



Human and Environmental Risk Assessment
on ingredients of Household Cleaning Products

Esterquats
Environmental Risk Assessment Report

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1. EXECUTIVE SUMMARY

Esterquats are a widely used class of cationic surfactants. They were introduced in the early 1980s when concerns were raised about the environmental profile of DHTDMAC (Di-Hardened Tallow Di-Methyl Ammonium Chloride) a fabric conditioner. Esterquats are similar to DHTDMAC except that ester links were introduced into the head-group of the molecules, making them more subject to degradation by hydrolysis and greatly facilitating biodegradation. Most, if not all, fabric conditioners marketed in Europe are now comprised of the three Esterquat groups, TEAQ (triethanol amine quat), DEEDMAC (diethoxyester dimethylammonium chloride), and HEQ ((Z)-2-hydroxy-3-[(1-oxo-9-octadecenyl)oxy]propyltrimethylammonium chloride). They combine a good environmental profile, especially in terms of ready and ultimate biodegradability (OECD criteria), with the structural features required for an effective fabric conditioner.

The total volume of Esterquat surfactants used in Europe is estimated to be 130,000 tonnes/year on an active matter basis [HERA, 2004].

Environmental assessment

A large environmental data set is available for esterquats. The ester quats under consideration are assessed according to a group approach, which is scientifically justified by close similarities with regard to physico-chemical properties, structural aspects, and a homogeneous ecotoxicity profile of relevant endpoints. On the environmental fate side this is based on standard biodegradation studies, advanced simulation studies of removal in treatment systems, and effluent monitoring data. On the environmental effects side acute as well as chronic single-species data are available tested with laboratory test water as well as natural river water.

To assess the Predicted Environmental Concentration (PEC), chemical removal in waste water treatment plants was determined from advanced simulation test data. Monitoring studies on sewage treatment plant effluents indicated that the exposure estimates in this assessment are in good agreement with each other.

The Predicted No-effect Concentration (PNEC) was based on chronic ecotoxicity.

Based on this higher tiers exposure and effects data, it could be shown that the use of esterquats in HERA applications (household detergents and cleaning products) results in risk characterization ratios less than one for the micro-organisms in a sewage treatment plant as well as aquatic, sediment and terrestrial organisms indicating no concern for any of these environmental compartments. _

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3. SUBSTANCE CHARACTERISATION

3.1 General substance information

Esterquat surfactants were introduced into the French market in the early 1980s and into the European market in the early 1990s when concerns were raised in Europe about the environmental profile of the predominant cationic surfactants used hitherto (Di-Hardened Tallow Di-Methyl Ammonium Chloride, or DHTDMAC). Esterquats are structurally similar to the unestrified dialkyl quats used previously except that ester links were introduced to link the alkyl chains to the head-group of the molecules, making them more accessible to hydrolysis and biodegradation.

Most, if not all, fabric conditioners marketed in Europe are now comprised of the three Esterquat types, TEAQ (triethanol amine quat), DEEDMAC (diethyloxyester dimethylammonium chloride), and HEQ (Hamburg Esterquat). They combine ready and ultimate biodegradability, with the structural features required for an effective fabric conditioner.

3.2 CAS No and Grouping information

There are several CAS numbers describing the different esterquats. A list is presented below in Table 1. This risk assessment does not address specific CAS numbers but is based on the environmental fate and effects of the product types. Esterquats are defined as reaction products of long chain fatty acids of different origin with substituted ammonium compounds..

Table 1: The CAS numbers of the esterquats under consideration in this risk assessment report

CAS No.	Substance name
	TEAQ
91995-81-2	Fatty acids, C ₁₀₋₂₀ and C ₁₆₋₁₈ -unsatd., reaction products with triethanolamine, di-Me sulfate-quaternized
93334-15-7	Fatty acids, tallow, reaction product with triethanolamine, diMe sulfate-quaternized
91032-11-0	Fatty acids, C ₁₂₋₂₀ , reaction products with triethanolamine, di-Me sulphate-quaternized
94095-35-9	9-octadecenoic acid (Z), reaction products with triethanolamine, di-Me sulphate-quaternized
85408-12-4	Octadecenoic acid, reaction products with triethanolamine, di-Me sulphate-quaternized
	DEEDMAC
67846-68-8	Dimethylbis[2-[(1-oxooctadecyl)oxy]ethyl]ammonium chloride
97158-31-1	Dimethylbis[2-[(1-oxohexadecyl)oxy]ethyl]ammonium chloride
	HEQ

3.3 Chemical structure and composition

3.3.1 Molecular description

The cationic surfactants used by the main manufacturers in Europe today are so-called *Esterquats* which are ammonium compounds having one or two long fatty ester chains.

Their basic structures contain one amine and two or three hydroxyl functions (triethanol amine, diethanol amine, or N,N-dimethyl-3-aminopropane-1,2-diol).

The hydroxyl functions are esterified with long-chained fatty acids, mostly tallow-based (C16–18) or similar carbon chains like Palmoil- based ones. The main reaction product is the dialkylester compound, next to that small amounts of the monoalkylester or monoalkyl- and trialkylester may be formed. The amine function is subsequently quaternised by methyl chloride or dimethyl sulfate."

Esterquats based on triethanol amine, diethanol amine or N, N-dimethyl-3-aminopropane-1, 2-diol are usually abbreviated by TEAQ (triethanol amine quat), DEEDMAC (diethoxyester dimethylammonium chloride), or HEQ (Hamburg Esterquat) respectively. The illustrative structures are shown in Figure 1.

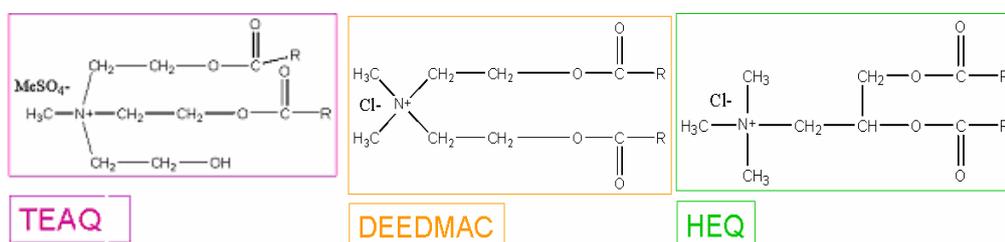


Figure 1: Graphical representation of the three esterquats

The alkyl chain length of the aliphatic chain varies from C16 to C18 and C18 double bond. For the TEAQ shorter chain lengths may be present-

Table 2: Typical carbon chain length distribution of the natural fats and oils used as starting materials in the manufacture of esterquats.

Substance Name	R = oleyl	R = tallow or unhardened	R = hydrogenated or hardened tallow
Typical carbon chain length	>80% C18 U _{1,2} *	±30% C16 S/ *	±30% C16

distrib.	<20% C16 S/ * balance C12, C14 C20	±65% C18 S/U ₁ * balance C12, C14, C20	±65% C18 balance C12, C14 C20
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*S = saturated, U₁ = mono unsaturated (one double bond), U₂ = di unsaturated (two double bonds).

3.3.2 Physico-chemical properties

Few data are available on the physico-chemical properties of the esterquats. All available data are provided in Table 3. Figures in bold are measured data. Other data are estimated using the EPISuite (v3.10) model. This model is one of the better models available to estimate physico-chemical properties and environmental end points [ECETOC, 2003]. For the calculated data a range is given which relates to the length of the carbon chain distribution of the esterquat.

Table 3: Carbon chain length related physico-chemical properties of Esterquat TEAQ, DEEDMAC and HEQ as calculated with EPISuite. The figures given in bold are measured data

		TEAQ	DEEDMAC	HEQ
Chain length	Unit	C16	C ₁₆₋₁₈ /Tallow	C ₁₈ /C ₁₈₌ ¹
Molecular weight	g/mol	613.01	643.12 – 699.23	691.16
Melting point	°C	395	/314 – 336	350
Boiling point	°C	818	717 – 771	809
Vapour pressure	Pa	<6*10 ⁻¹⁷	<6*10 ⁻¹⁵	/<6*10 ⁻¹⁷
log K _{ow}	-	6.86	3.1² /8.42 – 10.38	3.1² /9.29
Water solubility	mg/l	<0.001	<0.001	0.0028 / <0.001
log K _{oc}	-	8.20	11.78 – 12.84	10.15
BCF	-	70.8	13³ /70.8	13³ /70.8

1 is double bond

2 A log K_{ow} of 3.1 was measured for HEQ and this value will be used in the risk assessment for all esterquats.

3 No measured BCF data are available for esterquats. EPISuite calculates a BCF for cationic surfactants of 70.8. The measured BCF of the structurally very similar DODMAC of 13 [DODMAC, EU 2002] is included in the table as a worst-case. In contrast to DODMAC the esterquats will quickly hydrolyze which will result in a lower BCF for the esterquats.

