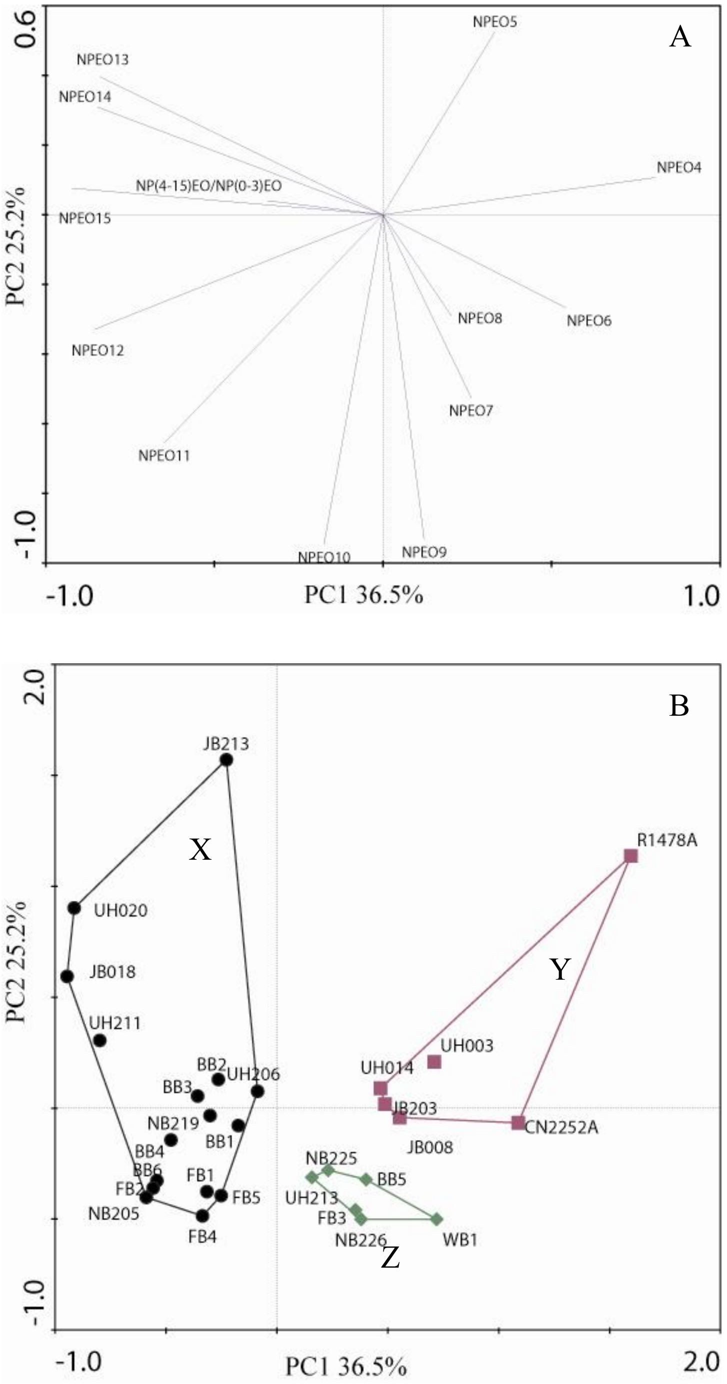


Figure 6.6. Average percentage of NP(4-15)EOs for the three groups separated in Figure 6.5.

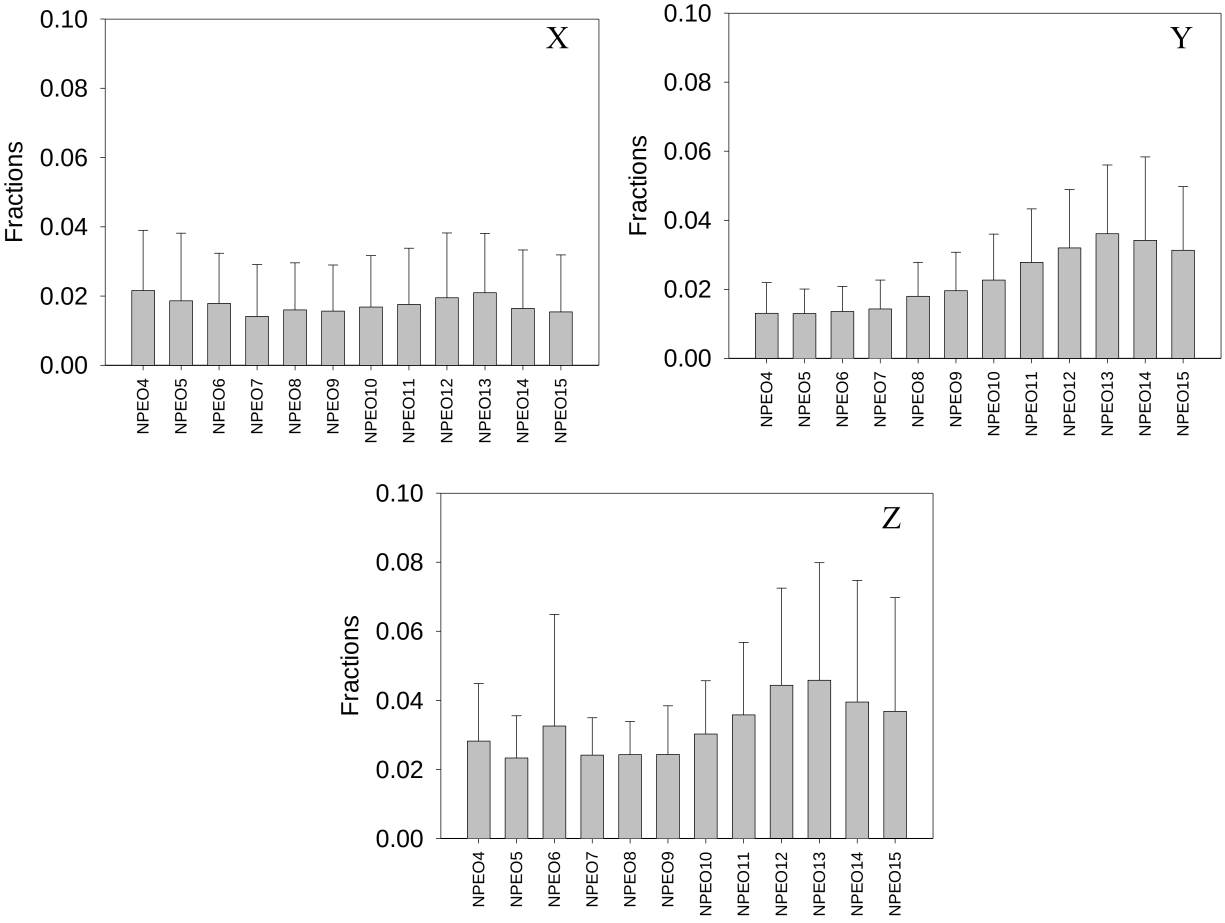
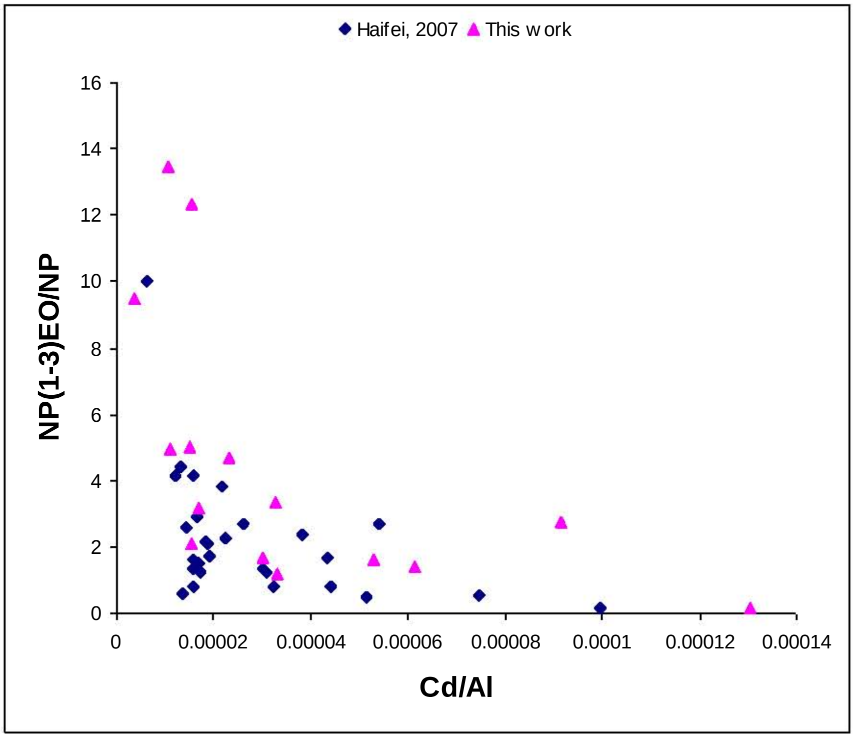


Figure 6.7. Correlation of redox tracer NP(1-3)EO/NP vs. Al normalized redox sensitive metals (Mn and Cd)



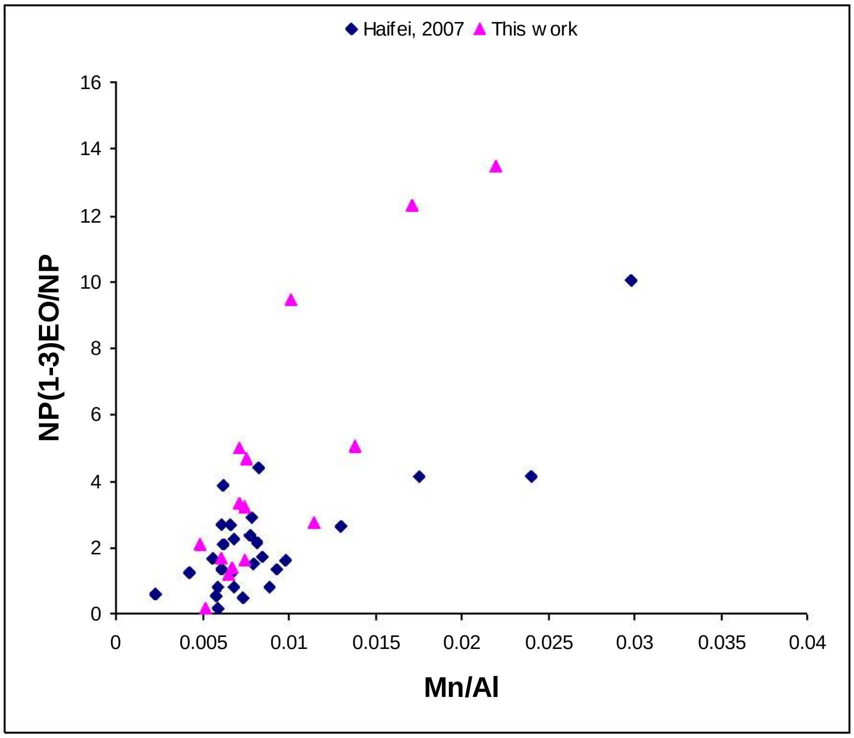


Figure 6.8 Plots of PCA loadings for NY/NJ harbor REMAP sediments in 1993 (a), and 1998 (b)

