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Occurrence of Alkyltrimethylammonium Compounds in Urban Estuarine Sediments: Behentrimonium As a New Emerging Contaminant

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The distribution of alkyltrimethylammonium compounds (ATMAC), cationic surfactants used in a wide variety of applications, has been determined in sediments from Jamaica Bay (NY). Total concentrations in surficial sediments collected between 1998 and 2008 ranged from 361 to 6750 ng/g. The highest values were found in samples from a deeper basin directly affected by treated wastewater discharges. Behentrimonium, a mixture dominated by a homologue having 22 carbon atoms in its alkyl chain (ATMAC 22), was identified for the first time using time-of-flight mass spectrometry and accounted for approximately 80% of the total ATMAC in recent sediment samples. Analyses of a dated sediment core and subsequent surface grab samples revealed an exponential increase in concentration over the last three decades with a doubling time of 3.9 years. Similar temporal trends were seen in surface samples from other sites in Jamaica Bay and Newton Creek (NY), another site greatly influenced by wastewater discharges. This dramatic increase in ATMAC 22 reflects greater use of behentrimonium and likely replacement of other products containing other ATMAC homologues in personal care products. Further monitoring is recommended to assess the environmental risk and fate of this persistent emerging contaminant.

Introduction

The emissions and environmental occurrence and fate of the vast majority of chemical substances in wide commercial use have not been determined. Muir and Howard (*1*) have presented many of the current challenges faced when screening a large number of compounds for potential risk, and prioritizing those that merit more detailed assessments. National and international programs have been developed for this purpose, screening especially those with higher production volumes: e.g., the Toxic Substance Control Act (TSCA) in the U.S., the goals of which are addressed in part by the High Production Volume Chemical (HPVC) program (a HPV chemical is defined as one with a production above 1 million pounds per year). Some of the screening criteria are designed to identify compounds that have potential to be persistent organic pollutants (POPs), many of them likely to be found in the list of chemicals widely used in commerce or as degradation products of these substances (*1*). Among them, surfactants, with an estimated total production above 10 million tons per year (*2*), include a large number of HPV chemicals, some of which, such as the extensively studied metabolite nonylphenol (NP), have been already added to the POP list (*3*). Cationic surfactants, such as quaternary ammonium compounds (QACs), have received much less attention (*4*). Among the most important structural classes of QACs are benzylalkyldimethylammonium (BAC), alkyltrimethylammonium (ATMAC), and ditallowdimethylammonium (DTDMAC) compounds. Although they are produced in lower amounts than anionic and nonionic surfactants, these chemicals can be more persistent, as they are hydrophobic cation exchangers that adsorb strongly to soils, sediments, and sewage sludge (*5, 6*), and their microbial degradation is minimal in the absence of oxygen (*7*). In a related study (*4*), this laboratory has reported on the distributions of homologous series of QACs in surficial sediments across the greater New York/New Jersey Harbor complex, where the median concentrations of total QACs was 29 μg/g ($n = 47$) (*4*).

Here we have focused our attention on ATMAC, chemicals that are often produced as chloride salts, but are also sold in significant amounts with other counterions such as bromide and methosulfate. These surfactants find a variety of uses, for example, in fabric softeners, antimicrobials, emulsifiers, phase transfer agents, and antistatics. ATMAC are also present in thousands of personal care products, especially hair care products, as they impart softness, manageability, and antistatic properties to hair (*8, 9*). Table S1 (Supporting Information) indicates production estimates for different ATMAC homologues and mixtures in the U.S. Data on their occurrence and fate in the environment are especially scarce. To our knowledge field measurements are limited to multimedia characterization of ATMAC 12−16 (*10, 11*), ATMAC 12−18 in river water (*12*), and the distributions of ATMAC 16−18 in surficial sediments of NY/NJ Harbor (*4*). Their removal in wastewater treatment plants (WWTPs) is thought to be dominated by a combination of sorption to sludge and microbial degradation (*11, 13*−*15*). Their degradation rate in seawater was also shown to decrease with increasing alkyl chain length, presumably the result of protection related to enhanced sorption (*16*). Similar to other QACs, ATMAC anaerobic biodegradation studies showed slow primary transformation and no detectable mineralization over 200 days (*17*).

