Environment Canada Environnement Canada

Canadian Environmental Protection Act, 1999

Federal Environmental Quality Guidelines

Alcohol Ethoxylates

Environment Canada

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Introduction

Federal Environmental Quality Guidelines (FEQGs) provide benchmarks for the quality of the ambient environment. Where the FEQG is met there is low likelihood of adverse effects on the protected use (e.g., aquatic life or the wildlife that may consume them). They are based on the toxicological effects or hazards of specific substances or groups of substances and do not take into account analytical capability or socio-economic factors. FEQGs serve three functions: first, they can be an aid to prevent pollution by providing targets for acceptable environmental quality; second, they can assist in evaluating the significance of concentrations of chemical substances currently found in the environment (monitoring of water, sediment, and biological tissue); and third, they can serve as performance measures of the success of risk management activities. The use of FEQGs is voluntary unless prescribed in permits or other regulatory tools. Thus FEQGs, which apply to the ambient environment, are not effluent limits or "never-to-be-exceeded" values but may be used to derive effluent limits. The development of FEQGs is the responsibility of the Federal Minister of Environment under the *Canadian Environmental Protection Act, 1999*. The intent is to develop FEQGs as an adjunct to risk assessment/risk management of priority chemicals identified in the Chemicals Management Plan (CMP) or other federal initiatives. This factsheet describes the Federal Water Quality Guidelines (FWQGs) for the protection of aquatic life for alcohol ethoxylates and some related substances (see Figure 1) and is based on information obtained to 2004. No FEQGs have been developed for the soil, sediment or biological tissue compartments at this time.

Federal Water Quality Guideline: 70 µg/L
(for representative alcohol ethoxylate homologue $C_{13.7}$ EO_5)

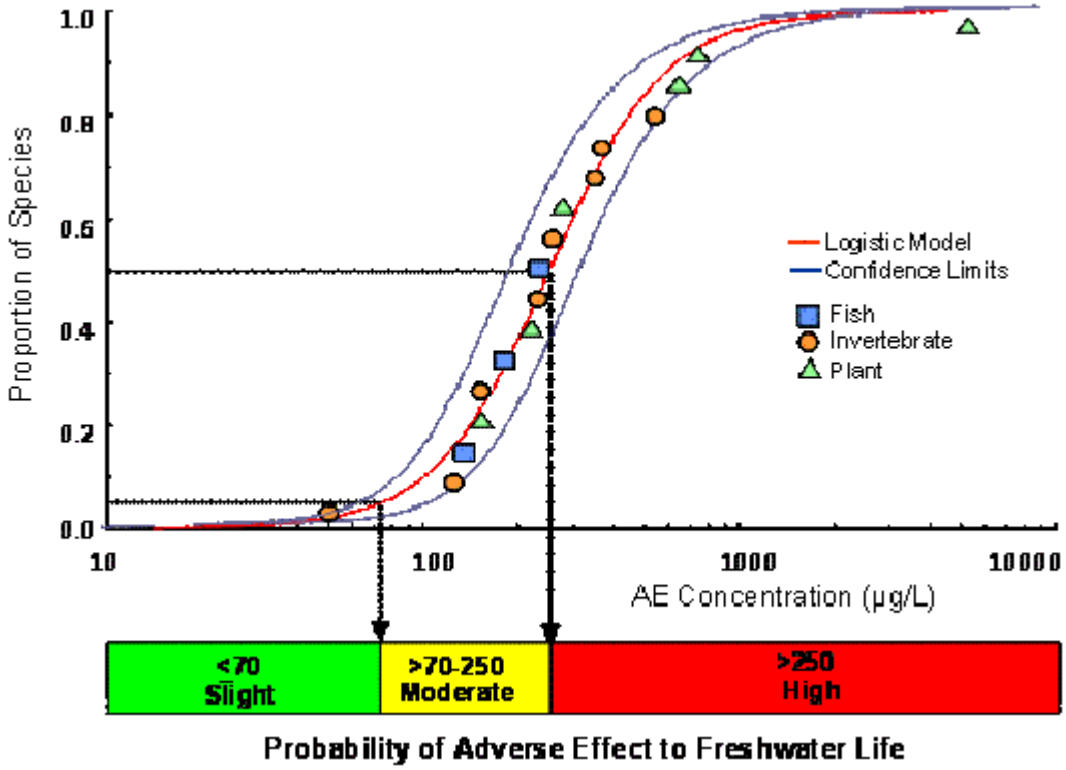

Figure 1. Species sensitivity distribution (SSD) for freshwater toxicity data for the representative alcohol ethoxylate homologue $C_{13.7}$ EO_5 and associated effect levels for freshwater life. Guidelines for individual homologues are given in Table 3.

