ALKYLPHENOL
ETHOXYLATE

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THE SOAP AND DETERGENT ASSOCIATION

ALKYLPHENOL ETHOXYLATE

INTRODUCTION

This monograph summarizes: 1) critical fate and effects data required for an environmental risk assessment on alkylphenol ethoxylate (APE); and 2) conclusions drawn from a risk assessment of APE in the United States. Although focused on conditions in the U.S., data from other parts of the world that are critical 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 APE, its chemical structure and U.S. consumption volumes. The second section describes the function of APE in cleaning products. The third section describes its 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.

This paper is made from 50% recycled fibers that include 10% post consumer waste.

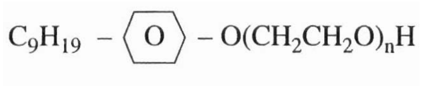
INGREDIENT IDENTIFICATION

Chemical Description

Alkylphenol ethoxylate (APE) is a nonionic surfactant composed of a branched alkylphenol (AP) coupled to a polyether chain consisting of ethylene oxide units. The alkylphenol is manufactured by reacting branched olefins with phenol in the presence of an acid catalyst.

By far the most commercially important alkylphenol is nonylphenol (NP); the nonene used in its manufacture is propylene trimer. NP is used primarily to produce nonylphenol ethoxylate (NPE) surfactants; other uses include phenolic resins, rubber curatives and antioxidants. NPE makes up about 80% of the total alkylphenol ethoxylate (APE) market. Also significant commercially are octylphenol (about 15-20%), dodecylphenol and dinonylphenol ethoxylates (about 1-2% each).

Commercial APE is manufactured by the base-catalyzed ethoxylation of alkylphenols. The reaction with ethylene oxide is rapid and consumes all of the alkylphenol. NPE surfactant is depicted as follows:



where $_n$ = the average number of moles of ethylene oxide per mole of nonylphenol and ranges from 1 to 100.

Relative amounts of the individual ethylene oxide (EO) oligomers follow a Poisson distribution with the peak at n.

Other nomenclature for NPE includes: nonoxynol; nonylphenol polyglycol ether; nonylphenoxy[poly (ethyleneoxy)]ethanol; an α-(p-nonylphenyl)-ω-hydroxy-poly(oxyethylene). Chemical Abstracts Service (CAS) numbers are 84852-15-3 for NP; 9016-45-9, 26027-38-3, 37205-87-1, 68412-54-4, 127087-87-0 and 152143-22-1 for NPE; 140-66-9 and 27193-28-8 for octylphenol; and 9002-93-1 and 9036-19-5 for octylphenol ethoxylate (TSCA Interagency Testing Committee, 1996a, 1996b).

Water solubility is directly proportional to n. NPE is water soluble for values of $n > 7$. The NPE most commonly used in cleaning products has $n = 9\text{-}10$ ($NPE_{9\text{-}10}$). Solubilities of NP and the lower NPE at 25°C are: 5 mg/L (NP), 3 mg/L (NPE_1), 6 mg/L (NPE_3), 10 mg/L (NPE_5) (Ahel and Giger, 1993a).

The octanol/water coefficients ($\log K_{ow}$) are: 4.5 (NP), 4.2 (NPE_1), 4.2 (NPE_3) (Ahel and Giger, 1993b). Partition coefficients (log K) of NP between three typical soils and water are: 3.60, 3.36 and 3.71 (Weston, 1991). The acid dissociation constant (pK_a) for NP is 10.7. Vapor pressure of NP at 25°C is 4.6×10^{-3} Pa (U.S. Environmental Protection Agency, 1997).

U.S. Consumption

Alkylphenol ethoxylate surfactants have been used in cleaning products and industrial processing for almost 50 years. Total U.S. consumption of APE now exceeds 500 million pounds per year (U.S. International Trade Commission, 1995). Major industrial applications for APE include latex paints and adhesives, inks, pesticide emulsions, textile and paper manufacturing, and institutional cleaners and detergents. APE (primarily NPE) is also used in household laundry and other cleaning products. Minor amounts may be found in personal care products, pharmaceuticals and cosmetics.

INGREDIENT FUNCTION

APE is an effective and economical emulsifier, wetting agent, dispersant and solubilizer. When APE is used in formulated cleaning products, levels can range up to 20% in liquid laundry detergents, and down to less than 1% in hard surface cleaners and personal care products. APE contributes to the performance of cleaning products by penetrating through oily soils, dislodging them and carrying them away, leaving the surfaces clean.

