APE RESEARCH COUNCIL

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ALKYLPHENOLS & ETHOXYLATES RESEARCH COUNCIL COMMENTS TO THE CALIFORNIA AIR RESOURCES BOARD ON PROPOSED RESTRICTIONS ON THE USE OF ALKYLPHENOL ETHOXYLATES IN CERTAIN CONSUMER CLEANING PRODUCT CATEGORIES SUBMITTED NOVEMBER 17, 2010

The Alkylphenols & Ethoxylates Research Council (APERC) provides the following comments in opposition to proposed regulations that would restrict the use of alkylphenol ethoxylates (APEs) in certain classes of consumer cleaning and degreaser products. For more than twenty years APERC and its member companies have been actively engaged in the conduct and review of toxicological and environmental fate and effects research on alkylphenol (APs) and APEs.[1] Consequently, APERC can contribute considerable information and expertise relevant to the environmental and toxicological assessment of these substances.

At the advice of the State Water Resources Control Board (SWRCB), the California Air Resources Board (ARB) is proposing regulatory measures to prohibit the use of APE surfactants in certain cleaning product categories. These prohibitions are proposed to ensure that cleaning products are not reformulated with APEs in an effort to meet VOC limits also being proposed by ARB. Specifically, APE surfactants would be prohibited from use in Oven or Grill Cleaner products and in the nonaerosol forms of general purpose cleaner, general purpose degreaser, and glass cleaner after December 31, 2012. A prohibition on use in nonaerosol heavy-duty cleaner or soap products would become effective in December 2013. ARB is proposing these measures for the following reasons:[2]

1. "APEs, in particular octylphenol and nonylphenol ethoxylates, have been found to be toxic to aquatic species;
2. They are hormone disruptors, with the primary concern focused on the estrogenic effects;
3. The SWRCB staff is 'concerned that any potential additional use of APEs could adversely impact aquatic life'; and,

[1] Current members of the Alkylphenols & Ethoxylates Research Council include: Dover Chemical Corporation; SI Group; TPC Group; and The Dow Chemical Company.

[2] California Air Resources Board (ARB). (2010, September 29). Initial Statement of Reasons: Proposed Amendments to the California Regulation for Reducing Emissions from Consumer Products and Test Method 310: Determination of Volatile Organic Compounds in Consumer Products and Reactive Organic Compounds in Aerosol Coating Products.

4. Replacements for APEs, which SWRCB considers to be 'more effective and environmentally safe', are available."

In its memo advising the ARB on this issue the SWRCB expressed concerns that:

1. "The level of aquatic toxicity posed by APEs is high enough to cause concern;
2. APEs are being discharged into coastal, estuarine, and freshwater by means of wastewater treatment plants, storm water and other sources in California (and elsewhere); and,
3. APEs seem to bioaccumulate in marine vertebrates and invertebrates and persist in environmental compartments such as sediments." [3]

The Alkylphenols & Ethoxylates Research Council provides the following comments to respond to the concerns raised by ARB and SWRCB and to inform the two Boards about additional available study results on APEs and their environmental degradants.

1.0 US EPA WATER QUALITY CRITERIA (WQC) FOR NP IN FRESH AND MARINE SURFACE WATERS AND PREDICTED NO EFFECT CONCENTRATIONS (PNECS) FOR NP IN SEDIMENT (CALCULATED ACCORDING TO GOVERNMENTAL GUIDELINES) ARE AVAILABLE AND PROVIDE A BASIS TO CONDUCT SCREENING RISK ASSESSMENTS IN CALIFORNIA

The fact that APEs are toxic to aquatic life is not surprising or unique among surfactants; all surfactants are toxic to aquatic life. In addition, the detection of AP/APEs in measurable quantities in California waters and/or sediment is not a sufficient basis for concern, particularly since NP-equivalent concentrations of these compounds found in the aquatic environment in California generally do not exceed the US EPA WQC and/or PNECs that have been calculated according to governmental guidelines for NP in sediment.