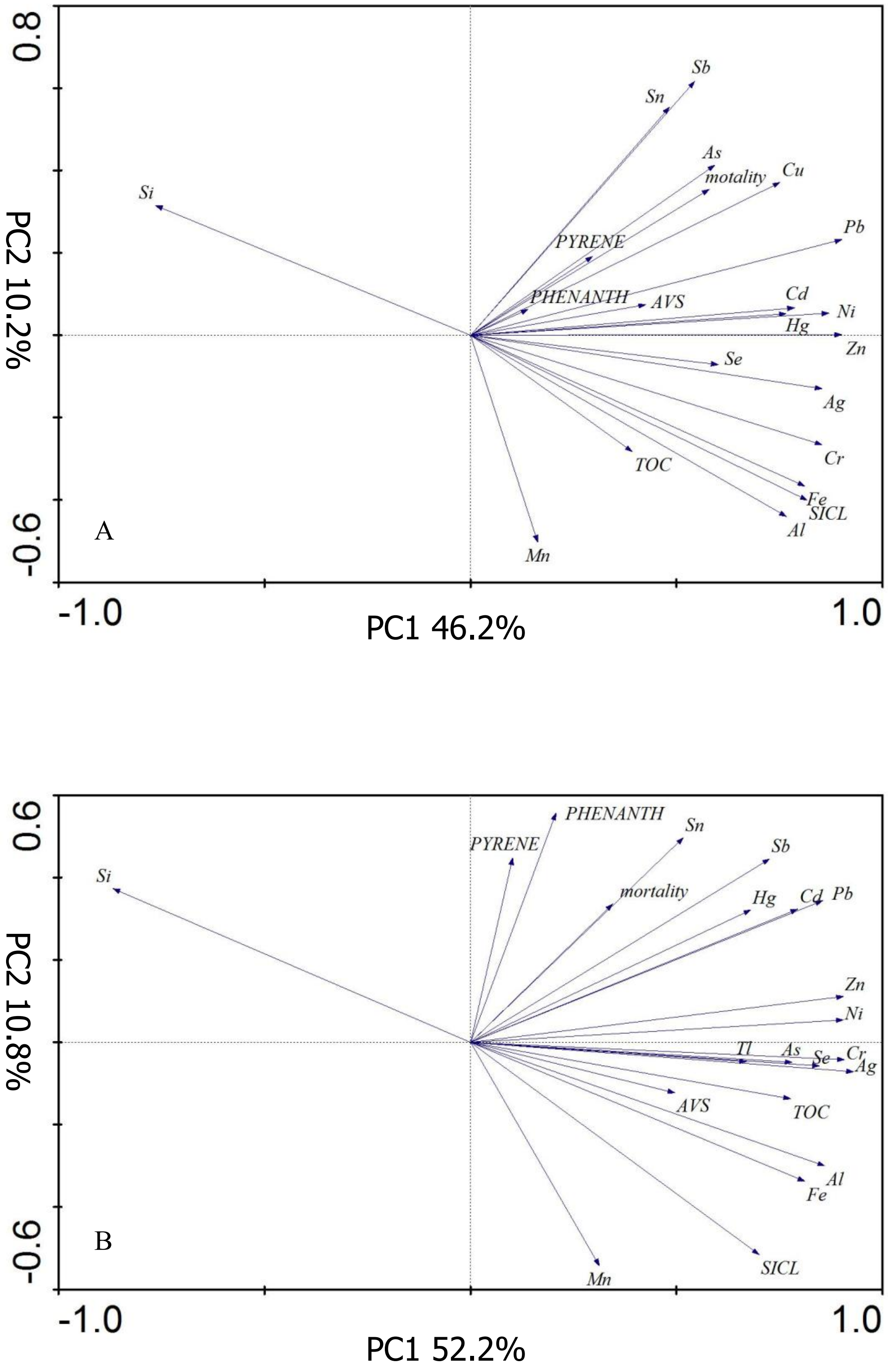
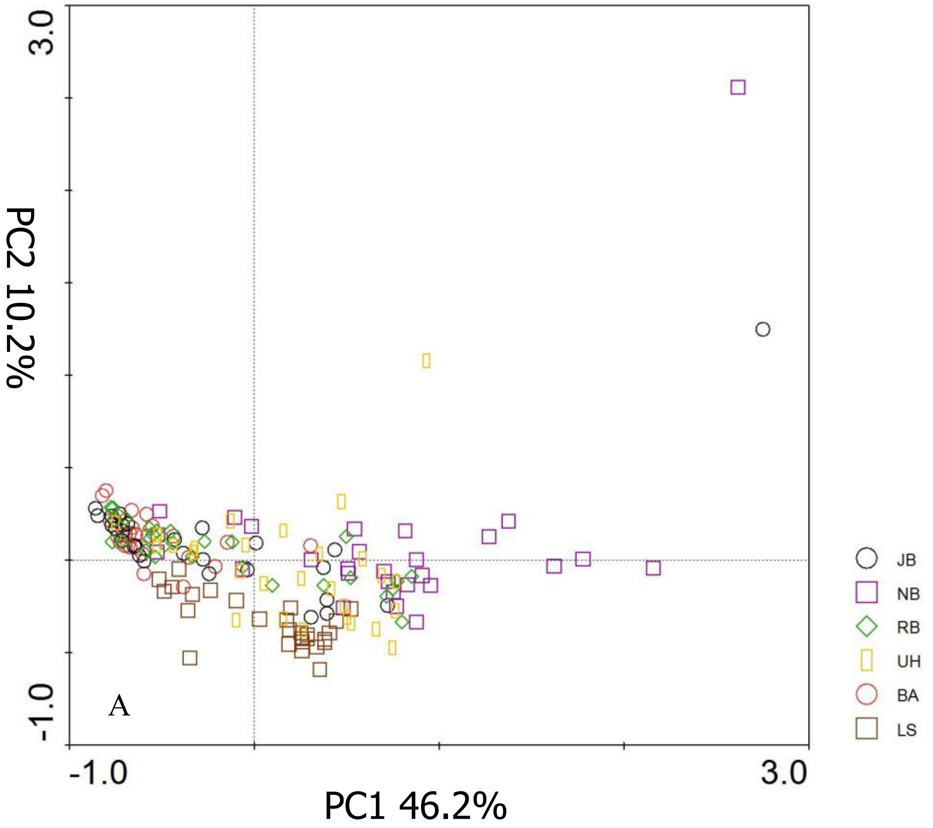


Figure 6.9. Plots of PCA scores for NY/NJ harbor REMAP sediments in 1993 (a), and 1998 (b)



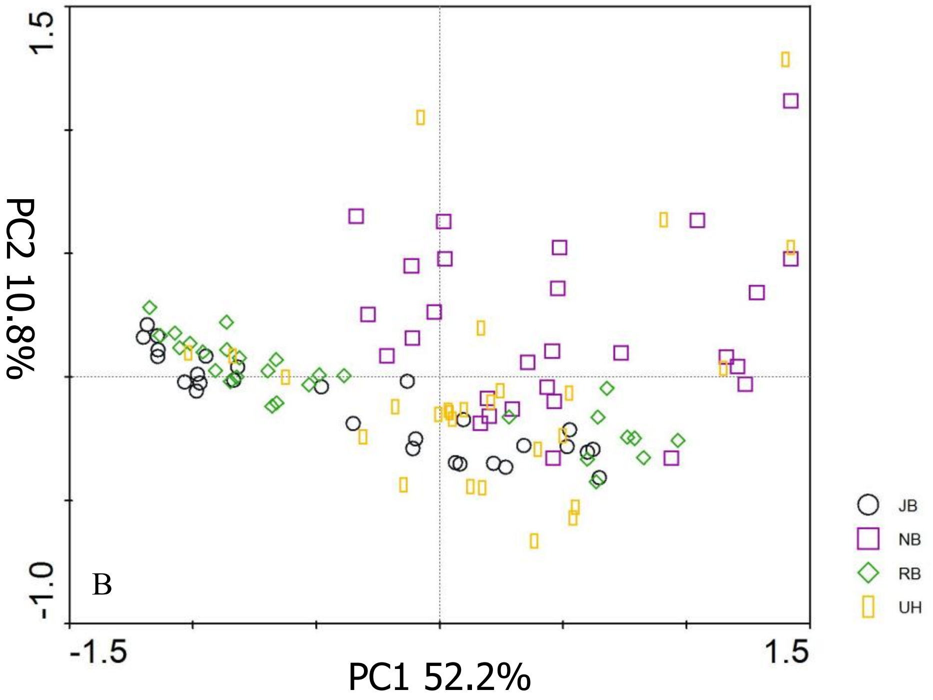


Figure 6.10. PCA loading and scores for all factors plus NP(1-3)EO/NP as redox tracer, DTDMAC and total NP(0-3)EO as sewage input tracers for samples from Jamaica Bay (black circle), Newark Bay (purple square) and Upper Harbor (green diamond).

