DIHYDROGENATED TALLOW DIMETHYL AMMONIUM CHEMICALS



THE SOAP AND DETERGENT ASSOCIATION

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INTRODUCTION

This monograph summarizes: 1) critical fate and effects data required for an environmental risk assessment on dihydrogenated tallow dimethyl ammonium chemicals (DHTDMA⁺), including the chloride (DHTDMAC) and the methyl sulfate salts (DHTDMAMS); and 2) conclusions drawn from a risk assessment of DHTDMA⁺ in the United States. Although focused on conditions in the U.S., data from other parts of the world that are relevant to a U.S. assessment are included in the monograph. The monograph is written for a technical audience, but not necessarily one familiar with environmental risk assessment.

The monograph is formatted into five sections. The first section describes DHTDMA⁺ chemicals, their chemical structure and U.S. consumption volumes. The second section describes the function of DHTDMA⁺ in fabric softening products. The third section describes their fate and exposure concentrations in the environment. The fourth section presents environmental effects information. The fifth section presents a comparison of exposure and effects concentrations in the framework of an environmental risk assessment.

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INGREDIENT IDENTIFICATION

Chemical Description

DHTDMA⁺ are cationic surfactants containing a mixture of saturated C_{14} to C_{18} alkyl chain lengths, with C_{16} to C_{18} being the most functional and abundant. DHTDMAC and DHTDMAMS are identified by the Chemical Abstract Service (CAS) numbers 61789-80-8 and 61789-81-9, respectively.

DHTDMA⁺ contain two hydrophobic alkyl chains and two methyl groups which are bonded to a hydrophilic, positively charged nitrogen. The molecules demonstrate strong surface active properties and have extremely low solubility in water, estimated to be $\leq 10^{-15}$ M (Laughlin, Munyon, Fu and Fehl, 1990; Laughlin, Munyon, Fu and Emge, 1991).

$$CH_3 \\ | \\ CH_3(CH_2)_{12-16}CH_2 - N^+ - CH_2(CH_2)_{12-16}CH_3 \quad CI^- \text{ or } MeSO_4^- \\ | \\ CH_3$$

DHTDMA+ Chemicals

The physical, chemical and biological fate of all the DHTDMA⁺ materials, including the chloride and methyl sulfate salts or ¹⁴C radiolabeled materials, are expected to be similar, if not identical, in laboratory test systems or environmental matrices. The anionic counter ion and the ¹⁴C radiolabel are not expected to significantly alter the fate/effects profile of this cationic surfactant. Therefore, reference to DHTDMA⁺ in various sections of the monograph will be made and may include any or all of these possible forms.

U.S. Consumption

The total estimated DHTDMA⁺ usage in the U.S. fabric softener industry is approximately 70 million pounds per year (MM lbs./yr.). It is estimated (Roes and de Groot, 1988) that DHTDMA⁺ usage in softener applications represents the largest single use for cationic surfactants in U.S. consumer products.

INGREDIENT FUNCTION

The positively charged DHTDMA⁺ have high affinity for negatively charged surfaces, making them suitable for a wide variety of commercial applications. In fabric softener applications, DHTDMA⁺ binds to the negatively charged fabric, reducing or eliminating the static charge while also softening the fabric via surface modifications of the fiber. These laundry products could not be functional without DHTDMAC/DHTDMAMS or suitable cationic alternatives.

The main uses of DHTDMA⁺ are in laundry fabric softener products, including rinse-added liquid fabric softeners (DHTDMAC), dryer-added softener sheets (DHTDMAMS) and detergent plus fabric softeners (DHTDMAC). These cationic materials are also used as conditioning agents in personal care products such as shampoos and hair conditioners and as emulsifiers in lotions.

DHTDMAC is the principal active in liquid rinse-added fabric softeners. "Single" strength products typically contain 5-10% DHTDMAC, while concentrated products may contain up to approximately 25-30% of a mixture of softener actives, including DHTDMAC.

In softener sheets, DHTDMAMS and other softener actives are used to provide the desired performance attributes. Levels of DHTDMAMS may range from approximately <10% to approximately 70% of sheet softeners.

ENVIRONMENTAL FATE AND EXPOSURE

Fate

The primary route of DHTDMA⁺ release to the environment is disposal of spent laundry wastewaters to municipal or on-site waste treatment systems.