ENVIRONMENTAL FATE AND EXPOSURE

Fate

Cleaning products containing APE are disposed of mainly by discharge into wastewater which receives biological treatment in municipal or on-site waste treatment systems. Residual amounts then enter the aquatic environment via wastewater discharges and the terrestrial environment via sludge amendment to soils.

Biodegradation

Biodegradability of APE has been a subject of vigorous debate for the past quarter-century. The highly branched alkyl chain and phenolic ring are both impediments to rapid biodegradability, but bacteria have demonstrated the capacity to metabolize APE after a period of acclimation. Numerous studies have indicated NPE to be slowly and incompletely biodegraded under laboratory conditions (Talmage, 1994; Taeger, 1996). Wide variability of results and generally much lower rates and degree of biodegradation are obtained in the laboratory compared to field studies. This may be due to the inherent differences in microbiological culture vitality and diversity between laboratory and natural conditions. These studies have been valuable, however, in elucidating biodegradation pathways and relative biodegradability.

Recent studies document the ring opening and degradation of the phenoxy group of NPE. $^{14}CO_2$ evolution was used as a measure of phenoxy ring mineralization of NPE ring-labeled with ^{14}C under simulated activated sludge treatment and river die-away conditions (Naylor, Williams, Varineau, Yunick, Serak, Cady and Severn, 1998). In both cases conversion of the ring carbon to CO_2, non-aromatic water-soluble metabolites and biomass was measured along with disappearance of NPE.

Biodegradation of NP, octylphenol (OP), nonylphenol ether carboxylates (NPEC) and octylphenol ether carboxylates (OPEC) using standard OECD 301 test protocols has been recently described (Staples, Williams, Blessing and Varineau, 1999). They are degraded to near or over 60%, but fall just short of passing the tests as "readily biodegradable" (defined as reaching 60% of theoretical mineralization within a 10-day window of the 28-day test), so may be termed "inherently biodegradable."

Treatability

AP and APE have no more than minor inhibitory effects on bacteria except at high concentrations. Sewage and soil microorganisms are not adversely affected by these surfactants at concentrations normally encountered. APE levels seen in influents to wastewater treatment plants showing high removal rates, both municipal and industrial plants, range from less than 1 mg/L to over 20 mg/L. Concentrations over 50 mg/L may be inhibitory (Talmage, 1994).

More definitive evidence of the high treatability of NPE under real-world conditions is a recent study of U.S. wastewater treatment plants. NPE removal ranged from 92.5% to 99.8% with approximately uniform loss of all EO oligomers, a strong indication that biodegradation was the primary mechanism of removal. Effluent concentrations were <5 to 200 ppb NPE_{1-18}. In most cases, the fraction of NPE removed through adsorption onto sludge was not determined; it is thought to be small in efficiently operating plants, since the one plant where the sludge was analyzed indicated 0.1% of the influent NPE ended up in the sludge as NP (The Alkylphenols and Ethoxylates Research Council, 1999; Naylor, 1992, 1995 and 1996; and Naylor, Williams, Varineau and Webb, 1996). There is still the potential for extensive partitioning into sludge when treatment plants are not operating optimally.

Removal of NPE by activated sludge and trickling filter treatment plants in Germany was 89% and 75%, respectively. Effluent concentrations were reported to be about 150 ppb. NPE removal was also measured at a number of Swiss plants. The extent of removal varied with operating conditions of the plants, from 1% to over 90%, and effluent NPE oligomer distributions were skewed toward the low-EO oligomers (Talmage, 1994). These distributions indicated reduced degradability of these species and their *ortho* isomers. This distribution pattern has been reported elsewhere, but is not universal and may indicate sub-optimum treatment conditions (Ahel and Giger, 1985; Giger, Ahel, Koch, Laubscher, Schaffner and Schneider, 1987; Kubeck and Naylor, 1990; Naylor, 1995).

NP, NPE_1 and NPE_2 accumulate in municipal sludge during anaerobic digestion (Giger, Brunner and Schaffner, 1984), and may biodegrade further, but slowly, under anoxic conditions. Once the sludge is applied to aerated soil, degradation resumes immediately and essentially proceeds to completion (Talmage, 1994; Marcomini, Capel and Giger, 1988). The data show that no accumulation of these species occurred in the soil from years of sludge loading. NPE applied directly to soil, in a simulation of soil exposure by pesticide spray adjuvant application, degrades completely within 63 days, as measured by disappearance of the aromatic ring (Hughes, Fisher and Brumbaugh, 1996). Therefore, composting and land farming of APE-containing sludge is an effective means for continued degradation of APE traces.

