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Quaternary Ammonium Compounds in Urban Estuarine Sediment Environments - A Class of Contaminants in Need of Increased Attention?

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The distributions of wastewater-derived quaternary ammonium compounds (QACs) were determined in surficial sediments ($n = 47$) collected from the urbanized lower Hudson River basin. The most abundant class of QACs were dialkyldimethylammonium compounds (DADMACs, with C8 to C18 carbon chain lengths; median ΣDADMAC = 26 μg/g), followed by benzylalkyldimethylammonium compounds (BAC, C12−C18; 1.5 μg/g), and alkyltrimethylammonium compounds (ATMAC, primarily C16 and C18; 0.52 μg/g). The concentrations of total QACs are higher than those of other conventional organic contaminants determined on the same samples (e.g., median ΣPAH level of 2.1 μg/g). Comparatively high concentrations, correlations with sewage derived contaminants, and the relatively constant compositions of QACs observed over large areas suggest that many sediment-sorbed QACs can be relatively persistent in receiving waters. Unusually large concentration-dependent sorption is considered as a mechanism that likely affects persistence of these intrinsically biodegradable chemicals under field conditions. There has been comparatively little field-based research on these classes of cationic surfactants; given the levels of QACs observed here, it is suggested that further investigation is warranted.

Introduction

Quaternary ammonium compounds (QAC) represent an important fraction of the cationic surfactant market and are widely used as ingredients in a host of industrial applications and find widespread use in household products, including fabric softeners, detergents, disinfectants, preservatives, and a range of personal care products (*1−3*). Although QACs have been measured in receiving waters (*4−8*), they are strongly sorbed (*9−12*), and relatively high concentrations of QACs have been reported in sludges and sediments (*3, 7, 11, 13−16*). These data suggest QACs have the potential to be persistent in receiving waters, especially when associated with solid phases (*13, 16*), yet there remains a paucity of field research on the occurrence and fate of QACs in the environment in comparison to work conducted on major classes of anionic and nonionic surfactants (*17*). One aim of this work was to characterize the occurrence and distribution in urban estuarine sediments of homologous series of different classes of QACs with widely varying hydrophobicity (e.g., alkyl chain length). The processes that affect the distributions of QACs are also considered, as is the potential use of QACs as particle-reactive tracers of sewage-derived contaminants or sediments affected by those sources.

This report focuses on three important classes of QACs including: dialkyldimethylammonium compounds (DADMAC), with even carbon n-alkyl chain lengths varying between C8 and C18; alkyltrimethylammonium compounds (ATMAC) possessing alkyl chain between C12 and C18; and benzylalkyldimethylammonium compounds (BAC) also with alkyl chain lengths between C12 and C18. Early studies of QAC occurrence and fate in the environment focused almost entirely on DADMAC used extensively as fabric softeners, with alkyl chain lengths primarily consisting of C14, C16, and C18 (*13, 14*). Derived primarily from hydrogenated animal fat and produced as chloride salts, they were commonly known as ditallowdimethylammonium chloride (DTDMAC) (*13*), a term retained here to distinguish these highly persistent DADMACs from more soluble and biodegradable DADMACs with C8 and C10 alkyl chains and used as disinfectants (*3, 18*).

Limited field data available to date indicates that the potential for acute toxicity from aqueous exposure of QACs to metazoans may be relatively low, although additional research on sublethal effects would help inform ecological risk assessments (*3, 7, 19*). Kreuzinger and co-workers (*19*) point out the fragmentary nature of field exposure data and that lowest ecotoxicologically effective concentrations for individual QACs only exceed the highest measured concentrations of the same QACs in receiving waters and sewage effluents by approximately 1 order of magnitude. There are also few studies of toxicity of mixtures of QACs or in sediment exposures. Many QACs have antimicrobial properties and a number are used as disinfectants, antimicrobials, and algaecides (*3, 18*). The potential for QACs to affect microbial communities or to play a role in the selection and spread of mobile gene element containing QAC-resistance genes (*20*) may prove to be of greater interest than direct toxicity for risk assessments. Finally, recent work has shown that BACs and other QACs may serve as potential precursors of n-nitrosodimethylamine (NDMA) formation during disinfection of wastewater-affected drinking waters (*21*).

It has been hypothesized that superhydrophobic DTDMAC would be an especially good tracer of sewage-affected sediment as well as relative sources and fate of other particle reactive contaminants (*22*). Despite facile microbial degradation of DTDMAC and other QACs in some laboratory studies (*1, 22*), other lab studies and mass balance considerations (*19, 24−26*) suggest that DTDMAC is not appreciably biodegradable within wastewater treatment plants (WWTPs) and that bioavailability and biodegradability is limited by sorption related to hydrophobicity (e.g., alkyl chain length and total number of carbons) (*3, 23−25*). These findings are consistent with very high levels of QACs measured in sewage sludges collected in Europe (typically between 2000−9000 μg/g) prior to a voluntary phase-out of DTDMAC as a fabric softener ingredient in those countries during the early 1990s (*11, 13, 14*). Research on the occurrence of QACs in sediments has been limited (*15*) before recent work on a broad selection of QACs in Austrian rivers (*11*). Unlike DTDMAC, biodegradation is a very important process within WWTPs for less hydrophobic QACs: DADMAC C10:C10, ATMAC 12−16, and BAC 12−18 (*25*), although they are still measured in downstream sediments in appreciable quantities (*11*).