DHTDMA⁺ are effectively removed during wastewater treatment practices, and removal is similar to those of other surfactants and biological oxygen demand (BOD). Removal (treatability) is attributed to both biodegradation by and sorption to the biological solids. DHTDMA⁺ are practically insoluble (Laughlin *et al.*, 1990; Laughlin *et al.*, 1991) in wastewaters and have a high partition coefficient from the wastewaters onto organic and inorganic sludge solids during wastewater treatment.

Only trace levels of DHTDMA⁺ are released in wastewater effluents into surface waters/sediments, where they are strongly associated with organic and inorganic materials via chemical complexation or physical sorption. DHTDMA⁺ are not volatile and are stable to chemical hydrolysis and photolysis. These low levels of DHTDMA⁺ are expected to be biodegraded and mineralized at various rates and extents in the surface waters and sediments, and accumulation is not expected (ECETOC, 1993).

Digested sludges (containing DHTDMA⁺) often are applied as a nutrient and conditioner for agricultural soils. DHTDMA⁺ are biodegraded in soil and are not expected to accumulate in plants, invertebrates or animals (ECETOC, 1993).

Biodegradation

It is difficult to evaluate DHTDMA⁺ biodegradation in standard screening level studies, such as CO₂ assays and BOD determinations which are commonly used for soluble organic materials (Larson and Vashon, 1983). DHTDMA⁺ are practically insoluble and difficult to dose to these test systems. DHTDMA⁺ are not readily "available" in solution and are not readily biodegradable in these laboratory assays.

More sophisticated biodegradation studies using ¹⁴Cdistearyl dimethyl ammonium chloride (¹⁴C-DSDMAC) labeled in all possible carbon positions confirm that all the carbon atoms are mineralized in activated sludge (Sullivan, 1983). Similar mineralization of all carbon positions in DHTDMA⁺ are expected to occur in other environmental matrices where DHTDMA⁺ may reside after consumer use and waste disposal. In these studies (Sullivan, 1983), mineralization of ¹⁴C-DSDMAC including methyl, alpha alkyl and uniformly labeled carbon atoms has been confirmed in activated sludge. Realistic concentrations of DSDMAC (0.5-5 mg/L; ppm) are mineralized with up to 30-40% ¹⁴CO₂ yields within approximately 30 days. Higher yields (40-50+%) may be achieved during extended 60-120 day incubations (ECETOC, 1993).

Large variations in ¹⁴CO₂ yields and rates of mineralization have been observed by various investigators (ECETOC, 1993; Sullivan, 1983). Variations are due to the extreme insolubility of DSDMA⁺ and different dosing/acclimation strategies used. The data do, however, confirm that DSDMA⁺/DHTDMA⁺ are ultimately biodegradable, albeit slowly, and no recalcitrant biodegradation intermediates are produced.

In sludge-amended soils, mineralization of both methyl and alpha ¹⁴C-labeled DSDMAC has been observed (ECETOC, 1993). Although mineralization of uniformly labeled DSDMA⁺ has not been tested in soil, complete biodegradation is expected based on the mineralization of the alpha alkyl carbon. In this study (ECETOC, 1993), alpha and methyl positions of ¹⁴C-DSDMAC are ultimately biodegraded in soil at realistic concentrations (0.1, 0.5, 1.0, 5.0 and 50.0 mg/kg). Extents of mineralization vary from approximately 20+% to over 50% depending on the dosing strategy and incubation period. In net, DSDMAC is ultimately biodegraded in soil and no recalcitrant intermediates are produced.

Limited biodegradation is available for aquatic sediments. However, slow but significant mineralization of alpha alkyl labeled ¹⁴C-DSDMAC in sediments (*in vitro*) previously exposed to this cationic material has been demonstrated (Federle and Pastwa, 1988). Limited or no mineralization was observed in unexposed sediments, or in deep sediments below those containing measurable levels of DSDMAC/DHTDMAC, suggesting that acclimation may play an important role for effective DSDMAC/DHTDMA⁺ mineralization *in situ*.

