



Review

Quaternary ammonium compounds (QACs): A review on occurrence, fate and toxicity in the environment



Chang Zhang^{*}, Fang Cui, Guang-ming Zeng^{**}, Min Jiang, Zhong-zhu Yang, Zhi-gang Yu, Meng-ying Zhu, Liu-qing Shen

College of Environmental Science and Engineering, Hunan University, Changsha 410082, China

Key Laboratory of Environmental Biology and Pollution Control, Hunan University, Ministry of Education, Changsha 410082, China

HIGHLIGHTS

- QACs occur in the aquatic and terrestrial environment all over the world.
- STPs are the main source of QACs released into environmental compartments.
- QACs removal is dependent on sorption and biotransformation processes.
- Excessive use of QACs results in the emergence of antibiotic-resistance bacteria.

ARTICLE INFO

Article history:

Received 18 December 2014

Received in revised form 10 February 2015

Accepted 1 March 2015

Available online xxx

Editor: Adrian Covaci

Keywords:

Quaternary ammonium compounds (QACs)

Biodegradation

Sorption

Toxicity

Determination

ABSTRACT

Quaternary ammonium compounds (QACs) are widely applied in household and industrial products. Most uses of QACs can be expected to lead to their release to wastewater treatment plants (WWTPs) and then dispersed into various environmental compartments through sewage effluent and sludge land application. Although QACs are considered to be aerobically biodegradable, the degradation is affected by its chemical structures, dissolved oxygen concentration, complexing with anionic surfactants, etc. High abundance of QACs has been detected in sediment and sludge samples due to its strong sorption and resistance to biodegradation under anoxic/anaerobic conditions. QACs are toxic to a lot of aquatic organisms including fish, daphnids, algae, rotifer and microorganisms employed in wastewater treatment systems. And antibiotic resistance has emerged in microorganisms due to excessive use of QACs in household and industrial applications. The occurrence of QACs in the environment is correlated with anthropogenic activities, such as wastewater discharge from WWTPs or single source pollutants, and sludge land application. This article also reviews the analytical methods for determination of QACs in environmental compartments including surface water, wastewater, sewage sludge and sediments.

© 2015 Elsevier B.V. All rights reserved.

Contents

1.	Introduction	353
2.	Occurrence and fate of QACs in different environmental media	353
2.1.	QACs in sewage and sludge	354
2.1.1.	QACs in sewage	354
2.1.2.	QACs in sludge	354
2.2.	QACs in surface water and sediments	354
2.2.1.	QACs in surface water	354
2.2.2.	QACs in sediments	355
2.3.	Fates of QACs in the environment	356
3.	Toxicity and risk assessments of QACs	357
4.	Overview of analytical methods for determination of QACs in environmental compartments	358

^{*} Correspondence to: C. Zhang, College of Environmental Science and Engineering, Hunan University, Changsha 410082, China.

^{**} Correspondence to: G.-m. Zeng, Key Laboratory of Environmental Biology and Pollution Control, Hunan University, Ministry of Education, Changsha 410082, China.

E-mail addresses: zhangchang@hnu.edu.cn (C. Zhang), zgming@hnu.edu.cn (G. Zeng).

5. Conclusion	360
Acknowledgments	360
References	360

1. Introduction

Currently, quaternary ammonium compounds (QACs) are the major class of cationic surfactants used as the ingredients in fabric softeners, antistatics, disinfectants, biocides, detergents, phase transfer agent and numerous personal care products, such as hair care products (Ding and Tsai, 2003; Lara-Martín et al., 2010; Tsai and Ding, 2004). Their structure contains at least one hydrophobic hydrocarbon chain linked to a positively charged nitrogen atom, and other alkyl groups which are mostly short-chain substituents such as methyl or benzyl groups. This structure gives them the property to readily adsorb to sewage sludge, soil and sediments, which are predominantly negatively charged (Ying, 2006; Clara et al., 2007). The three most frequently detected QACs in natural environments are dialkyldimethyl ammonium compounds (DADMACs) (with alkyl chain lengths from C8 to C18), alkyltrimethyl ammonium compounds (ATMACs) (C12–C18) and benzylalkyldimethyl ammonium compounds (BACs) (C12–C18) (Table 1).

Due to the extensive use of QACs in domestic and industrial products, they reach wastewater treatment plants in substantial amounts. The main sources of QACs released into the environment are the discharge of effluents and sludge from sewage treatment plants (STPs) (Clara et al., 2007; Martínez-Carballo et al., 2007a, 2007b; Merino et al., 2003a; Li et al., 2014). Other local point sources, such as hospitals, laundry wastewater (Kümmerer et al., 1997; Kreuzinger et al., 2007), and roof runoff (Van de Voorde et al., 2012) also lead to its presence in the environment.

The fate of QACs in aerobic treatment systems has been extensively studied (García et al., 2001; Games and King, 1982; Nishihara et al., 2000; Nishiyama and Nishihara, 2002; Tezel et al., 2012). QACs are generally considered to be biodegradable in an activated sludge system, however, its degradation varies depending on the QAC concentration, chemical structure, complexing with anionic surfactants, microbial acclimation, etc. Removal rates higher than 90% have been obtained for QACs in WWTPs (Clara et al., 2007; Kreuzinger et al., 2007). However, adsorption usually outcompetes biodegradation. And as the alkyl chain length of QAC homologues increased, an increased tendency to adsorb to sludge is observed for QACs and thus biodegradability is limited (Clara et al., 2007; García et al., 2001). Therefore, QACs are significantly enriched in sewage sludge. High concentrations of QACs would adversely impact the anaerobic digestion process by inhibiting

methanogenesis, resulting in methane inhibition and volatile fatty acid (VFA) accumulation (Tezel et al., 2006, 2008), then affect the performance of activated sludge systems and in turn result in the decrease of the system efficiency. Moreover, risk from QACs-containing biosolids recycling on land cannot be ignored (Fernández Cirelli et al., 2008). Although risk assessment results indicated that this practice would not impact human health (Clarke and Smith, 2011), long-term research is needed to support its security and sustainability.

WWTP effluents discharged into environment could result in contamination of marine sediments with QACs (Lara-Martín et al., 2010; Li and Brownawell, 2009, 2010). Moreover, residual QACs that are released into sewage treatment plants and natural environment are of great concern due to their toxic effect to a lot of organisms. The toxicity of QACs to aquatic organisms was higher than that of anionic surfactants (Qv and Jiang, 2013; Ying, 2006). QACs could inhibit the nutrients uptake by algae resulting in lower nutrient removal efficiency in wastewater treatment plants (Liang et al., 2013). Furthermore, increased use of QAC biocides and disinfectants has led to concern regarding reduction in bacteria susceptibility and biocide effectiveness (Buffet-Bataillon et al., 2012; Moore et al., 2008). In addition, long-term exposure of microbial communities to QACs not only increases selecting for QAC-resistant bacteria but also for antibiotic-resistance bacteria (Gaze et al., 2005; Tandukar et al., 2013), and multidrug resistance genes have been quantified in microbial communities (Tandukar et al., 2013). The enrichment and spread of these antibiotic-resistance bacteria which contain multidrug resistance genes are potentially adverse to both human and environmental health.

This paper reviews the occurrence of three major QACs in surface water, WWTP wastewater, sludge as well as sediments. It focuses on the fate and toxic effects of QACs in these environment compartments, and evaluates the risks that arise from its wide application, especially the increased antibiotic resistance. Furthermore, the analytical techniques used to determine QACs in various environmental compartments, such as surface water, sewage from WWTPs, sediments and sewage sludge are also reviewed in this article.

2. Occurrence and fate of QACs in different environmental media

The presence of QACs in the environment is the result of anthropogenic activities since high abundances of quaternary ammonium

Table 1
Acronym, CAS registry number, molecular mass and structure of QACs considered in this review.

QACs	Acronym	CAS-No	Molecular mass	Molecular structure
<i>Dialkyldimethylammonium compounds (DADMACs)</i>				
Dioctyldimethylammonium bromide	DADMAC C8	3026-69-5	350	$[\text{CH}_3(\text{CH}_2)_7]_2\text{N}(\text{CH}_3)_2\text{Br}$
Didecyldimethylammonium chloride	DADMAC C10	7173-51-5	362	$[\text{CH}_3(\text{CH}_2)_9]_2\text{N}(\text{CH}_3)_2\text{Cl}$
Didodecyldimethylammonium chloride	DADMAC C12	3401-74-9	418	$[\text{CH}_3(\text{CH}_2)_{11}]_2\text{N}(\text{CH}_3)_2\text{Cl}$
Ditetradecyldimethylammonium bromide	DADMAC C14	68105-02-2	518	$[\text{CH}_3(\text{CH}_2)_{13}]_2\text{N}(\text{CH}_3)_2\text{Br}$
Dihexadecyldimethylammonium bromide	DADMAC C16	70755-47-4	574	$[\text{CH}_3(\text{CH}_2)_{15}]_2\text{N}(\text{CH}_3)_2\text{Br}$
Diocetadecyldimethylammonium chloride	DADMAC C18 (DODMAC)	107-64-2	586	$[\text{CH}_3(\text{CH}_2)_{17}]_2\text{N}(\text{CH}_3)_2\text{Cl}$
<i>Alkyltrimethylammonium compounds (ATMACs)</i>				
Dodecyltrimethylammonium chloride	ATMAC C12 (DTAC)	112-00-5	264	$\text{CH}_3(\text{CH}_2)_{11}\text{N}(\text{CH}_3)_3\text{Cl}$
Tetradecyltrimethylammonium chloride	ATMAC C14 (TTAC)	4574-04-3	292	$\text{CH}_3(\text{CH}_2)_{13}\text{N}(\text{CH}_3)_3\text{Cl}$
Hexadecyltrimethylammonium chloride	ATMAC C16 (CTAC)	112-02-7	320	$\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3\text{Cl}$
Octadecyltrimethylammonium chloride	ATMAC C18 (OTAC)	112-03-8	348	$\text{CH}_3(\text{CH}_2)_{17}\text{N}(\text{CH}_3)_3\text{Cl}$
<i>Benzylalkyldimethylammonium compounds (BACs)</i>				
Dodecylbenzyltrimethylammonium chloride	BAC C12	139-07-1	339	$\text{CH}_3(\text{CH}_2)_{11}\text{N}(\text{Cl})(\text{CH}_3)_2\text{CH}_2\text{C}_6\text{H}_5$
Tetradecylbenzyltrimethylammonium chloride	BAC C14	139-08-2	368	$\text{CH}_3(\text{CH}_2)_{13}\text{N}(\text{Cl})(\text{CH}_3)_2\text{CH}_2\text{C}_6\text{H}_5$
Hexadecylbenzyltrimethylammonium chloride	BAC C16	122-18-9	396	$\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{Cl})(\text{CH}_3)_2\text{CH}_2\text{C}_6\text{H}_5$
Octadecylbenzyltrimethylammonium chloride	BAC C18	122-19-0	424	$\text{CH}_3(\text{CH}_2)_{17}\text{N}(\text{Cl})(\text{CH}_3)_2\text{CH}_2\text{C}_6\text{H}_5$

surfactants are annually produced in worldwide areas. After use, most of them are released into WWTPs and then dispersed into surface water and soil/sediments through WWTP effluents and sludge land application. The occurrence of QACs in aquatic and terrestrial environment has been reviewed in terms of their concentrations in surface water, wastewater, sewage sludge and sediments.

2.1. QACs in sewage and sludge

STPs are considered as the main source of QACs. Occurrence of QACs in STPs has been reported widely. Whether or not QACs can be removed by the wastewater treatment processes determines their final input into the receiving aquatic environment and related terrestrial environment.