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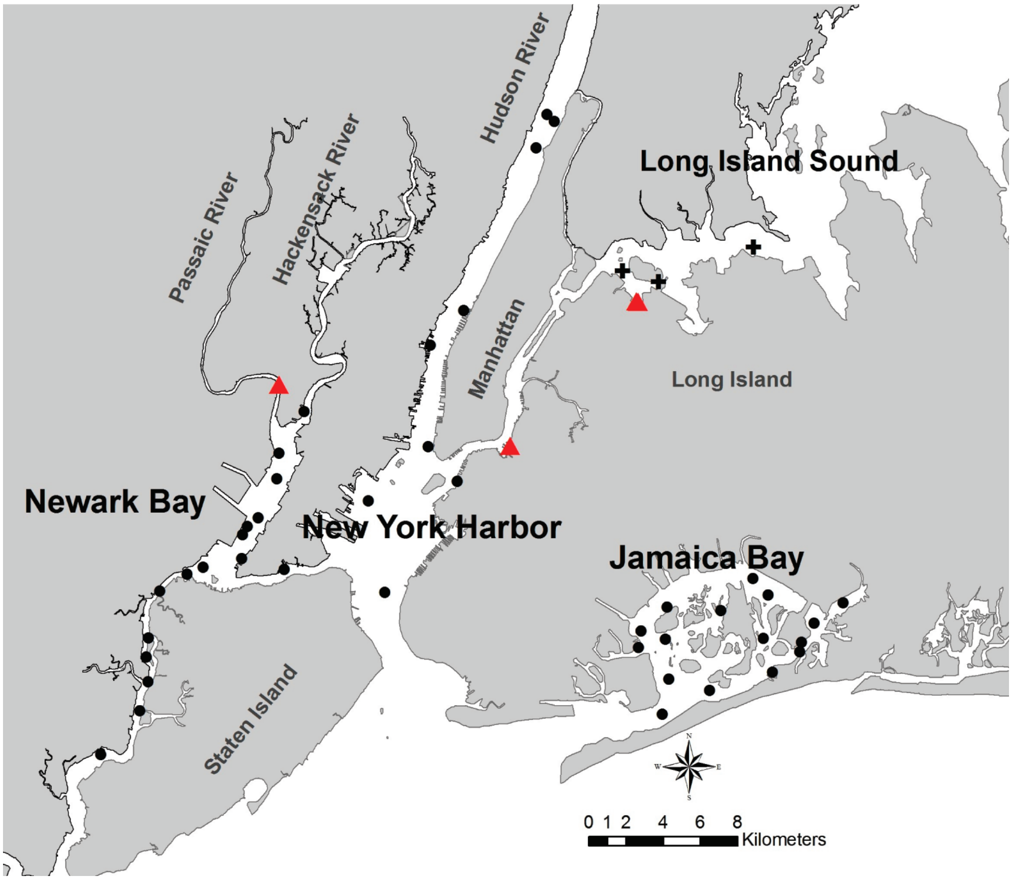

FIGURE 1. Surface sediment sample locations in the area of NY/NJ Harbor and Jamaica Bay (•); three from far western Long Island Sound (+); and four influenced by CSO outlets (▲), one of which superimposed with another station in far western Long Island Sound.

Concentrations of QACs in surficial sediments from the metropolitan region of the lower Hudson River Basin were determined in this work to assess their occurrence and provide insight into processes that affect their distributions. Sediment samples were also selected to allow comparisons of QAC concentrations to those of other classes of organic contaminants measured in the same samples. Comparisons of chemical compositions with selected sediments removed from sewage sources provide additional support for the hypothesis that some sediment-sorbed QACs can be very persistent, thus deserving of attention as sensitive tracers of sewage-derived sources of contaminants and sediments.

Experimental Section

Study Area and Sediment Samples. The metropolitan region of the lower Hudson Basin (Figure 1) is one of the most urbanized estuaries in the U.S. The watershed has a population of over 20 million people (*27*) that discharges 2.3 billion gallons of wastewater per day with additional inputs from combined sewer overflows (CSOs) through which largely untreated sewage is discharged during higher precipitation events.

Locations of 47 sediment grab sample (0−2 cm) stations are shown in Figure 1, with coordinates provided in the Supporting Information (Table S1). The majority of analyzed samples were collected as part of a larger EPA sponsored Regional Environmental Monitoring and Assessment Program (REMAP) sampling campaign conducted in 1998 ($n = 45$). Selection of the samples analyzed was based on availability of other data on sediment properties and a range of other metal and organic contaminants determined on splits of the same sediments (*22, 27, 28*). Most of the samples analyzed in this work were characterized as muddy with relatively high total organic carbon (TOC) and a relatively small range of aluminum (Al) contents (*27*). Two other surface samples were obtained at sites within 150 m of a combined sewer overflow (CSO) in 2004 (Table S1). To better illustrate the potential use of DTDMAC as a persistent sewage tracer, data are also presented from analysis of 13 samples collected in the area of the former Deep Water Dump Site 106 (DWDS106), where deep ocean disposal of sludge from the New York/New Jersey metropolitan region was conducted between 1986−1992 (Table S3). Detailed descriptions of the samples and study site are presented elsewhere (*29*).