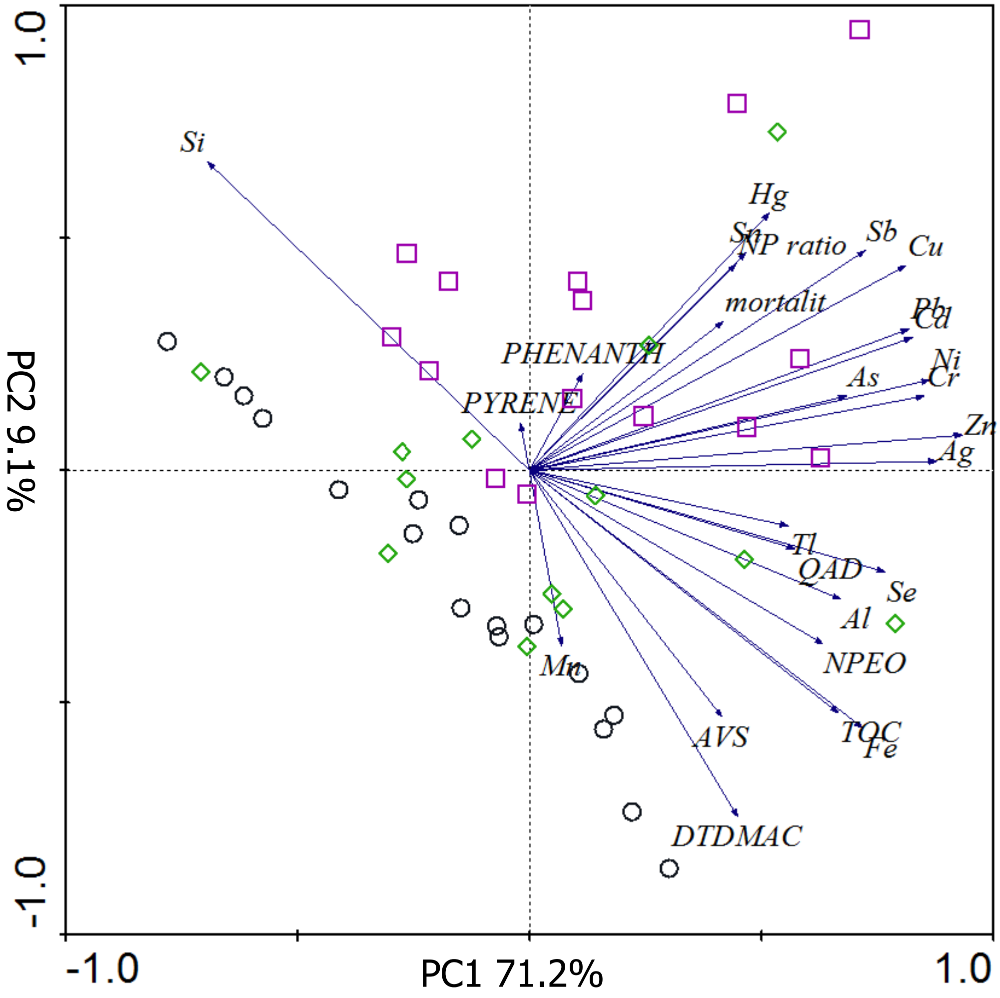


Table 6.1. NPEOs recoveries and method detection limits (MDL)

Compound	Average Recovery % (n=29)	MDL (ToF-MS) (ng/g)[a]	MDL (Quadrupole) (ng/g)[b]
NP	87±19	1.56	21.5
NP1EO	71±9	8.29	37.3
NP2EO	81±12	3.64	2.73
NP3EO	100±11	0.91	2.90
NP4EO	105±12	0.70	1.60
NP5EO	110±14	1.03	0.78
NP6EO	110±19	0.74	0.96
NP7EO	112±17	0.71	0.86
NP8EO	110±17	0.61	1.16
NP9EO	107±18	0.79	1.24
NP10EO	106±16	0.61	1.67
NP11EO	106±18	0.89	1.99
NP12EO	104±18	1.07	2.17
NP13EO	101±20	1.55	4.96
NP14EO	98±16	1.82	3.70
NP15EO	95±17	2.10	3.40

a. Calculated from the sample which has the lowest concentration as the concentration giving a peak with S/N =3; b. from previous report by Ferguson et al. (2001).

Table 6.2. Total NPEOs concentrations for all detected samples, the metabolites ratios and average EO chain length

Sample ID	NPEOs (μg/g)	$\frac{NP(4\text{-}15)EO}{NP(0\text{-}3)EO}$	Average EO chain
BB1	27	0.19	2.25
BB2	78	0.12	1.73
BB3	90	0.08	1.16
BB4	15	0.37	3.55
BB5	10	0.34	3.23
BB6	10	0.63	4.60
CN2252A	16	0.15	1.99
FB1	6.6	0.63	4.48
FB2	5.6	0.77	5.28
FB3	1.2	0.48	3.78
FB4	5.1	0.65	4.64
FB5	9.9	0.67	4.63
JB008	26	0.08	1.56
JB018	11	0.13	2.22
JB203	39	0.05	1.06
JB213	9.4	0.16	2.21
NB205	18	0.31	3.23
NB219	16	0.59	4.05
NB225	0.87	0.55	4.33
NB226	5.0	0.46	3.89
R1478A	15	0.13	2.00
UH003	6.2	0.96	5.43
UH014	5.2	0.69	4.94
UH020	14	1.11	6.51
UH029	0.070	2.03	7.09
UH206	89	0.14	1.90
UH211	3.2	3.39	8.65
UH213	3.6	0.65	4.78
WB1	26	0.04	0.49
Minimum	0.07	0.04	0.49
Maximum	90	3.39	8.65
Median	10	0.46	3.78
Mean	20	0.57	3.64

Table 6.3. Sediment toxicity in different region of NY/NJ Harbor complex in 1993 and 1998 – ad ones you analyzed

	Total sample number	Numbers of toxic[a]
1993 REMAP		
Bight apex	28	1
Long Island Sound	28	0
Raritan Bay	28	3
Jamaica Bay	28	7
Newark Bay	28	11
Upper Harbor	28	4
1998 REMAP		
Raritan Bay	28	1
Jamaica Bay	28 (17)[b]	9 (9)[c]
Newark Bay	28 (13)[b]	14 (12)[c]
Upper Harbor	28 (15)[b]	5 (4)[c]

a. Toxic sediment is defined by amphipod mortality % bigger than 20% relative to the controls. b. total numbers of samples analyzed in this chapter c. numbers of toxic sediments analyzed in this chapter

CHAPTER SEVEN: SUMMARY OF CONCLUSIONS

7.1 Summary

This thesis mainly focused on QACs, a major group of cationic surfactants that has been under the radar too long as major organic contaminants in natural environments. A robust analytical method was developed for determining QACs in estuarine sediments by HPLC-ESI-ToF-MS. The occurrence and biogeochemistry of QACs were extensively studied in sediments from the highly urbanized NY/NJ Harbor complex. Information on QACs sources and history of their (missing word) were well recovered from the sedimentary record. Further applications of QACs as tracers for sediment dating and for understanding the geochemistry of other organic contaminants have been described. In this chapter, the major findings and perspectives of this thesis are summarized and discussed below.

A sensitive and highly selective method by HPLC-ESI-ToF-MS has been developed for identification and quantification of major QAC homologs (more than 20 compounds) in sediments (Chapter 2). Extraction efficiency was evaluated by comparing other published methods and the method developed in this work. Greater efficiency was achieved with my method, especially for the sediment with lower QACs and TOC levels. The precision of the analytical method (4-20% RSD) and the recoveries (98-104%) from these organic matrix-rich samples were uniformly good. Great sensitivity was achieved given the small sample size (0.1g) extracted. LOQs for DADMACs and DTDMACs (0.1-2.0 ng/g) and BAC 14 and 16 (2-2.6 ng/g) are dramatically lower than those reported for methods available without ESI-MS. The detection limits are similar to, or lower than, prior methods employing ESI-MS detection o on much larger sample sizes. ToF-MS proved to be a powerful tool for the identification of targeted and un-targeted QACs. DADMAC C8:C8 and C8:C10 were first identified in sediments by retention time relative to the standard of DADMAC C10:C10. Accurate masses of the parent molecular and their CID fragments gave further confirmation of the two compounds. Unique positive mass defects of alkylammonium ions were discovered and the large positive defects of alkylammonium ions as a function of molecular weight and degree of saturations have been explored. The extraordinarily high positive mass defects associated with alkylammonium ions allow for the selective and sensitive HPLC-ToF-MS based measurement of the QACs studied in this work.

Accurate mass determination and great sensitivity under full mass spectrum scan mode are two major advantages for ToF-MS detector compared to other mass detectors that can be coupled with liquid chromatography. HPLC-ToF-MS was shown to be a powerful tool in the environmental analytical chemistry for identification of new organic contaminants from highly complex environmental matrix. Besides what I included in Chapter 2, there are more unidentified QACs (e.g. esterquats, TAMAC), which are also believed to be employed widely in commercial products, and my preliminary results showed the existence of some additional compounds; e.g., ethylbenzalkonium compounds. Esterquats (DEEDMAC and DEQ) as replacements of DTDMAC in fabric softeners have been found at trace levels in sewage sludge. Although they were not targeted in this study, a positive detection was evident in one CSO sample examined in this work. Considering esterquats are much more biodegradable than DTDMAC (that's why they are used to replace DTDMAC), it will be interesting to detect the occurrence of these compounds in sediments in order to provide more understanding of their biodegradation relative to DTDMAC in both sewage treatment and the natural environment.

In the analysis of the mass chromatograms of our sediment extracts, we confirmed the presence of high levels of another homologous series of QACs – TAMAC, whose members are even more hydrophobic than DTDMAC because of the triple alky chain structure. There is very limited knowledge of how these compounds have been used and treated within the wastewater treatment plants or their environmental fates. For future work, it would be very interesting to compare the distribution and geochronologies of TAMACs, given their potential as stable and particle-reactive tracers.

Chapter 3 represents the first comprehensive study of major QAC homologs in marine sediments. Total concentration of QACs in the surface sediments in the NY/NJ Harbor complex ranged between 0.98 and 114 μg/g. DTDMACs, primarily consisting of C16:C16, C16:C18 and C18:C18 DTDMACs, dominated the compositions of total QACs. Concentration level of DTDMAC in the harbor area was found to be more than 100 times higher than those recently determined in river sediments collected in Austria. BAC, including BAC12, 14, 16, and 18, was found to be the second most abundant class of QACs. Significantly higher concentrations and relative abundances of BAC 16 and 18 were found in this work compared to prior work, which could be due to differences in local sources, fractionation of BACs during WWTP treatment, and/or differences in extraction efficiency between this work and prior studies. ATMACs (16 and 18) and DADMACs (C8:C8, C8:C10 and C10:C10) were also measured in this study as important homologous series of QACs. QACs, as a class of organic contaminants, are present at much higher levels than other organic contaminants that have been measured in the same sediment samples. Excluding DTDMAC, even the other QACs were found to be most often higher than PAHs, various chlorinated hydrocarbons, NPEO metabolites, and the recently measured antimicrobials, triclosan and triclocarban.