Treatability

DHTDMA⁺ are extensively removed in biological, or secondary, wastewater treatment facilities commonly used in the U.S. and throughout Europe. Measured removals across the entire treatment systems are approximately 69% for trickling filters, 78% for rotating biological contactors (RBCs) and 94% for activated sludges (Versteeg, Feijtel, Cowan, Ward and Rapaport, 1992; ECETOC, 1993). Removals in oxidation ditches and lagoons are more extensive, exceeding 97%. These removals are similar to those of suspended solids and BOD (unpublished data, The Procter & Gamble Company).

Primary sewage treatment is used only on a limited basis in the U.S. However, DHTDMA⁺ removals (approximately 30%) are also similar to that of BOD (25-40%), and only slightly lower than that of suspended solids, approximately 50-65% (unpublished data, The Procter & Gamble Company). Removal for DHTDMA⁺ in European primary sewage treatment is similar, ranging from 20% to 50% depending on operating conditions (ECETOC, 1993).

Exposure

Aquatic

Measured levels of DHTDMA⁺ in surface waters downstream of discharges from treatment systems, including trickling filter, activated sludge and RBC units, range from <0.002 to 0.057 mg/L (Versteeg *et al.*, 1992). These levels correspond well with predicted levels. Using the previous treatability data and published exposure models (Cowan, Larson, Feijtel and Rapaport, 1993; Rapaport, 1988), the concentrations of DHTDMA⁺ in surface waters are predicted to range from 0.003 to 0.037 mg/L at the mixing zones of the wastewater treatment facilities in the U.S. Similar or slightly higher levels may be observed in European surface waters (Versteeg *et al.*, 1992; ECETOC, 1993).

Sediment

In U.S. sediments, DHTDMA⁺ have been monitored ranging from trace levels (<3 mg/kg) to approximately 128 mg/kg under worst case conditions where low (<10) dilution of sewage effluent is observed into the surface waters (unpublished data, The Procter & Gamble Company). In Europe, ranges of DHTDMA⁺ concentrations in sediments vary from approximately 10 mg/kg to 70 mg/kg (ECETOC, 1993).

Terrestrial

Limited data are available for DHTDMA⁺ in agricultural soils. Measured levels of DHTDMA⁺ in U.S. sludgeamended soils vary from trace levels up to approximately 164 mg/kg, with an average of 86 mg/kg (ECETOC, 1993). These results were obtained from triplicate soil grab samples taken at depths between 0 and 8 cm. DHTDMA⁺ are highly sorptive and were confined to the upper layers of soils. At a depth of 90 cm, DHTDMA⁺ levels were below detection limits (<1 mg/L). Levels of DHTDMA⁺ in European soils are generally lower, with ranges between 2 mg/kg and approximately 40 mg/kg.

ENVIRONMENTAL EFFECTS

Aquatic

It is difficult to evaluate the aquatic effects of DHTDMA⁺ in traditional standard aquatic tests which rely on delivering the test chemical in soluble form. In the case of highly insoluble DHTDMA⁺, which have often been dosed to these aquatic tests with solvents, the resultant exposure to the test organism may consist of low levels of soluble DHTDMA⁺, but with most of the exposure being in the form of aqueous dispersion or insoluble material. More recently, investigators have developed novel test systems to mimic the natural release mechanisms for DHTDMA⁺ in activated sludge effluent (see below).

Extensive aquatic toxicity testing with DHTDMA⁺ has been completed on a range of fresh and saltwater fish, invertebrates and algae using either well water, reconstituted water or, in limited situations, filtered surface waters (Versteeg *et al.*, 1992; ECETOC, 1993; Lewis and Wee, 1983; Roghair, Buijze and Schoon, 1992). Although these studies allow the determination of inherent toxicity of commercial DHTDMA⁺, they do not allow an accurate evaluation of the bioavailability and toxicity of DHTDMA⁺ in sewage effluent and, subsequently, in surface waters containing solids and humic acids.