Substance Identity

Alcohol ethoxylates (AEs) are part of the alcohol alkoxylates class which also includes alcohol propoxylates and butoxylates. Alcohol ethoxylates are a class of nonionic surfactants that contain a hydrophobic alkyl chain attached via an ether linkage to a hydrophilic ethylene oxide (EO) chain and have the general structure $R(OCH_2CH_2)_nOH$. The alkyl chain, R, can vary in length and in the degree of linearity, but is typically between 8 and 18 carbons long (for detergent range surfactants). The EO chain can also vary in length from 1 to 40 EO units. An AE with the structure $C_{9\text{-}11}EO_{6.5}$, for example, contains a range of alkyl chain lengths of 9-11 and averages 6.5 EO units per alkyl chain. It should be noted that, although this is the general description of the mixture, other homologues are present. For example, an AE produced from a $C_{12\text{-}15}$ alcohol mixture can yield up to 100 different surfactants (Raney 2000). Due to the large number of possible

AEs, many different CAS numbers and trade names exist for AEs (Table 1). Because of their ecological and/or human health concerns, many of these substances were identified as priorities for further action under the CMP.

The hundreds of different possible AEs each have slightly different chemical and physical properties (Hennes-Morgan and De Oude 1994), however, the presence of a strong hydrophilic (ethoxylate chain) and strong hydrophobic (alkyl chain) moiety linked together gives them their characteristic surfactant properties (Swisher 1987). AEs concentrate at surfaces and interfaces in aqueous solutions and create a surface film which reduces the surface tension of water and alters the wetting properties between water and solids (Aveyard 1984; Swisher 1987). The solubility of AEs in water results from the presence of the hydrophilic group (Aveyard 1984).

Uses

Alcohol ethoxylates are currently some of the most commonly manufactured and utilised nonionic surfactants in Canada and world-wide (Camford Information Services 1997; Campbell 2002). AEs are predominantly used in consumer and industrial products such as laundry detergents and all-purpose cleaners, and are used to a lesser extent by agriculture, cosmetic, textile, paper, and oil sectors (Talmage 1994; Camford Information Services 1997; Madsen et al. 2001). Total production capacity of AEs in Canada in 1996 was estimated at 72 000 t (Camford Information Services 1997). In 2000, a total of 216 800 t of AEs were consumed in Canada and the United States (Modler et al. 2002). Of this total, approximately 41% was used in laundry liquids, 20% in laundry powders, 3% in dishwashing liquids, 9% in other household cleaners, and the remaining 27% was consumed through other uses. In addition, another 411 408 t of AEs were consumed in Canada and the United States in 2000 in the production of alcohol ethoxysulfates, a group of anionic surfactants. In 2002, it is estimated that over 500 000 t of fatty alcohols and fatty-alcohol-based surfactants were consumed in North America (Modler et al. 2004). Of this, approximately 67% consisted of AEs or sulfated AE.

Table 1. Chemicals to which Federal Water Quality Guidelines for alcohol ethoxylates apply