DTDMAC appears to be stable in sewage treatment of estuarine sediments, and evidence is presented in Chapter 3 that DTDMAC may be acting as tracer of sewage derived sediment organic matter in the highly sewage impacted NY/NJ Harbor complex. However, the compositions of other more soluble QACs were more variable in sediments and greatly enriched in sediments nest to CSO. It was hypothesized that the composition of QACs could serve as an indicator of the efficiency of local sewage treatment.

To better understand environmental fates for DTDMAC and other more soluble QACs, and evaluate the basic hypothesis that QACs are persistent in sediments, more work needs to be done on the biodegradation of QACs. Previous biodegradation tests provided conflicting results, probably related to differences in bioavailability of these highly sorbed compounds in lab tests. This could be the result of less adsorption of QACs at very high concentrations used, or differences in the manner in which QACs are added in lab studies. In future work, C14-standard needs to be obtained for the detail biodegradation test under aerobic and anaerobic conditions, and these tests should be conducted at different concentrations and for different aging times.

In Chapter 4, the geochronologies of QACs were presented for dated sediment cores from WWTP-affected areas of Jamaica Bay and the Hackensack River. Similarly, QACs were measured in a time series of surface sediment samples collected from a site in Newtown Creek (1987 – 2003) and seven sites in Jamaica Bay, re-sampled in 1998, 2003 and 2008. Consistent results were found among sites, and the *in-situ* preservation of QACs at the Jamaica Bay site was determined by comparisons of two matched cores collected 8 years apart. The sediment profiles of different classes of QACs in the Jamaica Bay sediment cores were in agreement with differences in historical usage and production trends determined in part from USITC production data and other available references. In the case of times-of-first-appearance and peak concentrations, the profiles of QACs at the Hackensack site and Newtown Creek site were qualitatively similar to that seen in Jamaica Bay, as well illustrated in the normalized concentration profiles of the three sites. It is very interesting that ATMAC 22, commonly referred to as behentrimonium, was identified in the sediment core for the first time in natural environment with an exponential increase in concentrations over the last 30 years. The ratios of various classes of QAC homologs relative to each other as a function of sediment age were evaluated to determine the sensitivity of such ratios as potential time markers. The ratio of ATMAC22/ATMAC18 proves to be a highly sensitive time marker over the past 30 years for the sediments from different parts of the harbor, and QACs seemed to be persistent enough that this time marker worked for the samples collected from the deep water dump site in 1992. In conclusion, this chapter provided multiple lines of evidence that QACs can be conservative particle tracers that are specific to different time histories of the sewage derived inputs.

It will be important to seek out more complete production data from USITC, or other sources, for better comparison of geochronological record of QACs and historical use. If we can determine a good understanding of the relationship between loadings of

QACs to sewage treatment plants and the resultant concentrations in local sediments, it would then provide a powerful tool for assessing the relative fate in WWTPs or estuarine environments of other organic contaminants for which loading information is known. That would, in turn, provide a progressive approach useful for evaluating the possible risks of high and low volume production chemicals. Application of a sediment dating tracer discussed in Chapter 4 needs to be further explored with studies of sediment cores from additional areas. More comparisons of the dating tracer and other potential time markers (radio isotopes, metals, persistent contaminants) are also required for definitive confirmation.

In Chapter 5, DTDMAC has been used as particle-reactive and sewagesource-specific tracer for the source and fate study of three major endocrine disrupting compounds – PCB, PBDE, and NPEO metabolites. Previous conclusions by Benedict concerning the source of PBDEs to the lower Hudson Basin, utilizing PBDE congeners composition patterns, was further substantiated by comparing total PBDE concentrations with our sewage tracer DTDMAC. Industrial inputs of PBDE were the major sources at upstream Hudson River and upper Passaic River sites, and PBDE in the sediments from lower Hudson River was mostly influenced by sewage sources. Sources of PCB in the sediments of lower Hudson Estuary have been evaluated by comparing different (missing word) of PCB congener homologs with DTDMAC. For the upstream Hudson River sediments, the influence of contaminated sediments by the two GE factories was more obvious for mono- through tetraCB than the higher PCB congeners. In the lower Hudson Estuary, sewage inputs were indicated as major or dominant sources for all fractions of PCBs in the sediments, in agreement with what was found in prior studies indicating an increase in the relative importance of sewage-derived PCB over time, in comparison to upper Hudson River sources, in New York Harbor sediments since 1970s. The comparisons between DTDMAC and more soluble and labile NPEOs provided insights into how DTDMAC may be useful as a tracer to determine the relative transport or liability of other classes of less conservative or particle reactive wastewater contaminants. In the highly depositional area like NY/NJ harbor area, there was strong correlation between NPEO and DTDMAC, indicating that both two compounds were sewage derived and well preserved in the sediments. However, in other less depositional areas of the lower Hudson Basin, and especially in Jamaica Bay sediments, relative depletions of NPEOs and steroid estrogens were observed. Lower than predicted levels of these compounds in some sediments are probably due to less association of these compounds with suspended particles during transport and more microbial transformations that occurred in the water column. Such observations may also be related to losses of these potentially more bioavailable compounds once incorporated in sediment beds.

The concentrations and compositions of NPEOs and NPEO metabolites in sediments were studied to better understand how NPEOs can provide information about sources of wastewater contaminants, as well as other biogeochemical processes (Chapter 6). I compared a modified analytical method for NPEO analysis, which coupled HPLC with ToF-MS for determining NP(0-15)EO in sediments, with a previous method that employed a quadrupole-MS detector. Great recovery for NP to NP15EO (71-112%) and similar or lower method detection limit (0.61-8.29 ng/g) were achieved in this work. NPEOs were found to be ubiquitous in the NY/NJ Harbor complex, being detected in all 29 sediments with concentrations varying from 0.07-90 μg/g and a median value of 10 μg/g. The average EO chain lengths varied widely from 0.49-8.65, with median value around 3.78. It was predicted that NPEO ethoxymer distributions from less treated sources would be enriched in more highly ethoxylated compounds;however, the lowest values of average EO chain length were found for both the CSO impacted sediments (0.49-3.23) and the most sewage impacted sediments (1.06-2.00). Preliminary statistical analysis was applied to separate NPEO sources by the compositions of higher ethoxymers. More work is needed to statistically group different samples and understand the transformation mechanisms of these ethoxymers. Nonylphenol (NP) appears to be the persistent metabolite of NPEOs under more reducing sediment conditions. The NP(1-3)EO/NP ratios in sediments may be a useful redox sensitive tracer in the sediments, and this hypothesis was supported by comparison with other redox sensitive metals (Cd and Mn). Additional work needs to be done to evaluate the applications of NP(1-3)EO/NP as redox sensitive tracers. For example, more redox sensitive metals with minimum anthropogenic input (e.g. Mo and U) could be measured in the same set of samples for further comparison. These metals are less particle reactive and soluble (is it less soluble or more soluble?) in oxic seawater than is Cd, a metal that can also be affected by local pollution sources in the study.

Inter-correlations among sediment toxicity, inorganic and organic chemicals and other geochemical factors in REMAP sediments were integrated by the PCA analysis. Sediment toxicity was found to be strongly correlated with heavy metals (Sb, Sn, As, Cu, Cd, Pb) and our redox tracers. These results could provide hypotheses to be developed and tested in order to understand the causes of sediment toxicity observed in urban harbor sediments.

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APPENDIX: RAW DATA FIGURES AND TABLES

Table A1. Sample coordinates and concentrations of TOC, NPEO, and QAC homologs (Chapter 3)