Exposure

Aquatic

Concentrations of APE in streams that receive treated wastewater could be estimated using APE usage levels, household water usage, treatability under different treatment options and dilution into receiving streams. Alternatively and preferably, the actual concentrations measured in chemical monitoring programs can be used to describe their fate and to evaluate their potential effects on the aquatic environment.

A very extensive database on environmental occurrence of APE was generated involving 30 U.S. rivers (Naylor, Mieure, Adams, Weeks, Castaldi, Ogle and Romano, 1992). The sample locations were taken from the U.S. EPA River Reach File. The specific sites used in this study were selected randomly from a subset of reaches judged most likely to receive APE via effluents from municipal wastewater treatment plants or industrial discharges. The study was intended to provide a statistically valid set of sites of likely APE environmental exposure in the U.S., and the study design was sanctioned by the U.S. EPA. Both water and sediment were sampled from three points along perpendicular transects across the rivers and analyzed for NP, nonylphenol-1EO (NPE_1), nonylphenol-2EO (NPE_2) and the aggregate total of higher NPE oligomers (NPE_3 to NPE_{17}). Table 1 summarizes the measured NP and NPE concentrations in the Thirty River Study.

Nonylphenol, believed to be the most toxic of the monitored components to aquatic life, was not detected in 70% of the water samples taken in this study. The minimum detection limit for NP was 0.11 ppb (parts per billion or µg/L). Overall, 95% of the water samples contained 0.35 ppb or less of NP. The highest concentration observed was 0.64 ppb in a highly polluted stream draining an area of heavy industry (Grand Calumet River in Gary, Indiana). The 95th percentiles of NP concentrations in river water and sediments have also been derived from log normal distribution curves of the environmental measurements of NP to be 0.265 ppb in river water and 461 ppb in sediments (Weeks, Adams, Guiney, Hall and Naylor, 1996). The derived estimates, which are slightly lower than the 95th percentiles of the raw data summarized in Table 1, are considered more representative because they are based on consideration of all of the data.

NPE$_1$ was below the detection limit of 0.06 ppb in 67% of the water samples taken. Overall, 95% of the samples contained no more than 0.31 ppb of NPE$_1$, and the maximum concentration observed was 0.60 ppb. NPE$_2$ was present at less than the detection limit of 0.07 ppb in 58% of the water samples. Overall, 95% of the samples contained no more than 0.46 ppb, and the maximum observed concentration was 1.2 ppb.

The higher NPE oligomers (NPE$_3$ to NPE$_{17}$) were measured in the aggregate, with a detection limit of 1.6 ppb for the total of the oligomers in water. In this study, 76% of the water samples were below that detection limit, 95% contained no more than 6.6 ppb, and the maximum value observed in any sample was 14.9 ppb. This value was also found in the Grand Calumet River.

Sediment

Sediment samples from the 30 rivers contained higher levels of NP and NPE$_1$ than did the water samples (Naylor, Mieure, Adams, Weeks, Castaldi, Ogle and Romano, 1992), a consequence of the strong adsorption of these water-insoluble components into the organic fraction of the sediments. Twenty-eight percent of the sediment samples were below the detection limit for NP (2.9 µg/kg dry weight, or ppb), and 44% were below the detection limit for NPE$_1$ (2.3 µg/kg). Overall, 95% of the sediment samples contained less than 580 µg/kg NP and 89 µg/kg NPE$_1$. Maximum levels found were 2,960 ppb of NP (Grand Calumet River) and 175 ppb of NPE$_1$.

Nonylphenol concentrations in the pore water of the sediments were calculated from NP soil adsorption data (average soil/water partition coefficient = 3,800) to be essentially the same as the concentrations in the water flowing over the sediments.

NPE was extracted from marine sediments at the outfall of primary sewage discharge from Vancouver, British Columbia and analyzed using LC-MS (Shang, Ikonomou and Macdonald, 1999; Shang, Macdonald and Ikonomou, 1999). While levels were low (µg/kg dry solids for each oligomer, mg/kg total), a full distribution of NPE oligomers was seen. Not determined was how much was adsorbed onto the sediments and how much was in the pore water.