CAS Registry Number	Chemical Name
61791-28-4	Alcohols, tallow, ethoxylated
66455-14-9	Alcohols, C12-13, ethoxylated
68002-96-0	Alcohols, C16-18, ethoxylated propoxylated
66455-15-0	Alcohols, C10-14, ethoxylated
68002-97-1	Alcohols, C10-16, ethoxylated
68131-39-5	Alcohols, C12-15, ethoxylated
68154-96-1	Alcohols, C14-18, ethoxylated
68154-98-3	Alcohols, C14-18, ethoxylated propoxylated
68155-01-1	Alcohols, C16 and C18-unsatd., ethoxylated
68213-23-0	Alcohols, C12-18, ethoxylated
68213-24-1	Alcohols, C12-16, ethoxylated propoxylated
68439-45-2	Alcohols, C6-12, ethoxylated
68439-46-3	Alcohols, C9-11, ethoxylated
68439-50-9	Alcohols, C12-14, ethoxylated
68439-51-0	Alcohols, C12-14, ethoxylated propoxylated
68439-54-3	Alcohols, C11-13-branched, ethoxylated
68526-94-3	Alcohols, C12-20, ethoxylated
68551-12-2	Alcohols, C12-16, ethoxylated
68551-13-3	Alcohols, C12-15, ethoxylated propoxylated
68551-14-4	Alcohols, C11-15-secondary, ethoxylated propoxylated
68920-66-1	Alcohols, C16-18 and C18-unsatd., ethoxylated
68951-67-7	Alcohols, C14-15, ethoxylated
68991-48-0	Alcohols, C7-21, ethoxylated
69013-19-0	Alcohols, C8-22, ethoxylated
69227-20-9	Alcohols, C16-22, ethoxylated
69227-21-0	Alcohols, C12-18, ethoxylated propoxylated
70879-83-3	Alcohols, C6-10, ethoxylated
71243-46-4	Alcohols, C8-16, ethoxylated
73049-34-0	Alcohols, C16-20, ethoxylated propoxylated
106232-83-1	Alcohols, C12-15-branched and linear, ethoxylated
111905-53-4	Alcohols, C13-15-branched and linear, butoxylated ethox
111905-54-5	Alcohols, C13-15-branched and linear, ethoxylated propo
139626-71-4	Alcohols, C14-100, ethoxylated

Sources

Alcohol ethoxylates are synthetic chemicals that do not occur naturally. Since the majority of AEs are used in cleaners and detergents, the largest recipient of chemical inputs is the aquatic environment, primarily through wastewater effluent as a result of consumer disposal practices (Holt et al. 1992). Other potential sources of exposure exist within the industrial sectors where AEs are manufactured or used (industrial cleaners,

pulp and paper, chemical manufacture). Natural degradation processes and wastewater treatment techniques remove a large proportion of AE from water, however there is still potential for aquatic exposure. Due to the hydrophobic moiety of AE compounds, once introduced into the aquatic environment they have the potential to adsorb to particulate matter and be deposited to sediments (McAvoy and Kerr 2001). An additional pathway for environmental exposure to AEs is via direct application to soils such as in sewage sludge, and through the use of septic systems which use the soil to treat and disperse wastewater (Nielsen et al. 2002).

Fate, behaviour and partitioning in the environment

By far the most significant fate process for AEs is aerobic microbial biodegradation. Due to the down-the-drain disposal pattern of AEs, a majority of their biodegradation occurs in the sewage system (Nielsen et al. 2002), wastewater treatment plants (WWTP) (McAvoy et al. 1998), septic systems (Matthijs et al. 1995) and to a lesser extent in natural waters (Vashon and Schwab 1982). Multibranched AEs, which make up significantly less of the commercial AE market in Canada (Campbell 2002), are slower to degrade than linear AEs (Birch 1984; Marcomini et al. 2000) but can still be considered readily degradable. Intermediate degradation products of AEs can include free fatty alcohols, polyethylene glycols (PEG), and carboxylic fatty acids.

Adsorption of AEs plays a minor role in their aquatic fate, with sorption to humic materials in water, suspended and bed sediments, and sludge in wastewater treatment facilities. AEs are not expected to volatilize to the atmosphere (Kiewiet et al. 1997).

AEs are rapidly taken up across the gills in fish (Bishop and Maki 1980; Wakabayashi et al. 1987; Tolls et al. 1994; Newsome et al. 1995) and are rapidly metabolised and eliminated from fish (Bishop and Maki 1980; Wakabayashi et al. 1987; Newsome et al. 1995). Based on the high elimination rates, Tolls et al. (2000) concluded that rapid biotransformation was taking place in fathead minnows *(Pimephales promelas)*, and that AEs were not stored in the fish. Metabolites formed during biotransformation are of less concern than the parent compound as the short-chained metabolites have low lipophilicity and therefore are less toxic (Roberts 1991; Newsome et al. 1995). Bioconcentration factors reported for AEs are typically less than 300 (e.g., Tolls et al. 2000) and would not meet the criteria for *Persistence and Bioaccumulation Regulations* (Government of Canada 2000). However, log octanol/water partitioning coefficients (log K_{ow}) for various AEs have been estimated to range from approximately 3 to 7, suggesting that some AEs may tend to bioaccumulate (Müller et al. 1999b).

Ambient concentrations

Any AEs detected in the environment are the result of anthropogenic releases. Free fatty alcohols, however, which are found in mixtures of AE homologues, can also occur naturally. Free fatty alcohols are generally analysed with and quantified as AEs, and may therefore result in an over estimation of AE levels. There is currently no information on ambient concentrations of AEs in the Canadian environment.