The occurrence and distribution of ATMAC in sewage-affected marine sediments are reported below, showing the spatial and temporal trends of the most prevalent homologues (ATMAC 16−22), which have been monitored by means of repeated surface sediment sampling over a period of time, and analysis of a dated sediment core. Most significant is the discovery of relatively high concentrations of ATMAC 20 and, especially, ATMAC 22, a mixture sold under the name of behentrimonium chloride or methosulfate. Behentrimonium is derived from rapeseed oil, and has been used increasingly in personal care products, especially hair care products (*9*). As a result of increased hydrophobicity, it is hypothesized that ATMAC 20−22 will be less subject to microbial degradation in WWTPs and receiving waters, leading to greater potential for accumulation in sediments than might be

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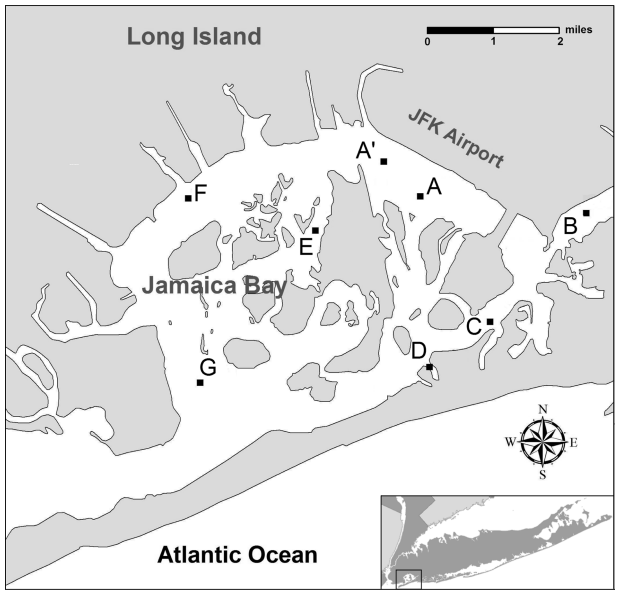


FIGURE 1. Location of Jamaica Bay in Long Island (NY) and of the sampling stations (A−G) inside the bay. Sediment core JB 16 was collected near station A.

expected from production estimates that are lower than those of ATMAC homologues with shorter alkyl chain lengths (Table S1).