Table 1. Nonylphenolic Concentrations in Thirty U.S. Rivers

Analyte	Range	Average	Highest value in lowest 95%	Percent of samples below DL[a]
Water	**µg/L**			
NP	<0.11-0.64	0.12	0.35[b]	70
NPE$_1$	<0.06-0.60	0.09	0.31	67
NPE$_2$	<0.07-1.2	0.10	0.46	58
NPE$_{3-17}$	<1.6-14.9	2.0	6.6	76
Sediment	**mg/kg dry weight**			
NP	<2.9-2,960	162	580[c]	28
NPE$_1$	<2.3-175	18.1	89	44

[a] DL = analytical detection limit

[b] Value derived from log normal distribution curve = 0.265 µg/L

[c] Value derived from log normal distribution curve = 461 mg/kg dry weight

Other Monitoring Studies

In separate studies (Talmage, 1994), significant levels (up to 18 ppb) of NPE_1 and NPE_2 were reported in a highly polluted Swiss river, along with up to 2 ppb of nonylphenol and up to 120 ppb of NPE carboxylates, another group of degradation intermediates. Swiss data for nonylphenol, collected in 1983-1985, contrast with U.S. data by being several-fold higher than the highest concentration found in U.S. rivers. A follow-up study of the same Swiss river in 1997 reported a large reduction of concentrations, attributed to both restrictions and bans of NPE from cleaning products and improved wastewater treatment (Ahel, Giger, Molnar, Ibric, Ruprecht and Schaffner, 1998). Recently NPE carboxylate levels were measured in some of the 30 rivers previously examined for NP and NPE concentrations, and were found to be low, similar to NPE levels (Field and Reed, 1996; Varineau, Williams and Field, 1996).

Extensive monitoring data on NP, NPE_1, NPE_2 and OP in Canada, including effluents, sludge and receiving waters, are generally consistent with U.S. data (Bennie, Sullivan, Lee, Peart and Maguire, 1997; Bennett and Metcalfe, 1998; Bennie, 1999; Maguire, 1999), except for a small number of highly polluted sites. OP levels were lower than NP, as expected. Higher ethoxylate oligomers and carboxylates were not included in the analyses. Similarly, limited monitoring in UK rivers and estuaries for NP showed very low levels except at points of untreated industrial wastewater discharge (Blackburn and Waldock, 1995).

Octylphenol and its ethoxylates have not previously been monitored separately from NP and NPE because the analytical methods used for trace level monitoring did not distinguish among them. NP and NPE reported values include any OP and OPE present. It was assumed that NP species are more prevalent than OP species in proportion to their relative market sizes.

Monitoring of a U.S. river receiving large volumes of wastewater from paper mills and cities, both major sources of NPE, demonstrated the levels of NPE in the environment that can result from biological wastewater treatment (Naylor, Williams, Varineau and Webb, 1996). All wastewater streams entering the lower Fox River of Wisconsin, and the river itself, were assayed for NPE over two years. NPE carboxylates (NPEC) were included in the last phase of the study, the summertime sampling (Field and Reed, 1996; Naylor, Varineau and Field, 1996). Average concentrations (sums of all oligomers) of NPE and NPEC in treated wastewaters were about equal, but the relative amounts varied widely, similar to previously published results (Ahel, Giger and Koch, 1994). Apparently, treatment conditions strongly influenced the ratio of NPE to NPEC. At the point of the highest Fox River water concentration of NPEC (13 ppb at the river mouth), the NPEC concentration was higher than that of NPE (4 to 8 ppb), partly because of greater influx of NPEC and partly because of more rapid degradation of NPE in the river (Ahel, Giger and Schaffner, 1994).

A monitoring study of NPE at a treatment plant in Rome, Italy found a wide range of effluent concentrations (NP, NPE and NPEC) over a period of one year. However, the effluent concentrations were within the range of concentrations found in the Fox River treatment plant effluents (Di Corcia, Samperi and Marcomini, 1994).

A survey of 16 Canadian primary and secondary treated wastewater streams (Bennie, Sullivan, Lee and Maguire, 1998) found varying levels of NP (<0.02 to 13 μg/L), NPE_1 (0.07 to 26 μg/L), NPE_2 (0.10 to 21 μg/L) and OP (<0.005 to 0.37 μg/L). A related study focused on ether carboxylate metabolites of NPE and OPE; total carboxylate levels in the eight final effluents analyzed ranged from 18 to 1,276 μg/L. No description of the plants was given, so no conclusions regarding treatability can be made (Lee, Weng, Peart and Maguire, 1998).