2.1.1. QACs in sewage

The analytical result from WWTPs in Austria revealed that high influent concentration levels were obtained for BAC C12 and C14 as well as DADMAC C10, with the maximum of 170 µg/L for BAC C12 (Martinez-Carballo et al., 2007a). In comparison to BAC and DADMAC, ATMAs were found in lower influent concentration levels with the highest concentration of 9.9 µg/L detected for ATMAC C16. Furthermore, unfiltered influents were generally higher polluted than the filtered ones, possibly due to strong adsorption of QACs onto suspended particulates. In comparison to the influents the effluents were generally below 1 µg/L, except for BAC C12 with a maximum concentration of 2.1 µg/L, which was comparable to the report of Kreuzinger et al. (2007) which detected a concentration of 4.1 µg/L for BAC C12 in WWTP effluent. The investigations in the WWTPs indicated that a mean elimination rate higher than 90% was obtained for QACs during sewage treatment (Kreuzinger et al., 2007; Martinez-Carballo et al., 2007a). Clara et al. (2007) reported the occurrence of ATMAC, BAC and DADMAC in nine WWTP sewages. BAC C12 and BAC C14 were measured with the maximum influent concentrations of 170 µg/L and 110 µg/L, respectively. From the ATMAC homologues, ATMAC C16 was the most abundant one with influent concentrations ranging between 7.7 and 27 µg/L. Among the DADMAC homologues, DADMAC C10 was detected with the highest concentrations of 200 µg/L, while DADMAC C18 was measured with a lower influent level of 74 µg/L, which can be explained by the reduced production of DADMAC C18 since 1989/90 (European Commission, 2002). The effluent concentrations of QACs were generally lower than 1 µg/L, except for ATMAC C16 (1.1 µg/L) and DADMAC C18 (3.5 µg/L). The removal rates were higher than 95% for most WWTPs for BACs and ATMAs, and biotransformation seems to be the major removal pathway (Clara et al., 2007). Meanwhile, lower removal rates but higher than 90% were obtained for DADMACs, with approximately 70% were due to adsorption to the sludge and removal via the excess sludge, and approximately 20% were due to biotransformation.

There is a lack of information concerning QAC concentrations in WWTP sewage in China. Limited data showed the presence of BAC C12–16 and ATMAC C12 in plant wastewater, sanitary wastewater and medical wastewater in Wuhan, China, with concentrations in the range of 0.9–3.7 µg/L (Peng et al., 2011).

Indirect discharger wastewaters and industrial effluent containing high concentrations of QACs may disrupt the treatment efficiency after releasing into WWTPs. Kreuzinger et al. (2007) reported that indirect discharge wastewaters from hospitals and laundries were highly contaminated with BAC C12 and DADMAC C10, with the highest effluent concentrations detected at 2800 and 210 µg/L, respectively. High levels of BAC C12–18 ranged from 0.5 µg/L to 100 µg/L were detected in industrial effluent from an industrial park located in Taiwan, with the highest concentration detected for BAC C18 (100 µg/L) (Ding and Liao, 2001). Merino et al. (2003a) studied the raw sewage and final effluent concentrations of BAC C12, C14 and C16 in two WWTPs in Spain. The concentrations of BACs in raw sewage were detected in the range of 0.14–49 µg/L. Between the two WWTPs, the one received 30% industrial effluents (mainly from laundries and olive oil industries) and 70%

domestic wastewaters showed higher BAC homologue concentration than the other which received mainly domestic effluents.

2.1.2. QACs in sludge

Mainly two pathways are responsible for the removal of QACs in STPs, namely biodegradation and adsorption by active sludge. However, an increased tendency to adsorb to the sludge is observed for QAC homologues as the alkyl chain length increased (Clara et al., 2007).

High abundances of QACs have been detected in sludge samples in the past time (Breen et al., 1996; Gerike et al., 1994). Mean concentrations of 3.67 g/kg (in 1991) of DTDMAC have been found in sludge from five WWTPs in Switzerland. After that, DTDMAC has been replaced in Europe by easily biodegradable diethyl ester dimethylammonium chloride (DEEDMAC) (Giuliano et al., 1995). And the concentration of DTDMAC detected in the same five WWTPs has dropped to 0.21 g/kg of dry sludge in 1994 (Fernández et al., 1996). In contrast, the concentrations of DADMAC, BAC and ATMAC in activated and dehydrated sludge collected from two WWTPs in Spain were significantly lower, ranged from 0.1 to 34 mg/kg (Merino et al., 2003b). Martinez-Carballo et al. (2007b) reported the total QAC concentration in sludge samples ranged from 22 to 103 mg/kg for the three WWTPs in Austria. The WWTP which was influenced remarkably by industrial wastewater showed higher QAC concentration in the sludge than that of the other two WWTPs which received mainly domestic wastewater. The sludges were mainly contaminated by BAC C12, BAC C14, DADMAC C10 and DADMAC C18, with maximum concentrations of 25 mg/kg, 23 mg/kg, and 27 mg/kg detected for BAC C12, BAC C14, and DADMAC C10, and the highest mean concentration of 10 mg/kg dry sludge for DADMAC C18. Among the ATMAC homologues, ATMAC C16 was the most abundant, with the highest concentration range of 0.16 to 8.4 mg/kg of dry sludge. While ATMAC C12 and ATMAC C14 were detected in the lower concentration range between not detected (<LOD) and 81 µg/kg of dry sludge.

Extremely high concentrations of QACs in the sludge were reported in the WWTP of Guangzhou, China, with total BAC, ATMAC and DADMAC concentrations of 3.6, 8.3 and 156 µg/g, respectively (Li et al., 2014). The total concentration of QACs (167 µg/g) was higher than that measured in the sludge samples of Austria (22–103 µg/g) (Martinez-Carballo et al., 2007b). Recently, Ruan et al. (2014) reported that the concentration of BAC, ATMAC and DADMAC in fifty-two municipal sewage sludge samples in China was in the range of 0.94–191 µg/g, 0.38–294 µg/g, and 0.64–343 µg/g dry weight respectively, with median values of 1.09 µg/g, 18.9 µg/g and 25.1 µg/g respectively. Among the ATMAC, ATMAC C18 was the most abundant homologue. The average proportion of ATMAC homologues constituted of total ATMAC concentrations in the decreasing order: ATMAC C18 (40%), ATMAC C22 (39%), ATMAC C16 (13%), and ATMAC C20 (4.9%). For the BAC homologues, BAC C12 was the most abundant (average percentage: 69%), followed by BAC C14 (23%), BAC C18 (5.4%), and BAC C16 (3.0%). The high concentration of BAC C12 and C14 detected in sewage sludge may be correlated with their wide usage in China. Similar to the composition of DADMACs reported in sewage sludge in European countries (Martinez-Carballo et al., 2007b; Merino et al., 2003b), DTDMAC (C16:C16, C16:C18 and C18:C18) was the most abundant homologues in China, which constituted 95% of total DADMAC concentrations.

These studies reveal QACs can be removed by adsorption onto sludge without being completely biodegraded. This also demonstrates the need to investigate the composition and distribution of QACs in sludge, since they could re-enter the ambient environment through sludge land application and thus become potentially hazardous (Clarke and Smith, 2011; Fernández Cirelli et al., 2008).

2.2. QACs in surface water and sediments

2.2.1. QACs in surface water

Generally, QACs are present in surface water bodies at concentrations in the µg/L ranges. In an earlier study, Ferrer and Furlong (2001)

detected BAC C12 and BAC C14 in the surface water downstream from five WWTPs in the US in the range of 2.7 to 5.8 µg/L and 6.3 to 36.6 µg/L, respectively. In the surface water of Austria, the highest concentrations of QACs were detected for BAC C12, BAC C14 and DADMAC C10, with a maximum of 1.9 µg/L (Martinez-Carballo et al., 2007a). QAC concentrations are correlated with rainfall for the reason that rainy weather results in a higher content of particulate matter in the rivers and thus more QAC adsorption occurs. Kreuzinger et al. (2007) reported that the concentrations of DADMAC in surface water samples in Austria were determined mainly below 0.1 µg/L, except for DADMAC C10 and DADMAC C18, with the highest concentration of 0.15 and 0.19 µg/L, respectively. Meanwhile, the concentrations of BAC in surface waters were mainly below 1 µg/L, except for BAC C12, with the highest concentration of 1.9 µg/L. The total concentrations of BAC in Taiwanese river water ranged from 2.5 to 65 µg/L (Ding and Liao, 2001). Among the compound, BAC C18 was the most abundant one with a level of 2.1–55 µg/L, followed by BAC C16 in the range of 0.4–5.3 µg/L. The data clearly indicated that high abundance of BAC C18 existed in household wastewaters in Taiwan and was directly discharged into the rivers. In contrast, the level of ATMAC homologues (C12–18) in Taiwanese river water was lower, with the total measured concentrations ranged from nondetectable to 1.24 µg/L (Ding and Tsai, 2003). Recently, Olkowska et al. (2013) detected that the total concentration of BACs (C12–16) in surface water samples ranged from 0.0725 ± 0.0014 to 0.342 ± 0.014 µg/mL in Poland. The samples were mainly contaminated by BAC C12, since they were detected almost in every sample with a concentration higher than 0.0188 µg/mL.

However, publications that monitored these compounds in the seawater are scarce. A recent study determined two biocidal QACs: DADMAC C10 and BAC C12, in seawater by liquid chromatography–mass spectrometry (LC–MS) for the first time (Bassarab et al., 2011). The sampling sites were chosen at three different locations along the North East coast of England. The level of DADMAC C10 correlated with distance from the mouth of the River Tyne, with concentration ranged from n.d. to 195 ng/L, whereas BAC C12 was not detected.

2.2.2. QACs in sediments

QACs can be found in sediments of surface water due to its strong adsorption and recalcitrance to biodegradation, but with much lower levels compared with sludge samples. The municipal wastewater input is considered to be the major source of the QACs in the sediments. The varied QAC compositions detected in sediments may be correlated with differences in the composition of QACs entering municipal

wastewaters and the efficacy of local sewage treatment. Table 2 listed some of the reported data on the levels of QACs measured in sewage sludge and sediments in some countries.

The maximum of 3.6 mg/kg and 2.1 mg/kg of dry sediment was detected for BAC C12 and DADMAC C18, respectively, in the sediment samples of Austria (Kreuzinger et al., 2007; Martinez-Carballo et al., 2007b). Higher concentration levels were achieved for DADMAC-C10, C16 and C18 as well as BAC-C12 and BAC-C14 with a mean concentration above 100 µg/kg, while BAC-C16 and BAC-C18 were determined with a mean concentration below 100 µg/kg (Martinez-Carballo et al., 2007b). This result was comparable to the study conducted by Ferrer and Furlong (2002), which detected BAC homologues in river sediment samples of the US in the concentration range of 22 to 206 µg/kg. However, QACs detected in estuarine sediments from the US showed higher contaminated total concentration (1.8 to 74 mg/kg) (Li and Brownawell, 2009), with BACs and DADMACs determined in the concentrations range of 0.12–21 mg/kg and 1.7–52 mg/kg, respectively. The much greater concentrations of DADMACs detected in estuarine sediments are likely attributed to its widely use as fabric softeners in the US and the chosen of the sampling sites, since two sampling sites are located in more sewage-affected areas. The occurrence of QACs in urbanized Hudson River Estuary (HRE) in the US was studied as well, with total concentrations ranged between 0.98 and 114 mg/kg (Li and Brownawell, 2010). The median values for BAC, ATMAC and DADMAC were 1.5, 0.52 and 26 mg/kg, respectively. Among the BAC homologues, the highest median concentration was measured for BAC C18 (490 µg/kg). The higher levels of BAC C18 reported in this study is likely attributed to its widely use in personal care products that may reach WWTPs. A related report which studied the evolution of ATMAC homologues in surficial sediments from Jamaica Bay detected behentrimonium homologues (ATMAC C20, and especially ATMAC C22) for the first time and indicated its increase use in personal care products in recent years (Lara-Martín et al., 2010). The concentrations of behentrimonium ranged from 93–1559 µg/kg in 1998 to 1232–5299 µg/kg in 2008, which were higher than those of other shorter alkyl chain homologues such as ATMAC C16 and ATMAC C18. This result may have been linked to replacement of shorter alkyl chain ATMACs in some personal care products.