1.1 In 2006, US EPA finalized acute and chronic aquatic life ambient WQC for NP (the most toxic of the NPE degradation intermediates) that are protective of aquatic species that dwell in fresh and salt water[4]

The US EPA Office of Water conducted a significant review of the available data for NP in support of its aquatic life ambient WQC for NP.[5] US EPA utilizes a statistical extrapolation procedure that draws upon both acute and chronic toxicity data from a wide

[3] Polhemus, D., State, Water Resources Control Board (SWRCB). (2010, Sept. 20) Memo to Air Resources Board: Water Quality Effects of Alkylphenol Ethoxylate Surfactants.

[4] US Environmental Protection Agency (US EPA). (2006, February 23). Notice of availability of final aquatic life ambient water quality criteria for nonylphenol. Federal Register, 71 (36), 9337-9339. http://www.epa.gov/EPA-WATER/2006/February/Day-23/w2558.htm.

[5] US Environmental Protection Agency (US EPA). (2005). Aquatic life ambient water quality criteria - nonylphenol. Report 822-R-05-005. US Environmental Protection Agency, Washington, DC, USA.http://www.epa.gov/waterscience/criteria/nonylphenol/final-doc.pdf

range of taxa and species to develop WQC that are "an estimate of the highest concentration to which an aquatic community can be exposed indefinitely without unacceptable effect."[6] In the case of NP, US EPA used results from acute studies (representing 18 freshwater species and 11 saltwater species) to statistically calculate a Final Acute Value (FAV) along with results for apical endpoints related to population level assessments of organism health (e.g., reproduction and growth) from chronic tests (representing 5 freshwater species and 1 saltwater species) to calculate acute-to-chronic ratios. Since the chronic endpoints used to derive the chronic NP WQC reflect the culmination of molecular, biochemical and tissue-level effects at the whole organism level, the NP WQC in turn addresses all mechanisms of action – including estrogenic effects – that result in measurable alterations in these apical endpoints. Although NP has been shown to have weak estrogenic activity, US EPA noted in the NP WQC document that "the ability of nonylphenol to induce estrogenic effects has seldom been reported at concentrations below the freshwater Final Chronic Value of 6.5965 µg/L."[7]

In 2006, EPA finalized the following acute and chronic criteria for NP in both fresh and salt waters:

> Acute WQC for NP: 28.0 µg/L (fresh water) and 7.0 µg/L (salt water)
> Chronic WQC for NP: 6.6 µg/L (fresh water) and 1.7 µg/L (salt water)[8]

The EPA WQC were developed using data available for NP as of 2005. EPA's conclusions were consistent with a species sensitivity distribution analysis based on essentially the same chronic data set conducted by Staples *et al*. (2004), which calculated a similar freshwater chronic value (5.7 µg/L at the lower bound 10th percentile) based on 90 chronic toxicity values for NP reported for 16 species of freshwater aquatic invertebrates and vertebrates.[9]

1.2. A review of studies published since finalization of the EPA WQC for NP found that more recent toxicity data do not contraindicate that the WQC are sufficiently protective of fresh and saltwater aquatic species

Since the finalization of the NP WQC additional ecotoxicity data have been reported; therefore, Coady *et al.*, (2010) completed a comprehensive literature search for the period between 1997 and 2009. [10] One purpose of the literature search was to identify any studies published on NP since EPA finalized the NP WQC. Also, in light of interest in other environmentally relevant metabolites of NPE (e.g., NPE1, NPE2, NPE>1, and NPEC) studies on these compounds were also identified and reviewed.

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[6] US EPA. (2005).
[7] US EPA. (2005).
[8] US EPA. (2006, February 23).
[9] Staples, C., Mihaich, E., Carbone, J., Woodburn, K., & Klečka, G. (2004). A weight of evidence analysis of the chronic ecotoxicity of nonylphenol ethoxylates, nonylphenol ether carboxylates, and nonylphenol. Human and Ecological Risk Assessment, 10 (6), 999-1017.
[10] Coady, K., Staples C., Losey B., & Klecka G. (2010). A Hazard Assessment of Aggregate Exposure to Nonylphenol and Nonylphenol Mono- and Di-ethoxylates in the Aquatic Environment. Human and Ecological Risk Assesment 16: 1066-1094.

Following the practices employed in the development of the 2006 EPA WQC for NP, studies were deemed valid and relevant for use in a hazard assessment – or development of WQC – if they contained a thorough description of the experimental design, had a clear linkage between reported findings and the experimental design, contained an ecologically relevant apical endpoint, such as growth, survival or reproduction, and exhibited adequate performance of controls.