4

Given the predicted high boiling points, it is most likely that the esterquats will decompose above 150°C.

a)

The octanol-water partition coefficient range is calculated using the log K_{ow} of 1.2 [Akzo Nobel, 1993] for didecyldimethyl ammonium chloride, measured in a GLP study, and applying the experimental

value adjusted method. This method calculates the log K_{ow} of the desired structure using the measured log K_{ow} of a similar substance as a starting point [EpiSuite, 2004].

The determination of octanol-water partition coefficient for surfactants and especially when they are poorly soluble is difficult because these substances tend to concentrate at the interface of both layers. It should be noted that the predictive power of the log K_{ow} of cationic surface-active substances for the partitioning to soil, sediment and sludge or its bioaccumulation potential is limited. The partitioning behaviour of a substance is independent from its stability and therefore despite the fact that DODMAC is far more stable in the environment than the esterquats, the measured DODMAC [DODMAC, EU 2002] values for both the partitioning to soil, sediment, sludge and the BCF are used in this risk assessment. However, the differences in vapour pressure, water solubility, melting point and boiling point between most of the esterquats will not influence the EUSES model- predicted partitioning behaviour significantly. It should be mentioned that while the calculation might be appropriate for estimating Kow for isolated (ie dissolved) molecules, molecular aggregates of various sorts are present at environmental temperatures and concentrations, and the measured Kow data are expected to reflect the partition properties of these aggregates

b)

The estimated water solubility is also influenced by this approach because the water solubility models use the log K_{ow} in their QSAR. The estimated water solubility is very low. The compounds form stable dispersions in water containing unilamellar or multilamellar particles such as vesicles, but also emulsions and micelles (surfactants). The size of the dispersed particles depends on temperature and the sheer forces applied when making the dispersion (e.g. by stirring or ultrasonication). The esterquats can also form mixed aggregates with other substances, e.g. anionic surfactants or humic substances [ECETOC, 1993].

c)

For ditallow ester of 2,3-dihydroxypropanetrimethyl ammonium chloride, a Hamburg Esterquat (HEQ), the vapour pressure, the octanol-water partition coefficient and its water solubility were measured. The data were not extracted from the original reports but from Waters *et. al.* [1991]. The vapour pressure was measured at an elevated temperature.

3.4 Manufacturing route and production/volume statistics

Market volume of all Esterquats used in detergent products is 130,000 Tons/year in the EU (based on the HERA inquiry [2004] to the major detergent producing companies). About 99% of this volume is covered by the use as fabrics conditioner.

3.5 Use application summary

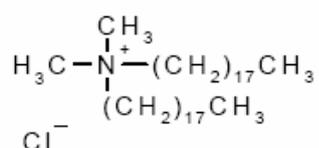
Almost all fabric conditioners marketed in Europe are now based on one of these three esterquat materials, TEAQ, DEEDMAC, and HEQ. They combine ultimate biodegradability, with the structural features required for an effective fabric conditioner.

4. ENVIRONMENTAL ASSESSMENT

Any environmental risk assessment is based on the comparison of exposure concentrations and effect concentrations. Structure-activity-relationship considerations are regarded to be an effective and valid tool in toxicology for comparing toxicological properties of structural closely related compounds. This is also recognized in the guidance documents for various HPV programmes and group approaches have been successfully used at the OECD level. According to the guidance document on the development of chemical categories in the HPV Challenge program from the EPA [Hefter *et al.*, 1999], a chemical category is a group of chemicals whose physico-chemical and toxicological properties are likely to be similar or follow a regular pattern as a result of structural similarity. The similarities should be based on the following:

- a common functional group
- the likelihood of common precursors and/or breakdown products
- an incremental and constant change across the category

When comparing the esterquats under consideration against above mentioned criteria, a grouping into one category is supported since all of above principles are fulfilled. The group approach for the esterquats under consideration is scientifically justified by close similarities with regard to physico-chemical properties, structural aspects, ecotoxicological considerations and a homogeneous ecotoxicity profile of relevant endpoints. Social-economic factors and animal welfare aspects also justify the grouping approach. Data gaps for sorption and bioaccumulation were filled with the measured values of DiOctadecyl DiMethyl Ammonium Chloride (DODMAC, CAS-No. 107-64-2) [DODMAC, EU 2002] for which a full risk assessment has been performed. Except for the intramolecular ester linkages, DODMAC exhibits large structural similarities with the esterquat surfactants (see figure of DODMAC below).



4.1 Environmental exposure assessment

4.1.1 Environmental fate

4.1.1.1 Partitioning

Esterquats are cationic aliphatic surface-active substances. Due to their cationic properties the environmental conditions like the pH, water hardness, humic acids or cation exchange capacity of sorbents will have a significant influence on the environmental fate of these substances.

Log K_{ow}

For substances that are ionogenic and surface active, such as the esterquats, the hydrophobicity is difficult to quantify by experimental measurement of the water/octanol partition because these substances tend to concentrate at the interface of the octanol and water layer. The calculated Log K_{ow} range, which relates to the length of the carbon chain distribution of the esterquat is presented in Table 3. The log K_{ow} as measured for HEQ is comparable with the measured log K_{ow} for DODMAC of 3.8 [DODMAC, EU, 2002]. Despite the fact that the experimental value adjusted method is used to calculate Log K_{ow} values they clearly differ from the measured values available. **The calculated values seem to be unrealistically high and therefore the measured log K_{ow} value of HEQ of 3.1 will be used in this risk assessment.**

Use of log K_{ow} for partition coefficients, distribution WWTP and bioconcentration factors

The predictive power of the log K_{ow} for the partitioning to soil, sediment and sludge or its bioaccumulation potential is considered to be limited, because the common K_{oc} derivations are not valid for surface active substances like the esterquats. Therefore the log K_{ow} values can not be used to derive the environmental distribution constants. Instead as a more reliable basis, the experimentally determined sorption and bioaccumulation figures of DODMAC are used.

4.1.1.1.1 Sorption

When esterquats enter the aquatic environment, it is likely that a large amount of the esterquats is not truly dissolved but is adsorbed onto suspended matter or included in vesicles together with other organics (e.g. humic acids, surfactants). The sorption behaviour of the esterquats in soils, sediment and sludge will be governed by two processes; partitioning to organic matter and ionic interaction with negatively charged particles. Under environmental conditions, sorption due to ionic interaction is expected to be the predominant process for cationic surfactants [Woltering *et al.*, 1989]. The higher the cationic exchange capacity (CEC) of the sorbent, the higher the sorption will be. Under these

conditions, the chain length of the esterquats is expected to be of minor importance for sorption/desorption behaviour onto soil, sediment or sludge. The sorption behaviour of Esterquats is expected to be comparable to that of DHTDMAC or DODMAC, due to structural similarities. Therefore, the value reported for DODMAC [DODMAC, EU 2002] of 10,000 l/kg dw is assumed to be a realistic estimate for the estimation of both $K_{p_{sed}}$ and $K_{p_{soil}}$ and has been taken in the absence of measured data for the Esterquats. With an assumed $K_{p_{susp}}$ of 10,000 l/kg and a concentration of 15 mg suspended matter per liter of river water about 87% of the esterquat would remain in the water phase. The sorption of the esterquats to sludge will be lower than to soil and sediment due to the lower CEC of sludge. Stearyl-labeled HEQ sorbed for 88 and 91% to settled liquor and between 90 and 92% for centrifuged settled mixed liquor taken from an STP [Unilever, 1997a]. Higher sorption was measured for raw sewage [Unilever, 1997b]. Unfortunately the available data in these reports are too limited to derive a reliable K_p . Based on the findings of these studies a significant amount of HEQ will be removed with the settled solids. For the assessment of the fate in the sewage treatment plant a value of 8,000 L/kg dw [DODMAC, EU 2002] is assumed to be realistic for raw sewage and settled sludge and of 5,000 L/kg dw [DODMAC, EU 2002] is assumed to be realistic for activated and effluent sewage sludge.

4.1.1.1.2 Volatilization

Volatilisation of a chemical from an aqueous compartment is described by its Henry's law constant, which can be calculated from the ratio of a chemical's vapour pressure and its water solubility. As no measured data are available for this calculation the values were calculated using EPIsuite. Considering the molecular structure and extremely low vapour pressure calculated for esterquats as presented in Table 3, volatilisation is expected to be negligible and therefore do not influence the environmental assessment.