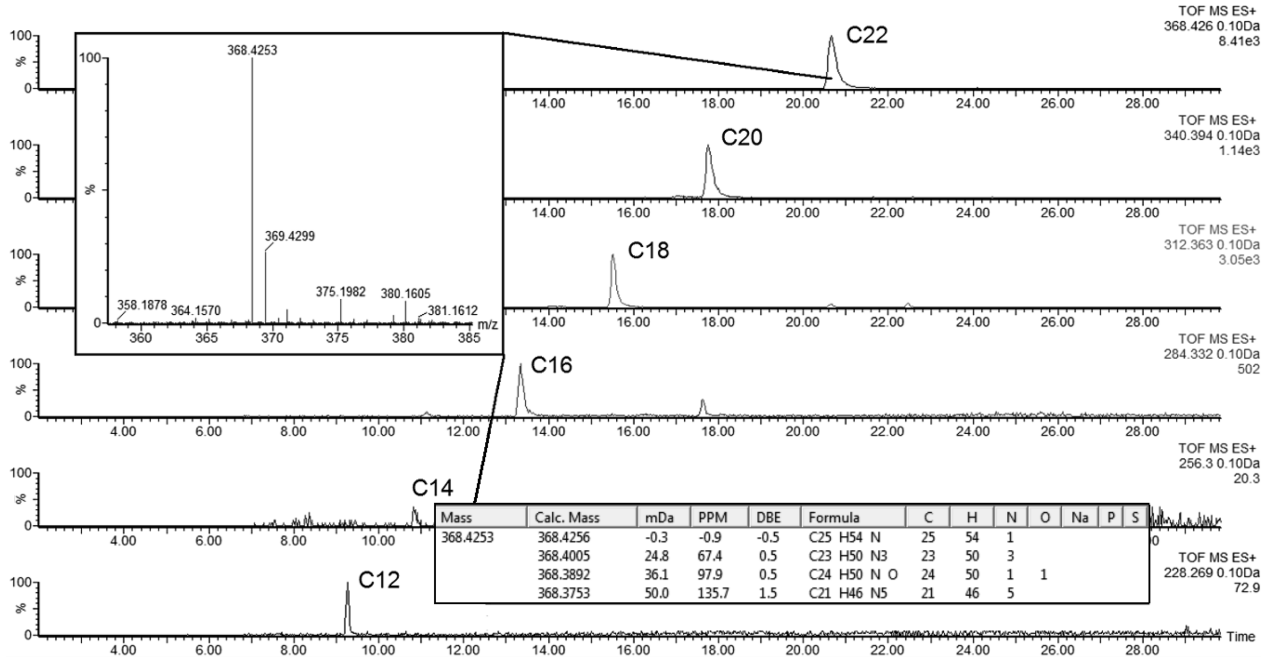
Experimental Section

Area Description and Sampling Collection. The main sampling area, Jamaica Bay, located on the Southwestern shore of Long Island, NY (Figure 1), has been the subject of a number of studies of wastewater derived contaminants (*4, 18−20*). Descriptions of the Bay and its sedimentary environment can be found in these references and in Supporting Information (SI). Only muddy and highly sulfidic muddy sediments were targeted, characterized by a narrow range of aluminum contents (SI). Surficial sediment (0−2 cm) samples were collected from station A to station G by means of Van Veen grabs during the summers of 1998, 2003, and 2008, as well as a sediment core, JB 16, in 1996 (less than 100 m from station A), within a depositional basin area known as Grassy Bay. The sediment core was sectioned at 2−4 cm intervals and dated (ref *19*; see SI for further details). Additional sediments samples (0−2 cm) analyzed were collected between 1987 and 2005 from another wastewater impacted site at Newton Creek (see SI for additional site and sample characterization).

Analytical Methodology. The methods for ATMAC analysis followed those described elsewhere (*21*), using high-performance liquid chromatography−time-of-flight−mass spectrometry (HPLC-ToF-MS). A more complete description of the methods is provided in the SI. Additionally, DTDMAC was analyzed in the same samples following published methods (*21*). The recovery of surrogate standard didodecyl dimethylammonium chloride was 106 ± 20%.

Results and Discussion

Identification of ATMAC Homologues in Sediments. ATMAC 12−18 were targeted analytes in a larger study on the biogeochemistry of QACs in urban estuarine sediments (*4*). Later examination of HPLC-ToF-MS data files suggested additional large peaks, hypothesized to correspond to ATMAC 20 and 22. Figure 2 displays extracted ion chromatograms corresponding to the different ATMAC homologues. ATMAC 12−18 were identified by means of measurement of their accurate masses and the coincidence in their retention times compared to authentic standards. The two later eluting peaks were tentatively identified as ATMAC 20 and 22 based on nominal mass and extrapolation of the effect of CH_2 addition on HPLC retention time. Confirmation of the elemental formulas was provided by accurate mass measurements of the peaks in a sediment sample (Figure 2) that agree with the exact masses of the putative ions (*m*/*z* 340.3943 and 368.4256 for ATMAC 20 and 22, respectively) to within 1 ppm. A search of other elemental formulas with ion masses closest to the accurate mass estimates provides unambiguous confirmation of the formula corresponding to ATMAC. For any ATMAC, there are no alternatives within 25.2 mDa when only even electron ions are considered, much greater than instrument



Mass	Calc. Mass	mDa	PPM	DBE	Formula	C	H	N	O	Na	P	S
368.4253	368.4256	-0.3	-0.9	-0.5	C25 H54 N	25	54	1				
	368.4005	24.8	67.4	0.5	C23 H50 N3	23	50	3				
	368.3892	36.1	97.9	0.5	C24 H50 N O	24	50	1	1			
	368.3753	50.0	135.7	1.5	C21 H46 N5	21	46	5				

FIGURE 2. Extracted HPLC-TOF-MS ESI+ chromatograms showing the presence of ATMAC homologues (12−22) in a sediment sample from station A taken in 2008. The mass spectrum for ATMAC 22 and its identification by accurate mass measurement are also displayed.