Analytical Methods. Details of the analytical methods are reported in Li and Brownawell (2009) for DADMAC C8:C8−C18:C18 and BAC C12−18 (*16*). ATMAC C12−18 was also determined with the same methods, as described in a related study (*30*).

Quantification of QACs was based on the response of pure standards for ten of the target analytes: DADMAC C10:C10, C14:C14, C16:C16, and C18:C18; ATMAC 12−18; and BAC 14 and 16. The response factors for DADMAC C14:C16 and C16:C18 were interpolated from the nearly equal response of most closely eluting DADMAC homologues. The concentrations of DADMAC C8:C8; C8:C10; BAC 12 and BAC 18 were calculated by assuming response factors of DADMAC C10:C10, BAC 14, and BAC 16, respectively. Given the alkyl chain length dependence on BAC instrumental response, the reported concentrations of BAC 12 and 18 are likely under- and overestimated, respectively by less than a factor of 2 (*16*). The limits of quantification (LOQ at $S/N = 10$) were determined by standard additions to a deeper QAC-free sediment core sample. With a sediment mass of 100 mg (dry wt) and a final sample extract volume of 15 mL, the LOQs of individual QACs range between approximately 1.5−30 ng/

g. The relative standard deviation of analysis of individual QACs in a low concentration sediment varied between 2 and 20% (*16*) and ranged between 1.2 and 9.2% for 3 urban estuarine sediments analyzed here. Recoveries of surrogate standard DADMAC 12:12 were 104 ± 19% ($n = 47$) in this study.

Results and Discussion

Occurrence of QACs in NYNJHC Sediments. The HPLC-ToF-MS method utilized for this study was highly sensitive, such that, 12 of the targeted QACs were easily measured in almost every sample (Table S1 includes complete data). However, DADMAC C8:C8, DADMAC C12:C14, ATMAC 12, and ATMAC 14 were present at much lower levels (rarely > LOQ) at the extract dilutions analyzed (*16*) and are not reported here.

Table 1 summarizes concentration ranges and median levels of targeted QACs determined in this study and in the few prior studies we are aware of (*3, 7, 11, 13*–*16*). Total concentrations of QACs range between 0.98 and 114 μg/g, with a median concentration of 29 μg/g. Total QACs in these samples are dominated by DTDMAC (median level of 26 μg/g). DTDMAC levels are relatively high throughout the urban estuary, with concentrations above 5 μg/g measured in samples from all but 3 of the 47 sites. Median concentrations of other classes of QACs were 1.5, 0.52, and 0.20 μg/g for ΣBAC, ΣATMAC, and ΣDADMAC, respectively. As discussed below, the concentrations of these more soluble and biodegradable classes of QACs were much greater at the 4 sites most affected by CSO inputs with maximum concentrations of 27, 5.2, and 4.5 μg/g determined for ΣBAC, ΣATMAC, and ΣDADMAC, respectively (Tables 1 and S1). Measurements of QACs in samples collected in 2008 at 7 of these sample sites indicate that the levels reported here changed little between 1998 and 2008 (*22, 30*).

DTDMAC Distributions. The alkyl homologue patterns primarily consist of DADMAC C16:C16, C16:C18, and C18:18, in expected relative proportions. A similar alkyl homologue distribution for trialkylamines (TAMs), dialkylmethyl analogs of DTDMACs present as impurities in commercial DTDMAC formulations, has also been observed (*31*). The concentrations of DTDMAC are within a similar range (with the exception of one highly contaminated estuarine sediment taken at a sewage outfall from Barcelona) of those determined in sediments collected before the phase-out of DTDMAC at the beginning of the 1990s (*3, 7, 13, 14*). The median concentration of DTDMAC measured here is 120 times higher than that reported in Austrian river sediments in a more recent study (*11*). This difference is likely due to three factors: 1) the drop in use of DTDMAC in fabric softeners in the U.S. was not mandated, nor nearly as great as in Europe (*2*); 2) the concentrations of DADMAC C14:16 and C16:C18 were not estimated in the Austrian study; and 3) the highly urbanized study area investigated in this study can be expected to be more impacted by municipal wastewater; similarly, sediment concentrations measured in Austrian rivers were much lower than those reported here for DADMAC C10:C10 and BACs (Table 1).

BAC Distributions. BACs were the second most abundant class of QACs measured in this work, with median concentrations of 140, 440, 320, and 490 ng/g for BACs 12–18, respectively (Table 1). BAC concentrations are again higher than those measured in riverine sediment studies (*11, 15*). The compositions of the BAC mixtures determined here reflect much greater proportions of BAC 16 and 18. The higher levels of BAC 16 could be due to a variety of factors including differential fate of BAC homologues during local WWTP treatment, or following discharge into receiving waters (*25*), or differences in uses of the major formulations of BACs for disinfection, possessing very different proportions of BAC