4.1.1.1.3 Bioconcentration

The purpose of the estimation of bioconcentration is to assess whether there is any potential for the chemical to accumulate in organisms to a high degree and hence, for further transfer up the food chain. In the absence of measured data, the bioconcentration potential for fish, based on the lipid solubility characteristics of chemicals can be estimated based on QSARs (Quantitative Structure Activity Relationships) using BCFWIN (EPIsuite v3.12). BCFWIN is based on an empirical model that was 'trained' using an extensive data set of measured BCFs for a wide range of organic chemicals (including several surfactants) which included class-specific corrections [ECETOC, 2003]. While it is recognised that the BCFWIN programme has limitations for use of BCF, it is used here as supporting

evidence that the BCF for these substances is expected to be low. Moreover, the BCFWIN QSAR does not include metabolism so it can be considered a conservative estimate of BCF.

Based on the measured Log BCF value of DODMAC (also considered to be a conservative estimate for esterquats (Table 3), the esterquats have a relatively low bioaccumulation potential. The low bioavailability of the esterquats (due to rapid and strong sorption to negatively charged surfaces in the aquatic environment) in combination with the rapid (bio)degradation of the bioavailable fraction (mainly due to the high probability of hydrolysis of the ester bond), make high bioaccumulation factors of esterquats even more improbable [Comber *et al.*, 2003]. Hydrolysis will lead to production of the more soluble degradation products and hence rapid elimination. For the fish eating human and predator exposure route a conservative DODMAC-based BCF for fish of 13 L/kg wwt will be used in the risk assessment. For the worm eating predator exposure route a BCF of 2.5 L/kg wwt (EUSES, based on the BCF of 13 L/kg for fish) will be used in the risk assessment.

4.1.1.2 Biotic and abiotic degradability

4.1.1.2.1 Biodegradation under aerobic conditions

Biodegradation of the esterquats and their hydrolysis products has been extensively studied in ready biodegradability tests. DEEDMAC is readily biodegradable; approximately 80% of the theoretical carbon dioxide formation was produced in 28 days [Giolando *et al.*, 1995]. With activated sludge, biodegradation of DEEDMAC reached 90% after 28 days in the manometric respirometry test [Unilever, 1991a]). In a Sturm test, >85% of HEQ degradation could be accounted for as carbon dioxide [Unilever, 1990a; Waters *et al.*, 1991]. Puchta *et al.* [1993] reported in their review that TEAQ is readily biodegradable in the Closed Bottle test and the BODIS test. Based on the consistently high degree of biodegradability test results of all esterquat types each representing a mixture of individual homologue constituents, the esterquats fulfil the OECD criteria of ready biodegradability. As expected, very high removal percentages due to biodegradation and adsorption were obtained in SCAS tests (Giolando *et al.*, 1995; Unilever 1991^a). Biodegradation data are compiled in Table 4 and Appendix 1. Studies used in this assessment are termed “key studies”. These are valid studies which have the lowest endpoint values and which are used to in the risk assessment. Other data, which did not represent the most representative values were not reviewed in detail.

Kommentar [WL1]:
Puchta hat den einzigen Review-Artikel geschrieben, alle anderen sind primärquelle. Daher unser Vorschlag, das auch im text kenntlich zu machen.

Table 4: Compilation of data on the biodegradation and removal of esterquats.

Substance	Test	Result	Validity	References
DEEDMAC	Ready (OECD 301 B)	80%		Giolando <i>et al.</i> (1995)
DEEDMAC	Ready (OECD 301 F)	90%	2	Unilever (1991a)
HEQ	Ready (OECD 301 B)	>85%		Waters <i>et al.</i> (1991)
TEAQ	Ready (OECD 301 D)	>60%		Puchta <i>et al.</i> (1993)
HEQ	ECETOC anaerobic screening test	73%	1	Unilever (1992 ^a)
HEQ	ECETOC anaerobic screening test	83%		Unilever (1992 ^b)
TEAQ	ECETOC anaerobic screening test	101±13%	2	Henkel (1988)
DEEDMAC	Inherent (OECD 302 B) (¹⁴ C ₂ evolution measured (not standard))	75%		Giolando <i>et al.</i> (1995)
HEQ	Inherent (OECD 302 A)	100%	2	Unilever (1991 ^a)
DEEDMAC	Inherent (OECD 302 A)	>99.7%		Giolando <i>et al.</i> (1995)
TEAQ	CAS- Study (OECD 303)	>90%		Puchta <i>et al.</i> (1993)
TEAQ	Coupled Unit test	>90%		Puchta <i>et al.</i> (1993)
HEQ	CAS- Study (OECD 303)	98.3%	1	Unilever (1993)
DEEDMAC	River Die away test (no protocol)	t _{0.5} = 1-2 days	4	Giolando <i>et al.</i> (1995)
HEQ	River Die away test (no protocol)	t _{0.5} = 0.5-8 days	4	Waters <i>et al.</i> (1991)
DEEDMAC	Biodegradation in soil (OECD 304)	57–71%	2	Unilever, 1999
DEEDMAC	Biodegradation in soil	52-62%		Giolando <i>et al.</i> (1995)
DEEDMAC	Biodegradation in soil	t _{0.5} = 18 days		Giolando <i>et al.</i> (1995)
HEQ	Biodegradation in soil (OECD 304)	>50%	1	Unilever 1991b

The biodegradability of the hydrolysis products of esterquats has also been tested. Sufficient degradation was measured to conclude that fatty acids resulting from the hydrolysis of these esterquats are readily biodegradable [Mix Spagl, 1990]. 2,3-Dihydroxypropyltrimethylammonium chloride, the hydrolysis product of HEQ, was biodegraded to carbon dioxide, with a level of 80% in the Sturm test [Waters *et al.*, 1991]. The biodegradation percentages for the hydrolysis product of TEAQ, methyltri-hydroxyethylammonium salts spanned a range of 76 to 94% in the OECD 301B (CO₂ evolution) test [Puchta *et al.*, 1993].

Total mineralization is assumed when biodegradation percentages of >60% are achieved in ultimate biodegradability screening test. Additional evidence for complete degradation may be obtained through the investigation of biodegradation pathways. Although detailed metabolic studies are not available for all esterquat types, a general degradation pathway of esterquats can be formulated based on research with mixed cultures and radiolabeled chemicals. Activated sludge extensively degraded ¹⁴C-methyl labeled DEEDMAC during 28 days of incubation under environmental conditions [Giolando *et al.*, 1995]. Solid phase extraction of quaternary ammonium salts, followed by thin layer

chromatography with radiochemical detection, showed that the disappearance of DEEDMAC was sequentially followed by the appearance of tallow fatty acid (mono-)ester of di-2-hydroxyethyltrimethylammonium chloride and then di-2-hydroxyethyltrimethylammonium chloride. Degradation of DEEDMAC was not detected in abiotic controls suggesting that the hydrolysis of the ester bonds is primarily biologically mediated. These results are consistent with the hydrolysis and degradation of fatty acids groups preceding mineralization of di-2-hydroxyethyltrimethylammonium chloride [Giolando *et al.*, 1995]. The proposed pathway for DEEDMAC is presented in Figure 2. The hydrolysis of the ester bonds, giving rise to fatty acids and a polyalcohol quaternary ammonium salt, is probably a general biodegradation mechanism for esterquats. The quaternary ammonium alcohols such as dimethyldihydroxyethylammonium are degraded by other microorganisms.

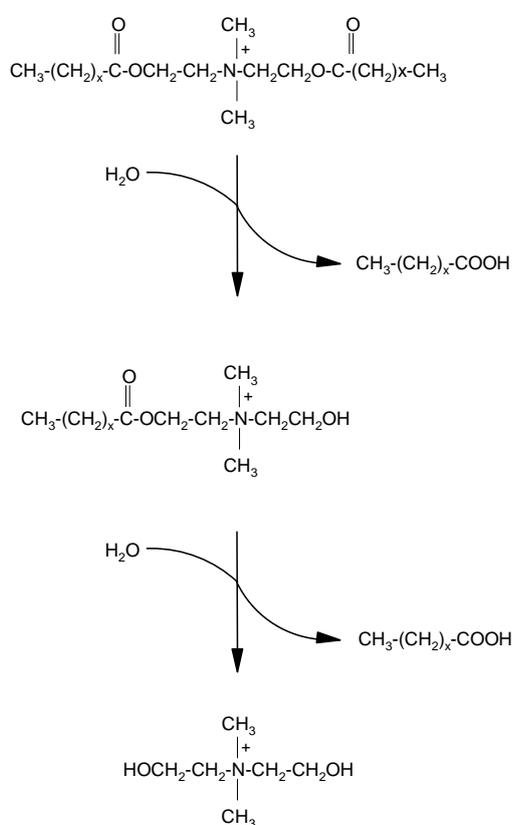


Figure 2: The microbial degradation pathway of DEEDMAC.