In August 2003, effluents were sampled from eight Canadian municipal WWTP (P&G – Shell 2003; Sherren et al. 2003; Eadsforth et al. 2006). The total AE concentrations for these eight plants ranged from 1.0 to 22.7 µg/L, with an average of 6.8 µg/L (Sherren et al. 2003). It is notable that the two highest concentrations occurred in effluents from the two plants that did not use activated sludge treatment. The measurements of total AEs included those species with no ethoxylate groups (i.e., free fatty alcohols). Among the eight municipal WWTP, free alcohols accounted for 21 to 62% of the total AE concentration. Although some of this free alcohol likely resulted from the degradation of AEs, some may also have originated from other sources including other alcohol-based surfactants such as alkyl sulfates and alcohol ethoxysulfates, other uses of alcohols, and as metabolic by-products from microbial degradation of animal and vegetable matter in the municipal WWTP (Scott Belanger, Procter & Gamble, pers. comm. 2004, Mudge et al. 2008). Ratios of the molar concentrations of free alcohol to AEs in the effluent were determined for each alkyl chain length. Using these ratios, it is therefore possible to determine "alcohol caps", that is, maximum concentrations of free alcohol in effluents that could have originated from AEs. The alcohol cap is defined as the ratio (for each chain length) between the effluent alcohol that could have been derived from AE and the total ethoxylated alcohols in the effluent (EO > 1). The cap values derived from Stephenson et al. (2004) were 0.58, 0.63, 0.33, 0.25, 0.26 and 0.05 for C_{12}, C_{13}, C_{14}, C_{15}, C_{16} and C_{18}, respectively. The cap is applied in any calculation only if the effluent measured alcohol concentration exceeds: cap x Sum (EO_{1-20}). When alcohol caps are applied to the monitoring data from the eight Canadian municipal WWTP, the concentrations of total AEs ranged from 0.8 to 11.5 µg/L with an average of 4.9 µg/L (P&G –Shell 2003).

From the study of AE concentrations in Canadian municipal wastewater effluents (P&G – Shell 2003; Sherren et al. 2003), it is also possible to determine the average homologue distribution. Applying an alcohol cap, the average alkyl chain length was 13.68 carbons long, and the average ethoxylate chain consisted of 5.03 ethoxylate units (Scott Belanger, Procter & Gamble, pers. comm. 2004). In other words, the average homologue distribution in Canadian municipal wastewater effluents is $C_{13.7}EO_5$.

Mode of action

Although the exact mechanism by which AEs affect aquatic organisms is not fully understood, it is likely that they act through nonspecific narcosis depending on the number of EO units (Roberts 1991; Dorn et al. 1997a; Müller et al. 1999a). Narcosis is a nonspecific, reversible mode of toxic action in which the presence of hydrophobic organic chemicals causes a disruption of cellular activity. Many researchers suspect that surfactants such as AE can disrupt gill membranes in fish, invertebrates and amphibians, and cause the gill epithelial cells to swell and secrete mucous (Moore et al. 1987; Cardellini and Ometto 2001). These cell membrane disruptions can affect diffusion of oxygen across the gills, ultimately resulting in suffocation (Moore et al. 1987; Cardellini and Ometto 2001).

In algal cells, surfactants such as AE are thought to denature and bind proteins in the cell wall, thereby altering the permeability of the cell membrane to nutrients and chemicals (Lewis 1990). The susceptibility of algal species can vary depending on the thickness and chemical composition of their cell walls. Algal species with thicker cell walls will be affected less by exposure to surfactants (Nyberg 1988; Lewis 1990). Hydrophobic surfactants will more easily penetrate algal species with high lipid and protein content in their cell walls (Lewis 1990).

In some cases, AE toxicity can also result from physical surface active effects. When applied to the surface of water bodies, AE can form a film that alters the water surface tension, thereby affecting surface breathing or water striding invertebrate larvae or adults (Mulla et al. 1983).