TABLE 1. Comparison of QAC Concentrations in Surficial Sediments in Different Published Reports[a]

sediment type	ref	DTDMAC (ng/g) C12:C12–C18:C18	DADMAC (ng/g) C8:C10	DADMAC (ng/g) C10:C10	ATMAC (ng/g) C10–C14	ATMAC (ng/g) C16–C18	BAC (ng/g) C12	BAC (ng/g) C14	BAC (ng/g) C16	BAC (ng/g) C18	total QAC(μg/g)
urban estuarine ($n = 47$) NY, NJ, U.S.	this work	690–110,000 (26,000)	n.d.–767 (10)	n.d.–4100 (190)	-	8.6–5300 (520)	40–1000 (140)	60–8900 (440)	n.d.–3800 (320)	n.d.–4000 (490)	0.98–114 (29)
remote estuarine ($n = 2$) NY, U.S.	(*16*)	1700–4700	n.d.	6.0–7.4	-	-	6.2–17	19–60	23–84	57–73	1.8–4.9
urban harbor ($n = 2$) Spain	(*13*)	42,300–1,140,000	-	-	-	-	-	-	-	-	42.3–1140
riverine ($n = 21$) Austria	(*11*)	5–2700 (140)	-	n.d.–510 (21)	n.d.–127 (6.8)	-	3.4–3600 (60)	n.d.–1600 (23)	1–510 (10)	n.d.–290 (7)	0.06–6.8 (0.88)
riverine SD, U.S.	(*7*)	3000–67,000	-	-	-	-	-	-	-	-	3.0–67
riverine Japan	(*3*)	6000–69,000	-	-	-	-	-	-	-	-	6.0–69
riverine ($n = 3$) Belgium	(*14*)	11,000–67,000	-	-	-	-	-	-	-	-	11–67
riverine ($n = 4$) KS, MO, CO, U.S.	(*15*)	-	-	-	-	-	23–105	22–206	21–260	-	0.066–0.57

[a] Where available median concentrations are indicated in parentheses.

12−16 homologues (*18*). More striking are the higher levels of BAC 18 reported here. As already mentioned, it is likely that the concentrations of BAC 18 are somewhat overestimated but not to the extent that would explain the differences in composition compared to prior studies (Table 1). Biocidal activity of BACs and skin irritancy of QACs generally decrease with alkyl chain lengths of the compound classes considered in this work (*3*). A survey of product formulations indicates that BAC 18, sometimes referred to as stearalkonium, is used in personal care products that may reach municipal wastewaters in higher proportions than BAC 12−16 often used as disinfectants applied to surfaces. BAC 18 was also the most abundant homologue detected in Taiwanese river and effluent samples, also interpreted to be related to use of this compound in shampoos and other personal care products (*4*).

ATMAC Distributions. ATMACs were the next most abundant class of QACs detected. ATMAC 16 and 18 are found in cetrimonium and stearyltrimonium formulations used in applications such as conditioners and hair care products (*5, 30*). Given the antimicrobial properties ATMACs and applications that include their use as preservatives (*3*), they may be environmental contaminants worthy of further study (*30*).

Near the completion of this study, it was discovered that there are much higher concentrations in recent surface sediments of previously unrecognized ATMAC 22 along with lower relative amounts of ATMAC 20 (*30*). Together ATMAC 20−22 make up behentrimonium, extensively used in hair care products. A much more detailed investigation of the occurrence and sediment geochronologies of behentrimonium, and other ATMACs, in lower Hudson River basin sediments is the subject of a related report (*30*).

DADMAC Distributions. Formulations of DADMACs with lower alkyl chain length (C8:C8, C8:C10, and C10:C10) than DTDMAC are used in more recent generations of QAC-based disinfectants (*18*). The presence of DADMAC C10:C10 has recently been reported in many sample types (*11, 19, 25*), and DADMAC C8:C8 and C8:C10 have been confirmed in marine sediments (*16*). In this survey, lower abundances of the C8:C10 homologue were measured (median concentration of 10 ng/g) in comparison to the C10:C10 homologue (190 ng/g). DADMAC C10:C10 was found to be efficiently removed by WWTPs, attributable to microbial degradation (*25*). Lower levels of less alkylated DADMACs may be related to greater biodegradation of more soluble homologues within WWTPs or in receiving waters.

Relationship of QACs to Sediment Total Organic Carbon (TOC). Concentrations of total QACs are comparatively high throughout the study area and, other than three samples from the highly eutrophied Long Island Sound, increase with sediment TOC on a Harbor complex-wide basis (Figure 2). Again, the total QAC concentrations are primarily comprised of DTDMAC (Table 1; Figure 3). There is a stronger relationship between these two properties ($r^2 = 0.80$) when only muddy sediments (defined as samples with TOC > 1.2% and Si/Al ratios <10) not proximate to CSO inputs are considered. Linear regression analysis of this data yields an intercept corresponding to a TOC of 1.68 ± 0.22% that falls within a range of background levels of TOC expected in muddy estuarine sediments not greatly affected by exceptionally high primary productivity or sewage inputs (*32, 33*).

There are many processes that affect relationships between QACs and TOC in these samples. It is hypothesized that the primary explanation for the observed correlation is that sewage-derived organic matter is the primary source of organic carbon enrichment in the samples analyzed and that DTDMACs and more persistent QACs serve as stable tracers of the transport and deposition of sediments co-contaminated with the more resistant fraction of sewage-derived organic matter. Based largely on correlation with sewage-derived metals, it was concluded that excess TOC in Jamaica Bay was sewage derived (*34*) and that excess sediment organic matter in the metropolitan region of the lower Hudson basin was due to sewage inputs (*33*). Neither QACs nor TOC levels in the samples analyzed are positively related to Al content (*22, 27*), as might be expected if the primary determinants on TOC and QACs were related to properties such as surface area or cation exchange capacity associated with Al-rich clays (*9*).