Field measurements on the levels of QACs in sediments of China are scarce. A recent study reported the occurrence of QACs in the surficial sediments of the Pearl River Estuary (PRE) (Li et al., 2014). The average composition patterns of QACs in the sediments were consistent with that detected in the sludge from the WWTP at Guangzhou, the biggest

Table 2
Occurrence of QACs in sediments/sewage sludge in different countries.

Countries	Concentration				Total QAC	Solid type	References	
	DTDMAC	DADMAC		ATMAC				BAC
		C8:C10	C10:C10					
China	159–7700 ng/g (median: 1120 ng/g) 156,000 ng/g			16.5–2010 ng/g (median: 176 ng/g) 8300 ng/g	49.3–1530 ng/g (median: 452 ng/g) 3610 ng/g	0.2–11.2 µg/g 167 µg/g	Surficial sediments Sludge	Li et al. (2014)
China	0.64–343 µg/g (median: 25.1 µg/g)			0.38–294 µg/g (median: 18.9 µg/g)	0.94–191 µg/g (median: 1.09 µg/g)	1.12–505 µg/g (median: 59.2 µg/g)	Sludge	Ruan et al. (2014)
Austria	582 ^a µg/kg; 709 ^b µg/kg (mean concentration)			35 ^a µg/kg; 19 ^b µg/kg (mean)	1023 ^a µg/kg; 351 ^b µg/kg (mean)	1640 ^a µg/kg; 1079 ^b µg/kg (mean)	Sediments	Martinez-Carballo et al. (2007b)
US	No data 1700–52,000 ng/g			0.16–8.5 mg/kg –	No data 121–21,000 ng/g	22–103 mg/kg 1800–74,000 ng/g	Sludge Urban estuarine sediment	Li and Brownawell (2009)
US	–			481–2820 ng/g (1998) 1600–6750 ng/g (2008)	–	1600–6750 ng/g (2008)	Urban estuarine sediment	Lara-Martín et al. (2010)
US	690–110,000 ng/g (median: 26,000 ng/g)	n.d.–767 ng/g (10 ng/g)	n.d.–4100 ng/g (190 ng/g)	8.6–5300 ng/g (median: 520 ng/g)	100–17,700 ng/g (median: 1400 ng/g)	0.98–114 µg/g (median: 29 µg/g)	Urban estuarine sediment	Li and Brownawell (2010)

^a June.

^b August.

city in the PRE, indicating that the major contribution of QACs in the sediments was from the municipal wastewater inputs. In the sediment samples, total BACs, ATMAs and DADMACs were in the range of 49.3–1050, 16.5–2010, and 159–7700 $\mu\text{g}/\text{kg}$ respectively, with median values of 452, 176 and 1120 $\mu\text{g}/\text{kg}$ respectively, which were relatively lower than those found in the HRE in the US (Li and Brownawell, 2010). Among the BAC homologues, BAC C12 was the most abundant with an average percentage of 69%, which was similar to the composition patterns of industrial BAC mixture. ATMAs C16 and ATMAs C18 were two major ATMA homologues with an average percentage of 36% and 64%, respectively. Among the DADMACs, DTDMACs (the alkyl chain length congeners primarily consist of C16:C16, C16:C18, C18:C18) possessed 94% of the total DADMACs detected in the sediments, which were similar to that found in the sediments of the HRE (Li and Brownawell, 2010). In contrast, DADMAC (C10:C10) only has an average percentage of 4% of the total DADMACs. All the sediments in the PRE showed uniform QAC average composition patterns, indicating its persistence in the estuary sediments. Furthermore, the total concentrations of QACs (0.24–10.3 $\mu\text{g}/\text{g}$) were higher than that of polychlorinated biphenyls (PCBs) (7.69–32.3 ng/g) detected in the same sediment samples (Li et al., 2014). Similarly, Li and Brownawell (2010) reported that the total concentrations of QACs (median $\Sigma\text{QACs} = 29 \mu\text{g}/\text{g}$) are higher than that of polycyclic aromatic hydrocarbon (median $\Sigma\text{PAH} = 2.1 \mu\text{g}/\text{g}$) detected in the same estuarine sediments. Moreover, QAC homologues are frequently found in freshwater sediment by nontarget analysis of emerging contaminants (Chiaia-Hernandez et al., 2013; Terzic and Ahel, 2011), which further demonstrates their persistence in the environment. All these findings suggest that the presence of QACs in the environment should receive great attention.

2.3. Fates of QACs in the environment

Sorption and biodegradation (biotransformation) are the two main processes influencing the fate of QACs in different environmental compartments. QACs have a high adsorption affinity onto a wide variety of materials such as sewage sludge, sediments, bacterial cell walls, clay, and humic materials (van Wijk et al., 2009). The adsorption ability of QACs in the environment not only depends on the QAC structure, but also depends on sediment/soil nature and environmental parameters (Ying, 2006). In wastewater treatment systems, an increased alkyl chain length of QAC homologues will result in an increased tendency to adsorb to the sludge and the proportion via excess sludge removal increases (Clara et al., 2007). Similarly, Ismail et al. (2010) reported the extent of sorption of four QACs on four sludges in the following order of decreased affinity: ATMA C16 > BAC C16 > BAC C12 > ATMA C12. Although a benzyl group further enhances the adsorption, this effect diminishes as the alkyl chain length increases. The decrease of temperature and sludge particle size could also increase the sorption of QAC onto activated sludge (Ren et al., 2011). Moreover, QACs and anionic surfactants can form complexes in STPs. These complexes have high adsorption affinity onto sludge, resulting in improved elimination of QACs in the presence of LAS (Sutterlin et al., 2008a). Nevertheless, biotransformation seems to be still the most relevant removal pathway for ATMAs, BACs and DADMAC C10 (Clara et al., 2007).

QACs are generally considered biodegradable under aerobic conditions (Nishihara et al., 2000; Nishiyama and Nishihara, 2002; Patrauchan and Oriel, 2003; Takenaka et al., 2007). The biodegradation of QACs can be affected by several factors, such as QAC chemical structure, concentration, and complexing with anionic surfactants and microbial community acclimatization (Brycki et al., 2014; Liffourrena et al., 2008; Qin et al., 2005). With increasing alkyl chain length or the substitution of a methyl group with a benzyl group, the biodegradation rate of QACs would decrease (García et al., 2001). The primary degradation of octadecyltrimethylammonium chloride (OTAC) occurred with a half-life of about 2.5 h in the laboratory scale activated sludge system (Games

and King, 1982). Long chain alkyltrimethylammonium salts were able to be ultimately biodegraded in activated sludge obtained from a municipal sewage treatment plant (Nishiyama et al., 1995). Initially, alkyltrimethylammonium salt is degraded to trimethylamine (TMA) through N-dealkylation, and TMA is further degraded to dimethylamine (DMA) and methylamine (MMA). These intermediates are finally mineralized to ammonium and carbon dioxide (Nishiyama et al., 1995). *Pseudomonas fluorescens* TN4, isolated from activated sludge, was demonstrated to be able to degrade didecyltrimethylammonium chloride (DDAC) as well as alkyltrimethylammonium and alkylbenzyltrimethylammonium salts in the similar N-dealkylation process (Nishihara et al., 2000). Nishiyama and Nishihara (2002) reported that *P. fluorescens* F7 and F2, isolated from the activated sludge of a municipal wastewater treatment plant, were able to completely degrade dodecyltrimethylammonium bromide (DTAB). In contrast, Liffourrena et al. (2008) reported that *Pseudomonas putida* A ATCC 12633 could degrade tetradecyltrimethylammonium bromide (TTAB) resulting in the formation of TMA. However, TMA accumulated inside the cell and ceased the biotransformation of TTAB. Continuous exposure of *Pseudomonas* sp. strains 7–6 in gradually increasing concentrations of dodecyltrimethylammonium chloride (DTAC) medium could lead to high tolerance and biodegradation of DTAC (Takenaka et al., 2007). Two pathways responsible for DTAC metabolism by strains 7–6 were proposed, with a main pathway and a minor pathway (Takenaka et al., 2007). Previous studies of QAC biotransformation pathways mainly focused on non-benzyl quaternary ammonium surfactants, the information on the biotransformation of BACs is limited. Recently, Tezel et al. (2012) reported that tetradecylbenzyltrimethylammonium chloride ($\text{C}_{14}\text{BDMA-Cl}$) was completely mineralized by an enriched *Pseudomonas* spp. community fed on benzalkonium chlorides (BACs) as the sole carbon and energy source. $\text{C}_{14}\text{BDMA-Cl}$ biotransformation starts with cleavage of the $\text{C}_{\text{alkyl}}\text{-N}$ bond resulting in the production of benzyltrimethylamine (BDMA) as the first intermediate. BDMA is then converted to ammonia through a debenzilation followed by N-demethylation processes. This biotransformation process is promising because the EC_{50} value of BDMA was 500-fold higher than that of $\text{C}_{14}\text{BDMA-Cl}$, which means the environment impact of $\text{C}_{14}\text{BDMA-Cl}$ is reduced (Tezel et al., 2012). Similarly, Tandukar et al. (2013) reported that long-term exposure of aerobic microbial communities to BACs leads to the enrichment of BAC-resistant/degrading species, which belongs to genus *Pseudomonas*. Other species that can degrade BACs is *Aeromonas hydrophila* sp. K, which was isolated from contaminated soil (Patrauchan and Oriel, 2003). BAC biodegradation starts with the fission of $\text{C}_{\text{alkyl}}\text{-N}$ bond, leading to the production of BDMA. Then, BDMA undergoes N-demethylation reactions to form benzylmethylamine (BMA) and benzylamine (BA). However, this degradation was not complete due to the inhibitory effect of BA (Patrauchan and Oriel, 2003). Microbial community adapted to BAC exposure is primarily due to selective enrichment of BAC-degrading *Pseudomonas nitroreducens* population, which may represent a useful inoculum for degrade BACs in both engineered and natural environment (Oh et al., 2013).

Biological nitrogen removal (BNR) is typically employed for the treatment of wastewater containing QACs. However, QACs have a detrimental influence on nitrification and denitrification processes, which leads to reduced nitrogen removal capacity (Hajaya and Pavlostathis, 2012; Kreuzinger et al., 2007; Yang, 2007). BAC was reported to inhibit denitrification at a concentration of 50 mg/L and above, and low temperatures exacerbate its inhibitory effect on nitrite reduction (Hajaya et al., 2011). However, microbial acclimation and enrichment would contribute to reduced inhibition and enhanced biodegradation of BACs in the laboratory scale BNR system (Hajaya and Pavlostathis, 2012, 2013). Respiratory inhibition is also responsible for the fate of QACs in activated sludge. BAC inhibits oxygen uptake and use by inhibition of the respiratory enzymes, thereby causing prolonged COD substrate utilization. After most of the readily degradable COD is utilized, the degradation of BAC begins (Zhang et al., 2011).