Discharge of NPE-containing raw sewage into an estuary resulted in traces being detectable for some time and distance from the outfalls. Biodegradation is apparently much slower because of lower bacteria concentrations in the estuary compared to biological treatment systems (Kvestak and Ahel, 1994; Kvestak, Terzic and Ahel, 1994).

Sewage Sludge

Nonylphenol and the water-insoluble lower oligomers of NPE adsorb onto sludge and sediments with an organic carbon component because of their hydrophobic character. Sewage sludge was reported to be a major sink for nonylphenol in Swiss wastewater treatment plants (Giger *et al.*, 1984); levels found were about 1 g/kg of dry sludge. Some values for NP levels in sludge have been reported recently (Williams and Varineau, 1996). Levels ranged from well below one hundred, up to a few hundred ppm, according to this report of preliminary findings. The wide variation of levels suggests that treatment plant operating conditions may be highly variable.

ENVIRONMENTAL EFFECTS

Aquatic

The toxicity of APE to aquatic life has been studied extensively (Talmage, 1994; Servos, 1999). In fish, the acute toxicity (LC_{50}) of APE ranges from 1,300 μg/L (or parts per billion, ppb) for NPE_4 to over 1,000,000 ppb for NPE_{30}. Most values are between 4,000 and 12,000 ppb. For fresh and salt-water invertebrates, the LC_{50} for APE range from 2,900 to >100,000 ppb. At less than 10,000 ppb, APE does not inhibit growth of most algae species.

Nonylphenol, a trace impurity in NPE and a biodegradation intermediate, is more toxic than the ethoxylates. NP inhibits growth of algae at concentrations as low as 40 ppb. Acute LC_{50} values for NP with fish vary from 130 to 1,400 ppb and NPE_9 from 1,000 to 10,000 ppb. With *Daphnia magna* (water flea), a representative aquatic invertebrate, LC_{50} values are 180 to 400 ppb and 14,000 for NP and NPE_9, respectively. The chronic NOEC (no-observable effect concentration) and MATC (maximum acceptable toxicant concentration) of NP for *Daphnia magna* are 24 ppb and 50 ppb, respectively; for fathead minnow 7 ppb and 10 ppb, respectively; for rainbow trout 6.3 ppb and 8.7 ppb, respectively; and for mysid shrimp 3.9 ppb and 5.1 ppb, respectively (Talmage, 1994). $NPE_{1,2,3}$ exhibit toxicity between NP and NPE_9, with LC_{50} values ranging from 1,000 to 3,000 ppb for aquatic organisms, although data are limited. Table 2 summarizes the pertinent data. The chronic NOEC and MATC of $NPE_{1.5}$ for mysid shrimp are 7.7 and 11 ppb, respectively (The Alkylphenols and Ethoxylates Research Council, 1999), showing it to be about half as toxic as NP.

The reproductive toxicity of NP toward *Ceriodaphnia dubia* is less than other chronic end points noted above. The NOEC for this effect is 89 ppb. $NPE_{1.5}$ is less toxic in the same 7-day reproduction test, with a NOEC of 285 ppb (England, Bucksath, Naylor and Varineau, 1995).

Nonylphenol may bioconcentrate to a moderate degree, but any concentration into organisms (fish, mussels) is rapidly reversible (Talmage, 1994). Recent studies of fish bioconcentration factors (BCF) report BCFs of 350 and 741 (fathead minnow) and 220 (bluegill) (Brooke, Thompson, Kahl and Cox, 1994).

An ambitious mesocosm study by the U.S. EPA has been reported. Dosing of nonylphenol into pond enclosures and following its effects on many classes of aquatic organisms over a period of months caused no measurable effects on community structure at or below 76 ppb. A conservative estimate of the MATC was 10 ppb (Liber, Knuth and Stay, 1999; Heinis, Knuth, Liber, Sheedy, Tunell and Ankley, 1999; O'Halloran, Liber, Gangl and Knuth, 1999; Schmude, Liber, Corey and Stay, 1999; Liber, Gangl, Corey, Heinis and Stay, 1999).

A 14-day toxicity study of midge larvae in nonylphenol-dosed sediment gave a NOEC of 20,100 µg/kg and MATC of 26,100 µg/kg (England and Bussard, 1993). Reviews of the aquatic toxicology and bioconcentration of APE were recently published (Staples, Weeks, Hall and Naylor, 1998; Servos, 1999).