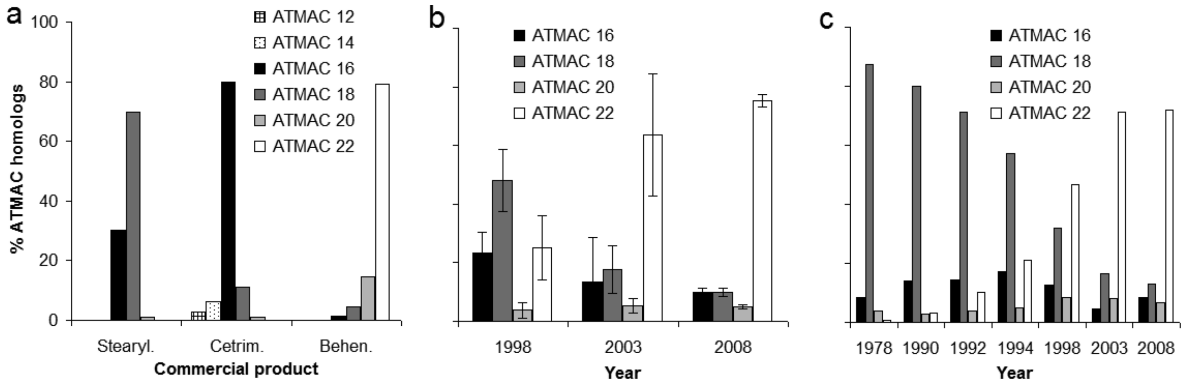


FIGURE 3. (a) Average distribution of ATMAC homologues in commercial products based on stearyltrimonium (*8*), cetrimonium (*8*), or behentrimonium, (b) evolution (1998−2008) in the average distribution of ATMAC homologues in surficial sediments from Jamaica Bay, and (c) evolution (1978−2008) of the same homologues in the JB 16 sediment core and station A samples collected between 1998 and 2008.

TABLE 1. ATMAC Concentrations (ng/g) in Sediment Grabs from Jamaica Bay (Stations A−G) from 1998 to 2008 (n.d. = Not Detected)

station	ATMAC 16	ATMAC 18	ATMAC 20	ATMAC 22	∑ ATMAC
			1998		
A	360	903	239	1320	2820
A′	340	855	203	1320	2720
B	201	497	40	231	969
C	191	425	21	197	834
D	161	376	11	97	644
E	169	284	41	220	714
F	154	174	8	85	421
G	154	459	14	119	746
			2003		
A	201	735	363	3200	4490
B	86	167	77	979	1310
C	78	117	51	651	897
D	74	155	50	608	886
E	171	129	n.d.	61	361
F	54	128	56	697	934
G	254	317	126	1360	2060
			2008		
A	578	870	439	4860	6750
B	206	213	102	1750	2280
C	244	222	115	1950	2530
D	199	181	110	1640	2130
E	197	168	72	1160	1600
F	211	193	91	1550	2050
G	259	229	103	1750	2340

specifications of 2 mDa mass accuracy. This unusually high mass resolution has been recently determined to be due to the characteristic high positive ion mass defect of alkyl amine ions possessing only C, H, and N, and few sites of unsaturation (*21*). The HPLC retention, accurate mass measurements, and the approximate relative abundance of ATMAC 20 and 22 for these two compounds were also in agreement with those found for these homologues in a commercial product containing behentrimonium (Figure 3a).

Distribution and Composition of ATMAC in Jamaica Bay Surface Sediments. The concentrations of ATMAC 16−22 in Jamaica Bay surface sediments are provided in Table 1. Shorter alkyl chain homologues such as ATMAC 12 and 14 are not reported since they were generally not detected or present at very trace levels at the most contaminated sites (Figure 2). The very low levels of these two homologues may be due to their lower use in personal care products (Figure 3a), or less persistence due to less sorption and higher biodegradation when compared to longer chain length ATMAC homologues (*14, 16*). The sum of ATMAC 16−22 (∑ATMAC) concentrations varied among sites and increases with time, with concentrations ranging from 481−2820 ng/g in 1998 to 1600−6750 ng/g in 2008. The highest ATMAC concentrations were found at site A during each year, and for nearby site A′ in 1998. These sampling stations are located within the Grassy Bay depositional basin. This finding agrees with results obtained in prior studies of the distribution of other particle reactive wastewater contaminants, that include nonylphenol ethoxylate (NPEO) metabolites, natural steroid estrogens, and a larger range of QACs at the same or nearby sites (*4, 18−20*). DTDMAC was also measured in all of the sediments analyzed here, as were NPEO metabolites in the 1998 samples (*4, 18*) (Table S2). The spatial variability of wastewater derived DTDMAC and NPEO metabolites was similar to that of the ATMAC, with a positive correlation found between ∑ATMAC and NPEO metabolites ($R^2 > 0.80$) and between ∑ATMAC and DTDMAC ($R^2 = 0.98$), suggesting commonalities in their sources, and the processes involved in the transport, deposition, and preservation of these contaminants in muddy Jamaica Bay sediments. It is also hypothesized elsewhere (*4*) that the correlation of ATMAC 16 and 18 with DTDMAC across the NY/NJ Harbor complex is indicative of persistence of both classes of hydrophobic QACs in sediments after deposition. The higher ATMAC concentrations in Grassy Bay may be attributed to the combination of their high sorption onto sewage or suspended particles (*13*) and the rapid settling of these particles within Grassy Bay. Furthermore, sediments from this area are characterized by very high burial rates, virtually no benthic infauna, and little biological or physical mixing, with anoxic or hypoxic conditions prevailing in the near-bottom waters (*20*). ATMACs are degraded much more slowly in the absence of oxygen (*17*), and a high degree of sorption to muddy sediments favors preservation of ATMACs and other potentially labile organic contaminants in muddy suboxic sediments of Jamaica Bay, especially in Grassy Bay.