The use of three differently positioned ^{14}C -labeled HEQ samples provided information on the degradation pathway of HEQ. Incubation with river water demonstrated >80% of all ^{14}C -labeled HEQs was mineralized to carbon dioxide. In these die-away experiments under environmental conditions, the microorganisms degraded the labeled HEQs within 10 days. The rate of disappearance varied with the position of the radiolabel. HEQ labeled in the fatty acid moiety was rapidly degraded without a detectable lag period. Mineralization of ^{14}C -methyl and ^{14}C -dihydroxypropyl labeled HEQ was preceded by a lag period, followed by extensive degradation. The mineralization of ^{14}C -methyl and ^{14}C -dihydroxypropyl labeled HEQ following that of the ^{14}C fatty acid labeled HEQ suggests the removal of fatty acid moieties prior to the degradation of the quaternary ammonium compound [Waters *et al.*, 1991].

Hydrolysis of HEQ results in the formation of 2,3-dihydroxypropyltrimethylammonium salts. This salt is ultimately biodegraded by a *Pseudomonas putida* strain. This compound served as growth substrate, and surplus nitrogen was excreted as ammonium by the isolate [Kaech and Egli, 2001]. Complete degradation of dihydroxyethyltrimethylammonium salts was demonstrated with another pure culture [Kaech, 2002].

4.1.1.2.2 Biodegradation under anaerobic conditions

Cleavage of the ester bonds can also take place in the absence of oxygen. Fatty acids undergo biodegradation under anaerobic conditions. As expected TEAQ is easily biodegraded under anaerobic conditions (>70%) in a screening test performed according to the ECETOC method [Garcia *et al.*, 2000]. Very high biodegradation percentages ($101 \pm 13\%$) were also achieved with TEAQ in another ECETOC test (Henkel, 1988). The standard ECETOC test was also used to assess the anaerobic degradation of DEEDMAC. At day 60, 90% of the DEEDMAC-carbon was recovered as carbon dioxide and methane [Giolando *et al.*, 1995]. HEQ was biodegraded 73 and 83% at day 28 in ECETOC tests [Unilever, 1992^a; 1992^b]. All esterquats can therefore be classified as anaerobically biodegradable. These results from conservative screening tests indicate that esterquats will be degraded to a very high extent in digesters.

4.1.1.2.3 Hydrolysis

Esterquats were introduced into the market as alternative cationic surfactants to DHTDMAC. Esterquats are structurally similar except that ester links have been introduced into the head-group of the molecules, which have the quality that they are susceptible to rapid degradation by hydrolysis. Hydrolysis due to biotic and/or abiotic mechanisms is likely to be the most important reaction (although it may be actually not just one, but the sum of three reactions: acid, neutral and basic

hydrolyses) of organic compounds with water in aqueous environments and is a significant environmental fate process for these compounds.

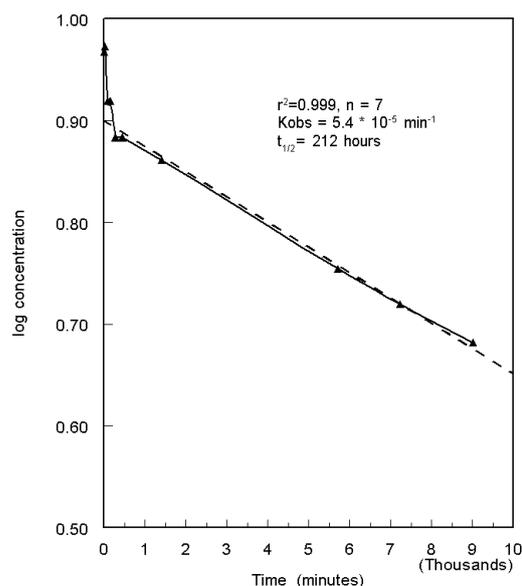


Figure 3

Figure 3. Rate of hydrolysis of DEEDMAC at 25°C and pH 8.2 in Dutch Standard Water from Akzo Nobel (1992)

Esterquats are a class of quaternary ammonium compounds characterized by hydrophobic parts of the moieties “R” linked to the charged head group via *ester bonds* $R-C(O)O^-$ or $ROC(O)^-$ and are therefore expected to be subject to degradation by chemical or biological hydrolysis. The half-life of DEEDMAC (10 mg/l) in Dutch Standard Water (synthetic surface water, pH 8.2) at 25°C, was 212 hours due to chemical hydrolysis (Figure 3: [Akzo Nobel, 1992]). During hydrolysis tests the DEEDMAC samples were stabilized by the addition of 1% v/v acetic acid [Akzo Nobel, 1992]. This rate corresponds well with a half-life of 330 hours found in an abiotic control of a biodegradation test performed at 20°C. In contrast, the measured half-life of TEAQ was less than 5 hours. After 5 hours

and 25 minutes at pH 7 and 20°C more than 99% of a 45 ppm solution was hydrolyzed. No measured half-life for HEQ was available although EPIsuite calculates a half-life even shorter than for TEAQ. The hydrolysis rates of Esterquats depend on the pH of the test system. Under acidic conditions (pH<4), they are not susceptible to hydrolysis. The observed difference in the hydrolysis rate as measured for DEEDMAC and TEAQ cannot be caused by the orientation of the ester bond because they are all of the *ROC(O)*- type. It is probably due to the difference in test conditions like the pH.

4.1.1.2.4 Photodegradation

Due to the very low emissions of the esterquats to air the extent of photodegradation in air is of low relevance for the environmental fate of this class of chemicals.

4.1.2 Removal in Sewage Treatment Plants

4.1.2.1 Removal in sewers

It is known that surfactants can be subject to high levels of in-sewer removal (Matthijs et. al., 1995). The degradation of DEEDMAC was examined through laboratory die-away studies (Matthijs et. al., 1995) and rapid disappearance was observed with a half-life in the order of hours (between 8 and 10 hours).

The difference between the expected raw sewage concentration (calculated by EUSES, 2004 and on the basis of data in table 6, considering the tonnage used in household applications of 130,000 tons/year) and the measured raw sewage concentrations from monitoring studies (table 5) demonstrate that the concentrations of the esterquats can be significantly reduced in the sewer, resulting in a rapid reduction of the environmental loading.

In addition to the removal during its travel in the sewer, partial degradation or removal of esterquats is also expected to occur before reaching the sewer pipeline due to:

1. Degradation in the wash process. Due to their ester linkage, hydrolysis in the presence of water is an important decomposition reaction for esterquats. In neutral to alkaline conditions (which are the typical wash conditions), the esterbond hydrolyzes quickly to yield fatty acid and a small hydrophilic quaternary. The diester quats hydrolyze in the same way in which case 2 fatty acid molecules are released.

2. Deposition onto textiles. A study on the removal of quats on treated fabric (Steiger, et. al., 2002) showed that a part of hydrogenated TEAQ remained on the fabric after washing. Therefore, it is expected that a part of the esterquats present as fabric conditioners will not reach the sewer system.

The evidence of removal in the wash and sewer systems was confirmed by Waters et. al., 2000. Comparisons of estimated and measured influent concentrations of STPs (see table 5) indicated that >50% of HEQ is already removed in the wash and sewers.

Based on the above listed arguments, a 50% in sewer removal is considered justified and taken into account in the PEC calculations of the HERA risk assessment.

4.1.2.2 Modelling

Based on the ready biodegradability (according to OECD criteria), the extremely low vapour pressure and the relatively strong sorption of the esterquats to sludge, Simpletreat (STP module in EUSES) predicts a removal by sorption in an STP of 55% (identical to DODMAC) and a removal by biodegradation of 38.3% resulting in a calculated total removal of 93.3%.

4.1.2.3 Sewage treatment plant Simulation tests

The removal of esterquats and their degradation products has been studied using continuous activated sludge (CAS) tests. High removals of all three esterquats and their biodegradation products are expected during sewage treatment. Indeed, in CAS studies very high substance removals of >98% for HEQ and DEEDMAC [Waters *et al.*, 1991; Giolando *et al.*, 1995; Unilever, 1993] and of >90% for TEAQ [Puchta *et al.*, 1993] were found. High degrees of biodegradability results obtained for all esterquats justify the assumption that the removal of all esterquat types is comparable.