Terrestrial

Nonylphenol at levels of 100 mg/kg or less in soil, dosed via sewage sludge, has no effect on microorganisms in the soil (Trocme, Tarradellas and Verdy, 1988). No soil macroorganism effect or plant root uptake studies have been reported.

Estrogenic

Alkylphenols and ethoxylates have been reported to exhibit estrogenic effects in fish, both *in vitro* and *in vivo* (White, Jobling, Hoare, Sumpter and Parker, 1994; Jobling, Sheahan, Osborne, Matthiessen and Sumpter, 1996; Tyler and Routledge, 1998). Rainbow trout hepatocytes produced the egg yolk protein vitellogenin at levels of these compounds close to their cytotoxic thresholds. Nonylphenol, OP, NPE_2 and NPE_1C were specifically studied. Increased blood levels of vitellogenin were found in male rainbow trout after exposure for three weeks to NP at 20 µg/L, OP at 5 µg/L, NPE_2 at 30 µg/L and NPE_1C at 30 µg/L. Testis growth in juvenile male fish was reduced by the four compounds at 30 µg/L, but no consistent effect on testis size was seen in full-grown fish exposed to OP at concentrations up to 44 µg/L. A dose-response study of gonad growth in maturing males indicate the NOEC is 10.1 µg/L and the MATC is 33.2 µg/L (Jobling *et al.*, 1996). The apparent estrogen potency of NP is 10^{-4} to 10^{-6} as strong as that of estradiol (Nimrod and Benson, 1996).

A recent study isolated and identified the estrogenically-active substances present in seven United Kingdom wastewater treatment plants (Desbrow, Waldock, Sheahan, Blackburn, Routledge, Sumpter and Brighty, 1996). They were 17ß-estradiol, estrone (both in all effluents) and ethinyl estradiol (in at least one sample of three effluents). All of these estrogen hormones are believed to be anthropogenic and were present in unbound, biologically-active forms. Concentrations of the first two were high enough (0.010 to 0.076 µg/L) in some of the effluents to elicit the vitellogenin response in male fish. The nonylphenol-containing fractions from treatment plant effluents were all estrogenically inactive. The UK Environment Agency recognizes the need for improved sewage treatment to give greater protection to the aquatic environment, but does not exonerate NPE as a possible causative agent at highly contaminated sites.

A similar result was recently reported at U.S. sites, the Las Vegas Wash and Las Vegas Bay of Lake Mead, Nevada, and downstream from a number of wastewater treatment plant effluents in Michigan (Renner, 1998; Snyder, Keith, Verbrugge, Snyder, Gross, Kannan and Giesy, 1999). Estrogen steroids were identified as the estrogenically active components, and NP was not in the active fractions.

RISK ASSESSMENT

A risk assessment is made by a comparison of toxicity data with the water and sediment concentrations found in the U.S. river survey described above. The levels of nonylphenol and NPE in the most polluted rivers in the survey were well below the no-observable effect concentration of the most sensitive species. Table 2 summarizes some key toxicity values and concentrations of NP and NPE from the Thirty River Study. The comparison of quantitative measures of exposure concentrations to effects concentrations are based on NP rather than on NPE or NPEC, because NP is the most toxic and thus provides a worst case for environmental risk assessment. While quantitative assessments of risks posed by NPE and NPEC have not been done, the values in Table 2 illustrate that exposure levels for these two substances are well below concentrations found to cause effects, due to their lower toxicity and, in the case of NPEC, much greater water solubility and lower adsorptivity.

The exposure concentrations used in the risk assessment are appropriately based on the 95th percentiles of the log normal distributions of NP concentrations in river water and sediments, 0.265 ppb and 461 mg/kg, respectively (Weeks, 1996, 1998). The critical comparisons for assessing the safety of NP using both MATC (maximum acceptable toxicant concentration) and NOEC values for the most sensitive species are:

- the mysid shrimp effect threshold (length at 28 days; MATC = 5.1 µg NP/L; NOEC = 3.9 µg NP/L) is 19 to 15 times higher, respectively, than the 95th percentile estimate of NP in river water (0.265 µg NP/L);
- the midge larvae effect threshold (14 day sub-chronic; MATC = 26,100 µg NP/kg; NOEC = 20,100 µg NP/kg) is 57 to 43 times higher, respectively, than the 95th percentile estimate of NP in sediment (461 µg NP/kg); and
- the rainbow trout estrogenic effects threshold (inhibition of testicular growth; MATC = 33.2 µg NP/L; NOEC = 10.1 µg NP/L) is 125 to 38 times higher, respectively, than the 95th percentile estimate of NP in river water (0.265 µg NP/L) and higher than the chronic toxic effect threshold (MATC = 8.7 µg NP/L, NOEC = 6.3 µg NP/L).