Large changes in ATMAC concentrations and composition were observed over the sampling time frame. A progressive increase in the ∑ATMAC concentration in Jamaica Bay sediments is apparent; e.g., increasing from 2820 to 6750 ng/g at station A (Table 1). Similar increases were seen throughout the Bay, as average ∑ATMAC concentrations for the other sampling stations rose from 721 ± 184 in 1998 to 2150 ± 320 in 2008. In contrast, DTDMAC levels were relatively stable over this time period (e.g., 108, 139, and 106 μg/g at station A in years 1998, 2003 and 2008, respectively) (Table S2). The increase in ∑ATMAC concentration in sediments is clearly related to a change in the homologue composition (Figure 3b). ATMAC 16 and 18 homologues comprised a large portion of the total ATMAC in 1998, averaging 23 and 48% of ∑ATMAC, respectively. However,

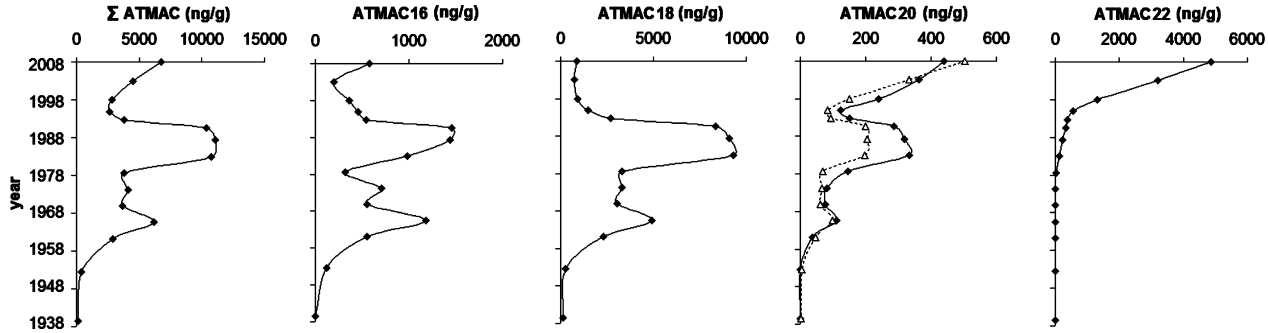


FIGURE 4. Concentration (ng/g) profiles for ∑ATMAC and ATMAC homologues in dated sediments from station A. The dotted line for ATMAC 20 represents a prediction (see text) assuming the concentrations result from a linear combination of sources derived from behentrimonium and other ATMAC mixtures.

the relative abundance of these homologues drops markedly over time to less than 10% in 2008, primarily due to the increase in the concentration of behentrimonium homologues (ATMAC 20, and especially ATMAC 22) from 1560 to 5300 ng/g at station A, and from 181 ± 79 to 1730 ± 282 ng/g at the other sites in the Bay.

Geochronologies of ATMAC Homologues Derived from a Dated Sediment Core and Surface Grab Samples. More detailed insight into the changes in ATMAC inputs to Jamaica Bay and homologue compositions are obtained from examining the geochronology of ATMAC determined in a dated and well studied sediment core collected in Grassy Bay (*19*), a site within 100 m of station A. Figure 4 shows the temporal changes for ∑ATMAC and individual ATMAC homologues between ~1939 and 2008. The sediment core was collected in 1996, and the time history profiles shown are extended to more recent times using data from 1998, 2003, and 2008 grab samples at station A (Table 1). The argument for combining results from the sediment core and subsequent surface grab samples is supported by the close similarity in concentrations of each ATMAC homologue in grab samples collected at both Grassy Bay stations A and A′ in 1998 (Table 1) and of ATMAC 16−18 and other QACs (*23*) in the upper sediment layer from the 1996 core (Figure 4). Sediment type was similar within a sediment core (e.g., TOC values between 6 and 7.2%; *19*) and in grab samples collected in 1998 (7.05%) and 2008 (7.52%) from this site (see Supporting Information). Moreover, the increase in ATMAC 20 and 22 between the 1996 core top and the 1998 sample (Figure 4) is consistent with rapidly increasing concentrations observed in surface grab samples throughout the Bay (Table 1), and that observed at the Newtown Creek site discussed below.