Freshwater toxicity

Fish and invertebrates are generally more sensitive to AE than plants or algae (Bisop and Perry 1981; Dorn et al. 1997b). The toxicity of individual AE homologues is a function of their chemical structure. The toxicity of AE increases with increasing alkyl chain length (Wong et al. 1997; Dorn et al. 1997a; Lizotte, Jr. et al. 1999; Ghirardini et al. 2001), and with decreasing ethoxylate chain length (Macek and Krzeminski 1975; Maki and Bishop 1979; Yamane et al. 1984; Wong et al. 1997; Raney 2000). In addition, to the length of the alkyl chain, the structure of the chain can also affect its toxicity as linear AEs are more toxic than branched AEs (Dorn et al. 1993; Kaluza and Taeger 1996; Ghirardini et al. 2001). Other factors that have been demonstrated to affect toxicity are the location of attachment between the alcohol and ethoxylate chains (e.g., primary vs. secondary alcohols) (Kurata et al. 1977), the homologue distribution of the ethoxylate chain (Garcia et al. 1996), water hardness (Tovell et al. 1975), and temperature (Lewis and Hamm 1986).

Commercial AEs consist of a mixture of various AE homologues which differ in their relative toxicity. As a result, direct comparisons cannot be made among all of the available AE toxicity studies because they involve tests on numerous different mixtures. Commercial AE mixtures that are used in toxicity testing will also differ in their homologue distributions from the AE mixtures that are found in the aquatic environment following varying degrees of biodegradation. Therefore, direct comparisons cannot be made between results of laboratory toxicity tests and total AE concentrations that are measured in ambient waters. For the purpose of assessing acceptable levels of AE in water, a solution is to normalize the toxicity data to a common homologue distribution.

A monitoring survey of Canadian municipal wastewater effluents identified the average AE homologue distribution, in Canadian effluents, adjusted for an alcohol cap, to be $C_{13.7}EO_5$ (Scott Belanger, Procter & Gamble, pers. comm. 2004). Where the exact homologue distribution of AEs at a particular site is unknown, this average distribution can be used as the structure to which all acceptable reported AE toxicity data are normalized. It should be noted, however, that this average distribution is based solely on analyses of municipal wastewater effluents. Where AEs in ambient Canadian waters

originate from other types of sources, such as discharges from industries, it is possible that the average homologue distribution will differ, due to differences in the types of parent AEs that are used.

AE toxicity data were normalised based on the predicted effect concentrations for both the test structure and the normalized structure as determined through the use of quantitative structure-activity relationship models (QSARs). A number of QSARs have been developed for AEs, both for acute and chronic exposure, as well as various types of organisms.

The general formula used to normalize AE toxicity data to a common homologue distribution is as follows:

$$normalizedEC_{env} = reportedEC_{test} * \left(\frac{predictedEC_{env}}{predictedEC_{test}} \right)$$

where,

normalized EC_{env}= normalized effect concentration for environmental distribution
reported EC_{test} = effect concentration from a toxicity test on a commercial distribution
predicted EC_{env} = effect concentration from a QSAR based on environmental distribution
predicted EC_{test} = effect concentration from a QSAR based on a commercial distribution

In normalizing the aquatic toxicity data, corrections were also made for sorption. The sorption correction was made to account for homologue-specific sorption to effluent suspended solids, with the assumption that sorbed fractions are not bioavailable, and therefore are not contributing to the toxicity of the AE distribution. Adjustments for sorption were made using a QSAR based on a regression between K_d or K_{oc} and chain length and ethoxylate number (van Compernolle et al. 2006). This is made possible because all sorption studies have utilized pure materials and not mixtures. The sorption corrections were used to adjust the average environmental homologue distribution. Corrections for solubility were made using a QSAR developed by Hansch et al. (1968) based on log K_{ow}. Both the solubility and sorption corrections were used to adjust the average environmental homologue distribution. The solubility corrections, however, were found to have little effect since the AE homologue concentrations measured in Canadian municipal wastewater effluents never exceeded solubility limits. For the AEs used in the toxicity tests it was assumed that all homologues were bioavailable and below solubility limits, so no corrections were needed.

The sensitivities for AEs overlap among taxa (Table 2). The most sensitive species reported for AE is an invertebrate species bivalve (*Corbicula fluminea*), followed by the water flea (*Daphnia magna*). A mayfly (*Isonychia bicolour*) was the least sensitive invertebrate species in the data set. Among fish species, rainbow trout (*Oncorhynchus mykiss*) and bluegill (*Lepomis macrochirus*) were the most and least sensitive species, respectively. In general, plants tend to be less sensitive than invertebrates and fish,

though some plant species may be quite sensitive (i.e., rotifers). Among plants, *Navicula pelliculosa* was most sensitive whereas *Chlorella vulgaris* was least sensitive.