4.1.2.4 Monitoring studies in STPs

Confirmation of high removal percentages obtained in CAS tests is provided by two monitoring studies showing very low levels of esterquats in effluents. An overview of the concentrations of the esterquats found in influents, and effluents of sewage treatment plants (STPs) and removal percentages calculated are given in Table 4. The data are obtained from properly operated conventional activated sludge treatment plants in the Netherlands and Germany. The removal efficiency of HEQ was higher than 98% and the corresponding effluent values were determined to be <10 µg/L [Waters *et al.*, 2000]. Radke *et al.* [1999] also reported very high removal percentages i.e. >99 % for HEQ and DEEDMAC in a STP in Bayreuth, Germany (Table 5). These monitoring studies support the assumption that at least 98 % esterquat removal occurs in properly operated biological treatment systems. The concentrations of the typical primary biodegradation intermediates of the esterquats i.e.

methyltrihydroxyethylammonium salts, dimethyldihydroxyethylammonium salts and 2,3-dihydroxypropyltrimethylammonium salts in effluents of STPs ranged from 0 to 4 µg/L (Table 5).

Table 5: Concentrations of esterquats (grey) and their intermediates (methyltrihydroxyethylammonium salts (MTEA), dimethyldihydroxyethylammonium salts (DMDEA), 2,3-dihydroxypropyltrimethylammonium salts (DHPTMA)) in influents and effluents of STPs and removal percentages calculated [Radke *et al.*, 1999; Waters *et al.*, 2000].

STW site (country)	Compound	Influent (µg/L)	Effluent (µg/L)	Removal (%)
Bayreuth (G)	HEQ and DEEDMAC	140 ± 4.3	0.40 ± 0.04	>99
Kralingseveer (NL)	HEQ	325 ± 35	7.5 ± 1.1	98
Horstermeer (NL)	HEQ	240 ± 16	5.2 ± 1.0	98
Kralingseveer (NL)	DHPTMA	103-109 ^a	0.9-1.4	
Kralingseveer (NL)	MTEA	116-230 ^a	0.5-1.8	
Kralingseveer (NL)	DMDEA	51-54 ^a	0-2.9	
Horstermeer (NL)	DHPTMA	116-128 ^a	0.7-2.2	
Horstermeer (NL)	MTEA	246-272 ^a	1.7-3.9	
Horstermeer (NL)	DMDEA	58-63 ^a	0.1-3.0	

^a Predicted concentration in raw sewage calculated from per capita use, population served and prevailing plant flows. These calculations were based on the estimated market shares of the substances. The accuracy is therefore limited and the data should rather be considered as semi-quantitative estimates.

In the absence of actually measured data for the contribution of sorption to the removal in STPs, removal is estimated according to the Simpletreat model i.e. 55%. The total removal is 98% and removal by biodegradation is therefore 43% as a worst-case.

4.1.2.5 Digesters

Esterquats are predicted to sorb strongly to sludge. The surplus sludge originating from municipal waste water treatment plants is commonly treated anaerobically in digesters. Esterquats will biodegrade under anaerobic conditions prevailing in digesters. As fast and extensive ultimate biodegradation by digested sludge has been demonstrated for esterquats (see 4.1.1.2), **for the exposure assessment 90% primary degradation is assumed to occur in digesters.**

4.1.3 Biodegradation in soils, surface waters and sediments

Low levels of undegraded esterquats may reach the soil compartment via agricultural use of digester sludge. Degradation of DEEDMAC in sludge amended soils was investigated by Giolando *et al.* [1995]. The evolution of ¹⁴CO₂ was monitored for up to 142 days. The extent of mineralisation ranged

from 52 to 72% and the half-life for mineralisation was 14-18 days [Giolando *et al.*, 1995]. The intermediate of DEEDMAC was more than 67% degraded over 112 days in two soils [Unilever, 1999]. DEEDMAC and its intermediate can therefore be classified as biodegradable in soils. Over 50% of carbon of three differently labeled ¹⁴C-labeled HEQ samples added to soil was recovered as carbon dioxide within 10 weeks [Unilever, 1991a]. The rate of disappearance did only slightly vary with the location of the radiolabel strongly indicating degradation to carbon dioxide, water and biomass. This result strongly suggests that the half-life for mineralisation of HEQ in soil is 2 to 3 weeks. Comparably high biodegradability test results of all esterquats under aerobic and anaerobic conditions justify a **half-life of 18 days in soils for all esterquats.**

Based on their ready biodegradability, a default half-life value of all esterquats in surface waters of 15 days may be used as proposed by the TGD. However, it is obvious that the removal of the parent material (primary biodegradation) representing the basis for the exposure assessment within the environmental risk assessment process is at least as fast and effective as the ultimate biodegradation of these chemicals. Therefore, mineralisation kinetics data of esterquats obtained in river die-away tests can be considered a very conservative estimate of the removal rate of the esterquats in surface waters. The biodegradation study of (¹⁴C-methyl-) radiolabelled DEEDMAC in a river die-away test system revealed a mineralisation half-life time of 1.1 days (Giolando *et al.*, 1995). A similar investigation using HEQ radiolabelled in different positions of the molecule revealed mineralisation half-lives of <1 day (¹⁴C-stearyl-labelled) - ca. 8 days (¹⁴C-methyl) (Waters *et al.*, 1991). The 8 day result was found in a study with radio-labeled head-group, while degradation of the unlabeled chain would actually determine the primary biodeg rate. This allows to conclude that the half-life of the parent materials will be rather in an order of hours instead of days. This conclusion is supported by the observation that the primary biodegradation kinetics of another surfactant, LAS, in rivers corresponds to a half-life of 1-3 hours (Takada *et al.*, 1992; Schröder, 1995) while the mineralisation half-life in a river die-away study was 18 h (HERA, 2004: RA of LAS). Based on these facts, a conservative half-life of 16 h will be used for the esterquats in this HERA risk assessment.

No concrete data for the biodegradation kinetics of esterquats in sediments are available. A conservative estimate can be based on the approach suggested by the TGD (2003), i.e. using the half-life time for aerated soils. This approach is justified due to the ready biodegradability (according to the OECD criteria), as well as the good anaerobic biodegradability. **Therefore, a half-life of 18 days in sediments for all esterquats is used as a conservative estimate.**

4.1.4 PEC calculations

The environmental concentrations are calculated using the HERA EUSES input spreadsheet version 2.3 (18 July 2000) as developed by Geert Boeije (P&G) in the default detergent setting [HERA, 2004] but assuming 80% of the consumers to be connected to the sewer (according to the new TGD 2003), in combination with EUSES 2.0. The essential input data for these calculations are presented in Table 6 below. These data are based on the available data as discussed previously in this report following a realistic worst-case approach. The exposure assessment is performed only once and not for the different esterquats separately, because the essential datapoints like the environmental half-life, removal in a STP, partitioning behaviour are for all esterquats chosen to be identical.

Table 6: Essential Input data for PEC calculations

	Unit	Value	References
Use volume in the EU	Tons/year	130000	§ 3.3
Regional volume of substance (6.5% of use volume)	Tons/year	8450	HERA (2004)
Industrial category	-	5: Personal domestic use	HERA (2004)
Use category	-	9: Cleaning/washing agent	HERA (2004)
Molecular weight (TEAQ C ₁₆)	g/mol	669.11	-
Kd soil, sediment	L/kg	10,000	§ 4.1.1.1
Kd raw sewage, settled sludge	L/kg	8,000	§ 4.1.1.1
Kd activated, effluent sewage sludge	L/kg	5,000	§ 4.1.1.1
Half-life surface water	Hours	16	§ 4.1.3
Half-life soil	Days	18	§ 4.1.3
Half-life bulk sediment	Days	18	§ 4.1.3
Half-life in air	Days	0.25	§ 4.1.1.2
Fraction removed in sewer	-	0.5	§ 4.2.1
Fraction release to waste water	-	1	HERA (2004)
Fraction of the main local source	-	7.5* 10 ⁻⁴	HERA (2004)
Fraction degraded in STP	-	0.43	§ 4.1.2
Number of emission days	D	365	HERA (2004)
Removal in STP	%	98	§ 4.1.2
Removal by sorption	%	55	§ 4.1.2
Removal in digester	%	90	§ 4.1.2
Direct emission to surface water (regional)	%	20	TGD (2003)

The environmental half-lives as presented in Table 5 were used to override the default values. The resulting PEC values for the local and regional scenario are presented in Table 7. The PEC values are calculated based on wet weight (wwt) and converted to dry weight (dwt) using the conversion factors wet-dry for soil and sediment of respectively 1.13 and 2.6 (EUSES defaults).