As part of the literature review the authors examined studies investigating the effects of NPE and NP on secondary endpoints, such as behavioral effects, induction of biochemical markers, or alterations in cells within tissue. From these studies, the types of endpoints being measured, the range of effect concentrations associated with NPE and its breakdown products, and the possible mechanisms of action of these compounds in various aquatic species were examined. In summary, there were a total of 30 recent studies (17 with freshwater and 13 with marine species) that examined apical endpoints (survival, growth and reproduction) relevant for risk assessment of NP in a broad range of species (i.e., fish, frogs, echinoderms, crustaceans, mollusks, and diatoms). The review found that these recent studies add to the weight-of-evidence that supports EPA's current fresh and saltwater WQC for NP.[11]

In summary, an abundant data set of apical and secondary endpoints in aquatic species exists for NP and is summarized in Table 1 along with the results for other NPE metabolites. Furthermore, there are no definitive data in the recent literature to contraindicate that the current fresh and saltwater chronic WQC for NP are sufficiently protective of aquatic communities. [12]

1.3 Adequate data are available to calculate sediment PNECs for NP using established governmental methodologies; these can be used to conduct screening assessments of concentrations of NP/NPE and OP/OPE in sediment

In comments to SWRCB, the Southern California Coastal Water Research Project (SCCWRP) expressed concern that "we do not have a good idea of sediment threshold levels that would be protective of aquatic marine or freshwater life". [13] However, adequate data exist and PNECs can – and have been – calculated. These are discussed below.

1.3.1 Sediment PNECs have been calculated using the equilibrium partitioning method

[11] Coady. (2010).
[12] Coady. (2010).
[13] Maruya, K., Southern California Coastal Water Research Project (SCCWRP).(2010, July 15). Letter to SWRCB: Effects on Water Quality of Alkylphenol Ethoxylate Surfactants.

PNEC (sediment) values have been calculated for NP by the Canadian government using Equilibrium Partitioning methods. [14, 15] In 2001, Environment Canada calculated an Environmental No Effect Value (ENEV) for NP in sediment of 2 µg/g (2000 ng/g) and, using Relative Toxicity Factors, calculated an ENEV of 4.0 µg/g (4000 ng/g) for NPE1 and NPE2.[16] Also in 2001, the Canadian Council of Ministers of the Environment (CCME) calculated interim sediment quality guidelines (ISQGs) for NP and its ethoxylates of 1.4 mg/kg-dw (1400 ng/g-dw) in freshwater sediment and 1.0 mg/kg-dw (1,000 ng/g-dw) in marine sediments.[17] These CCME ISQGs are expressed on a Toxicity Equivalence Basis.

While equilibrium partitioning is useful to provide a rough estimate of the potential ecotoxity of a compound in the absence of ecotoxicity data in benthic species, this approach is subject to shortcomings due to its reliance on basic physical and chemical properties to determine partitioning of the chemical between water and sediment. Therefore, more accurate and relevant PNECs are derived using guidelines based on actual ecotoxicity studies in living organisms and are discussed below.

1.3.2 Sediment PNECs have been calculated using chronic ecotoxicity data from benthic organism studies conducted on NP in sediment

Since an adequate number of ecotoxicity studies are now available to calculate toxicity-based PNECs for benthic organisms with sediment-dosed concentrations of NP, Staples *et al*. (2010) recently calculated freshwater and marine PNECs for NP of 6,150 ng/g-dw and 2,130 ng/g-dw, respectively. In addition, Staples *et al*. (2010) conducted an assessment of potential risk of NP to sediment dwelling organisms that considered the available sediment monitoring data from the literature, including data cited by SWRCB.[18]

Table 2 summarizes the short-term acute and sub-chronic ecotoxicity studies on NP in sediment dwelling organisms, which demonstrate the wide range of ecotoxity data that are available for this compound; however acute and sub-chronic data were not used to derive the chronic sediment PNECs for NP.