I.D.	Lat.	Lon.	TOC (%)	NPEO	8:10	10:10	14:14	14:16	16:16	16:18	18:18	BA12	BA14	BA16	BA18	AT16	AT18
BB1	40.7758	-73.8871	6.74	21.93	0.38	2.38	0.76	0.86	5.14	18.71	26.38	6.47	5.73	2.07	3.14	1.56	1.26
FB1	40.7847	-73.8635	3.90	3.20	0.04	0.45	0.39	0.79	4.02	11.10	16.55	0.33	1.29	0.63	1.81	0.25	0.63
FB2	40.7819	-73.8647	4.60	8.59	0.07	0.68	0.38	0.55	2.64	7.31	10.20	0.21	0.96	0.56	1.35	0.18	0.35
JB008	40.6409	-73.8162	6.35	24.29	0.03	0.34	0.64	1.20	8.80	34.76	53.80	0.83	0.66	0.60	1.33	0.30	0.85
JB018	40.6096	-73.7860	5.10	9.44	0.01	0.13	0.30	0.44	3.33	12.11	17.78	0.22	0.21	0.20	0.44	0.17	0.35
JB033	40.6161	-73.8879	4.52	1.68	0.01	0.10	0.53	0.95	5.11	17.95	35.10	0.27	0.15	0.14	0.31	0.19	0.41
JB039	40.5870	-73.8450	3.04	1.06	0.01	0.13	0.32	0.54	2.83	8.99	11.91	0.01	0.20	0.16	0.29	0.11	0.27
JB043	40.5756	-73.8751	0.19	0.05	0.00	0.05	0.01	0.01	0.08	0.25	0.34	0.00	0.07	0.06	0.00	0.05	0.05
JB202	40.6118	-73.8101	4.82	2.46	0.01	0.15	0.39	0.79	4.58	13.56	20.06	0.01	0.21	0.19	0.38	0.15	0.30
JB203	40.6328	-73.8067	7.05	37.48	0.03	0.34	0.75	1.37	10.91	39.35	56.15	0.96	0.64	0.64	1.47	0.36	0.90
JB204	40.6082	-73.8898	4.90	4.10	0.02	0.20	0.58	1.16	5.44	19.50	36.79	0.54	0.38	0.32	0.73	0.24	0.62
JB206	40.5954	-73.8047	3.18	0.74	0.01	0.16	0.27	0.73	4.52	10.08	14.07	0.01	0.28	0.22	0.50	0.16	0.38
JB207	40.6286	-73.7591	5.29	4.88	0.02	0.22	0.61	1.56	8.52	26.88	36.91	0.01	0.37	0.31	0.79	0.20	0.50
JB209	40.6051	-73.7872	5.03	1.66	0.01	0.17	0.42	0.85	4.53	14.58	19.58	0.02	0.27	0.22	0.44	0.19	0.42
JB210	40.6275	-73.8712	0.47	0.30	0.00	0.06	0.04	0.12	0.64	1.96	2.72	0.00	0.09	0.07	0.02	0.00	0.09
JB211	40.6120	-73.8725	0.57	0.29	0.00	0.00	0.01	0.08	0.45	1.45	1.76	0.00	0.00	0.00	0.00	0.00	0.00
JB213	40.6189	-73.7777	4.70	8.06	0.01	0.13	0.35	0.69	5.69	22.34	33.27	0.19	0.19	0.20	0.54	0.15	0.39
JB215	40.6256	-73.8370	1.86	1.18	0.00	0.07	0.45	0.62	3.12	11.39	26.21	0.20	0.08	0.09	0.12	0.17	0.28
JB216	40.6330	-73.8734	0.34	0.22	0.00	0.05	0.39	0.34	1.65	7.24	18.70	0.14	0.04	0.07	0.03	0.15	0.17
JB223	40.5926	-73.8707	3.53	2.40	0.01	0.16	0.34	0.44	2.12	7.61	10.18	0.01	0.27	0.22	0.40	0.15	0.46
NB201	40.6651	-74.1409	2.04	1.86	0.00	0.24	0.12	0.57	2.69	8.43	10.71	0.03	0.56	0.52	1.02	0.11	0.37
NB202	40.6461	-74.1765	4.55	6.85	0.00	0.45	0.35	1.28	6.09	18.21	23.08	0.24	1.68	0.91	1.54	0.30	0.75
NB203	40.6154	-74.2015	2.55	4.26	0.00	0.18	0.03	0.32	1.13	4.90	5.50	0.04	0.61	0.33	0.47	0.11	0.25
NB204	40.5942	-74.2022	2.00	3.25	0.00	0.19	0.02	0.25	0.72	2.52	1.95	0.14	0.78	0.36	0.49	0.13	0.24
NB205	40.7377	-74.1170	7.20	13.59	0.02	1.34	0.73	0.55	2.94	12.18	18.10	2.85	4.75	2.06	2.46	0.75	1.27
NB207	40.6481	-74.1148	0.76	1.33	0.00	0.10	0.00	0.17	0.34	2.63	2.94	0.04	0.31	0.22	0.31	0.07	0.16
NB211	40.6381	-74.1940	2.52	5.65	0.00	0.14	0.02	0.24	0.66	3.14	3.22	0.15	0.69	0.33	0.49	0.20	0.25

Table A1 (continued). Sample coordinates and concentrations of TOC, NPEO, and QAC homologs (Chapter 3)

I.D.	Lat.	Lon.	TOC (%)	NPEO	8:10	10:10	14:14	14:16	16:16	16:18	18:18	BA12	BA14	BA16	BA18	AT16	AT18
NB212	40.6689	-74.1380	2.38	1.85	0.00	0.22	0.16	0.68	3.13	10.63	13.91	0.05	0.50	0.41	0.71	0.10	0.29
NB214	40.5800	-74.2075	1.11	1.12	0.00	0.11	0.00	0.17	0.46	2.59	2.97	0.05	0.30	0.18	0.21	0.07	0.13
NB217	40.6919	-74.1188	1.15	0.69	0.00	0.13	0.06	0.21	0.96	2.67	3.04	0.03	0.34	0.23	0.27	0.06	0.15
NB219	40.5590	-74.2327	2.28	12.61	0.01	0.11	0.59	0.43	2.34	7.79	11.83	1.57	1.18	0.54	1.26	0.46	0.54
NB222	40.6535	-74.1417	3.03	5.16	0.00	0.31	0.28	0.97	4.64	13.05	16.13	0.07	0.80	0.64	1.38	0.08	0.29
NB223	40.6495	-74.1663	3.83	7.11	0.00	0.33	0.30	1.20	5.64	16.89	18.43	0.33	1.76	0.88	1.31	0.26	0.59
NB224	40.6061	-74.2030	2.18	7.07	0.00	0.19	0.02	0.23	0.52	2.21	2.19	0.17	0.88	0.38	0.49	0.16	0.26
NB225	40.7244	-74.1009	1.57	2.73	0.00	0.04	0.02	0.04	0.26	0.98	1.42	0.10	0.11	0.07	0.09	0.08	0.11
NB226	40.6732	-74.1311	2.88	0.56	0.01	0.24	0.32	0.39	2.96	9.95	15.38	0.33	0.60	0.40	0.73	0.19	0.39
NB227	40.7044	-74.1172	1.74	1.62	0.00	0.14	0.00	0.22	0.75	4.36	5.18	0.05	0.45	0.29	0.38	0.10	0.19
UH003	40.8672	-73.9439	3.29	3.19	0.02	0.26	0.59	0.33	2.26	7.80	11.87	0.37	0.44	0.31	0.58	0.20	0.34
UH008	40.8018	-73.8132	6.21	1.15	0.00	0.21	0.00	0.23	0.84	3.91	4.92	0.07	0.51	0.27	0.41	0.07	0.20
UH010	40.7911	-73.8970	3.89	0.38	0.00	0.09	0.01	0.06	0.28	0.93	1.14	0.00	0.11	0.12	0.08	0.04	0.09
UH011	40.7855	-73.8741	5.98	1.02	0.00	0.12	0.00	0.12	0.27	2.62	2.81	0.02	0.22	0.15	0.17	0.07	0.13
UH014	40.7560	-74.0201	4.15	2.36	0.02	0.26	0.33	0.51	3.62	13.31	20.77	0.45	0.51	0.39	0.91	0.21	0.40
UH018	40.7067	-74.0223	5.25	4.32	0.00	0.30	0.23	0.94	4.63	15.23	20.03	0.03	0.50	0.45	0.90	0.12	0.33
UH020	40.6897	-74.0039	5.66	6.46	0.05	0.65	0.78	0.97	6.74	27.55	37.91	1.48	1.56	0.90	2.07	0.45	0.83
UH029	40.6364	-74.0509	2.27	0.03	0.00	0.05	0.05	0.02	0.08	0.35	0.64	0.03	0.04	0.07	0.03	0.12	0.15
UH204	40.8637	-73.9394	1.79	2.81	0.00	0.10	0.00	0.13	0.22	2.81	3.68	0.00	0.11	0.12	0.09	0.04	0.09
UH206	40.7761	-73.8884	10.32	77.61	0.69	2.84	1.38	1.30	7.18	29.44	37.47	11.43	8.85	2.83	4.00	2.66	2.50
UH211	40.8511	-73.9510	3.02	0.72	0.16	0.50	0.29	1.89	6.85	10.30	0.34	0.34	0.24	0.43	0.19	0.29	0.72
UH213	40.7726	-73.9985	1.83	2.16	0.15	0.53	0.22	1.53	5.32	8.44	0.27	0.28	0.20	0.32	0.18	0.27	2.16
UH214	40.6808	-74.0607	2.08	1.71	0.20	0.22	0.60	2.68	5.68	7.66	0.01	0.44	0.49	1.09	0.06	0.16	1.71
WB1	40.7068	-73.9700	5.92	24.76	0.37	4.13	0.53	0.65	4.43	13.26	22.11	5.96	8.19	2.53	3.80	1.44	1.18

Table A2. JB core sample information and organics concentrations (Chapter 4)

Sample ID	Date	Location	NPEO	DTDMAC	DADMAC	ATMAC16-18	ATMAC22	BAC
JB16 0-2 cm	1995	Jamaica Bay	41.35	116.37	0.52	1.96	0.55	4.10
JB16 2-4 cm	1993	Jamaica Bay	40.93	222.83	0.49	3.25	0.39	5.56
JB16 4-6 cm	1991	Jamaica Bay	50.18	352.63	0.77	9.78	0.33	12.86
JB16 6-8 cm	1987	Jamaica Bay	42.22	512.04	0.58	10.54	0.23	11.78
JB16 8-12 cm	1983	Jamaica Bay	34.66	432.97	0.54	10.28	0.13	11.22
JB16 12-16cm	1979	Jamaica Bay	15.39	223.71	0.45	3.64	0.02	9.40
JB16 16-20 cm	1974	Jamaica Bay	11.24	255.12	0.18	4.03	n.d.	14.47
JB16 20-24 cm	1970	Jamaica Bay	13.84	176.98	0.20	3.58	n.d.	13.22
JB16 24-28 cm	1966	Jamaica Bay	16.13	280.13	0.12	6.07	n.d.	24.26
JB16 28-32 cm	1961	Jamaica Bay	16.49	185.18	0.11	2.85	n.d.	8.21
JB16 36-40 cm	1953	Jamaica Bay	9.21	8.96	0.10	0.39	n.d.	0.90
JB16 48-52cm	1939	Jamaica Bay	2.70	0.18	0.09	0.11	n.d.	0.26
JB203	1998	Jamaica Bay	0.05	108.52	0.37	2.82	1.32	3.71
JB206	1998	Jamaica Bay	-	29.83	0.17	0.81	0.23	1.02
JB207	1998	Jamaica Bay	-	74.70	0.25	0.92	0.20	1.49
JB209	1998	Jamaica Bay	-	40.13	0.18	0.72	0.10	0.96
JB215	1998	Jamaica Bay	-	41.79	0.07	0.71	0.22	0.49
JB216	1998	Jamaica Bay	-	28.32	0.05	0.42	0.09	0.29
JB223	1998	Jamaica Bay	-	20.84	0.17	0.75	0.12	0.90
JB303	2003	Jamaica Bay	-	139.56	0.48	4.49	3.20	4.24
JB306	2003	Jamaica Bay	-	29.50	0.17	1.28	0.98	0.90
JB307	2003	Jamaica Bay	-	69.14	0.22	0.95	0.65	1.10
JB309	2003	Jamaica Bay	-	33.73	0.14	0.85	0.61	0.66
JB315	2003	Jamaica Bay	-	1.82	0.23	0.36	0.06	0.19
JB316	2003	Jamaica Bay	-	32.36	0.15	0.93	0.70	0.75
JB323	2003	Jamaica Bay	-	32.91	0.45	2.06	1.36	1.73
JB303 08	2008	Jamaica Bay	-	106.08	1.01	6.32	4.87	3.42
JB306 08	2008	Jamaica Bay	-	20.10	0.31	2.35	1.75	0.60
JB307 08	2008	Jamaica Bay	-	63.06	0.36	2.48	1.95	0.81
JB309 08	2008	Jamaica Bay	-	25.02	0.39	2.24	1.64	0.68
JB315 08	2008	Jamaica Bay	-	10.32	0.30	1.64	1.17	0.42
JB316 08	2008	Jamaica Bay	-	16.56	0.35	2.06	1.55	0.58
JB323 08	2008	Jamaica Bay	-	19.26	0.39	2.36	1.75	0.64
R1397A	2001	Newtown Creek	10.60	84.14	2.62	1.64	2.09	28.94
R1227A	1998	Newtown Creek	14.20	94.75	1.61	2.12	1.68	25.31
R1093A	1996	Newtown Creek	14.60	112.88	1.12	2.69	0.67	26.69
CN2168A	1992	Newtown Creek	15.90	235.14	1.09	7.57	0.26	49.59
CN2102A	1990	Newtown Creek	10.30	164.45	0.66	6.12	0.18	33.74
CN2019A	1987	Newtown Creek	12.60	358.01	1.07	6.39	0.14	58.01
R1487A	2003	Hackensac	13.40	36.13	0.47	0.88	3.07	3.63
CN2252A	1995	Hackensac	14.00	52.24	0.45	1.62	0.38	4.65
CN2252E	1980S	Hackensac	16.30	106.39	0.46	4.67	0.15	8.16
CN2252I	1970S	Hackensac	5.59	18.56	0.09	0.71	n.d.	2.63
CN2252L	1960S	Hackensac	5.96	6.59	0.09	0.55	n.d.	4.27
CN2252N	1950S	Hackensac	1.82	1.17	n.d.	0.13	n.d.	5.42
BC6	1992	DWD-106	-	1.41	0.003	0.02	0.003	0.05
DIVE2556	1992	DWD-106	-	7.17	0.01	0.11	0.001	0.19