Table 7: Calculated environmental concentrations of esterquats

	Unit	Local scenario	Regional scenario
Concentration influent	mg/l	4.34	-
Concentration effluent (= PEC _{stp} microorganisms)	mg/l	0.087	-
Concentration dry sewage sludge	mg/kg	604	-
PEC in surface water (total)	mg/l	0.0105	0.0018
PEC in surface water (dissolved)	mg/l	0.0091	0.0016
PEC in sediment (total)	mg/kg wwt	19.9	0.425
PEC in agricultural soil (total) 30 days	mg/kg wwt	0.53	0.011
PEC in agricultural soil (total) 30 days	mg/kg dwt	0.60	0.012

4.2 Environmental effects assessment

4.2.1 Ecotoxicity

Ecotoxicity studies are available for all three esterquat types under consideration, DEEDMAC, TEAQs and HEQs, all carried out above the level of solubility. The database provides information on both acute and chronic toxicity and some work has also been performed on breakdown products of parent compounds. Validity ratings based on Klimisch scores have been included in the tables for all studies validated during the compilation of this risk assessment. Studies used in this assessment are termed “key studies”. These are valid studies which have the lowest endpoint values and which are used to generate a PNEC. Other data, which did not represent the most conservative values were not reviewed in detail.

Data are also available to assess the ecotoxicity of the principal breakdown products or metabolites of the esterquat classes, DEEDMAC, TEAQs and HEQ (see Appendix I). Several data are available for the principal TEAQ primary degradation product, MTEA and for the HEQ degradation by-product, DHPA. An acute toxicity effect concentration of these substances was observed several orders of magnitude above that of the parent compounds. Data are also available for two other major degradation products of esterquats, the DEEDMAC monoester, EEDMAC, and the HEQ 3 monoester. Toxicity values for these substances appear to be similar to those found for the parent compounds. Moreover, Waters *et al.* [1991] showed that primary degradation of the Hamburg esterquat, to the fatty acid was rapid. This suggests that at least for the algae studies, in this case the most sensitive species, the major degradation product was present during some or all of the test period. However, Waters *et al.* considered that degradation would be too rapid for significant concentrations of either the 2- or 3-monoester intermediate to build up so the relevance of the toxicity data of the 3-monoester intermediate is therefore very limited. As the DEEDMAC algae study used for this risk assessment

was found to have a lower NOEC at 72 h than 96 h, it can be assumed that the substance degraded to the by-product during the study and toxicity of the degradation product is also taken into account. Given the lower or at worst equal toxicity of the metabolites and their biodegradability, the conclusion can be drawn that the HERA RA does not need to address them further in this environmental risk assessment.

4.2.1.1 Ecotoxicity – aquatic: acute test results

Acute data for TEAQs, DEEDMACs and HEQs are provided in Appendix I. Valid data are available for the three trophic levels required for the base set for all the classes of compound. In order to improve comparability and clarity, only 72 h values were used for algae data and the effects concentrations based on biomass are not used, in accordance with the recommendations of the Technical Guidance Document. In some cases the data were recalculated in order to provide these values. The lowest acute toxicity value found is the 72 h ErC₅₀ of 0.93 mg/l for *Selenastrum capricornutum* (now known as *Pseudokirchmeriella subcapitata*) for DEEDMAC [Akzo Nobel, 1991b]. TEAQs had a 72 h ErC₅₀ of 3.1 mg/l performed using the algal species, *Scenedesmus subspicatus* [KAO Corporation, 1990]. The lowest HEQ value was the 96 h LC₅₀ for *Oncorhynchus mykiss* of 7 mg/l [Unilever, 1990c]. Valid EC₅₀ data on faunal species tend to lie between 1 and 10 mg/l supporting the supposition that acute toxicity for these substances is of the same order for the three esterquat groups.

However, based on measured values for HEQ data, the esterquats appear to have a real water solubility in the low µg/L range. These water solubility data are supported by calculations from EPIsuite [2004]. The effects found in the acute studies may not only be due to toxicity of the parent compound but could also be attributed to physical effects (e.g. micelle or lamellar formation leading to direct contact of the undissolved substance with the delicate gill membranes of the organisms and eventual suffocation) . The more soluble, transiently present intermediates may also have contributed to the toxicity observed in certain cases.

4.2.1.2 Ecotoxicity – aquatic: chronic test results

A full set of valid chronic studies based on Klimisch scores (key studies are noted) are also available for TEAQs, DEEDMACs and HEQs and are summarized in Table 8.

Five key studies are available, including an ELS fish study on DEEDMAC with a NOEC of 0.63 mg/l [Procter & Gamble, 1996b] and three 21 d daphnid reproduction studies with a NOEC of 1 mg/l (for

HEQ [Unilever, 1991c], DEEDMAC [Procter & Gamble, 1996a] and TEAQs [Procter & Gamble, 1999a]) all with a Klimish score of 1. However, the lowest value with high reliability is the TEAQ algae study with a 72 h ErC₁₀ of 0.43 mg/l (KAO Corporation, 1990) based on nominal concentrations. The value is supported by the 72 h ErC₁₀ data from the DEEDMAC algae study which, recalculated from the original 96 h value, is only slightly greater than the TEAQ value (0.48 mg/l) [Akzo Nobel, 1991b]. No analytical monitoring was undertaken for either of these studies so they are considered reliable with restrictions. There is approximately a factor of 2 difference between the algae results and the next lowest NOECs from fauna (the TEAQ, DEEDMAC and HEQ daphnid reproduction studies, all with a NOEC of 1 mg/l). For this reason and supported by the comparability of the acute toxicity data, it is considered that read across between TEAQs, HEQ and DEEDMAC is justified and the esterquats can be taken as a group for the purposes of aquatic risk assessment.

Consideration of the Bulk Approach

For risk assessment it is essential to compare results from studies which have been conducted in a similar way. A number of EU risk assessments on cationic surfactants (EU risk assessment on Primary amines), use data for the effects chapter based on the bulk approach. This method is considered more appropriate for compounds that sorb strongly to negatively charged surfaces such as clays and suspended solids than the approach recommended which considers partitioning based only on hydrophobic interactions. The bulk approach uses effect values from studies based on nominal concentrations and which have been performed in natural river water containing a known quantity of suspended solids. In this case the approach could not be used as the relative proportion of adsorption to suspended solids cannot be readily calculated from the available data.

Thus nominal value of the 72h ErC₁₀, 0.43 mg/l, is considered to be a reasonable estimate of the lowest toxicity value despite the lack of analytical monitoring because this study was performed using synthetic medium. Using the more environmentally relevant bulk approach the ErC₁₀ result would be expected to be higher than this. **The value of 0.43 mg/l is used for a conservative calculation of the PNEC.**

The acute to chronic ratios of key studies is 2.4 times for daphnids and 4.4 times for fish based on measured values, and EC₁₀ to EC₅₀ ratio for the algae study is 2.2 times, suggesting that specific modes of action or unexpected long term effects are unlikely.

Table 8a: TEAQ chronic aquatic data

CAS no.	Substance (R-group description)	Species	Endpoint	Test type*	Result (mg a.i./l)	Validity	Reference
93334-15-7	Tallow reaction products (C16-18)	<i>Scenedesmus subspicatus</i>	72 h NOEC	N; S; L	0.43	2 Key	KAO Corporation, 1990
91995-81-2	C10-20 & C16-18 unsaturated	<i>Daphnia magna</i>	21 d NOEC	M; D; R	1 (N)	1 Key	Procter & Gamble, 1999a
91995-81-2	C10-20 & C16-18 unsaturated	<i>Pimephales promelas</i>	34 d NOEC	M; D; R	8 (N)	1	Procter & Gamble, 1999b

* N = nominal; M = measured; S = static; D = flow-through; R = river water; L = synthetic medium (N) = nominal values presented

Table 8b: DEEDMAC chronic aquatic data

CAS no.	Substance	Species	Endpoint	Test type*	Result (mg a.i./l)	Validity	Reference
67846-68-8 / 97158-31-1	DEEDMAC	<i>Selenastrum capricornutum</i>	72 h ErC10	N; S; L	0.48	2	Akzo Nobel, 1991b
67846-68-8 / 97158-31-1	DEEDMAC	<i>Daphnia magna</i>	21 d NOEC	M; D; R	1.0	1 Key	Procter & Gamble, 1996a
67846-68-8 / 97158-31-1	DEEDMAC	<i>Pimephales promelas</i>	35 d NOEC (post fry mortality)	M; D; R	0.63 (N)	1 Key	Procter & Gamble, 1996b

* N = nominal; M = measured; S = static; SS = semi-static; D = flow-through; R = river water; L = synthetic medium; (N) = nominal values presented

Table 8c: HEQ chronic aquatic data

CAS no.	Substance	Species	Endpoint	Test type	Result (mg a.i./l)	Validity	Reference
NI	HEQ #	<i>Scenedesmus subspicatus</i>	28 d NOEC	M; S; L	1.8	1	Unilever, 1991h
NI	HEQ #	<i>Daphnia magna</i>	21 d NOEC	M; SS; L	1.0	1 Key	Unilever, 1991c
NI	HEQ #	<i>Oncorhynchus mykiss</i>	28 d NOEC	M; SS; L	≥3.5	1	Unilever, 1991d

NI = no information; M = measured; S = static; SS = semi-static; L = synthetic medium

= 2,3-Bis(C12-C22 Acyloxy)-N,N,N-trimethyl-1-propan-ammonium chloride (the alkyl groups are tallow derived)

4.2.1.3 Terrestrial: acute test results

Terrestrial data are available for TEAQ and DEEDMAC (see Table 9a & b) but not for HEQ. All data are considered valid for risk assessment purposes. While no effects were observed at the highest concentration tested, the DEEDMAC values are not directly comparable with TEAQs as the highest concentration tested of the former was only 47.4 mg a.i./kg dw. Nevertheless, based on available data,

as no effect of TEAQ was observed at 1000 mg a.i./kg and as the aquatic toxicity values are considered comparable for all esterquat types, the EC₅₀ of esterquats for terrestrial studies is considered >1000 mg/kg and this figure is used for the PNEC derivation.