Federal Water Quality Guideline Derivation

The FWQGs developed here identify benchmarks for aquatic ecosystems that are intended to protect all forms of aquatic life for indefinite exposure periods. Although AEs are rapidly degraded in water under field conditions, aquatic organisms may be chronically exposed to AEs due to their continuous release in municipal wastewater effluents. The acceptable data identified for developing the AE guidelines consist of three fish species, eight invertebrate species, and six plant species (Table 2).

Table 2. Toxicity data used for developing the Federal Water Quality Guideline for alcohol ethoxylates. Concentrations were normalised to $C_{13.7}EO_5$.

Species	Group	Endpoint	Concentration (µg/L)
Bivalve (*Corbicula fluminea*)	●	56d EC_{20} (length gain)	50
Water Flea (*Daphnia magna*)	●	21d EC_{20} (reproduction)	124
Rainbow trout (*Oncorhynchus mykiss*)	■	56d EC_{20} (dry weight)	135
Rotifer (*Brachionus calyciflorus*)	●	48h EC_{20} (population size)	153
Diatom (*Navicula pelliculosa*)	▲	96h EC_{20} (cell density)	153
Fathead minnow (*Pimpehales promelas*)	■	35d EC_{20} (percent hatch)	181
Blue-green algae (*Microcystis aeruginosa*)	▲	96h EC_{20} (cell density)	221
Mayfly (*Elimia* sp.)	●	56d MATC (weight gain)	229
Bluegill (*Lepomis macrochirus*)	■	35d EC_{20} (percent hatch)	233
Freshwater copepod (*Ceriodaphnia dubia*)	●	7d EC_{20} (reproduction)	257
Green algae (*Selenastrum capricornutum*)	▲	72h EC_{20} (growth rate)	278
Midge (*Chironomus tentans*)	●	10d LC_{20} (survival)	346
Amphipod (*Hyalella azteca*)	●	10d LC_{20} (survival)	370
Mayfly (*Isonychia bicolour*)	●	4d LC_{20} (survival)	542

Species	Group	Endpoint	Concentration (µg/L)
Green algae (*Scenedesmus subspicatus*)	△	72h EC_{20} (growth rate)	646
Duckweed (*Lemna minor*)	△	7d EC_{20} (frond count)	741
Green algae (*Chlorella vulgaris*)	△	72h EC_{20} (growth rate)	5281

Legend: ■ = Fish; ● = Invertebrate; △ = Plant

Notes: EC_{20}= Concentration at which there is an adverse effect on 20% of the population; LC_{20} = concentration lethal to 20% of the population; MATC = maximum acceptable toxicant concentration.

The species sensitivity distribution (SSD) curve was fitted using the toxicity data (Figure 1). Each species for which appropriate toxicity data were available was ranked according to sensitivity, and its centralized position on the SSD was determined. Following the CCME protocol (CCME 2007), several cumulative distribution functions (CDFs) were fit to the data using regression methods and the best model was selected based on consideration of goodness-of-fit and model feasibility (for details see CCME 2007). The logistic model provided the best fit of the models tested and the 5th percentile (HC_5) of the SSD plot is 70 µg/L, with lower and upper confidence limits of 50 and 110 µg/L, respectively (Figure 1).

The recommended FWQG is 70 µg/L. The guideline represents the concentration below which you would expect either no, or only a low likelihood of adverse effects on aquatic life. In addition to this guideline, two other concentration ranges are provided for use in risk management. At concentrations between greater than the 5th and 50th percentile of the SSD (>70-250 µg/L) there is a moderate likelihood of adverse effects to aquatic life. Concentrations greater than the 50th percentile (>250 µg/L) have a higher likelihood of causing adverse effects. Risk managers may find these additional concentration ranges useful in defining short-term or interim risk management objectives for a phased risk management plan. The moderate to higher concentration range may also be used in setting less protective objectives for waters that are already highly degraded or where there are socio-economic considerations that preclude the ability to meet the FWQG (i.e., the 5th percentile).

This FWQG represents the average homologue distribution of AEs and can be used where the average homologue distribution of AE in the ambient water is known to be $C_{13.7}EO_5$, or this can be used as a default guideline if the average AE homologue distribution at a site is unknown. Guideline values have also been determined for a suite of individual AE homologues that could occur in the environment (Table 3). These were determined using the same method used for the default guideline, by normalizing the toxicity data to each individual homologue and creating a SSD distribution for each individual homologue. Where possible, it is recommended that

concentrations of each individual AE homologue at a site be determined and then compared with the corresponding guideline value given in Table 3 through the use of a Toxic Unit approach.