DHTDMA⁺ are highly sorptive and readily complex with other anionic organic matter in sewage effluent, surface waters and sediments. These physical/chemical processes have been shown to mitigate the inherent toxicity of DHTDMA⁺ demonstrated in the well water, reconstituted water and filtered natural water studies (Versteeg *et al.*, 1992; ECETOC, 1993; Lee, 1986; Pittinger, Woltering and Masters, 1989). In these studies, investigators have used sewage effluent toxicity assays and unfiltered surface waters containing humic acids to better mimic the effects of DHTDMA⁺ on aquatic life (Versteeg *et al.*, 1992; ECETOC, 1993; Versteeg and Shorter, 1992; Versteeg and Woltering, 1990). The effluent toxicity assays (Versteeg *et al.*, 1990) allow for the most realistic dosing form of DHTDMA⁺ and have been evaluated using the invertebrate *Ceriodaphnia dubia* and the alga *Selenastrum capricornutum*. The resulting chronic no-observed effect concentration (NOEC) for the most sensitive species, *Ceriodaphnia*, was 4.53 mg/L. Traditional toxicity tests in well water, reconstituted waters and filtered river waters yield chronic NOECs of <1 mg/L (Versteeg *et al.*, 1992; ECETOC, 1993). The chronic toxicity of DHTDMA⁺ to fish and invertebrates appears to be similar (Versteeg *et al.*, 1992; ECETOC, 1993).

Sediment

Studies in aquatic sediments (Lee, 1986; Pittinger *et al.*, 1989) demonstrate that the aquatic toxicity of DHTDMA⁺ is mitigated by adsorption onto sediments composed of sand, kaolin and natural organic matter. The chronic NOEC for the benthic invertebrate *Chironomus*, or sediment midge, is approximately 876 mg/kg (Pittinger *et al.*, 1989).

Terrestrial

Several phytotoxicity studies have been completed by various investigators over the last 10 years. Test species included important commercial crops such as tomato, lettuce, barley, radish, sorghum, sunflower and mung bean. Effects measured were growth/viability or effects on fresh and dry weights of plants, roots, fruits and/or seed. Effect concentrations impairing viability, growth or weight by 50% (EC₅₀) ranged from approximately 2,500 to over 40,000 mg/kg DHTDMA⁺ (ECETOC, 1993). A 38-day plant uptake study with up to 4 mg/kg DHTDMA⁺ in sludge-amended soil indicated very little (<0.03%) accumulation in a wide range of vegetables.

Earthworms (*Eisenia foetida*) exposed to up to 1,000 mg/kg DHTDMA⁺ in soil for 14 days showed no adverse effects in survival, behavior or body weight (ECETOC, 1993). There was also no evidence of bioaccumulation.

Sludge-amended soil containing up to 365 mg/kg DHTDMA⁺ supported microbial respiration, including oxygen uptake and carbon dioxide (CO₂) production similar to those in control soil (no added DHTDMA⁺). These studies were conducted for up to 14 weeks (ECETOC, 1993).

RISK ASSESSMENT

Aquatic

The most environmentally relevant aquatic assessment is determined by comparing the toxicity value in the effluent toxicity assays to either predicted or monitored exposure levels for DHTDMA⁺. Since the 4.53 mg/L chronic NOEC is much greater than the monitored surface water concentrations of DHTDMA⁺ (<0.002 to 0.057 mg/L), no aquatic hazard is expected.

Sediment

DHTDMA⁺ measured in U.S. sediments have been observed up to approximately 128 mg/kg (ECETOC, 1993) under worst case conditions where dilution factors for sewage effluent into the overlying surface water are <10. Under more typical dilution scenarios where higher effluent dilutions are observed, sediment concentrations often are lower. Since the chronic NOEC for DHTDMA⁺ is 876 mg/kg in the sediment bioassay, no sediment hazard is expected even under the worst case scenario.

Terrestrial

Since measured concentrations of DHTDMA⁺ in sludgeamended soils are less than the toxicity thresholds for plants, earthworms and soil microbial respiration, and because DHTDMA⁺ biodegrade and show minimal potential to bioaccumulate, no terrestrial hazard is expected.

CONCLUSION

DHTDMA⁺ have an adequate margin of environmental safety for usage by the U.S. and European fabric softener industry as well as all consumer uses of DHTDMA⁺. Recent publications (Versteeg *et al.*, 1992; ECETOC, 1993) summarize environmental fate, exposure and effects data for DHTDMA⁺, and confirm that DHTDMA⁺ are effectively removed in wastewater treatment and that no aquatic or terrestrial risks are expected due to typical consumer use of these materials in the U.S. or Europe. Commercial uses for DHTDMA⁺ have begun to decline significantly both in Europe and the U.S. Therefore, this assessment will further improve as actual environmental releases of DHTDMA⁺ are significantly reduced.

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