Table 9a: TEAQ acute terrestrial data

CAS no.	Substance	Species	Endpoint	Test type*	Result (mg a.i./kg)	Validity	Reference
91995-81-2	C10-20 & C16-18 unsaturated	<i>Avena sativa</i>	22 d EC ₅₀ ; growth	N; soil	>1000	2	Henkel KgaA a
91995-81-2	C10-20 & C16-18 unsaturated	<i>Eisenia fetida</i>	14 d EC ₅₀ mortality, weight	N; soil	>1000	2	Henkel KgaA a

* N = nominal

Table 9b: DEEDMAC acute terrestrial data

CAS no.	Substance	Species	Endpoint	Test type*	Result (mg a.i./kg)	Validity	Reference
67846-68-8 / 97158-31-1	DEEDMAC	<i>Avena sativa</i>	17 d NOEC	N; soil	>47.4	2	Procter & Gamble, 1993d
67846-68-8 / 97158-31-1	DEEDMAC	<i>Lactuca sativa</i>	17 d NOEC	N; soil	>47.4	2	Procter & Gamble, 1993d
67846-68-8 / 97158-31-1	DEEDMAC	<i>Eisenia fetida</i>	14 d EC ₅₀ (weight and mortality)	N; soil	>47.4	2	Procter & Gamble, 1993c

* N = nominal

4.2.1.4 Terrestrial: chronic test results

No data available.

4.2.1.5 Micro-organisms

Five valid tests on micro-organisms were found. Two for TEAQ, one for DEEDMAC and two for HEQ (see Table 10 a, b & c). In all cases EC₅₀s were greater than 48.6 mg/l and EC₁₀s and NOECs were at least 35 mg a.i./l. For all esterquat classes, toxicity to micro-organisms is of the same order. The lowest endpoint used for risk assessment for acute effects in the sewage treatment plant was the 30 min EC₁₀ of 35 mg/l and this figure is used for the PNEC derivation.

Table 10a: TEAQ micro-organism data

CAS no.	Substance	Species	Endpoint	Test type*	Result (mg a.i./kg)	Validity	Reference
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91995-81-2	C10-20 & C16-18 unsaturated ⁺	<i>Pseudomonas putida</i>	30 min EC ₁₀	N; S	35	2	Henkel KGaA, 1998b
93334-15-7	C16-18 [#]	Raw and digester sludges mixed 2:1	16 h NOEC	Anaerobic inhibition	>3.75% w/w dried sludge	2	Unilever, 1989c

* N = nominal; S= static

⁺ = Bis(acyloxyethyl)hydroxyethyl methylammonium methosulfate

[#] = Di(C16-C18 alkyloyl-oxyethyl)methyl-hydroxyethyl ammonium methosulphate

Table 10b: DEEDMAC micro-organism data

CAS no.	Substance	Species	Endpoint	Test type*	Result (mg a.i./kg)	Validity	Reference
67846-68-8/ 97158-31-1	DEEDMAC	Activated sludge	3 h NOEC	N; S	48.6	2	Procter & Gamble, 1993b

* N = nominal; S= static

Table 10c: HEQ micro-organism data

CAS no.	Substance	Species	Endpoint	Test type	Result (mg a.i./l)	Validity	Reference
NI	HEQ #	<i>Pseudomonas putida</i>	16 h NOEC	Growth inhibition	>130	1	Unilever, 1991g
NI	HEQ #	Raw and digester sludges mixed 2:1	16 h NOEC	Anaerobic inhibition	>2.5% w/w dried sludge	1	Unilever, 1991f

2,3-Bis(C12-C22 Acyloxy)-N,N,N-trimethyl-1-propan-ammonium chloride Sediment data

No data on sediment dwelling organisms were available for any of the esterquats.

4.2.2 Effect assessment: PNEC calculations

The PNECs derived are considered to adequately cover the group of esterquats:

4.2.2.1 Aquatic PNEC

Using the method described in the TGD, sufficient chronic data are available to use the lowest NOEC divided by 10.

$$PNEC_{aquatic} = 0.43/10 = 43 \mu\text{g/L}$$

4.2.2.2 Sediment PNEC

In the absence of measured data for sediment dwelling organisms the TGD recommends that a provisional PNEC_{sediment} can be calculated from PNEC_{surface water} using the equilibrium partitioning (EP) equation as given in the TGD [TGD, 2003, Part II: eq. 70 pg. 113]:

$$PNEC_{\text{sediment}} = \frac{K_{\text{susp-water}}}{(\text{RHO}_{\text{susp}})} * PNEC_{\text{water}} * 1000$$

Table 11a: PNEC derivation for organisms living in the sediment compartment.

	Unit	Value
PNEC Aquatic organisms	µg/L	43
$K_{\text{susp-water}}$	m^3/m^3	2500
Rho_{susp}	kg/m^3	1150
PNEC sediment organisms (equilibrium partitioning method)	Mg/kg wwt	93.5

For compounds with a log Kow greater than 5 or with a corresponding adsorption or binding behaviour, e.g. ionisable substances, the equilibrium method is used in a modified way [TGD 2003]. In order to take uptake via ingestion of sediment into account, the $\text{PEC}_{\text{sed}}/\text{PNEC}_{\text{sed}}$ ratio should be increased by a factor of 10.

It is recognized that no directly applicable QSAR is available in the TGD which relates log Kow with log Koc. However, in the absence of such a relationship, the “predominantly hydrophobics” QSAR in the TGD [TGD, 2003, Part III: Table 4 pg. 26] was used for esterquats to calculate the Kd that corresponds with a log K_{ow} of 5. Accordingly, a $\text{PNEC}_{\text{sediment}}$ would result which is by a factor of 10 lower than the originally calculated value (Table 11a). However, it must be taken into account that the scientific justification for increasing the $\text{PEC}_{\text{sed}}/\text{PNEC}_{\text{sed}}$ ratio, i.e. implying the presence of a metabolically stable compound in the biota, does not apply to esterquats. Based on the existing information about the high susceptibility of the ester bonds in these compounds to biotic and abiotic hydrolysis and considering the abundance of hydrolytic enzymes in the digestive tract of sediment organisms (Mayer *et al.*, 1997), it can be excluded that the parent structure of esterquats will prevail in biota. The soundness of this assumption is supported by the existing knowledge about the metabolism of esterquats (HERA internal report). It should also be mentioned that the EP method is based on sorption of organic substances to organic matter by weak binding such as van der Waal’s forces. In the case of esterquats, binding is by ionic interaction with inorganic matter (especially clay) which is stronger than van der Waal’s forces (Schwarzenbach *et al.*, 2003). Currently the exact extent of desorption in the gut of adsorbed cationics to clays is not yet known but preliminary research suggests that much of the cationic surfactant is not desorbed by invertebrates such as *Caenorhbditis elegans*

(which live in both soils and sediments) in natural soils or soils tested under sediment conditions [Thomas *et al.*, 2005].

Taking the discussed esterquat properties and their implications for the presence and effects in sediment biota into account, the application of an assessment factor of 10 is scientifically not justified. The use of the EP method is recognized in the TGD to be only considered as a screening approach to generating a PNEC_{sediment} in the absence of measured data. Where measured data are available these should prevail in the risk assessment. Therefore, in this risk assessment we use read across values from DODMAC. Structural similarities between DODMAC and the esterquats, in particular considering DEEDMAC, and the comparable effects on aquatic organisms (see Tables 11b, 11c, 11d) suggest that these data can be used in the assessment of the sediment compartment with higher confidence that the assessment is more realistic, than when using a value generated using the EP method. There is additional confidence in the data since these are from a published EU risk assessment and as such have already undergone scrutiny. The EQs might be slightly more bioavailable but are on the other hand also considerably more rapidly degraded than DODMAC [DODMAC, EU 2002].