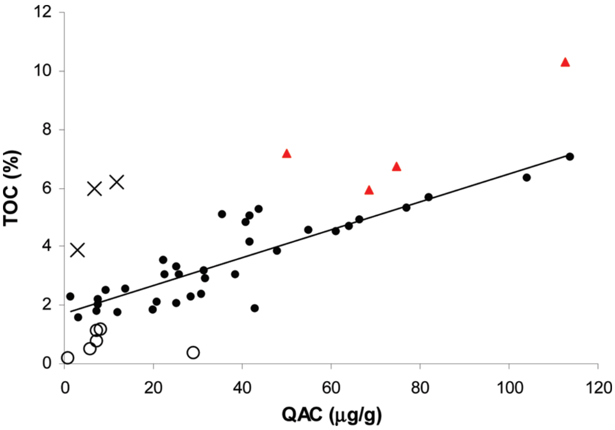

FIGURE 2. Relationship between sediment TOC and total QAC concentrations at sites from western Long Island Sound (×); sandier sediments (○) (defined by TOC < 1.2% with Si/Al > 10); CSO-impacted samples (▲); and all other muddy samples in the urban harbor complex (•). The linear regression plotted is only calculated from the latter ($y = 0.05x+1.7$, $r^2 = 0.80$), standard error for the intercept is 0.22, and the p-value that the intercept is greater than zero is 1.01×10^{-8}.

Sediment-Sorbed QACs as Potential Source Tracers. There is further support that DTDMAC, and perhaps other QACs, can serve as useful tracers of the sources or transport of sewage-derived contaminants, organic matter, or affected sediments. Bayona and co-workers (*31*) reviewed the evidence that TAMs, which also exist as protonated cations at seawater pH, can serve as powerful particle-reactive tracers of sewage sources. For example, TAMs are transported farther from sewage sources than either coprostanol or linear alkyl benzenes, both of which that have a long history of use as particle-reactive sewage tracers (*31*). In sewage dominated Jamaica Bay sediments, all classes of QACs correlate proportionally with silver (Ag) (Figure S1), a metal which has served as a diagnostic and sensitive sewage tracer in sediments (*29, 35*); DTDMAC was also determined on continental slope sediments from the former DWDS106 (at approximately 2600 m depth). With no natural background signal, the concentration of DTDMAC at the most sewage-affected site (7.2 μg/g) was over 100 times greater than concentrations determined at the most remote site (Table S2). In contrast, Ag enrichment in that sample is much less: 7 times a low natural background of 0.03 μg/g. Most interesting is that the DTDMAC-Ag relationship overlays closely the relationship in near-shore Jamaica Bay (Figure S1). Additional evidence suggesting that QACs are relatively persistent and have potential to be powerful sewage-source particle-reactive tracers include 1) the close similarity in QAC compositions in Jamaica Bay sediment and a sediment sample from central Long Island Sound over 50 miles from major sewage inputs (*16*); 2) the similarity in QAC compositions across wide areas of the urban harbor complex (Figure 3) suggesting lack of dramatic hydrophobicity-dependent fractionation during local transport or across variable deposition regimes; 3); postdepositional *in situ* preservation in suboxic sediments is indicated from matched sediment