QACs usually showed no or poor biodegradation under anaerobic/anoxic conditions (García et al., 1999, 2000; Hajaya et al., 2011; Tezel et al., 2006, 2007, 2008; Tezel, 2009; Tezel and Pavlostathis, 2009). No anaerobic biodegradation was observed for di (hydrogenated tallow) dimethylammonium chloride (DHTDMAC) at a concentration of 32 mg/g dry sludge, whereas high biodegradation levels were obtained for two ester quaternary ammonium compounds (esterquats) at the same test conditions (García et al., 2000). Similarly, Watson et al. (2012) reported biotransformation of two esterquats by the mixed methanogenic culture, below their inhibitory concentrations.

QACs were reported to adversely impact the anaerobic digestion process by inhibiting methanogenesis, and the inhibition depended on the QAC concentration and structure (García et al., 1999; Tezel et al., 2006). High concentrations of QAC may affect the stability of an anaerobic digester resulting in accumulation of VFAs and a decrease of the COD removal efficiency (Watson et al., 2012). Tezel and Pavlostathis (2009) reported that long-term inhibition of methanogenesis and accumulation of VFAs were observed at and above 50 mg/L BAC concentration. Inhibitory effects of QACs on biogas production increased with decreasing alkyl chain length, while the substitution of a benzyl group for a methyl group did not have significant differences on biogas production (García et al., 1999). Similar results were obtained by Tezel et al. (2006) who reported that the inhibitory effects of four QACs on methanogenesis decreased according to the following order: dioctyl > octyl decyl > alkyl benzyl > didecyl. Conversely, the adsorption affinity of QACs on the biomass decreased according to the following series: didecyl > alkyl benzyl > octyl decyl > dioctyl. Additionally, complete recovery of methanogenesis was observed in this reactor over seven feeding cycles, probably due to enhanced microbial community acclimatization after exposure to QACs.

3. Toxicity and risk assessments of QACs

The wide occurrence of QACs in different environmental compartments raises concerns about their potential harm to ecosystem and human health. The toxicity of QACs has received considerable attention and reviews have focused on the toxicity of QACs both in wastewater treatment systems and in receiving waters (Boethling, 1984; Ying, 2006). QACs are toxic to aquatic organisms such as fish, daphnids, rotifer, algae and protozoan and a lot of microorganisms (Chen et al., 2014; Jing et al., 2012; Kreuzinger et al., 2007; Liang et al., 2013; Nalecz-Jawecki et al., 2003; Sandbacka et al., 2000; Sanchez-Fortun et al., 2008; Zhu et al., 2010). The biocidal mechanism of QACs can differ according to their structures. Typically, QACs kill bacteria by penetrating their alkyl chains into the microorganism's membrane and altering the phospholipid bilayer, thereby causing a membrane disruption that results in the leakage of intracellular constituent (Ioannou et al., 2007; Pérez et al., 2009; Sutterlin et al., 2008b).

Excessive use of QACs in household and industrial products leads to the concern that antibiotic resistance might emerge in engineered and natural systems (Hegstad et al., 2010; Ishikawa et al., 2002; Pruden et al., 2006). Mc Cay et al. (2010) stated that subinhibitory concentrations of BACs could select for microbes resistant to these compounds as well as antibiotics. Similarly, Gaze et al. (2005) reported that antibiotic and QAC resistance genes are both carried on class 1 integrons, which were screened from isolates lived in QAC-polluted environment. Thus, the chance for coselection of antibiotic resistance bacteria is increased. Long term exposure of aerobic microbial communities to BACs results in increased antibiotic resistance and reduced community diversity, which is predominantly attributed to degradation or transformation of BACs by enriched *Pseudomonas* species (Tandukar et al., 2013). While McBain et al. (2004) reported long-term exposure of domestic drain microorganisms to a QAC-containing domestic detergent (QD) did not significantly alter the antimicrobial susceptibility. Furthermore, there are studies that indicated the potential genotoxic effects of QACs to exposed eukaryotic cells at concentrations commonly found in

wastewaters and employed in commercially available nasal preparations (Deutschle et al., 2006; Ferk et al., 2007). An in vitro study conducted by Inacio and coworkers has shown that QACs cause mitochondrial dysfunction in the mammalian epithelial cell (Inacio et al., 2013). Melin et al. (2014) also reported that exposure of mice to QAC disinfectant significantly damaged its reproduction health. In contrast, Grabinska-Sota (2011) indicated that three groups of newly synthesized quaternary ammonium salts (QAS) and their biodegradation products will not create any carcinogenic health hazards to humans at concentrations normally found at natural bodies of water. Study also indicated that inhalation of QAC aerosols caused lung effects to mice, which may pose a potential threat to human beings (Larsen et al., 2012). However, further studies are required to support these findings since most of the experiments were conducted in vitro, they did not reflect the situation in vivo. Besides, the safety of more QAC groups as well as their release into the environment warrants further investigations.

Algae are more sensitive to the presence of QACs than fish and crustaceans (van Wijk et al., 2009). Studies under standard laboratory conditions showed that QACs have a high toxicity to algae (Jing et al., 2012; Liang et al., 2013; Zhu et al., 2010), since QACs are readily binded to negatively charged algal cell walls. However, the toxic effects will mitigate under realistic environmental conditions due to the presence of other sorbents such as clay, humic acid, sediments and suspended matter (van Wijk et al., 2009). 96 h EC₅₀ of alkyl trimethyl ammonium halides and alkyl benzyl dimethyl ammonium halides on *Chlorella vulgaris* ranged from 0.11 to 0.203 mg/L (Zhu et al., 2010), which decreased with the length of the alkyl chain. This result was comparable to the study which reported that the calculated EC₅₀ values of cetyltrimethyl ammonium chloride (CTAC) for *C. vulgaris* were 145 ± 13.35 µg/L (Ge et al., 2010). The inhibition effect mechanism of cetyltrimethyl ammonium bromide (CTAB) towards *C. vulgaris* is: with the increase of CTAB concentration, alga cell activities were inhibited, resulting in decreased uptake efficiencies of ammonia nitrogen (NH₄⁺) and total phosphorus (TP) by *C. vulgaris* (Liang et al., 2013).

Different species have different sensitivities towards the same QAC (see Table 3). The short term median effective concentration values (EC₅₀) of BAC and dimethylditetradecylammonium bromide (DADMAC C14) on algae, daphnids, rotifers and protozoans varied from 21 to 4427 µg/L (Kreuzinger et al., 2007). Jing et al. (2012) compared the sensitivities of two green alga *Chlorella pyrenoidosa* and *Scenedesmus quadricauda* towards 13 QACs by testing their EC₅₀ values. The results indicated that *S. quadricauda* was more tolerant to most of the tested QACs, whereas *C. pyrenoidosa* was proved to be more sensitive. The toxicity of benzalkonium to aquatic organisms is more intense than that of bacteria, with obtained EC₅₀ of 280 µg/L and 5.9 µg/L for fish and invertebrate, respectively (Van de Voorde et al., 2012). In contrast, EC₅₀ values of BAC for *Vibrio fischeri* and *P. putida* were reported at the concentration of 0.5 mg/L and 6.0 mg/L respectively (Sutterlin et al., 2008b). Acute toxicity tests on *Daphnia magna* and *Photobacterium phosphoreum* obtained EC₅₀ values in the range of 0.1–1 mg/L for alkyl trimethyl ammonium halides (ATMAC C12–16) and alkyl benzyl dimethyl ammonium halides (BAC C12–16) (García et al., 2001). In addition, the substitution of a benzyl group for a methyl group increases slightly the toxicity to *P. phosphoreum* and appears to be more toxic to *D. magna*. However, an incremental difference in toxicity between homologues of different chain lengths was not observed.

In aquatic environment, QACs usually combined with other chemical contaminants as mixtures, such as aromatic hydrocarbons (AHs), anionic surfactants, and heavy metals. The toxic effect of binary mixtures is significantly different from that of the QAC individuals. The binary mixtures of CTAC and AHs displayed a synergetic toxic effect on *C. vulgaris* in the low AH concentration range, however, when at high concentrations of AHs, the joint action of mixtures changed from synergetic effect to antagonistic effect due to competitive adsorption between CTAC and AHs (Ge et al., 2010). Similar result was observed in

Table 3
Aquatic toxicity values for quaternary ammonium compounds (QACs).

QAC	Species	Test	Value (mg/L)	References
Alkyltrimethylammonium halides (ATMAC C12–16)	<i>Daphnia magna</i>	IC ₅₀	0.13–0.38	García et al. (2001)
	<i>Photobacterium phosphoreum</i>	EC ₅₀	0.24–0.63	
Dodecyltrimethylammonium bromide (DTAB/DADMAC C12)	<i>D. magna</i>	24 h-EC ₅₀	0.37	Sandbacka et al. (2000)
	Rainbow trout	24 h-LC ₅₀	40.53	
	<i>C. vulgaris</i>	96 h EC ₅₀	0.188	
Tetradecyltrimethylammonium bromide (TTAB/ATMAC C14)	<i>D. magna</i>	24 h-EC ₅₀	0.091	Sandbacka et al. (2000)
	Rainbow trout	24 h-LC ₅₀	2.51	
	<i>C. vulgaris</i>	96 h EC ₅₀	0.182	
Hexadecyltrimethylammonium bromide (CTAB/ATMAC C16)	<i>D. magna</i>	24 h-EC ₅₀	0.058	Sandbacka et al. (2000)
	Rainbow trout	24 h-LC ₅₀	0.6	
	<i>C. vulgaris</i>	96 h EC ₅₀	0.156	
Hexadecyltrimethylammonium chloride (CTAC/ATMAC C16)	<i>C. vulgaris</i>	96 h EC ₅₀	0.137	Zhu et al. (2010)
	<i>C. vulgaris</i>	96 h-EC ₅₀	0.15	
	<i>C. vulgaris</i>	96 h EC ₅₀	0.11	
Octadecyltrimethylammonium bromide (STAB/ATMAC C18)	<i>C. vulgaris</i>	96 h EC ₅₀	0.11	Zhu et al. (2010)
	<i>Daphnia magna</i>	IC ₅₀	0.13–0.22	
Alkylbenzyltrimethylammonium halides (BAC C12–16)	<i>Photobacterium phosphoreum</i>	EC ₅₀	0.15–0.55	García et al. (2001)
	<i>P. subcapitata</i>	72-h EC ₅₀	0.041	
Benzalkonium chlorides (BAC)	<i>D. magna</i>	48-h EC ₅₀	0.041	Kreuzinger et al. (2007)
	<i>B. calyciflorus</i>	48-h EC ₅₀	0.13	
	<i>T. thermophila</i>	24-h EC ₅₀	2.94	
	<i>C. vulgaris</i>	96 h EC ₅₀	0.203	
	<i>C. vulgaris</i>	96 h EC ₅₀	0.174	
Benzyltrimethylhexadecylammonium chloride (BAC C14)	<i>C. vulgaris</i>	96 h EC ₅₀	0.161	Zhu et al. (2010)
	<i>C. vulgaris</i>	96 h EC ₅₀	0.161	
Dimethylditetradecylammonium bromide (DADMAC C14)	<i>P. subcapitata</i>	72-h EC ₅₀	0.021	Kreuzinger et al. (2007)
	<i>D. magna</i>	48-h EC ₅₀	0.023	
	<i>B. calyciflorus</i>	48-h EC ₅₀	0.025	
	<i>T. thermophila</i>	24-h EC ₅₀	4.43	
	<i>C. vulgaris</i>	96 h EC ₅₀	0.203	

a recent study which indicated that the joint toxicity of CTAC (100 µg/L) and fluoranthene (Flu) (0–200 µg/L) on the algae changed from a synergistic effect to an antagonistic effect as the concentration of Flu increased from 0–50 µg/L to 50–200 µg/L (Yu et al., 2013). The toxic interaction mechanism lies in Flu can affect the uptake of CTAC by the algae, resulting in different levels of CTAC toxicity. Sutterlin et al. (2008b) found that the toxicity of BAC in the presence of anionic surfactants was different from that of individual BAC. The toxicity was not only influenced by chemical structures of the anionic compounds, but also correlated with the compound mixture ratios. Similarly, Wong et al. (2012) reported that the alkyl chain lengths of the surfactants and the mixing ratios play a crucial role in determining the toxicity of alkyltrimethylammonium bromide (C_nTAB)/sodium alkyl methyl ester α-sulfonate (C_nMES) mixtures against bacteria.