Table 3 summarizes long-term chronic sediment toxicity data for nonylphenol using aqueous exposure and dosed sediments, which were used to derive the PNEC (sediment) values for NP. The lowest chronic No Observed Effect Concentration (NOEC) was 61,500 ng/g-dw, as determined from a 28-day survival and reproduction study on NP in the Amphipod (M) *Leptocheirus plumulosus*, published by Zulkowski *et*

[14] Environment Canada and Health Canada (EC and HC). (2001). Priority substances list assessment report for nonylphenol and its ethoxylates. ISBN: 0-662-29248-0. http://www.hc-sc.gc.ca/ewh-semt/pubs/contaminants/psl2-lsp2/nonylphenol/index-eng.php.
[15] CCME PNEC
[16] EC/HC CEPA Assessment, 2001
[17] CCME ISQGs for Sediment 2001
[18] SCCWRP.(2010, July 15)

al. (2002). [19] An assessment factor (AF) of 10 was applied in accordance with the guidance to derive the PNEC (sediment, fresh) as three chronic tests with species with different feeding and living conditions were available and a PNEC (sediment, fresh) of 6,150 ng/g-dw was derived. An AF of 50 was applied to the lowest sediment-based NOEC, since only one marine species was available, to derive the PNEC sediment (marine) of 1,230 ng/g-dw.

Table 4 summarizes available environmental monitoring data for NP in freshwater and marine sediment (ng/g-dry weight). The whisker graphs in Figure 1 compare the sediment monitoring results to the PNEC (sediment, freshwater) or PNEC (sediment, marine). From nine studies, 327 sediment samples were collected from fresh surface water systems in North America and Europe. From 12 studies, 132 sediment samples were collected from estuarine and coastal marine sites. Most freshwater (~93%) and marine (~96%) data are below their respective PNEC (sediment) values. Of those samples taken in California, only one sample from a coastal wastewater treatment outfall site exceeded the PNEC (sediment, marine).

2.0 AP/APE ARE HIGHLY TREATABLE IN WASTEWATER TREATMENT PLANTS AND THEIR DEGRADATION INTERMEDIATES ARE NOT PERSISTENT OR BIOACCUMULATIVE IN THE ENVIRONMENT; THEIR LIKELIHOOD OF EXCEEDING THE EPA WQC FOR NP IS LOW NATIONALLY AND IN CALIFORNIA; AND APES ARE NOT POSING A RISK IN CALIFORNIA SURFACE WATERS AND SEDIMENTS

In its memo to the ARB the SWRCB expressed concerns that "APEs are being discharged into coastal, estuarine, and freshwater by means of wastewater treatment plants, stormwater and other sources in California (and elsewhere); and APEs seem to bioaccumulate in marine vertebrates and invertebrates and persist in environmental compartments such as sediments."[20] The ARB Staff report states "once into wastewater, alkylphenol ethoxylates do not readily degrade and they and/or their degradation products enter aquatic environments through wastewater treatment facilities or storm water." [21]

While APEs and their degradation intermediates are not "readily biodegradable" as defined by OECD guidelines[22] they are highly treatable and removed from the effluent stream in wastewater treatment plants and they are inherently biodegradable.

2.1 NP and NPE are treatable in wastewater treatment plants and their degradation metabolites and are not persistent or bioaccumulative

[19] Zulkowsky AM, Ferguson PL, McElroy AE. (2002) Effects of sewage-impacted sediment on reproduction in the benthic crustacean Leptocheirus plumulosus. Marine Environ Res 54: 615-619
[20] SWRCB (2010. September 20)
[21] ARB (2010, September 29)
[22] Organization for Economic Cooperation and Development (OECD). (1996) OECD Guidelines for the Testing of Chemicals. Paris, France.