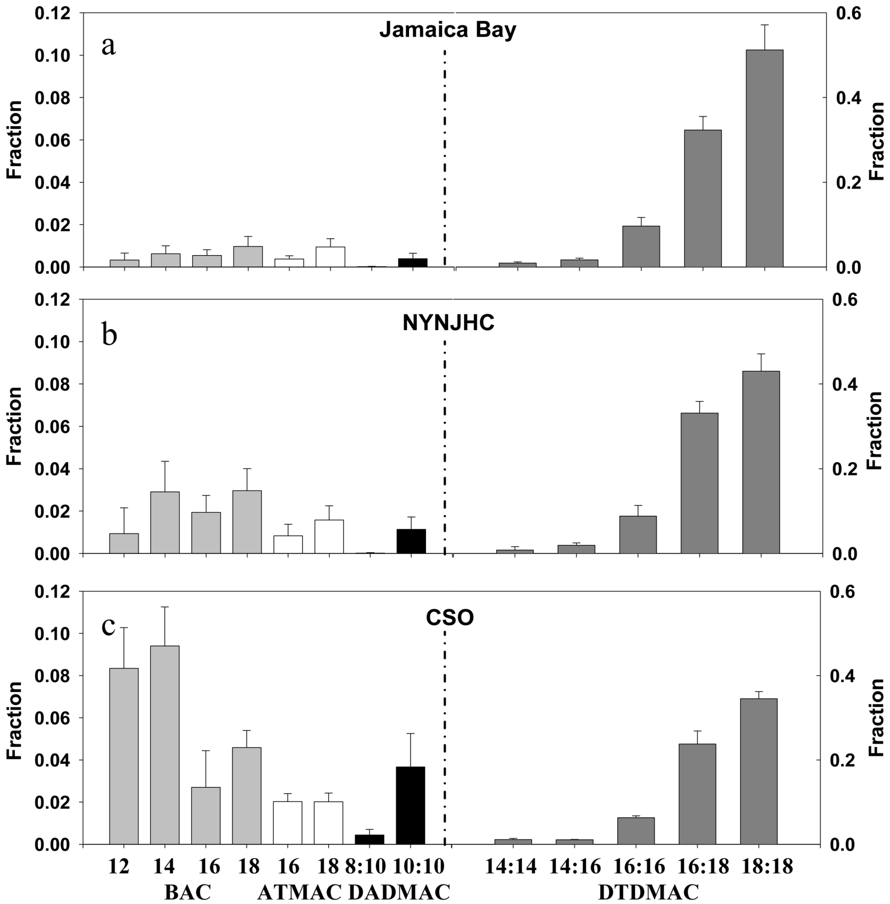

FIGURE 3. Average compositions of detected QAC in the samples from (a) Jamaica Bay ($n = 15$); (b) NY/NJ Harbor Complex ($n = 28$); (c) CSO influenced samples ($n = 4$); DTDMAC compositions and other QACs are plotted in different scales; error bars represent standard deviations. Note that fractions of DTDMAC (right) and other QACs (left) are presented in different scales.

cores, collected 8 years apart, where sediment deposited at the same time period possess indistinguishable concentrations and compositions of QACs (*22*); and 4) DTDMAC distributions were able to separate the relative sources of particle reactive PCBs and PBDEs in the lower Hudson Basin, consistent with conclusions from independent geochemical indicators (*22*). Sediment-sorbed QACs are seen to be transported over significant distances, but there must be a discernible fraction of QACs which exist in dissolved phases in receiving waters, especially near sources. In order to better understand the bioavailability of QACs or the limitations on their use as particle-reactive tracers, research is needed to characterize and understand *in situ* speciation of QACs and the conditions under which sorbed compounds desorb.

Composition of QACs in Sediments - Insights into Sources and Differential Preservation. The composition of the QACs determined in each sample are illustrated in Figure 3, which divides the samples into three defined areas: a) Jamaica Bay (JB; $n = 15$); b) the rest of the New York New Jersey Harbor Complex (NYNJHC, $n = 28$); and c) those most affected by proximal CSO sources. The small differences in DTDMAC composition within and across geographical regions suggests a lack of appreciable alkyl chain length-dependent fractionation, similar to that seen for TAMS on suspended particles and sediments tens of miles from shore (*31*).

The composition of other more soluble QACs differs between the three areas. DTDMAC represents 95, 87, and 66% of the total QACs detected in sediments from JB, NYNJHC, and CSO affected sites, respectively. It is unclear why the relative abundance of DTDMAC is greater in JB than in the NYNJHC samples. Differences in the composition of QACs entering municipal wastewaters in different sewersheds or the efficacy of local sewage treatment may be responsible.

Pronounced differences in concentrations and composition of more soluble QACs are observed in CSO-affected sediments (Figure 3c; Figure 4). In these samples, the composition within a homologous series is characterized by relative enrichment of more soluble QACs with shorter alkyl chain lengths, reflecting a less treated municipal wastewater source (*8, 25*). Biodegradation of more soluble QACs is also consistent with laboratory-based degradation studies examining effects of alkyl chain length (*19, 23, 24*). Following discharge, it is not clear how much additional biodegradation occurs, although it is of interest to note that the composition of more soluble BAC 12−18 and DADMAC C10:C10 in river sediments near WWTPs were similar to those measured in effluents (*8, 11*). Our working hypothesis is that the differences in QAC composition observed in sediments from this study are affected more by differences in sources to the local sewersheds and different levels of sewage treatment rather than the processes affecting fate in receiving waters, which would be expected to be highly dependent on structure or alkyl chain lengths. Each QAC increases positively with DTDMAC concentration (Figure 4), with correlation coefficients of linear regression between 0.82 and 0.92 for JB samples. Correlations were often less good for the larger area of NYNJHC, specifically for more soluble BAC 12 ($r = 0.58$), BAC 14 (0.66), and ATMAC 16 (0.65); correlation coefficients for other, largely more hydrophobic, QACs in NYNJHC ranged between 0.79 and 0.88. It is hypothesized that one reason for the similarity in QAC compositions in sediments sampled at different distances from sources is that after association with suspended particles and surficial sediments the intense