The aquatic toxicity of QACs has been studied by many literatures. However, the toxicity of QACs-containing sludge towards soil microbial activity is also in need of attention, as sewage sludge land application has become one of the major disposal routes in many countries (Clarke and Smith, 2011; Scott and Jones, 2000). These QACs-containing biosolids together with many other contaminants would be a potential risk to soil organisms, since they may accumulate in soil over time due to its long half-life degradation. Changes in the soil environment caused due to the presence of QACs can be measured by soil quality parameters, since microbial activities are sensitive indicators to the disturbances in soil (Sarkar et al., 2010). Hexadecyl trimethyl ammonium bromide (CTAB) is demonstrated to be more toxic than octadecyl trimethyl ammonium bromide (OTAB) on the dehydrogenase and potential nitrification activities in three different types of soils (Sarkar et al., 2010). CTAB and OTAB inhibited dehydrogenase activity at a concentration of 50 and 100 mg/kg soil, respectively, whereas potential nitrification was inhibited at 50 mg/kg soil of CTAB and OTAB. However, the nature of QAC molecules is not the only factor affecting its toxicity, the organic carbon content of soil is also responsible for its behavior in soil. Bioaccumulation of QACs has been reported in earthworm tissues due to the use of organoclay minerals for remediating contaminants in soil (Sarkar et al., 2013). However, whether long term exposure of QACs can cause chronic toxic effects to earthworms through DNA damage warrants further investigation.

In addition to the potential toxicity to soil organisms caused by QACs, its toxic effect on the freshwater sediment dwelling organisms is studied as well. Thomas et al. (2009) reported that the 72 h NOEC for *Caenorhabditis elegans* for didecyldimethylammonium bromide (DADMAC C10) is 3344 mg/kg at 5 cmol/kg cationic exchange capacity (CEC) level based on field sediment. NOECs of dioctadecyldimethylammonium chloride (DODMAC) for *Lumbriculus variegatus*, *Tubifex tubifex* and *C. elegans* were greater than 5738, 1515 and 1351 mg/kg dw, respectively (Comber et al., 2008). Moreover, the accumulation factors of DODMAC for *L. variegatus* and *T. tubifex* were 0.22 and 0.78, respectively, indicating its low tendency to accumulate in these sediment dwelling organisms (Comber et al., 2008). These results demonstrate the relative low toxicity (>100 mg/kg dw) and bioaccumulation of QACs in the test organisms, which were probably due to strong adsorption of QACs onto particulate matters, and thus bioavailability is limited.

The database on the toxicity of QACs to aquatic and soil/sediment organisms is still fragmentary. Different species have varied responses to QACs, thus, laboratory studies conducted with single species are inadequate for predicting the toxic effects of QACs in natural environment. Therefore, laboratory studies conducted with more aquatic and soil/sediment species could be much more helpful in the QAC risk assessment process. Additionally, the long term exposure effects of QACs on reproduction and growth of organisms as well as the toxic effects of binary mixtures still need further research.

4. Overview of analytical methods for determination of QACs in environmental compartments

QACs are widely applied in domestic and industrial applications. Therefore, QACs will inevitably get into different compartments of ecosystems. Their toxicity and persistence are such that an accurate and sensitive analytical method must be developed to better understand the occurrence, distribution and fate of trace level QACs in various environmental samples.

Over the last decades, numerous methods for analysis of QACs in different compartments have been developed. QACs are commonly treated

with anionic dyes or chromogenic reagents resulting in ion associates, which can be measured by a spectrophotometry technique (Li and Zhao, 2004; Yamamoto et al., 2002). This technique is quick and simple in determining QACs without use of complicated equipment. However, it is readily affected by several interfering compounds, such as anionic surfactants. In environmental compartments where anionic surfactants are also present, QACs have a higher affinity for anionic surfactants than that for the dyes (Ding and Liao, 2001). Moreover, this technique is unable to determine individual QACs, which also limits its widespread use.

Nowadays, chromatographic techniques (gas chromatography and high performance liquid chromatography) coupled with various types of detectors have become the most widely used analytical methods for the determination of QACs in various environmental compartments (Bassarab et al., 2011; Ding and Liao, 2001; Ding and Tsai, 2003; Lara-Martín et al., 2010; Li and Brownawell, 2010; Martínez-Carballo et al., 2007a, 2007b; Van de Voorde et al., 2012). These techniques are capable of separating, detecting and quantitatively determining individual QACs from complex mixtures. The general analytical procedures were summarized in Table 4, which involve application of chromatographic techniques for determination of QACs in different environmental samples.

High-performance liquid chromatography (HPLC) is the most promising method for analyzing alkyl benzyl quaternary ammonium surfactants in the past (Norberg et al., 2000). However, this technique is not suitable for the analysis of these non-chromophoric surfactants, such as mono- and dialkyl quaternary ammonium surfactants, because these surfactants cannot absorb ultra-violet (UV). HPLC should be coupled with conductometric detection to analyze non-UV absorbing surfactants (Wee and Kennedy, 1982). Furthermore, capillary electrophoresis (CE) using indirect UV detection offers a convenient analytical technique for determining non-chromophoric QACs, i.e. ATMAC and DADMAC, in hair conditioners and fabric softeners (Liu and Ding, 2004).

Gas chromatography/mass spectrometry (GC/MS) is readily available in many environmental laboratories. GC/MS has been used for qualitative determination of BACs and ATMACs in river

water and sewage effluent (Ding and Liao, 2001; Ding and Tsai, 2003), with quantitation at less than 0.01 µg/L in 500 mL of the water samples. However, GC/MS needs a complex pretreatment of QACs before injecting them into the system. The long-chain cationic surfactants should be converted to the corresponding tertiary amines by thermal decomposition in the injection port and then used for analysis (Ding and Tsai, 2003).

Compared with GC/MS, HPLC coupled with single quadrupole (MS) or tandem mass spectrometers (MS–MS) is more suitable for determining these non-volatile cationic surfactants with large-molecules, since derivatization is unnecessary in most cases. In addition, with the combination of HPLC and MS, both the separation of different cationic surfactants through HPLC and the specific detection of QAC homologues through MS can be used. LC–MS/MS working in positive electrospray ionization (ESI+) mode is typically employed for determining trace amounts of QACs in environmental samples (Ferrer and Furlong, 2001, 2002; Martínez-Carballo et al., 2007a, 2007b; Núñez et al., 2004a, 2004b; Vidal et al., 2004). This method represents a new and powerful tool for the analysis of cationic surfactants in the environment. Different kinds of surfactants such as cationic, anionic, nonionic and amphoteric surfactant can be analyzed simultaneously by applying mixed-mode reversed-phase HPLC (RPLC)–ESI–MS combined with evaporative light scattering detection (ELSD), with detection limit in the range of 2.5–8.5 µg/mL achieved for cationic surfactants (Im et al., 2008). Furthermore, on-line polymer monolith microextraction (PMME) coupled with HPLC–ESI–MS achieved automated determination of QACs in water samples, making the whole analysis procedure simple, accurate and time-saving (Peng et al., 2011).

Literatures reported about determination of QACs in aquatic compartments are mainly focused on river water samples. Recently, a research about analysis of QACs in seawater samples was conducted by applying solid-phase extraction (SPE) combined with LC–MS, which is demonstrated to be sensitive in determination of QACs in marine environment with LOD in the µg/L range (Bassarab et al., 2011). The presence of QACs in other compartments such as urban runoff was also

Table 4
General information on the analytical procedures for determining QACs in environmental samples.

Analytes	Sample type	Sample preparation	Recovery [%]	Detection technique	LOD/LOQ	References
ATMAC (C12–16) BAC (C12–18)	Surface water Waste water	Ion-pair LLE	80–99	LC/ESI(+)-MS/MS	4–19 ng/L	Martínez-Carballo et al. (2007a)
DADMAC (C10–18) BAC C12	Indirect discharge water Sea water	SPE	80–105	LC/ESI(+)-MS	At ng/L level	Bassarab et al. (2011)
DADMAC C10 ATMAC (C12–18) BAC (C12–18)	River water River water sewage effluent	Ion-pair LLE SPE derivatization (potassium tert-butoxide)	70–94 81–92	GC–MS (EI and PCI) GC–MS (EI)	≤0.01 µg/L ≤0.1 µg/L	Ding and Tsai (2003) Ding and Liao (2001)
BAC (C12–16)	Wastewater samples Stream samples Surface water	SPE SPE	71–78 79–93	LC/ESI(+)-MS/MS Ion chromatography–conductivity detection (IC–CD)	3–5 ng/L 0.0018–0.038 µg/mL	Ferrer and Furlong (2001) Olkowska et al. (2013)
ATMAC (C12–16) BAC (C12–14) DADMAC (C12–16)	Sewage sludge	Acid-induced cloud-point extraction (ACPE)	91–100	RPLC/ESI(+)-MS	40–75 ng/g	Merino et al. (2003b)
QACs [ATMAC (C10–16) BAC (C12–18) DADMAC (C10–18)]	Sediment Sludge	Soxhlet extraction	67–95	HPLC/ESI(+)-MS/MS	0.6–3 µg/kg 2–5 µg/kg	Martínez-Carballo et al. (2007b)
BAC (C12–18) DADMAC (C8–C18)	Estuarine sediments	Ultrasonically assisted extraction (UAE)	98–104	HPLC–ESI(+)/ToF–MS	2–2.6 ng/g 0.1–2.0 ng/g	Li and Brownawell (2009)
ATMAC (C16–18) BAC (C12–18) DADMAC (C8–C18)	Estuarine sediments	UAE	104 ± 19%	HPLC–ESI(+)/ToF–MS	1.5–30 ng/g	Li and Brownawell (2010)
ATMAC (C12–22) BAC (C12–18)	Estuarine sediments Sediment	UAE Accelerated solvent extraction (ASE) followed by on-line SPE	106 ± 20% 79–85	HPLC–ESI(+)/ToF–MS LC/ESI(+)-MS–MS	1.5–30 ng/g 0.16 µg/kg	Lara-Martín et al. (2010) Ferrer and Furlong (2002)

reported by applying LC–MS/MS, with detection for both dissolved and particulate fractions (Van de Voorde et al., 2012).

HPLC–ESI coupled with time-of-flight (ToF)–MS is powerful for the identification of QACs in estuarine sediments (Lara-Martín et al., 2010; Li and Brownawell, 2009, 2010). It not only identified the targeted QACs and gave information for the molecular ion as well as the typical fragment ions, but also identified non-targeted DDMAC C8:C8 and C8:C10 (Li and Brownawell, 2009). Recently, solid phase extraction coupled with ion chromatography and conductometric detection (SPE–IC–CD) is applied for determining BACs in surface water sample (Olkowska et al., 2013). In comparison with liquid–liquid extraction (LLE) coupled with LC–MS, this method is simpler, time-saving, less expensive, and avoids use of toxic reagents like chloroform.