Table A3. Ratio of ATMAC homologs and calculated date for REMAP sediment samples collected by grab sampler (0-5cm). Sediment dates are caculated from the regression of samples from RPI (Figure A1.).

Date	ID	22/18	Log(22/18)	Calculated date	Date difference
1998	JB008	1.40	0.15	1999.16	1.16
1998	JB018	2.03	0.31	2000.34	2.34
1998	JB033	1.78	0.25	1999.92	1.92
1998	JB039	0.67	-0.17	1996.85	-1.15
1998	JB202	0.45	-0.35	1995.58	-2.42
1998	JB203	1.46	0.16	1999.30	1.30
1998	JB204	2.46	0.39	2000.95	2.95
1998	JB206	0.26	-0.59	1993.81	-4.19
1998	JB207	0.47	-0.33	1995.69	-2.31
1998	JB209	0.47	-0.33	1995.68	-2.32
1998	JB213	1.49	0.17	1999.37	1.37
1998	JB215	0.77	-0.11	1997.29	-0.71
1998	JB216	0.49	-0.31	1995.82	-2.18
1998	JB223	0.26	-0.59	1993.84	-4.16
1998	NB201	0.82	-0.09	1997.46	-0.54
1998	NB202	1.47	0.17	1999.32	1.32
1998	NB203	2.38	0.38	2000.85	2.85
1998	NB204	2.86	0.46	2001.43	3.43
1998	NB205	0.79	-0.10	1997.35	-0.65
1998	NB207	0.43	-0.37	1995.44	-2.56
1998	NB211	0.77	-0.11	1997.27	-0.73
1998	NB212	0.93	-0.03	1997.89	-0.11
1998	NB214	3.85	0.59	2002.37	4.37
1998	NB217	0.33	-0.48	1994.63	-3.37
1998	NB219	1.11	0.05	1998.44	0.44
1998	NB222	0.61	-0.22	1996.54	-1.46
1998	NB223	1.15	0.06	1998.54	0.54
1998	NB224	1.33	0.12	1999.01	1.01
1998	NB225	1.49	0.17	1999.36	1.36
1998	NB226	1.61	0.21	1999.62	1.62
1998	NB227	0.60	-0.22	1996.51	-1.49
1998	NB250	0.54	-0.27	1996.17	-1.83
1998	UH003	1.82	0.26	2000.00	2.00
1998	UH008	0.24	-0.63	1993.54	-4.46
1998	UH011	0.29	-0.53	1994.24	-3.76
1998	UH014	1.76	0.25	1999.90	1.90
1998	UH018	0.55	-0.26	1996.20	-1.80
1998	UH020	1.21	0.08	1998.72	0.72
1998	UH029	0.81	-0.09	1997.42	-0.58
1998	UH206	1.87	0.27	2000.08	2.08
1998	UH211	1.69	0.23	1999.77	1.77
1998	UH213	2.11	0.32	2000.46	2.46
1998	UH214	0.27	-0.57	1993.99	-4.01

Table A3. continued.

Date	ID	22/18	Log(22/18)	Calculated date	Date difference
2003	JB303	4.35	0.64	2002.75	-0.25
2003	JB306	3.94	0.59	2002.44	-0.56
2003	JB307	5.88	0.77	2003.71	0.71
2003	JB309	5.57	0.75	2003.54	0.54
2003	JB316	5.46	0.74	2003.48	0.48
2003	JB323	4.31	0.63	2002.73	-0.27
2008	JB303	5.59	0.75	2003.55	-4.45
2008	JB306	9.06	0.96	2005.08	-2.92
2008	JB307	8.23	0.92	2004.77	-3.23
2008	JB309	8.79	0.94	2004.98	-3.02
2008	JB315	6.95	0.84	2004.24	-3.76
2008	JB316	8.03	0.90	2004.69	-3.31
2008	JB323	7.62	0.88	2004.53	-3.47

Figure A1. Historical changes in the concentration of ATMAC 22 normalized to ATMAC 18 from RPI with better confirmed date by ^{137}Cs and ^{7}Be (blue dots). The solid line represents the linear regression of all RPI samples. Average ratios and standard deviations of REMAP samples collected by grab samplers are showed in different symbols. (Calculated date for each REMAP samples are showed in Table A3).

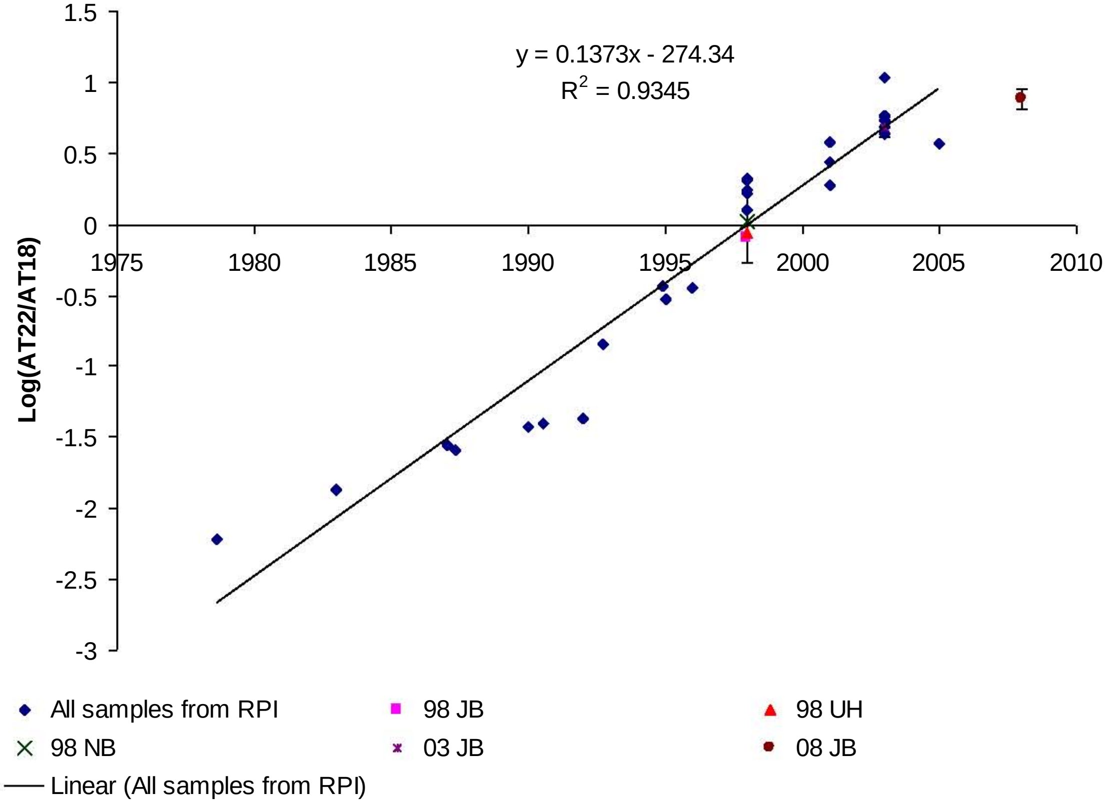


Figure A2. 137Cs profile in the sediment core collected from Hackensack River in 1995 (Hack 14B).