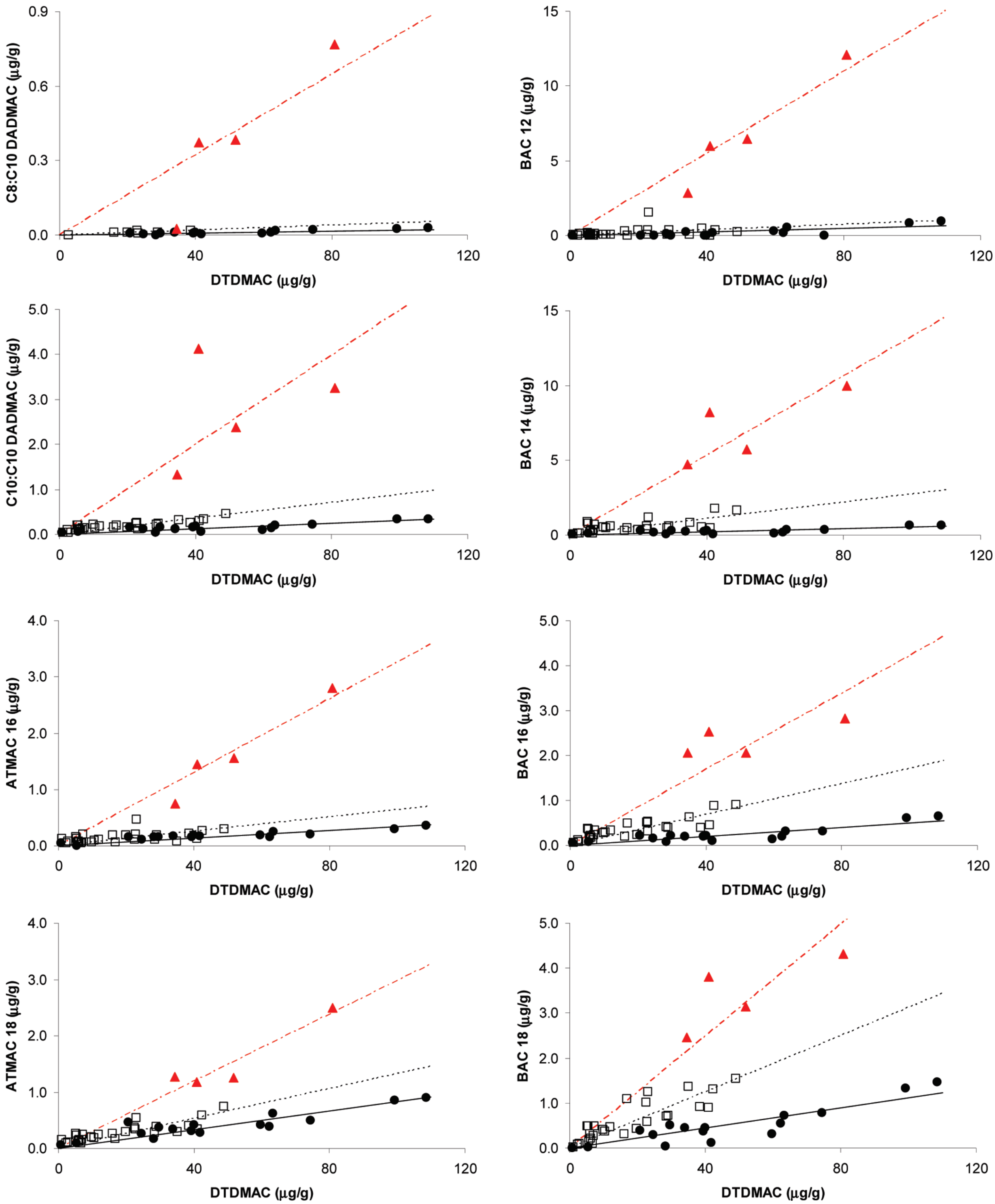

FIGURE 4. Relationships between sediment concentrations of more soluble QACs vs DTDMAC indicating alkyl homologue-dependent enrichments of less hydrophobic QACs in CSO-impacted sediment (▲), in comparison to those in Jamaica Bay (•) and the rest of NY/NJ Harbor Complex (□). Linear regression results are illustrated for the model ($y = ax$), with solid and dashed lines corresponding to Jamaica Bay (black solid), NY/NJ Harbor Complex (black dashed) and CSO (red dashed), respectively.

sorption of QACs is magnified to an extent that leads to greater resistance to biodegradation and desorption in receiving waters (discussed below). The positive relationships between less soluble QACs and DTDMAC are illustrated in Figure 4 with linear regression lines determined for the model $C_i = a_{ir}C_{DTDMAC}$, where C is the sediment concentration of each QAC (i) and the defined region (r) of the samples (i.e., CSO, NYNJHC, JB). The slopes of these regressions were also determined as a means to provide a proxy for the degree of relative depletion (RD) compared to DTDMAC of more soluble QACs in NYNJHC and JB samples, when compared to CSO-influenced sites. QACs with lower RD values ($RD_i = a_{i(JB/NYNJHC)}/a_{i(CSO)}$) are interpreted to have been more biodegraded or otherwise removed prior to, or following, discharge to JB or NYNJHC. As shown in Figure 5, the QACs with the lower values of RD are those that are less hydrophobic, as estimated by alkyl chain length within a structural class of QACs, and by the reverse-phase HPLC retention time

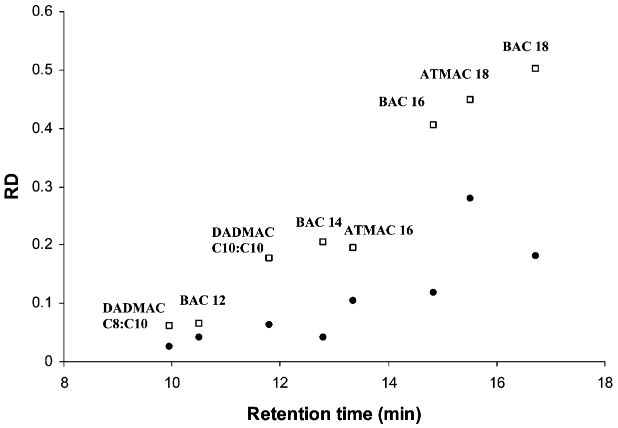

FIGURE 5. The relative depletion (RD) of more soluble QACs in comparison to less treated CSO-affected sites vs HPLC retention time as an indicator of QAC hydrophobicity (see text for details). The magnitude of RD is different for Jamaica Bay (●) the rest of the urban harbor complex (□), although the trend with retention time is similar.

as an estimator of relative hydrophobicity (*36*). The trends shown in Figure 5 provide some evidence that biodegradation of QACs may be more affected by hydrophobicity than QAC structural class, a result consistent with relative losses from biodegradation in Austrian WWTPs (*25*).