5. Conclusion

Industrial and domestic usage of QACs-containing products are the main source for the presence of QACs in wastewater treatment plants, surface water and sediments. Generally, the contamination levels of QACs in sewage and surface water are in the range of ng/L to µg/L, while the levels of QACs in sludge, sediments are in the range of µg/kg to mg/kg (dw). Although QACs are able to be biodegraded in aerobic conditions, their sorption is faster than degradation. Therefore, high abundances of QACs were accumulated in the environment, especially in anoxic/anaerobic compartments. The presence of QACs in the environment is not only toxic to both aquatic and terrestrial organisms, but also increases the chance for coselection of antibiotic resistant bacteria, which is considered as a pressing problem for both human and environment health. Therefore, it is of necessity to improve the elimination of QACs in wastewater treatment plants, especially in activated sludge, before they were released into the environment. Henceforth, there is an urgent need to develop strategies to enhance the QAC removal in activated sludge as well as sediments, where they are readily accumulated.

Acknowledgments

The project is financially supported by the National Natural Science Foundation of China (51179068, 51039001).

References

- Bassarab, P., Williams, D., Dean, J.R., Ludkin, E., Perry, J.J., 2011. Determination of quaternary ammonium compounds in seawater samples by solid-phase extraction and liquid chromatography–mass spectrometry. *J. Chromatogr. A* 1218, 673–677. <http://dx.doi.org/10.1016/j.chroma.2010.11.088>.
- Boethling, R.S., 1984. Environmental fate and toxicity in wastewater treatment of quaternary ammonium surfactants. *Water Res.* 18, 1061–1076. [http://dx.doi.org/10.1016/0043-1354\(84\)90220-3](http://dx.doi.org/10.1016/0043-1354(84)90220-3).
- Breen, D., Horner, J.M., Bartle, K.D., Clifford, A.A., Waters, J., Lawrence, J.G., 1996. Supercritical fluid extraction and off-line HPLC analysis of cationic surfactants from dried sewage sludge. *Water Res.* 30, 476–480. [http://dx.doi.org/10.1016/0043-1354\(95\)00185-9](http://dx.doi.org/10.1016/0043-1354(95)00185-9).
- Brycki, B., Waligorska, M., Szulc, A., 2014. The biodegradation of monomeric and dimeric alkylammonium surfactants. *J. Hazard. Mater.* 280, 797–815. <http://dx.doi.org/10.1016/j.jhazmat.2014.08.021>.
- Buffet-Bataillon, S., Tattevin, P., Bonnaure-Mallet, M., Jolivet-Gougeon, A., 2012. Emergence of resistance to antibacterial agents: the role of quaternary ammonium compounds—a critical review. *Int. J. Antimicrob. Agents* 39, 381–389. <http://dx.doi.org/10.1016/j.ijantimicag.2012.01.011>.
- Chen, Y., Geurts, M., Sjollem, S.B., Kramer, N.J., Hermens, J.L., Droge, S.T., 2014. Acute toxicity of the cationic surfactant C12-benzalkonium in different bioassays: how test design affects bioavailability and effect concentrations. *Environ. Toxicol. Chem.* 33, 606–615. <http://dx.doi.org/10.1002/etc.2465>.
- Chiaia-Hernandez, A.C., Krauss, M., Hollender, J., 2013. Screening of lake sediments for emerging contaminants by liquid chromatography atmospheric pressure photoionization and electrospray ionization coupled to high resolution mass spectrometry. *Environ. Sci. Technol.* 47, 976–986. <http://dx.doi.org/10.1021/es303888v>.
- Clara, M., Scharf, S., Scheffknecht, C., Gans, O., 2007. Occurrence of selected surfactants in untreated and treated sewage. *Water Res.* 41, 4339–4348. <http://dx.doi.org/10.1016/j.watres.2007.06.027>.
- Clarke, B.O., Smith, S.R., 2011. Review of 'emerging' organic contaminants in biosolids and assessment of international research priorities for the agricultural use of biosolids. *Environ. Int.* 37, 226–247. <http://dx.doi.org/10.1016/j.envint.2010.06.004>.
- Comber, S.D., Rule, K.L., Conrad, A.U., Hoss, S., Webb, S.F., Marshall, S., 2008. Bioaccumulation and toxicity of a cationic surfactant (DODMAC) in sediment dwelling freshwater invertebrates. *Environ. Pollut.* 153, 184–191. <http://dx.doi.org/10.1016/j.envpol.2007.07.032>.
- Deutschle, T., Porkert, U., Reiter, R., Keck, T., Riechelmann, H., 2006. In vitro genotoxicity and cytotoxicity of benzalkonium chloride. *Toxicol. In Vitro* 20, 1472–1477. <http://dx.doi.org/10.1016/j.tiv.2006.07.006>.
- Ding, W.H., Liao, Y.H., 2001. Determination of alkylbenzyltrimethylammonium chlorides in river water and sewage effluent by solid-phase extraction and gas chromatography/mass spectrometry. *Anal. Chem.* 73, 36–40. <http://dx.doi.org/10.1021/ac000655i>.
- Ding, W.H., Tsai, P.C., 2003. Determination of alkyltrimethylammonium chlorides in river water by gas chromatography/ion trap mass spectrometry with electron impact and chemical ionization. *Anal. Chem.* 75, 1792–1797. <http://dx.doi.org/10.1021/ac020536y>.
- European Commission, 2002. European Union Risk Assessment Report: Dimethyldioctadecylammonium Chloride (DODMAC) vol. 14 (EUR 20397 EN. <http://echa.europa.eu/documents/10162/6434698/orats_summary_dimethyldioctadecylammoniumchl_en.pdf>).
- Ferk, F., Misik, M., Hoelzl, C., Uhl, M., Fuerhacker, M., Grillitsch, B., et al., 2007. Benzalkonium chloride (BAC) and dimethyldioctadecyl-ammonium bromide (DDAB), two common quaternary ammonium compounds, cause genotoxic effects in mammalian and plant cells at environmentally relevant concentrations. *Mutagenesis* 22, 363–370. <http://dx.doi.org/10.1093/mutage/gem027>.
- Fernández Cirelli, A., Ojeda, C., Castro, M.J.L., Salgot, M., 2008. Surfactants in sludge-amended agricultural soils: a review. *Environ. Chem. Lett.* 6, 135–148. <http://dx.doi.org/10.1007/s10311-008-0146-1>.
- Fernández, P., Alder, A.C., Suter, M., Giger, W., 1996. Determination of the quaternary ammonium surfactant ditallowdimethylammonium in digested sludges and marine sediments by supercritical fluid extraction and liquid chromatography with postcolumn ion-pair formation. *Anal. Chem.* 68, 921–929. <http://dx.doi.org/10.1021/ac9505482>.
- Ferrer, I., Furlong, E.T., 2001. Identification of alkyl dimethylbenzylammonium surfactants in water samples by solid phase extraction followed by ion trap LC/MS and LC/MS/MS. *Environ. Sci. Technol.* 35, 2583–2588. <http://dx.doi.org/10.1021/es001742v>.
- Ferrer, I., Furlong, E.T., 2002. Accelerated solvent extraction followed by on-line solid-phase extraction coupled to ion trap LC/MS/MS for analysis of benzalkonium chlorides in sediment samples. *Anal. Chem.* 74, 1275–1280. <http://dx.doi.org/10.1021/ac010969l>.
- Games, L.M., King, J.E., 1982. Fate and distribution of a quaternary ammonium surfactant, octadecyltrimethylammonium chloride (OTAC), in wastewater treatment. *Environ. Sci. Technol.* 16, 483–488. <http://dx.doi.org/10.1021/es00102a011>.
- García, M.T., Campos, E., Sanchez-Leal, J., Ribosa, I., 1999. Effect of the alkyl chain length on the anaerobic biodegradability and toxicity of quaternary ammonium based surfactants. *Chemosphere* 38, 3473–3483. [http://dx.doi.org/10.1016/S0045-6535\(98\)00576-1](http://dx.doi.org/10.1016/S0045-6535(98)00576-1).
- García, M.T., Campos, E., Sanchez-Leal, J., Ribosa, I., 2000. Anaerobic degradation and toxicity of commercial cationic surfactants in anaerobic screening tests. *Chemosphere* 41, 705–710. [http://dx.doi.org/10.1016/S0045-6535\(99\)00455-5](http://dx.doi.org/10.1016/S0045-6535(99)00455-5).
- García, M.T., Ribosa, I., Guindulain, T., Sánchez-Leal, J., Vives-Rego, J., 2001. Fate and effect of monoalkyl quaternary ammonium surfactants in the aquatic environment. *Environ. Pollut.* 111, 169–175. [http://dx.doi.org/10.1016/S0269-7491\(99\)00322-X](http://dx.doi.org/10.1016/S0269-7491(99)00322-X).
- Gaze, W.H., Abdoullam, N., Hawkey, P.M., Wellington, E.M., 2005. Incidence of class 1 integrons in a quaternary ammonium compound-polluted environment. *Antimicrob. Agents Chemother.* 49, 1802–1807. <http://dx.doi.org/10.1128/AAC.49.5.1802-1807.2005>.
- Ge, F., Xu, Y., Zhu, R., Yu, F., Zhu, M., Wong, M., 2010. Joint action of binary mixtures of cetyltrimethyl ammonium chloride and aromatic hydrocarbons on *Chlorella vulgaris*. *Ecotoxicol. Environ. Saf.* 73, 1689–1695. <http://dx.doi.org/10.1016/j.ecoenv.2010.06.003>.
- Gerike, P., Klotz, H., Kooijman, J.G.A., Matthijs, E., Waters, J., 1994. The determination of dihardened tallow dimethyl ammonium compounds (DHTDMAC) in environmental matrices using trace enrichment techniques and high performance liquid chromatography with conductometric detection. *Water Res.* 28, 147–154. [http://dx.doi.org/10.1016/0043-1354\(94\)90128-7](http://dx.doi.org/10.1016/0043-1354(94)90128-7).
- Giolando, S.T., Rapaport, R.A., Larson, R.J., Federle, T.W., Stalmans, M., Masscheleyn, P., 1995. Environmental fate and effects of DEEDMAC: a new rapidly biodegradable cationic surfactant for use in fabric softeners. *Chemosphere* 30, 1067–1083. [http://dx.doi.org/10.1016/0045-6535\(95\)00005-5](http://dx.doi.org/10.1016/0045-6535(95)00005-5).
- Grabinska-Sota, E., 2011. Genotoxicity and biodegradation of quaternary ammonium salts in aquatic environments. *J. Hazard. Mater.* 195, 182–187. <http://dx.doi.org/10.1016/j.jhazmat.2011.08.026>.
- Hajaya, M.G., Pavlostathis, S.G., 2012. Fate and effect of benzalkonium chlorides in a continuous-flow biological nitrogen removal system treating poultry processing wastewater. *Bioresour. Technol.* 118, 73–81. <http://dx.doi.org/10.1016/j.biortech.2010.05.050>.
- Hajaya, M.G., Pavlostathis, S.G., 2013. Modeling the fate and effect of benzalkonium chlorides in a continuous-flow biological nitrogen removal system treating poultry processing wastewater. *Bioresour. Technol.* 130, 278–287. <http://dx.doi.org/10.1016/j.biortech.2012.11.103>.
- Hajaya, M.G., Tezel, U., Pavlostathis, S.G., 2011. Effect of temperature and benzalkonium chloride on nitrate reduction. *Bioresour. Technol.* 102, 5039–5047. <http://dx.doi.org/10.1016/j.biortech.2011.01.080>.
- Hegstad, K., Langsrud, S., Lunestad, B.T., Scheie, A.A., Sunde, M., Yazdankhah, S.P., 2010. Does the wide use of quaternary ammonium compounds enhance the selection and spread of antimicrobial resistance and thus threaten our health? *Microb. Drug Resist.* 16, 91–104. <http://dx.doi.org/10.1089/mdr.2009.0120>.