Table 3. Federal Water Quality Guideline values (mg/L) for specific AE homologues* (see text for explanation).

EO#	C9	C10	C11	C12	C13	C14	C15	C16	C18
0	0.179	0.121	0.080	0.051	0.032	0.019	0.011	0.006	0.002
1	0.225	0.149	0.096	0.061	0.037	0.022	0.013	0.007	0.002
2	0.303	0.199	0.128	0.080	0.049	0.029	0.017	0.009	0.003
3	0.394	0.257	0.164	0.102	0.062	0.037	0.021	0.012	0.003
4	0.498	0.323	0.206	0.128	0.078	0.046	0.026	0.015	0.004
5	0.617	0.400	0.254	0.158	0.096	0.057	0.033	0.018	0.005
6	0.753	0.488	0.310	0.193	0.118	0.070	0.040	0.023	0.007
7	0.909	0.588	0.374	0.233	0.142	0.084	0.049	0.028	0.008
8	1.085	0.703	0.447	0.279	0.170	0.102	0.059	0.033	0.010
9	1.285	0.832	0.531	0.332	0.203	0.121	0.071	0.040	0.012
10	1.511	0.980	0.625	0.392	0.240	0.144	0.084	0.048	0.014
11	1.766	1.146	0.732	0.460	0.283	0.170	0.100	0.057	0.017
12	2.052	1.333	0.853	0.537	0.331	0.200	0.117	0.067	0.020
13	2.374	1.544	0.990	0.624	0.386	0.233	0.138	0.079	0.024
14	2.735	1.781	1.144	0.723	0.448	0.272	0.161	0.093	0.029
15	3.139	2.047	1.317	0.834	0.518	0.316	0.188	0.109	0.034
16	3.590	2.344	1.511	0.959	0.598	0.365	0.218	0.127	0.040
17	4.094	2.677	1.728	1.099	0.687	0.421	0.252	0.147	0.046
18	4.656	3.048	1.971	1.257	0.788	0.484	0.291	0.171	0.054
19	5.280	3.462	2.243	1.433	0.901	0.555	0.335	0.197	0.063
20	5.975	3.923	2.546	1.630	1.027	0.635	0.385	0.228	0.074

* Homologue-specific guideline values were determined by calculating the HC_5 from a species sensitivity distribution plotted with EC_{20} effect data normalized to the particular homologue.

To derive the guideline for specific homologues (each cell) shown in Table 3, the following steps were taken. First, for each homologue, the calculated log P (C log P) (a theoretical measure of hydrophobicity based on structural modelling) value was determined as a function of carbon chain length and ethoxylate length measure. The C log P was used in place of log K_{ow} as it is difficult to obtain octanol-water partitioning coefficients (K_{ow}s) for AEs because, as surfactants, they do not partition well into either liquid, but rather tend to emulsify the octanol-water interface. With the tendency to form micelles, determination of the K_{ow} for a surfactant will also be strongly dependent on its concentration (Müller et al. 1999b). Instead, the C logP based on the structure of the chemical can be determined using a modified version of the fragment method of Leo and Hansch (Roberts 1991; Roberts and Marshall 1995). In this method, using linear $C_{12}EO_1$ with a logP of 5.23 as the parent compound, an increment of 0.54 is added

for each additional carbon unit, and an increment of –0.10 is used for each additional EO group. To adjust for branching in the carbon chain, the term [1.44 log (C_s + 1)] is subtracted, where C_s is the carbon number of the shorter chain (Roberts and Marshall 1995).

Next, for each specific homologue in question, the appropriate QSAR equation found in Table 4 was used to predict the toxicity for each of the available toxicity endpoints listed in Table 2 (for 17 species = three fish species, eight invertebrate species and six plant species) given the toxicity of the original AE tested. A species sensitivity distribution was then constructed for each specific homologue. The HC_5 from the species sensitivity distribution was determined as the FWQG for each specific AE homologue which appears in each cell of Table 3.

Table 4. Quantitative Structure Activity Relationships (QSARs) used to convert toxicity data shown in Table 1 for default homologue to homologues shown in Table 3.