A conservative assessment can be done for NP in terrestrial compartments. Assuming sludge application to soil at a typical rate of 10 tons per hectare mixed into the top 10 cm of soil, with NP present in sludge at the highest levels reported (1,000 µg/kg; Ahel, Giger and Koch, 1994), the initial NP concentration would be about 10 µg/kg in the soil. This concentration would be 10,000 lower than the level known to cause no effects in microorganism (100 mg/kg).

CONCLUSION

APE undergoes rapid breakdown during conventional wastewater treatment and continues to degrade in aerated water and soil. APE was not detected in most water samples gathered in a comprehensive survey of U.S. rivers receiving wastewater discharges. The highest level in river water of nonylphenol, the most toxic APE biodegradation product, was less than 1 µg/L (0.64 µg/L). This level was about an order of magnitude below the chronic toxicity threshold for the most sensitive freshwater organism (NOEC of 6.3 µg/L, MATC 8.7 µg/L).

APE bioaccumulation potential is low, since nonylphenol uptake by fish and mussels is modest and reversible, the ethoxylates are more water soluble than nonylphenol, and the ethoxylates are not metabolized to nonylphenol *in vivo*. Levels of nonylphenol in river sediments are at least an order of magnitude below the toxicity threshold to benthic organisms, and ethoxylate levels in sediment are still lower.

While the potential hazard of manmade compounds which may disrupt endocrine function must be taken seriously, and much research is underway to understand their modes of action, the risk to aquatic organisms and wildlife due to APE surfactant residues appears to be very low. Other, more conventional, measures of environmental toxicity are more sensitive and the data base is much more extensive.

The impact of APE on the aquatic environment is minimal when disposed of properly, that is, into wastewater biological treatment systems. Concentrations of APE in the environment are well below thresholds of toxicity, except possibly where wastewater treatment is poor or absent.

Table 2. Aquatic Toxicity and Environmental Concentrations of APE[a]

	NP				NPE9			NPEC	
	LC_{50}	NOEC	MATC	**Environmental Concentration**	LC_{50}	MATC	**Environmental Concentration**	LC_{50}	**Environmental Concentration**
Aquatic Toxicity - Water (µg/L)									
Fathead minnow, 96 hr acute	300				4,600				
Killifish, 96 hr acute								9,000	
Fathead minnow, 7 day chronic						1,400			
Fathead minnow, 28 day chronic		7.4	10.0						
Rainbow trout, 91 day growth		6.3	8.7						
Rainbow trout, testicular growth		10.1	33.2						
All fish, LC_{50} acute range	130-1,400				1,300-1,000,000				
Daphnia magna, 48 hr acute	440				14,000				
Daphnia magna, 7 day chronic						14,000			
Daphnia magna, 28 day chronic		24	50						
Mysid shrimp, 28 day growth		3.9	5.1						
All invertebrates, LC_{50} acute, range	20-1,590				2,900-100,000				
Selenastrum capricornutum, EC_{50} 96 hr acute	400				12,000				
All algae, EC_{50} acute, range	25-750				210-5,000,000				
Aquatic Concentrations - Water (µg/L)									
U.S. Thirty River Study, highest level in lowest 95%				0.35			6.6		
U.S. Thirty River Study, highest level				0.64			14.9		
U.S. Thirty River Study, 95% value from log normal distribution				0.265					
Limited U.S survey, highest value									13
Aquatic Toxicity - Sediment (µg/kg)									
Midge, 14 day sub-chronic		20,100	26,100						
Aquatic Concentrations - Sediment (µg/kg)									
U.S. Thirty River Study, highest level in lowest 95%				580					
U.S. Thirty River Study, highest level				2,960					
U.S. Thirty River Study, 95% value from log normal distribution				461					

[a] Talmage, 1994; The Alkylphenols and Ethoxylates Research Council, 1999; Jobling *et al.*, 1996; Weeks *et al.*, 1996; Staples *et al.*, 1998

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