- Im, S.H., Jeong, Y.H., Ryou, J.J., 2008. Simultaneous analysis of anionic, amphoteric, nonionic and cationic surfactant mixtures in shampoo and hair conditioner by RP–HPLC/ELSD and LC/MS. *Anal. Chim. Acta* 619, 129–136. <http://dx.doi.org/10.1016/j.aca.2008.03.058>.
- Inacio, A.S., Costa, G.N., Domingues, N.S., Santos, M.S., Moreno, A.J., Vaz, W.L., et al., 2013. Mitochondrial dysfunction is the focus of quaternary ammonium surfactant toxicity to mammalian epithelial cells. *Antimicrob. Agents Chemother.* 57, 2631–2639. <http://dx.doi.org/10.1128/AAC.02437-12>.
- Ioannou, C.J., Hanlon, G.W., Denyer, S.P., 2007. Action of disinfectant quaternary ammonium compounds against *Staphylococcus aureus*. *Antimicrob. Agents Chemother.* 51, 296–306. <http://dx.doi.org/10.1128/AAC.00375-06>.
- Ishikawa, S., Matsumura, Y., Yoshizako, F., Tsuchido, T., 2002. Characterization of a cationic surfactant-resistant mutant isolated spontaneously from *Escherichia coli*. *J. Appl. Microbiol.* 92, 261–268. <http://dx.doi.org/10.1046/j.1365-2672.2002.01526.x>.
- Ismail, Z.Z., Tezel, U., Pavlostathis, S.G., 2010. Sorption of quaternary ammonium compounds to municipal sludge. *Water Res.* 44, 2303–2313. <http://dx.doi.org/10.1016/j.watres.2009.12.029>.
- Jing, G., Zhou, Z., Zhuo, J., 2012. Quantitative structure–activity relationship (QSAR) study of toxicity of quaternary ammonium compounds on *Chlorella pyrenoidosa* and *Scenedesmus quadricauda*. *Chemosphere* 86, 76–82. <http://dx.doi.org/10.1016/j.chemosphere.2011.09.021>.
- Kreuzinger, N., Fuerhacker, M., Scharf, S., Uhl, M., Gans, O., Grillitsch, B., 2007. Methodological approach towards the environmental significance of uncharacterized substances – quaternary ammonium compounds as an example. *Desalination* 215, 209–222. <http://dx.doi.org/10.1016/j.desal.2006.10.036>.
- Kümmerer, K., Eitel, A., Braun, U., Hubner, P., Daschner, F., Mascart, G., et al., 1997. Analysis of benzalkonium chloride in the effluent from European hospitals by solid-phase extraction and high-performance liquid chromatography with post-column ion-pairing and fluorescence detection. *J. Chromatogr. A* 774, 281–286. [http://dx.doi.org/10.1016/S0021-9673\(97\)00242-2](http://dx.doi.org/10.1016/S0021-9673(97)00242-2).
- Lara-Martín, P.A., Li, X.L., Bopp, R.F., Brownawell, B.J., 2010. Occurrence of alkyltrimethylammonium compounds in urban estuarine sediments: behentrimonium as a new emerging contaminant. *Environ. Sci. Technol.* 44, 7569–7575. <http://dx.doi.org/10.1021/es101169a>.
- Larsen, S.T., Verder, H., Nielsen, G.D., 2012. Airway effects of inhaled quaternary ammonium compounds in mice. *Basic Clin. Pharmacol.* 110, 537–543. <http://dx.doi.org/10.1111/j.1742-7843.2011.00851.x>.
- Li, X., Brownawell, B.J., 2009. Analysis of quaternary ammonium compounds in estuarine sediments by LC–ToF–MS: very high positive mass defects of alkylamine ions as powerful diagnostic tools for identification and structural elucidation. *Anal. Chem.* 81, 7926–7935. <http://dx.doi.org/10.1021/ac900900y>.
- Li, X., Brownawell, B.J., 2010. Quaternary ammonium compounds in urban estuarine sediment environments—a class of contaminants in need of increased attention. *Environ. Sci. Technol.* 44, 7561–7568. <http://dx.doi.org/10.1021/es1011669>.
- Li, S., Zhao, S., 2004. Spectrophotometric determination of cationic surfactants with benzothiazolidiazobenzene. *Anal. Chim. Acta* 501, 99–102. <http://dx.doi.org/10.1016/j.aca.2003.09.014>.
- Li, X., Luo, X., Mai, B., Liu, J., Chen, L., Lin, S., 2014. Occurrence of quaternary ammonium compounds (QACs) and their application as a tracer for sewage derived pollution in urban estuarine sediments. *Environ. Pollut.* 185, 127–133. <http://dx.doi.org/10.1016/j.envpol.2013.10.028>.
- Liang, Z., Ge, F., Zeng, H., Xu, Y., Peng, F., Wong, M., 2013. Influence of cetyltrimethyl ammonium bromide on nutrient uptake and cell responses of *Chlorella vulgaris*. *Aquat. Toxicol.* 138–139, 81–87. <http://dx.doi.org/10.1016/j.aquatox.2013.04.010>.
- Liffourrena, A.S., Lopez, F.G., Salvano, M.A., Domenech, C.E., Lucchesi, G.I., 2008. Degradation of tetradecyltrimethylammonium by *Pseudomonas putida* A ATCC 12633 restricted by accumulation of trimethylamine is alleviated by addition of Al^{3+} ions. *J. Appl. Microbiol.* 104, 396–402. <http://dx.doi.org/10.1111/j.1365-2672.2007.03591.x>.
- Liu, H.-Y., Ding, W.-H., 2004. Determination of homologues of quaternary ammonium surfactants by capillary electrophoresis using indirect UV detection. *J. Chromatogr. A* 1025, 303–312. <http://dx.doi.org/10.1016/j.chroma.2003.10.108>.
- Martinez-Carballo, E., Sitka, A., Gonzalez-Barreiro, C., Kreuzinger, N., Fuerhacker, M., Scharf, S., et al., 2007a. Determination of selected quaternary ammonium compounds by liquid chromatography with mass spectrometry. Part I. Application to surface, waste and indirect discharge water samples in Austria. *Environ. Pollut.* 145, 489–496. <http://dx.doi.org/10.1016/j.envpol.2006.04.033>.
- Martinez-Carballo, E., Gonzalez-Barreiro, C., Sitka, A., Kreuzinger, N., Scharf, S., Gans, O., 2007b. Determination of selected quaternary ammonium compounds by liquid chromatography with mass spectrometry. Part II. Application to sediment and sludge samples in Austria. *Environ. Pollut.* 146, 543–547. <http://dx.doi.org/10.1016/j.envpol.2006.07.016>.
- Mc Cay, P.H., Ocampo-Sosa, A.A., Fleming, G.T., 2010. Effect of subinhibitory concentrations of benzalkonium chloride on the competitiveness of *Pseudomonas aeruginosa* grown in continuous culture. *Microbiology* 156, 30–38. <http://dx.doi.org/10.1099/mic.0.029751-0>.
- McBain, A.J., Ledder, R.G., Moore, L.E., Catrenich, C.E., Gilbert, P., 2004. Effects of quaternary-ammonium-based formulations on bacterial community dynamics and antimicrobial susceptibility. *Appl. Environ. Microbiol.* 70, 3449–3456. <http://dx.doi.org/10.1128/AEM.70.6.3449-3456.2004>.
- Melin, V.E., Potinini, H., Hunt, P., Griswold, J., Siems, B., Werre, S.R., et al., 2014. Exposure to common quaternary ammonium disinfectants decreases fertility in mice. *Reprod. Toxicol.* 50, 163–170. <http://dx.doi.org/10.1016/j.reprotox.2014.07.071>.
- Merino, F., Rubio, S., Pérez-Bendito, D., 2003a. Solid-phase extraction of application to the concentration of benzalkonium surfactants in sewage and river water. *Anal. Chem.* 75, 6799–6806. <http://dx.doi.org/10.1021/ac030224a>.
- Merino, F., Rubio, S., Pérez-Bendito, D., 2003b. Mixed aggregate-based acid-induced cloud-point extraction and ion-trap liquid chromatography–mass spectrometry for the determination of cationic surfactants in sewage sludge. *J. Chromatogr. A* 998, 4825–4834. <http://dx.doi.org/10.1128/AEM.00573-08>.
- Moore, L.E., Ledder, R.G., Gilbert, P., McBain, A.J., 2008. In vitro study of the effect of cationic biocides on bacterial population dynamics and susceptibility. *Appl. Environ. Microbiol.* 74, 4825–4834. <http://dx.doi.org/10.1128/AEM.00573-08>.
- Nalecz-Jawacki, G., Grabinska-Sota, E., Narkiewicz, P., 2003. The toxicity of cationic surfactants in four bioassays. *Ecotoxicol. Environ. Saf.* 54, 87–91. [http://dx.doi.org/10.1016/S0147-6513\(02\)00025-8](http://dx.doi.org/10.1016/S0147-6513(02)00025-8).
- Nishihara, T., Okamoto, T., Nishiyama, N., 2000. Biodegradation of didecylmethylammonium chloride by *Pseudomonas fluorescens* TN4 isolated from activated sludge. *J. Appl. Microbiol.* 88, 641–647. <http://dx.doi.org/10.1046/j.1365-2672.2000.01007.x>.
- Nishiyama, N., Nishihara, T., 2002. Biodegradation of dodecyl trimethyl ammonium bromide by *Pseudomonas fluorescens* F7 and F2 isolated from activated sludge. *Microbes Environ.* 17, 164–169. <http://dx.doi.org/10.1264/jsm.2.17.164>.
- Nishiyama, N., Toshima, Y., Ikeda, Y., 1995. Biodegradation of alkyltrimethylammonium salts in activated sludge. *Chemosphere* 30, 593–603. [http://dx.doi.org/10.1016/0045-6535\(94\)00406-K](http://dx.doi.org/10.1016/0045-6535(94)00406-K).
- Norberg, J., Thordarson, E., Mathiasson, L., Jonsson, J.A., 2000. Microporous membrane liquid–liquid extraction coupled on-line with normal-phase liquid chromatography for the determination of cationic surfactants in river and waste water. *J. Chromatogr. A* 869, 523–529. [http://dx.doi.org/10.1016/S0021-9673\(99\)01219-4](http://dx.doi.org/10.1016/S0021-9673(99)01219-4).
- Núñez, O., Moyano, E., Galceran, M.T., 2004a. Determination of quaternary ammonium biocides by liquid chromatography–mass spectrometry. *J. Chromatogr. A* 1058, 89–95. <http://dx.doi.org/10.1016/j.chroma.2004.08.085>.
- Núñez, O., Moyano, E., Galceran, M.T., 2004b. Time-of-flight high resolution versus triple quadrupole tandem mass spectrometry for the analysis of quaternary ammonium herbicides in drinking water. *Anal. Chim. Acta* 525, 183–190. <http://dx.doi.org/10.1016/j.aca.2004.08.006>.
- Oh, S., Tandukar, M., Pavlostathis, S.G., Chain, P.S., Konstantinidis, K.T., 2013. Microbial community adaptation to quaternary ammonium biocides as revealed by metagenomics. *Environ. Microbiol.* 15, 2850–2864. <http://dx.doi.org/10.1111/1462-2920.12154>.
- Olkowska, E., Polkowska, Z., Namiesnik, J., 2013. A solid phase extraction-ion chromatography with conductivity detection procedure for determining cationic surfactants in surface water samples. *Talanta* 116, 210–216. <http://dx.doi.org/10.1016/j.talanta.2013.04.083>.
- Patrauchan, M.A., Oriel, P.J., 2003. Degradation of benzyldimethylalkylammonium chloride by *Aeromonas hydrophila* sp.K. *J. Appl. Microbiol.* 94, 266–272. <http://dx.doi.org/10.1046/j.1365-2672.2003.01829.x>.
- Peng, X.T., Shi, Z.G., Feng, Y.Q., 2011. Rapid and high-throughput determination of cationic surfactants in environmental water samples by automated on-line polymer monolith microextraction coupled to high performance liquid chromatography–mass spectrometry. *J. Chromatogr. A* 1218, 3588–3594. <http://dx.doi.org/10.1016/j.chroma.2011.04.009>.
- Pérez, P., Fernández, E., Beiras, R., 2009. Toxicity of benzalkonium chloride on monoalgal cultures and natural assemblages of marine phytoplankton. *Water Air Soil Pollut.* 201, 319–330. <http://dx.doi.org/10.1007/s11270-008-9947-x>.
- Pruden, A., Pei, R.T., Storteboom, H., Carlson, K.H., 2006. Antibiotic resistance genes as emerging contaminants: studies in northern Colorado. *Environ. Sci. Technol.* 40, 7445–7450. <http://dx.doi.org/10.1021/es060413l>.
- Qin, Y., Zhang, G.Y., Kang, B.A., Zhao, Y.M., 2005. Primary aerobic biodegradation of cationic and amphoteric surfactants. *J. Surfactant Deterg.* 8, 55–58. <http://dx.doi.org/10.1007/s11743-005-0330-x>.
- Qv, X.Y., Jiang, J.G., 2013. Toxicity evaluation of two typical surfactants to *Dunaliella bardawil*, an environmentally tolerant alga. *Environ. Toxicol. Chem.* 32, 426–433. <http://dx.doi.org/10.1002/etc.2073>.
- Ren, R., Li, K., Zhang, C., Liu, D., Sun, J., 2011. Biosorption of tetradecyl benzyl dimethyl ammonium chloride on activated sludge: kinetic, thermodynamic and reaction mechanisms. *Bioresour. Technol.* 102, 3799–3804. <http://dx.doi.org/10.1016/j.biortech.2010.12.032>.
- Ruan, T., Song, S., Wang, T., Liu, R., Lin, Y., Jiang, G., 2014. Identification and composition of emerging quaternary ammonium compounds in municipal sewage sludge in China. *Environ. Sci. Technol.* 48, 4289–4297. <http://dx.doi.org/10.1021/es4050314>.
- Sanchez-Fortun, S., Marva, F., D'Ors, A., Costas, E., 2008. Inhibition of growth and photosynthesis of selected green microalgae as tools to evaluate toxicity of dodecylethylmethylammonium bromide. *Ecotoxicology* 17, 229–234. <http://dx.doi.org/10.1007/s10646-007-0189-2>.
- Sandbacka, M., Christianson, I., Isomaa, B., 2000. The acute toxicity of surfactants on fish cells, daphnia magna and fish – a comparative study. *Toxicol. in Vitro* 14, 61–68. [http://dx.doi.org/10.1016/S0887-2333\(99\)00083-1](http://dx.doi.org/10.1016/S0887-2333(99)00083-1).
- Sarkar, B., Megharaj, M., Xi, Y., Krishnamurti, G.S., Naidu, R., 2010. Sorption of quaternary ammonium compounds in soils: implications to the soil microbial activities. *J. Hazard. Mater.* 184, 448–456. <http://dx.doi.org/10.1016/j.jhazmat.2010.08.055>.
- Sarkar, B., Megharaj, M., Shanmuganathan, D., Naidu, R., 2013. Toxicity of organoclays to microbial processes and earthworm survival in soils. *J. Hazard. Mater.* 261, 793–800. <http://dx.doi.org/10.1016/j.jhazmat.2012.11.061>.
- Scott, J.M., Jones, M.N., 2000. The biodegradation of surfactants in the environment. *Biochim. Biophys. Acta* 1508, 235–251. [http://dx.doi.org/10.1016/S0304-4157\(00\)00013-7](http://dx.doi.org/10.1016/S0304-4157(00)00013-7).
- Sutterlin, H., Alexy, R., Coker, A., Kummerer, K., 2008a. Mixtures of quaternary ammonium compounds and anionic organic compounds in the aquatic environment: elimination and biodegradability in the closed bottle test monitored by LC–MS/MS. *Chemosphere* 72, 479–484. <http://dx.doi.org/10.1016/j.chemosphere.2008.03.008>.
- Sutterlin, H., Alexy, R., Kummerer, K., 2008b. The toxicity of the quaternary ammonium compound benzalkonium chloride alone and in mixtures with other anionic