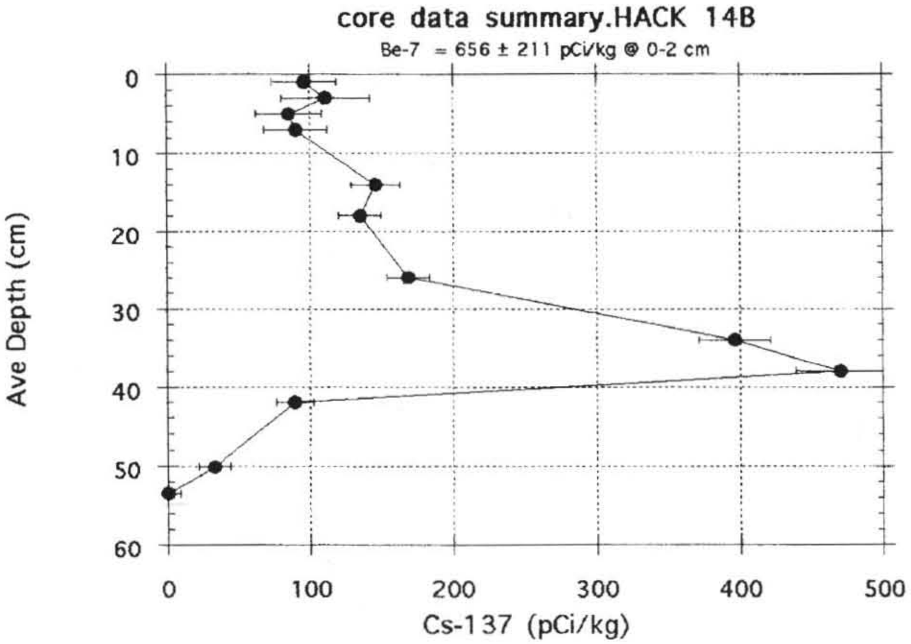
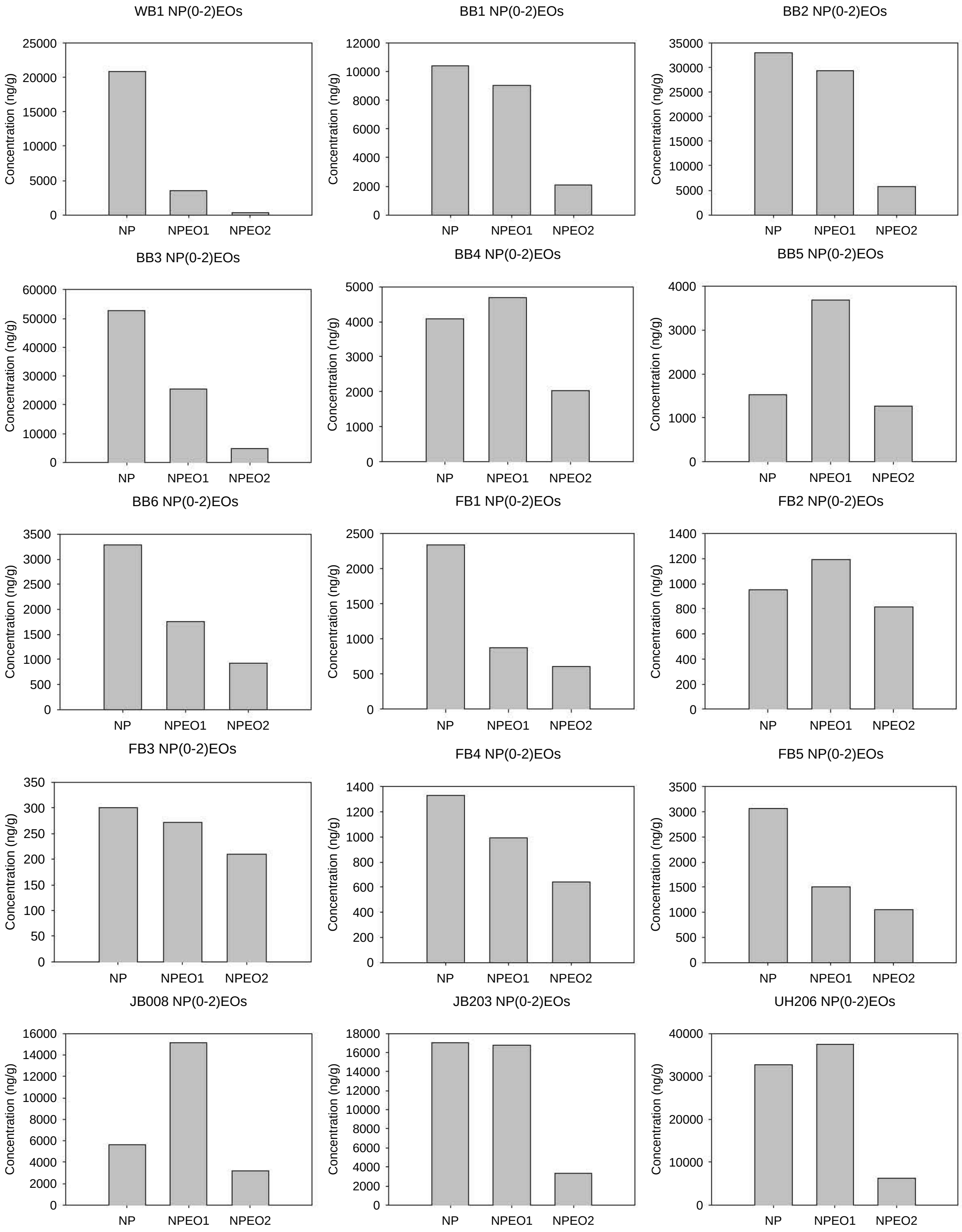
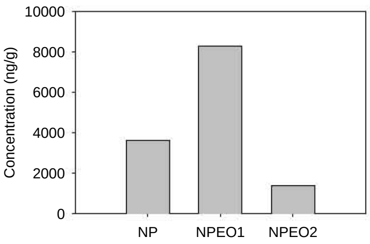


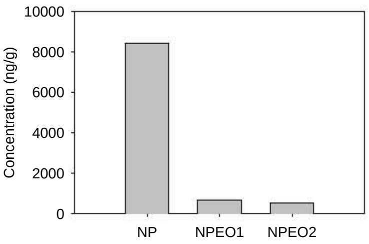
Figure A3 NP(0-2)EOs concentrations in the samples from NY/NJ Harbor complex (Chapter 6)



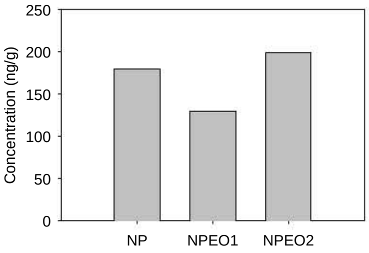
NB205 NP(0-2)EOs



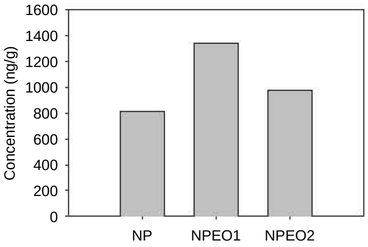
NB219 NP(0-2)EOs



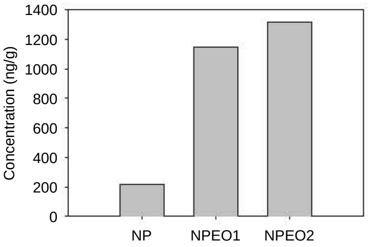
NB225 NP(0-2)EOs



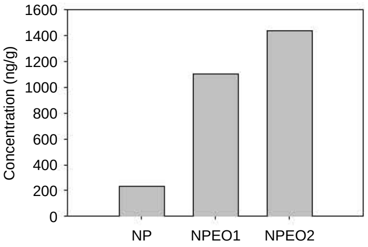
NB226 NP(0-2)EOs



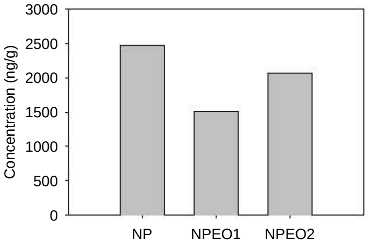
UH003 NP(0-2)EOs



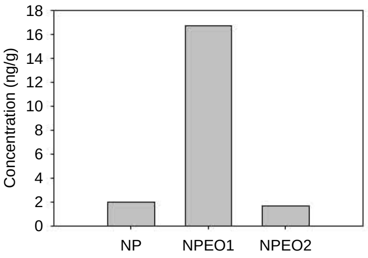
UH014 NP(0-2)EOs



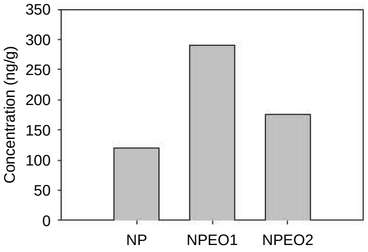
UH020 NP(0-2)EOs



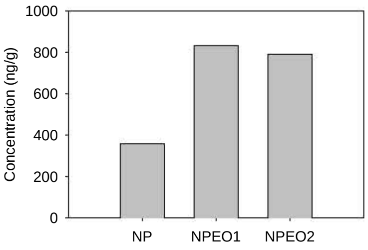
UH029 NP(0-2)EOs



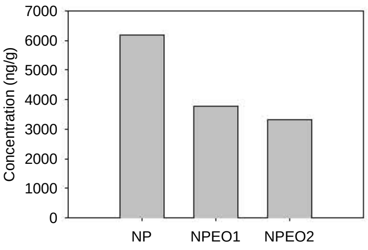
UH211 NP(0-2)EOs



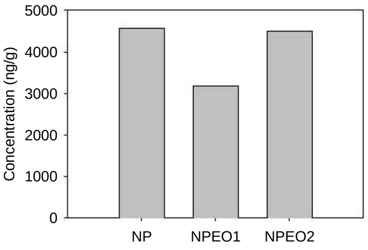
UH213 NP(0-2)EOs



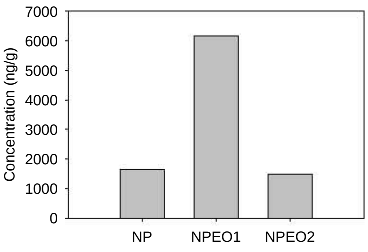
CN2252A NP(0-2)EOs



R1478A NP(0-2)EOs



JB018 NP(0-2)EOs



JB213 NP(0-2)EOs

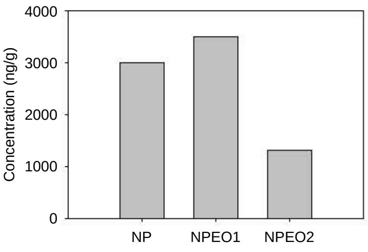
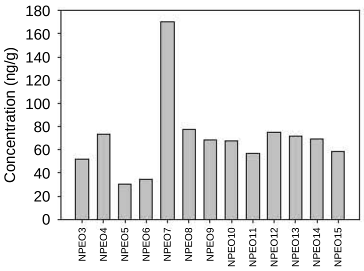
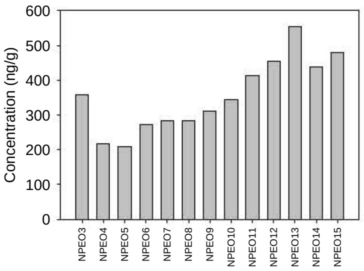
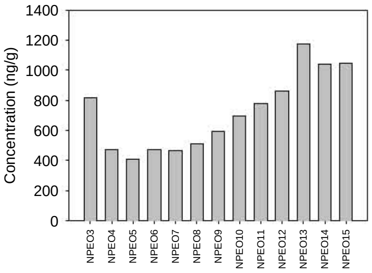
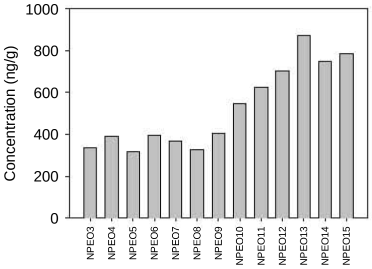