Biodegradation has been shown to be the dominant mechanism responsible for removal of NP, NPE, alkylphenol (AP) and alkylphenol ethoxylates (APE) during wastewater treatment and in the environment.[23,24,25,26] While NPE is highly treatable in wastewater treatment plants, with removal rates commonly greater than 90%, low levels of its degradation metabolites have been reported in effluent and surface waters.[27] Under anaerobic conditions, the major metabolites of NPE include: NPE1, NPE2 and, to a lesser extent, NP. Under aerobic conditions, nonylphenol monoethoxycarboxylate (NPEC1) and nonylphenol diethoxycarboxyoxylate (NPEC2) also occur. [28,29] These intermediates continue to degrade in the environment, including mineralization of the phenolic ring, to carbon dioxide. [30,31,32,33,34]

It is important to remember that the terms "persistent" and "bioaccumulative" have very specific meanings and are based on measurable criteria. Assessments of the persistence and bioaccumulation of NP/NPE relative to these recognized criteria have been conducted by the European Union (EU), Environment Canada, Washington State and the State of Oregon.[35,36,37,38,39, 40] All of these concluded that NP and/or NPE, along with

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[23] Staples, C.A., Williams, J.B., Blessing, R.L., & Varineau, P.T. (1999). Measuring the biodegradability of nonylphenol ether carboxylates, octylphenol ether carboxylates, and nonylphenol. Chemosphere, 38, 2029-2039.
[24] Staples, C.A., Naylor, C.G., Williams, J.B., & Gledhill, W.E. (2001). Ultimate biodegradation of alkylphenol ethoxylate surfactants and their biodegradation intermediates. Environmental Toxicology and Chemistry, 20, 2450-2455.
[25] Staples, C.A., Klecka, G.M., Naylor, C.G., & Losey, B.S. (2008). C8- and C9-alkylphenols and ethoxylates: I. identity, physical characterization, and biodegradation pathways analysis. Human and Ecological Risk Assessment, 14, 1007- 1024.
[26] Melcer, H., Klecka, G., Monteith, H., & Staples, C. (2007). Wastewater treatment of alkylphenols and their ethoxylates: A state of the science review. Water Environment Federation, Alexandria, VA.
[27] Melcer et al. (2007).
[28] Klecka, G., Zabik, J., Woodburn, K., Naylor, C., Staples, C. & Huntsman, B. (2007). Exposure analysis of C8- and C9-alkylphenols, alkylphenol ethoxylates, and their metabolites in surface water systems within the United States. Human and Ecological Risk Assessment, 13, 792-822.
[29] Staples. (2008).
[30] Ahel, M., Giger, W., & Koch, M. (1994). Behaviour of alkylphenol polyethoxylate surfactants in the aquatic environment. I: Occurrence and transformation in sewage treatment. Water Research, 28 (5), 1131-1142.
[31] Staples et al. (1999).
[32] Staples et al. (2001).
[33] Staples et al. (2008).
[34] Naylor, C.G., Staples, C.A., Klecka, G.M., Williams, J.B., Varineau, P.T., & Cady, C. (2006). Biodegradation of [^{14}C] ring-labeled nonylphenol ethoxylates. Archives of Environmental Contamination and Toxicology, 51, 11-20.
[35] European Chemicals Bureau (ECB). (2003). PBT Working Group Substance Information Sheets for Nonylphenol (CAS 25154-52-3) and Phenol, 4-Nonyl, branched (CAS 84852-15-3).
[36] Environment Canada (EC). (2006). Ecological categorization of substances on the Domestic Substance List; Categorization Decisions. (Completed in September 2006). http://www.ec.gc.ca/substances/ese/eng/dsl/cat_index.cfm.
[37] Environment Canada (EC). (2005, November 21). Response to APERC's proposal regarding Environment Canada's preliminary categorization of nonylphenol, octylphenol and their ethoxylates.
[38] Washington State Department of Ecology (2006a, January) Rule Adoption Notice: Persistent Bioaccumulative Toxins Chapter 173-333 WAC. http://www.ecy.wa.gov/biblio/0607007.html
[39] Oregon Department of Environmental Quality (OR DEQ). (2009, October). Final Report: Senate Bill 737: Development of a Priority Persistent Pollutant (P3) List for Oregon. No. 09-WQ-013. http://www.deq.state.or.us/wq/SB737/docs/P3LReportFinal.pdf.
[40] Environment Canada (EC). (2007). Ecological categorization of substances on the Domestic Substance List; Categorization decisions (Completed in September 2006). http://www.ec.gc.ca/substances/ese/eng/dsl/cat_index.cfm.

other AP and APEs, are not persistent or bioaccumulative. Companion papers by Staples *et al.* (2008) and Klecka *et al.* (2008), summarize and provide references to the available data on the persistence and bioaccumulative properties of NP and NPE.[41,42] As such, numerous high quality studies are available to ARB and the SWRCB to confirm that NP and NPE are not persistent or bioaccumulative.