Why Might Sediment Sorbed QACs Be Especially Persistent. All classes of QACs, even DTDMAC, are intrinsically biodegradable in laboratory studies, even in suspensions of sediment or inoculums of activated sludge sorbents that could greatly reduce bioavailability (*1, 23, 24*), and less hydrophobic QACs can be substantially biodegraded in WWTPs utilizing biological treatment (*25*). However there is no evidence of appreciable biodegradation of ultrahydrophobic DTDMAC within WWTPs, and the relatively high concentrations and generally uniform compositions of QACs away from sewage sources leads us to hypothesize a high degree of persistence for an even larger range of more soluble QACs once associated with sediments in urban estuarine and marine settings.

Possible explanations for greater persistence of sediment-sorbed QACs in the field are manifold. However, very strong sorption and resistance to desorption of even the most soluble QACs must contribute to the relatively high levels and uniform composition of many QACs measured. Two major differences between conditions in the field and many lab experiments that affect sorption include the time of exposure to sediment and the concentration of solute and sorbate. "Aging effects" for sorption are seen in extraction efficiency for QACs (*13, 16*) e.g., their ability to adsorb to sites within clay lattices could be one factor (*12, 13*). While, it is well-known that substrate levels can affect rates and routes of biodegradation of organic chemicals, it is also known that concentration-dependent sorption of QACs to soils and sediments can be very large (*9, 10, 12*). Sorption studies of QACs, especially with phase distributions measured at both low sorbate and solute concentrations, are generally lacking. Sorption isotherms for dodecylpyridinium (DP) were very nonlinear compared to other organic contaminants (*10*) and could be described using a multisite cation-exchange model (*9*). In one experiment spanning over 6 orders of magnitude of solute concentration, sorption was reasonably well described with a single Freundlich isotherm. The measured concentration distribution ratios of DP were approximately 1000 times greater at low sorbate concentration than at the highest sorbate concentrations near the cation exchange capacity. Most of the QACs detected in this work are much more hydrophobic than DP, such that distribution ratios will be greater at low solute concentrations. This may lead to even greater nonlinearity in sorption isotherms and very difficult to experimentally determine distribution ratios.

QAC Concentrations in Comparison to Other Organic Contaminants of Concern. Total concentrations of QACs are much greater than summed concentrations of chlorinated pesticides, PCBs, and PAHs measured in the same EPA collected samples ($n = 45$; ref *29* with comparisons found in Table S3). The median ratio of QACs to ΣPAHs is 25; the sum of the concentrations of NPEOs with one to three ethoxomers was also determined (*22*), and the median QAC/NPEO ratio is 2.1 (Table S2). The only class of organic contaminants in these sediments that has been found at higher concentrations are total petroleum hydrocarbons, characterized as unresolved complex mixtures consistent with the composition of used motor oil [(*22*) Table S2]. Finally, a comparison can be made of the levels of QACs that can be labeled as disinfectants (BAC 12−16 and shorter chain DADMACs) or are used in preservative formulations (ATMACs) with that of triclosan and triclocarban, antimicrobials that are not used as disinfectants. Triclosan (<LOQ) and triclocarban ($\sim$2.5 μg/g) were measured at the surface of a 1996 collected sediment core obtained in a depositional basin in Jamaica Bay (*37*), similar to QAC concentrations determined in samples analyzed here from two nearby sites: ΣBAC (3.4−3.7 μg/g), ΣDADMAC (0.35−0.37 μg/g), and ΣATMAC (1.2−1.3 μg/g).

There are presently very few field measurements of QACs (*19*), illustrated here for sediments (Table 1) which serve as an important reservoir for these particle-reactive contaminants. Greater understandings are required to estimate the fate and bioavailability of sediment-sorbed QACs, especially under field conditions where concentrations are lower than those considered in most lab studies. Given the comparatively high concentrations, exciting potential for applications of QACs as source-specific tracers, and antimicrobial properties of several classes of QACs measured in urban estuarine sediments, the question is raised as to whether these chemicals should receive increased attention within the environmental research community.

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Supporting Information Available

Detailed station locations, TOC and individual QAC data (Table S1); station locations, TOC, Ag, and DTDMAC for the former 106 mile Deep Water Dump Site (Table S2); a comparison of QAC levels with other organic contaminants determined on the same EPA collected surface sediments (Table S3); and Figures (S1) illustrating the relationships between different classes of QACs with the Ag in Jamaica Bay sediments as well as the relationship between DTDMAC and Ag determined at the former 106-mile Deep Water Dump Site. This material is available free of charge via the Internet at http://pubs.acs.org.

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