The vertical profile for ∑ATMAC concentrations (Figure 4) indicates a first appearance of ATMAC in the sediment record around 1950, consistent with the first appearance of papers describing them, including the use of cetrimide (mixtures containing ATMAC 14−18; Figure 3a) as an antimicrobial in shampoos (*22*). Three different maxima are observed in the time history of ∑ATMAC concentrations corresponding to the most recent sample in 2008 (6.7 μg/g), the mid- to late-1980s (11.1 μg/g), and the mid-1960s (6.2 μg/g). There is no detectable ATMAC 22 that contributes to the earlier two subsurface maxima, whereas the recent increase is driven by the rapidly growing concentrations of ATMAC 20 and especially ATMAC 22. The changes in sediment concentrations over time may be affected by inputs from the Jamaica WWTP and postdepositional transformations. Comparisons have been made between the concentrations and compositions of NPEO metabolites (*19*) and QACs (*23*) in samples from the core studied here (sampled in 1996) and in corresponding "age matched" sediment samples from another core sampled at the same site collected in 1988. Based on the close agreements in concentrations between samples deposited at the same time (but sampled 8 years apart), it was concluded that most NPEO metabolites and all measured QACs are persistent in the anoxic sediment column at this site over the intervening 8-year time period. In the case of NPEO metabolites, the changes over time in the ethoxymer composition could be attributed to upgrades in treatment performance of the local Jamaica WWTP that occurred in 1963 and 1978 (*19*). The change in flow capacity during the first upgrade (during which there was only partial treatment of flow) may have led to the subsurface ATMAC maxima seen in the 1960s. However, the profiles of individual and ∑ATMAC concentrations following 1978 are interpreted as resulting primarily from changing inputs to the WWTP from the sewer-shed of the Jamaica Plant, which covers largely residential portions of Queens and Brooklyn Boroughs of New York City.

There have been large changes in the patterns of ATMAC inputs since 1978 (Figures 3c and 4). First, ATMAC 18 was the most abundant homologue until 1995, reaching a maximum in the mid- to late-1980s (9.3 μg/g), followed by a sharp decline to more constant levels by the mid-1990s. The profile of ATMAC 16 was similar to that of ATMAC 18, although the relative abundance of ATMAC 16 has risen over more recent times; i.e., the ATMAC 16/ATMAC 18 ratio (0.18 ± 0.05) was relatively constant between the 1950s and the early 1990s (Figure 3c), and increased to 1.03 ± 0.17 in Jamaica Bay surface samples collected in 2008 (Table 1). On the other hand, ATMAC 20 was very low and ATMAC 22 was undetected in sediments until about 1980. Together they comprised only about 3% of total ATMAC in a sample dated near 1990, and continued to increase since that time (Figure 3c). As described further below, some of this shift in pattern seen in sediment core and grab samples is likely due to substitutions of ingredients in hair care or other personal products.

The sedimentary record of ATMAC 20 is intermediate between that of ATMAC 16−18 and ATMAC 22. This appears to be due to the fact that trace levels of ATMAC 20 exist in commercial formulations of ATMAC other than behentrimonium (Figure 3a). Thus the time history of ATMAC 20 mirrors that of ATMAC 16 and 18 at deeper depths in the core (Figure 4), prior to the appearance of measurable levels of ATMAC 22. ATMAC 20 was found in a much greater proportion (approximately 15% of ATMAC 22) in the behentrimonium-based hair care product analyzed (Figure 3a), thus the recent increase in ATMAC 22 explains why the surficial maximum for ATMAC 20 is higher than the one corresponding to the 1980s. Based on the average relative percentages of ATMAC 20 as compared to ATMAC 18 measured in sediment horizons from the 1960s and to ATMAC 22 in the past decade (2 and 10%, respectively), a very simple model was able to predict its depositional trends in sediments:

$$[\text{ATMAC 20}]_t = [\text{ATMAC 18}]_t \times 0.02 + [\text{ATMAC 22}]_t \times 0.10$$

The resulting predicted time history of ATMAC 20 matches well the measured concentrations in the sediment core and grab samples (Figure 4), consistent with the interpretation that this homologue was derived in the past from ATMAC mixtures with shorter average alkyl chain lengths (Figure 3a) (*9*).