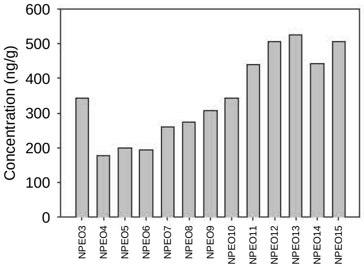
Figure A4 NP(3-15)EOs concentrations in the samples from NY/NJ Harbor complex (Chapter 6)

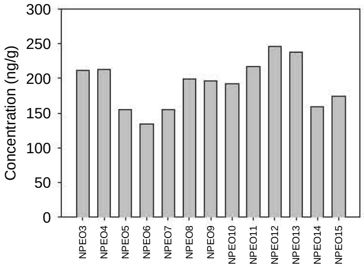

WB1 NP(3-15)EOs

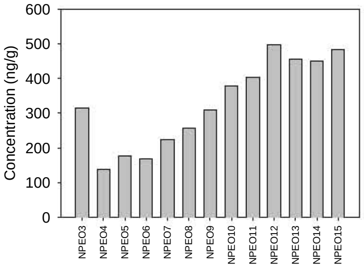

BB1 NP(3-15)EOs

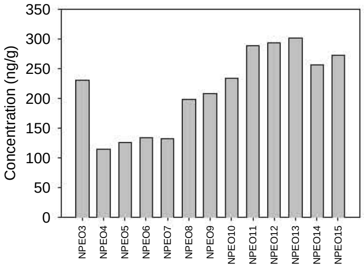

BB2 NP(3-15)EOs

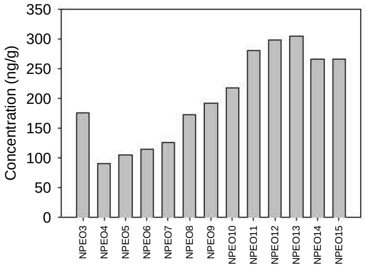

BB3 NP(3-15)EOs

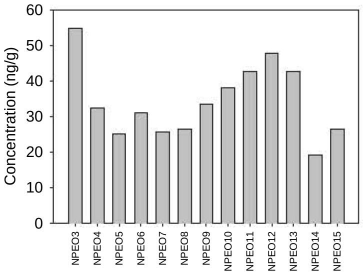

BB4 NP(3-15)EOs

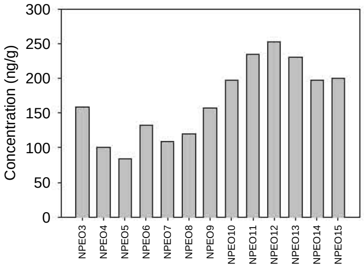

BB5 NP(3-15)EOs

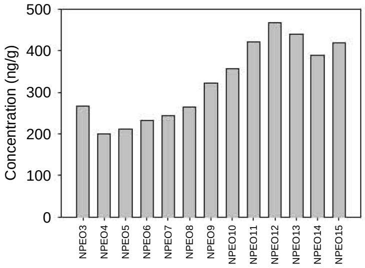

BB6 NP(3-15)EOs

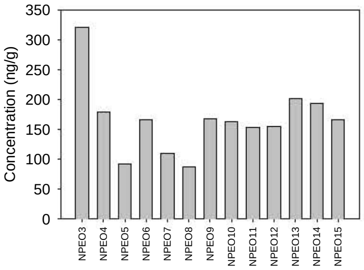

FB1 NP(3-15)EOs

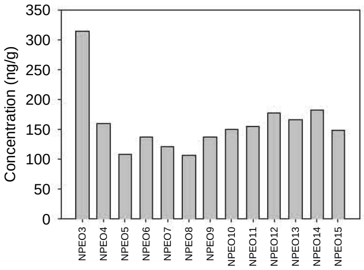

FB2 NP(3-15)EOs

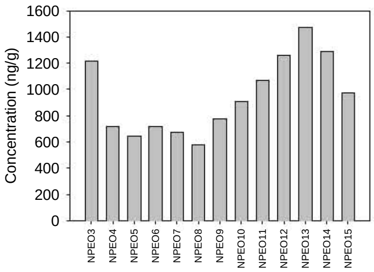

FB3 NP(3-15)EOs

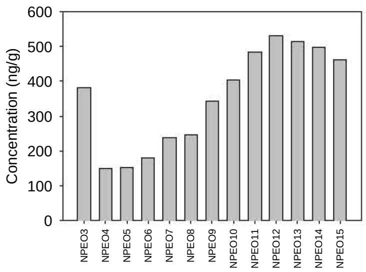

FB4 NP(3-15)EOs

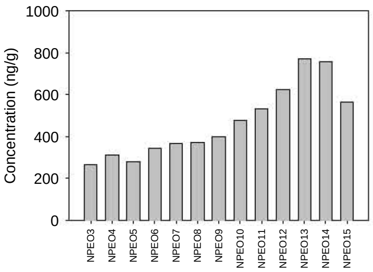

FB5 NP(3-15)EOs

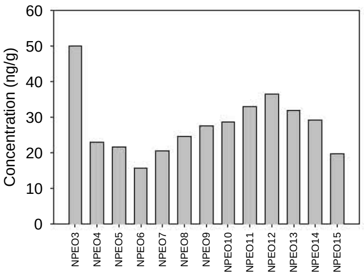

JB008 NP(3-15)EOs

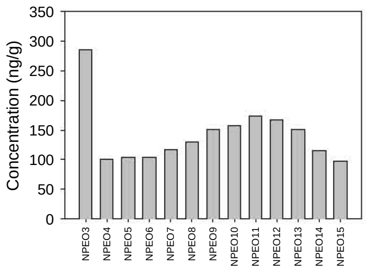

JB203 NP(3-15)EOs

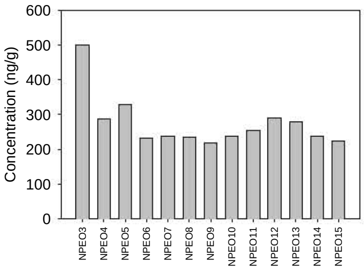

UH206 NP(3-15)EOs

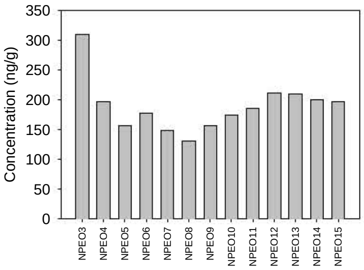

NB205 NP(3-15)EOs

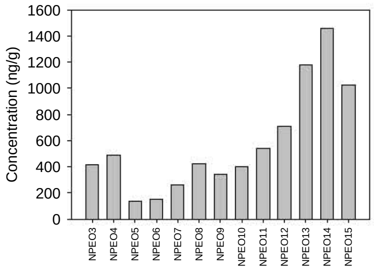

NB219 NP(3-15)EOs

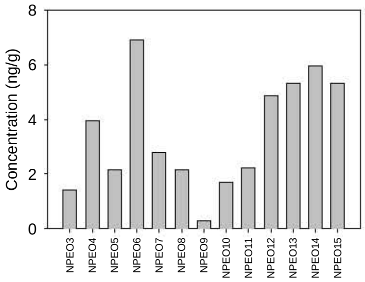

NB225 NP(3-15)EOs

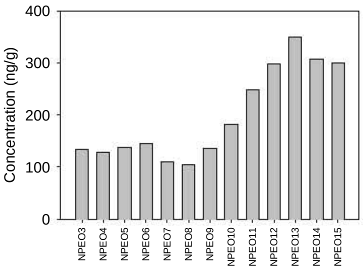

NB226 NP(3-15)EOs

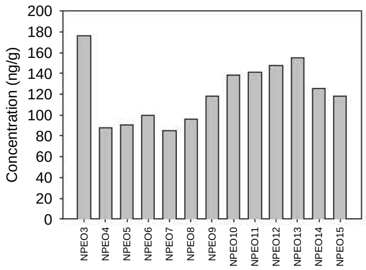

UH003 NP(3-15)EOs

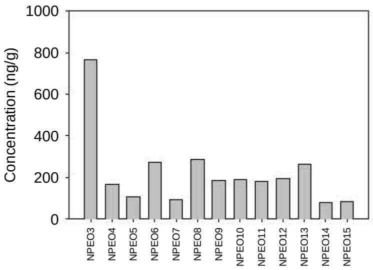

UH014 NP(3-15)EOs

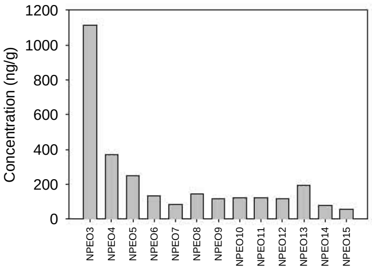

UH020 NP(3-15)EOs

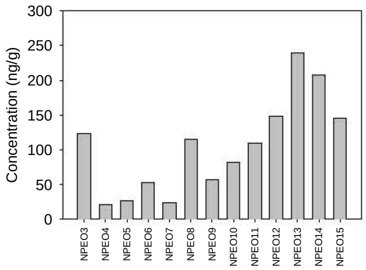

UH029 NP(3-15)EOs

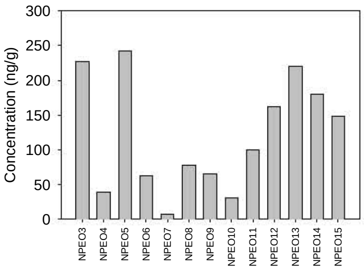

UH211 NP(3-15)EOs


UH213 NP(3-15)EOs


CN2252A NP(3-15)EOs


R1478A NP(3-15)EOs


JB018 NP(3-15)EOs


JB213 NP(3-15)EOs