Table 11b: Selected comparable key algae data for DODMAC [DODMAC, EU, 2002] and esterquats : additional to data already in Tables 8a, b and c

CAS no.	Substance	Purity	Species	Endpoint	Test type*	Result (mg a.i./l)	Validity	Reference
NI	DODMAC	NI	<i>S. capricornutum</i> (<i>P. subcapitata</i>)	96hr EbC50	N; L	0.46	n.a.	DODMAC EU, 2002
NI	DODMAC	NI	<i>S. capricornutum</i> (<i>P. subcapitata</i>)	96hr NOEC	N; L	0.16	n.a.	DODMAC EU, 2002
NI	DODMAC	NI	<i>S. capricornutum</i> (<i>P. subcapitata</i>)	96hr EbC50	N; R	1.17	n.a.	DODMAC EU, 2002
NI	DODMAC	NI	<i>S. capricornutum</i> (<i>P. subcapitata</i>)	96hr NOEC	N; R	0.6	n.a.	DODMAC EU, 2002
NI	DODMAC	NI	<i>S. capricornutum</i> (<i>P. subcapitata</i>)	96hr EC50	N; L	0.06	n.a.	DODMAC EU, 2002
93334-15-7	TEAQ Tallow reaction products	85% in 15% propan-2-ol	<i>Scenedesmus subspicatus</i>	72 h ErC50	N; S	3.1	2	KAO Corporation
93334-15-7	TEAQ Tallow reaction products	85% in 15% propan-2-ol	<i>Scenedesmus subspicatus</i>	72 h EbC50	N; S	1.62	2	KAO Corporation
67846-68-8/97158-31-1	DEEDMAC	83.4% in 15% ethanol	<i>Selenastrum capricornutum</i>	72 h ErC50	N; S	0.93	2 key Study	Kroon, A.G.M. and Van Ginkel, C.G., 1991
67846-68-8/97158-31-1	DEEDMAC	83.4% in 15% ethanol	<i>Selenastrum capricornutum</i>	72 h EbC50	N; S; L	0.24	2	Kroon, A. Adn Van Ginkel, C,1991

*N = nominal; M = measured; S= static; SS = semi-static; D = flow-through; R = river water; L = synthetic water
 NI = no information

Table 11c: Selected comparable key *Daphnia magna* data for DODMAC [DODMAC, EU, 2002] and esterquats additional to data already in Tables 8a, b and c

CAS no.	Substance	Purity	Species	Endpoint	Test type*	Result (mg a.i./l)	Validity	Reference
91995-81-2	TEAQ	100%	<i>Daphnia magna</i>	48 h EC50	M; S; L	2.4	1 key study	Rieche H, 1998
NI	HEQ	87.3%	<i>Daphnia magna</i>	48 h EC50	NI	7.7	1	Unilever
67846-68-8/97158-31-1	DEEDMAC	83.4% in 15% ethanol	<i>Daphnia magna</i>	48 h EC50	N; S; L	4.0	2	Mark, U. and Arends, I., 1991
NI	DODMAC	NI	<i>Daphnia magna</i>	21d NOEC	M; R	0.38	n.a.	DODMAC EU, 2002

*N = nominal; M = measured; S= static; SS = semi-static; D = flow-through; R = river water; L = synthetic water; W = well water; WH = well water + humics
 NI = no information

Table 11d: Selected comparable key fish data for DODMAC [DODMAC, EU, 2002] and esterquats additional to data already in Tables 8a, b and c

CAS no.	Substance	Purity	Species	Endpoint	Test type*	Result (mg a.i./l)	Validity	Reference
67846-68-8/97158-31-1	DEEDMAC	91.4% in 9.4% isopropanol	<i>Danio rerio</i>	96 h LC50	M; SS; L	2.8	2 Key study	Unilever
NI	HEQ	87.3%	<i>Oncorhynchus mykiss</i>	96 h EC50	NI	7.0	1	Unilever
NI	DODMAC	NI	<i>P. promelas</i>	96hr LC50	N; W	3.55	n.a.	DODMAC EU, 2002
NI	DODMAC	NI	<i>P. promelas</i>	96hr LC50	N; WH	6.3-13.8	n.a.	DODMAC EU, 2002
NI	DODMAC	NI	<i>P. promelas</i>	96hr LC50	N; R	21.3-36.2	n.a.	DODMAC EU, 2002

*N = nominal; M = measured; S= static; SS = semi-static; D = flow-through; R = river water; L = synthetic water; W = well water; WH = well water + humics
 NI = no information

For DODMAC several chronic sediment test results are available [DODMAC, EU, 2002]. The $PNEC_{sed}$ of 55 mg/kg dw for DODMAC is based on the EC_{10} value of 550mg/kg for *Tubifex tubifex* and applying a safety factor of 10 since long term tests are available for species representing three different living and feeding conditions. Therefore the $PNEC_{sediment}$ as a dry weight measurement for esterquats is taken as:

$$PNEC_{sed} = 55 \text{ mg/kg dwt}$$

This $PNEC_{sediment}$ is converted to a wet weight value for comparison with the wet weight $PEC_{sediment}$. A conversion factor of 2.6 for this calculation is based on the TGD properties for sediment. Thus the $PNEC_{sediment}$ as a wet weight measurement for calculation of RCRsed is taken as:

$$PNEC_{sed} = 21.2 \text{ mg/kg wwt}$$

4.2.2.3 Terrestrial PNEC

The acute EC_{50} values for *Avena sativa* or *Eisenia fetida* as found for TEAQ are used to calculate the PNEC for long term effects in soil.

$$PNEC_{terrestrial} \geq 1000/1000 = 1 \text{ mg/kg dwt}$$

4.2.2.4 STP PNEC

The 30 min EC_{10} for *Pseudomonas putida* as found for TEAQ is used to calculate the PNEC for effects in the sewage treatment plant.

$$PNEC_{microorganisms} = 35/10 = 3.5 \text{ mg/L}$$

4.3 Environmental risk characterization

The risk characterization ratios were calculated using the PEC estimations, based on the household use tonnage of the product with the highest consumption tonnage in the EU+ of 130 Ktons based on 100% active ingredient.. The RCR values are presented in Table 12.

Table 12: RCR values for each compartment

	Private use –Local	Regional
RCR water (dissolved)	0.21	0.037
RCR soil	0.60	0.012
RCR sed	0.94	0.36
RCR STP	0.025	-

4.4 Discussion and conclusions

The group approach used in this report is based on a comparison of the available data provided by the companies involved in the HERA risk assessment consortium. Close examination of environmental and toxicological data provided convincing evidence that a read across approach could be used for the

three esterquat groups. However, derivation of sediment effects data is recommended to confirm this approach with measured values for the sediment compartment.

Based on a total use volume of 130 Ktons of esterquats in the EU and applying a conservative exposure and effects assessment, no environmental risks are predicted for the local and regional scale for any of the environmental compartments.

List of Symbols and Abbreviations

BCF	Bio Concentration Factor
CAS	Chemical Abstracts System
CEC	Cation Exchange Capacity
DEEDMAC	diethoxyester dimethylammonium chloride
DEQ	2,3-Bis(C12-C22 Acyloxy)-N,N,N-trimethyl-1-propan-ammonium chloride
DHTDMAC	Di-Hardened Tallow Di-Methyl Ammonium Chloride
DODMAC	Di-Octadecyl Di-Methyl Ammonium Chloride
dw	dry weight
GLP	Good Laboratory Practice
HDQ or DHQ	ditallow ester of 2,3,dihydroxypropanetrimethyl ammonium chloride
HEQ	Hamburg Esterquat
IPA	Isopropyl alcohol (isopropanol)
K _p	Partition coefficient solid-water
PEC	Predicted Environmental Concentration
PNEC	Predicted No Effect Concentration
TEAQ	triethanol amine quat
TGD	Technical Guidance Document
wwt	wet weight

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6. CONTRIBUTORS TO THE REPORT

- **Leading company**

Stepan Europe

- **Consultant company**

Akzo Nobel Chemicals Research

(Department Environmental Chemistry and Regulatory Affairs)

- **Other contributors**

Akzo Nobel Surface Chemistry AB

CECA Arkema

Clariant GmbH

Cognis Deutschland GmbH & Co. KG

Colgate Palmolive Co

Degussa Goldschmidt GmbH

Henkel KGaA

Kao Corporation S.A.

Procter & Gamble, Eurocor

Unilever Home & Personal Care Europe

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