ATMAC as Sediment Contaminants of Potential Concern. There have been very few reports on the presence and distribution of ATMAC in receiving waters or sediments, no measurements of ATMAC in marine settings, and to our knowledge, no mention of behentrimonium compounds in the peer-reviewed literature. The concentrations of ATMAC 16−18 measured in other urban harbor sites from the NY/NJ Harbor complex (from 8.6 to 5300 ng/g) bracketed the concentrations reported here (*4*). However, ∑ATMAC concentrations determined in Jamaica Bay sediments (Table 1) were much greater than those measured in riverine sediments (usually below 100 ng/g) collected downstream of WWTPs in Austria (*10*). Much of this disparity can be attributed to the fact that only ATMAC 12−16 homologues were determined in sediments and not prominent ATMAC 18−22 homologues (*10, 11, 14*). More soluble homologues such as ATMAC 12 have been found to be predominant in the dissolved phase in surface waters (*11, 12*), whereas the more hydrophobic ATMAC 16 homologue was detected at higher levels in sewage sludges and sediments (*10*), consistent with greater removal of this compound to sewage sludge (*14*). The enrichment in sediments of the more hydrophobic, longer alkyl chain length homologues has been previously noted for other classes of surfactants, such as linear alkylbenzene sulfonates and alcohol ethoxylates (*24*). With the exception of selected aqueous phase studies that included ATMAC 18 (*12, 13*), other field and laboratory studies have ignored ATMAC 18, which along with newly discovered behentrimonium homologues, are more likely to be persistent solid-phase contaminants (*10, 11, 16, 17*).

The levels of ∑ATMAC measured in recently collected Jamaica Bay surface sediments are similar to or approach those of organic contaminants of potential concern measured in the same samples, such as NPEO metabolites and polycyclic aromatic hydrocarbons (PAH) (Table S2). It is also noted that ∑ATMAC levels in 2008-collected Grassy Bay sediment (6750 ng/g) were higher than those of the antimicrobials triclosan (less than 100 ng/g) and triclocarban (approximately 2000 ng/g at the top of the same JB 16 core (*25*)). Concentrations of DTDMAC (Table S2) are much higher than ATMAC, and levels of BACs (*4*) are comparable to that of ATMAC 16−22, illustrating the potential for QACs to accumulate to comparatively high levels in wastewater affected sediments. The ecotoxicological risks associated with part per million concentrations of ATMAC (and other QACs) in sediments are not fully characterized. These compounds have long been used as antimicrobials, and can select for QAC resistant genes in bacteria (*26*). Phytoplankton appears to be among the groups of eukaryotic organisms most sensitive to ATMAC and other QACs (*27*), and the acute toxicity of ATMAC 12−16 to marine bacteria and invertebrates is greater than for anionic or nonionic surfactants (*16*). Given the relatively high levels of ATMAC in these sediments, additional ecotoxicological study may be prudent. In this sense, the European Water Framework Directive (WFD) adopted in December 2000, identified some QACs as potentially hazardous chemicals selected for further investigation and assessment.

Emergence of Behentrimonium As a Newly Discovered Emerging Contaminant. Figure 5 shows the exponential increase over recent time of ATMAC 22 in sediments from Jamaica Bay (1979−2008) as well as in surficial sediments collected at a site in Newtown Creek between 1987 and 2005. Doubling times (t_2) of 3.9 years and 2.8 years are

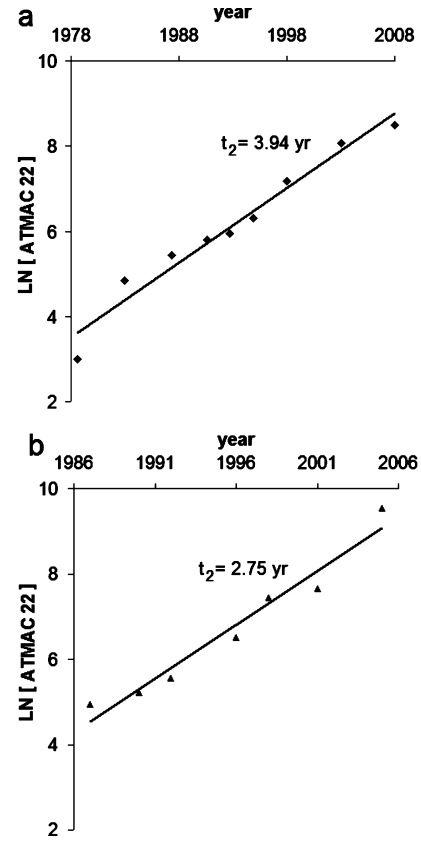


FIGURE 5. Concentrations of behentrimonium as a function of sediment age in (a) Grassy Bay and (b) Newton Creek, showing the doubling time of its concentration in sediments.