- compounds to bacteria in test systems with *Vibrio fischeri* and *Pseudomonas putida*. *Ecotoxicol. Environ. Saf.* 71, 498–505. <http://dx.doi.org/10.1016/j.ecoenv.2007.12.015>.
- Takenaka, S., Tonoki, T., Taira, K., Murakami, S., Aoki, K., 2007. Adaptation of *Pseudomonas* sp. strain 7–6 to quaternary ammonium compounds and their degradation via dual pathways. *Appl. Environ. Microbiol.* 73, 1797–1802. <http://dx.doi.org/10.1128/AEM.02426-06>.
- Tandukar, M., Oh, S., Tezel, U., Konstantinidis, K.T., Pavlostathis, S.G., 2013. Long-term exposure to benzalkonium chloride disinfectants results in change of microbial community structure and increased antimicrobial resistance. *Environ. Sci. Technol.* 47, 9730–9738. <http://dx.doi.org/10.1021/es401507k>.
- Terzic, S., Ahel, M., 2011. Nontarget analysis of polar contaminants in freshwater sediments influenced by pharmaceutical industry using ultra-high-pressure liquid chromatography–quadrupole time-of-flight mass spectrometry. *Environ. Pollut.* 159, 557–566. <http://dx.doi.org/10.1016/j.envpol.2010.10.009>.
- Tezel, U., 2009. *Fate and Effect of Quaternary Ammonium Compounds in Biological Systems*. (Ph.D. Dissertation). Georgia Institute of Technology, Atlanta, GA.
- Tezel, U., Pavlostathis, S.G., 2009. Transformation of benzalkonium chloride under nitrate reducing conditions. *Environ. Sci. Technol.* 43, 1342–1348. <http://dx.doi.org/10.1021/es802177f>.
- Tezel, U., Pierson, J.A., Pavlostathis, S.G., 2006. Fate and effect of quaternary ammonium compounds on a mixed methanogenic culture. *Water Res.* 40, 3660–3668. <http://dx.doi.org/10.1016/j.watres.2006.06.019>.
- Tezel, U., Pierson, J.A., Pavlostathis, S.G., 2007. Effect of polyelectrolytes and quaternary ammonium compounds on the anaerobic biological treatment of poultry processing wastewater. *Water Res.* 41, 1334–1342. <http://dx.doi.org/10.1016/j.watres.2006.12.005>.
- Tezel, U., Pierson, J.A., Pavlostathis, S.G., 2008. Effect of didecyl dimethyl ammonium chloride on nitrate reduction in a mixed methanogenic culture. *Water Sci. Technol.* 57, 541–546. <http://dx.doi.org/10.2166/wst.2008.068>.
- Tezel, U., Tandukar, M., Martinez, R.J., Sobecky, P.A., Pavlostathis, S.G., 2012. Aerobic biotransformation of n-tetradecylbenzyltrimethylammonium chloride by an enriched *Pseudomonas* spp. community. *Environ. Sci. Technol.* 46, 8714–8722. <http://dx.doi.org/10.1021/es300518c>.
- Thomas, P.C., Velthoven, K., Geurts, M., van Wijk, D., 2009. Bioavailability and detoxification of cationics: II. Relationship between toxicity and CEC of cationic surfactants on *Caenorhabditis elegans* (Nematoda) in artificial and natural substrates. *Chemosphere* 75, 310–318. <http://dx.doi.org/10.1016/j.chemosphere.2009.02.003>.
- Tsai, P.-C., Ding, W.-H., 2004. Determination of alkyltrimethylammonium surfactants in hair conditioners and fabric softeners by gas chromatography–mass spectrometry with electron-impact and chemical ionization. *J. Chromatogr. A* 1027, 103–108. <http://dx.doi.org/10.1016/j.chroma.2003.10.047>.
- Van de Voorde, A., Lorgeoux, C., Gromaire, M.C., Chebbo, G., 2012. Analysis of quaternary ammonium compounds in urban stormwater samples. *Environ. Pollut.* 164, 150–157. <http://dx.doi.org/10.1016/j.envpol.2012.01.037>.
- van Wijk, D., Gyimesi-van den Bos, M., Garttner-Arends, I., Geurts, M., Kamstra, J., Thomas, P., 2009. Bioavailability and detoxification of cationics: I. Algal toxicity of alkyltrimethyl ammonium salts in the presence of suspended sediment and humic acid. *Chemosphere* 75, 303–309. <http://dx.doi.org/10.1016/j.chemosphere.2008.12.047>.
- Vidal, J.L.M., Vega, A.B., López, F.J.S., Frenich, A.G., 2004. Application of internal quality control to the analysis of quaternary ammonium compounds in surface and groundwater from Andalusia (Spain) by liquid chromatography with mass spectrometry. *J. Chromatogr. A* 1050, 179–184. <http://dx.doi.org/10.1016/j.chroma.2004.08.023>.
- Watson, M.K., Tezel, U., Pavlostathis, S.G., 2012. Biotransformation of alkanoylcholines under methanogenic conditions. *Water Res.* 46, 2947–2956. <http://dx.doi.org/10.1016/j.watres.2012.03.021>.
- Wee, V.T., Kennedy, J.M., 1982. Determination of trace levels of quaternary ammonium compounds in river water by liquid chromatography with conductometric detection. *Anal. Chem.* 54, 1631–1633. <http://dx.doi.org/10.1021/ac00246a037>.
- Wong, S.P., Lim, W.H., Cheng, S.F., Chuah, C.H., 2012. Biological properties of sodium alkyl methyl ester sulfonate/alkyltrimethylammonium bromide surfactant mixtures. *Colloids Surf. B: Biointerfaces* 89, 48–52. <http://dx.doi.org/10.1016/j.colsurfb.2011.08.021>.
- Yamamoto, K., Oka, M., Murakami, H., 2002. Spectrophotometric determination of trace ionic and non-ionic surfactants based on a collection on a membrane filter as the ion associate of the surfactant with Erythrosine B. *Anal. Chim. Acta* 455, 83–92. [http://dx.doi.org/10.1016/S0003-2670\(01\)01560-4](http://dx.doi.org/10.1016/S0003-2670(01)01560-4).
- Yang, J., 2007. *Fate and Effect of Alkyl Benzyl Dimethyl Ammonium Chloride in Mixed Aerobic and Nitrifying Cultures*. (MS Thesis). Georgia Institute of Technology, Atlanta, GA.
- Ying, G.G., 2006. Fate, behavior and effects of surfactants and their degradation products in the environment. *Environ. Int.* 32, 417–431. <http://dx.doi.org/10.1016/j.envint.2005.07.004>.
- Yu, F., Ge, F., Zhou, W., Tao, N., Liang, Z., Zhu, L., 2013. Subcellular distribution of fluoranthene in *Chlorella vulgaris* with the presence of cetyltrimethylammonium chloride. *Chemosphere* 90, 929–935. <http://dx.doi.org/10.1016/j.chemosphere.2012.06.032>.
- Zhang, C., Tezel, U., Li, K., Liu, D., Ren, R., Du, J., et al., 2011. Evaluation and modeling of benzalkonium chloride inhibition and biodegradation in activated sludge. *Water Res.* 45, 1238–1246. <http://dx.doi.org/10.1016/j.watres.2010.09.037>.
- Zhu, M., Ge, F., Zhu, R., Wang, X., Zheng, X., 2010. A DFT-based QSAR study of the toxicity of quaternary ammonium compounds on *Chlorella vulgaris*. *Chemosphere* 80, 46–52. <http://dx.doi.org/10.1016/j.chemosphere.2010.03.044>.