QSAR Equation	Units	Type of Data to Which the QSAR is Applied	Reference
CHRONIC DATA			
log (72h EC_{20} algae) = -0.378 x log Kow – 4.072	$mmol \cdot L^{-1}$	Chronic Plant/Algae Toxicity	Wind and Belanger 2006
log (21d EC_{20} *Daphnia magna*, reproduction) = -0.532 x log Kow – 3.025	$mol \cdot L^{-1}$	Chronic Invertebrate Toxicity	Boeije et al. 2006
log (30d EC_{20} *Pimephales promelas*) = -0.307 x log K_{ow} – 3.92	$mol \cdot L^{-1}$	Chronic Fish Toxicity	Boeije et al. 2006
log (mesocosm NOEC) = -0.74 x logKow – 2.78	$mol \cdot L^{-1}$	Mesocosm	Boeije et al. 2006
ACUTE DATA			
log (48h EC_{50} *Daphnia magna*) = -0.38 x alkyl-length + 0.1 * EO-length – 1.77	$mol \cdot L^{-1}$	Acute Invertebrate Toxicity	Wong et al. 1997
log (96h LC_{50} *Pimephales promelas*) = -0.34 x alkyl-length + 0.05 x EO-length -1.65	$mol \cdot L^{-1}$	Acute Fish Toxicity	Wong et al. 1997

Considerations in Guideline Implementation

The default FWQG for the protection of freshwater life from adverse effects of AEs is 0.07 mg/L normalized to the average homologue distribution of $C_{13.7}EO_5$. Together with the other values shown in Figure 1, these guidelines can be used when the average homologue distribution of AEs at a particular site are unknown. A simple measurement of total AE in the ambient waters can be compared with the guideline values to determine whether there is an exceedence. This is the most simple and cost effective approach, as chemical analyses for individual homologues can be costly, and very few analytical laboratories are currently set up to do them. Although analyses of individual homologues are not required to use the default guidelines, the analytical method used should be capable of detection at low ppb concentrations, as well as detection of free fatty alcohols and AEs with short EO chains.

The default guidelines are based on an environmental distribution expressed for convenience as a $C_{13.7}EO_5$ AE, which is likely characteristic of many sites where the main source of AEs is through municipal wastewater effluents. Where AEs in the ambient water are originating from other sources, such as industrial outflows, the average homologue distribution may be considerably different. If an initial measurement of total AE at the site has been found to exceed the default guidelines, then more in-depth evaluation through analysis of specific homologues could be considered. Use of the homologue-specific guidelines will give a better indication of whether AEs present at a particular site are in fact likely to cause adverse effects or not. In these cases, it would be advisable to use the homologue-specific guideline values presented in Table 3.

For determining the concentrations of individual AE homologues in ambient water at a particular site, the current recommended analytical approach is the pyridinium LC/MS method (Dunphy et al. 2001). Concentrations should be determined, at a minimum, for homologues with alkyl chains between 12 and 18 carbons long (excluding C_{17} AEs), and ethoxylate chains ranging from 0 to 18 EO units long. The measured concentrations of the homologues can then be compared with the homologue -specific guideline values in Table 3 using a Toxic Unit approach (see Boeije et al. 2006 for additional background on the construction of Toxic Unit approaches for AEs). For each individual homologue, the measured concentration is divided by the corresponding homologue -specific guideline listed in Table 3 to obtain the toxic unit for that particular homologue. The toxic units for all homologues present in the sample are then summed. If the total of all toxic units is less than or equal to one, then the AE guideline has not been exceeded. If the total of all toxic units is greater than one, this indicates an exceedence of the guideline.

For alcohol alkoxylates, where the hydrophilic chain of the surfactant contains a mix of ethoxylate, propoxylate, and/or butoxylate groups, the FWQGs for AEs may also be applied. This recommendation is based on data (see Roberts et al. 2007) that suggest that alcohol alkoxylates have similar aquatic toxicity to AEs of the same parent alcohol and with similar numbers of ethoxylate groups.

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List of Acronyms

AEs – alcohol ethoxylates
CAS – Chemical Abstracts Service
CCME – Canadian Council of Ministers of the Environment
CMP – Chemical Management Plan
DOM – dissolved organic matter
EC – effects concentration
EO – ethylene oxide
FWQG – Federal Water Quality Guidelines
LC – lethal concentration
MATC – maximum acceptable toxicant concentration
QSAR – quantitative structure activity relationship
SSD – **s**pecies sensitivity distribution
WWTP – **w**astewater treatment plant