estimated from the Jamaica Bay and Newtown Creek data, respectively. At the latter site, ATMAC 22 values increased 1000-fold (from 141 to 13,900 ng/g), whereas ATMAC 18 decreased from 5060 to 1110 ng/g over the same time. While limited to data from only three time points (Table 1), an average t_2 for the 8 Jamaica Bay stations is estimated to be 3.1 years. Thus, complementary approaches yield similar results concerning the rise in behentrimonium inputs to wastewater-affected sediments. It is hypothesized that the increase in behentrimonium was directly related to use of this compound in personal care products. This interpretation is based on the following: relatively stable sewage treatment conditions and population in the area (U.S. Bureau of Census data); primary use of behentrimonium in hair care products, much of which is likely washed directly to WWTPs; and the likely high persistence of ATMAC 22 in muddy, suboxic sediments.

The rise of behentrimonium may have been linked to replacement of cetrimonium or stearyltrimonium in some personal care products. Recommendations have been made that cetrimonium and stearyltrimonium chloride concentrations in personal care products should not exceed 0.5%, whereas a maximum level of 3% is allowed if behentrimonium chloride is used (*9*). An older study reports that cetrimonium and stearyltrimonium chlorides are considered safe for use in rinse-off cosmetic products but only at concentrations of up to 0.25% (*28*). ATMAC 22 causes less irritation to the skin and eyes, and also exhibits a better performance than other ATMAC homologues when applied to hair (*9*). The historical production estimates provided by EPA are given often as wide ranges (see Table S1). For chemicals containing ATMAC these estimates appear to be too wide to detect decreases in production of ATMAC 16−18 between 1986 and 2006. Moreover, the production data for behentrimonium (Table

S1) appear to be incomplete at best, reporting increases in production from 10−500 thousand pounds in 1986 to 1−10 million pounds in 1998 (the only time that production exceeded the HPVC threshold volume). Given the geochronologies presented, there is little doubt that the decreased production reported in 2002 and nonreportable levels in 2006 are in error (Table S1). In addition, the methosulfate salt of behentrimonium is not reported, although popular in many products. This review of the EPA TSCA database for chemicals containing ATMAC (Table S1) illustrates another challenge associated with screening chemicals for potential environmental exposure and risks: many chemicals are sold in multiple formulations that carry separate CAS (or other identifying) numbers, a fact that can become even more complex in the case of ionic compounds sold as different salts. Some of the year-to-year inconsistencies in production data for ATMAC (seen for many CAS numbers in Table S1) could be the result of confusion on how industry or government reports which mixtures are produced. The ability to aggregate such data to estimate the sales or production volume histories of individual or mixtures of surfactants is impeded by the nature of these data reporting difficulties.

ATMAC 22 is not the first organic chemical that has been observed to increase rapidly in sediments without significant previous attention to potential for environmental persistence. For comparison, the estimated doubling times of this compound (2.8−3.9 years) are somewhat faster than those that were reported for polybrominated diphenyl ethers (PBDE), as recorded in Great Lake sediments (5−10 years) (*29*). However, despite the fact that behentrimonium concentrations (approaching or exceeding 5−10 μg/g in highly sewage impacted sediments) are more than an order of magnitude greater than those of total PBDEs in sediments from the same area (*23*), it would have been more difficult to predict the occurrence of behentrimonium as a contaminant of potential concern. First, PBDEs are polyhalogenated "PCB-like" POPs with U.S. production estimated in the range of 150 million pounds per year (*30*), and, unlike behentrimonium, clearly qualify as HPVC, a designation that can lead to more careful regulatory review. Other factors that would make it difficult to recognize a potential need to screen for the presence of chemicals such as behentrimonium, include (1) a lack of peer-reviewed literature on this compound and many other personal care product ingredients; (2) the nontargeting of ionic substances in some chemical database screening exercises because they have little potential for long-range atmospheric transport and are not thought to be highly bioaccumulative; and (3) the assumption that available data from standard biodegradation assays are adequate, when such experiments are conducted at high substrate levels, and may rely on data for more soluble and likely more biodegradable ATMACs. This study of behentrimonium and other ATMAC homologues illustrates difficulties with estimating production and environmental fate common to other chemicals. As such, it points to the need for more reasoned approaches during the assessment of household or personal care products that enter wastewaters so easily.

Acknowledgments

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Supporting Information Available

Details on the analysis of ATMAC by HPLC-TOF-MS, sampling areas and sediment description (aluminum content and total organic carbon), ATMAC sales (Table S1), and concentrations of DTDMAC, NPEO metabolites, and PAH at each sampling station (Table S2). This information is available free of charge via the Internet at http://pubs.acs.org/.

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