In addition, SCCWRP has noted that concentrations in the livers of *P.verticulis* were similar to those in the sediment and points out that "[t]hese findings are consistent with most other studies and provide very strong evidence that APEs do not biomagnify like so-called persistent organic pollutants (e.g. DDE, PCBs and PBDEs) do." [43]

2.2 The degradation intermediates of APE occur at low levels in wastewater effluent and the aquatic environment nationally; however the likelihood of their occurrence exceeding EPA's WQC for NP is low.

The breakdown products of NPE (i.e., NP, NPE1 and NPE2) are known to co-occur at low concentrations in the aquatic environments; therefore, Klecka *et al*. (2007) conducted an assessment of surface water and/or sediment monitoring studies available in the published or publicly available literature to develop a statistical understanding of exposures to APE, including NPE and its metabolites in US surface waters. A literature search was conducted to identify environmental monitoring studies published during the 15 year period between 1990 and 2005, which contained information on surface water and/or sediment concentrations of APE and its metabolites in US waters. Nineteen reliable monitoring studies, most of which were conducted by the US Geological Survey (USGS), were reviewed and the highest concentrations of all NPE metabolites were generally observed for rivers in heavily urbanized or industrialized locations with average concentrations of 1.7 µg/L, 1.2 µg/L, 2.3 µg/L, and 8.1 µg/L for NP, NPE1, NPE>1, and nonylphenol ethoxycarboxylate (NPEC) respectively reported. Klecka *et al.* (2007) reported NPE>1 as a group because the US Geological Survey (USGS), which provided much of the data analyzed in this paper, frequently reported in this manner. However, a review of the database that catalogued all of the raw data analyzed by Klecka et al. (2007) confirmed that the majority (87%) of the data points categorized as NPE>1 do in fact represent concentrations of NPE2. [44]

Klecka *et al*. (2007) also used the available data to examine changes in reported concentrations of NPE metabolites over the 15 year sampling period ending in 2005. While noting that the data were drawn from a diverse set of studies with different

[41] Staples, C.A., Klecka, G.M., Naylor, C.G., and Losey, B.S. (2008). C8- and C9-Alkylphenols and Ethoxylates: I. Identity Physical Characterization, and Biodegradation Pathways Analysis Human and Ecological Risk Assessment, 14: 1007–1024.

[42] Klecka, G.M., Staples, C.A., Naylor, C.G., Woodburn, K.B., and Losey, B.S. (2008). C8- and C9-Alkylphenols and Ethoxylates: II. Assessment of Environmental Persistence and Bioaccumulation Potential Human and Ecological Risk Assessment, 14: 1025–1055.

[43] SCCWRP(2010, July 15)

[44] Klecka, G., Zabik, J., Woodburn, K., Naylor, C., Staples, C. & Huntsman, B. (2007). Exposure analysis of C8- and C9-alkylphenols, alkylphenol ethoxylates, and their metabolites in surface water systems within the United States. Human and Ecological Risk Assessment, 13, 792-822.

sampling strategies and analytical methods, the authors found that maximum concentrations varied widely; however, the mean and 90th percentiles for concentrations of NPE and its metabolites remained relatively constant during this time period. Therefore, it was assumed that any apparent shifts in maximum concentrations represented a bias in sampling locations toward effluent-dominated streams. These findings together with APERC's understanding that use of NPE in consumer cleaning products has declined in recent years, make it likely that concentrations of NPE metabolites in US surface waters have not increased since this study was conducted.

2.3 APEs are not posing a risk in California's surface waters and sediments: Concentrations of AP and APEs in California fresh and marine surface waters and sediment do not reach levels of concern relative to US EPA Water Quality Criteria (WQC) and PNECs (sediment) for NP in fresh and marine surface waters and sediment

Aside from a few samples, concentrations of NP and other NPE degradation intermediates reported in California surface waters and sediment have not been show to reach levels that warrant concern relative to the US EPA WQC or PNEC (sediment) values.

Levels of NP and NPE reported by SCCWRP and the San Francisco Estuary Institute (SFEI) are generally in the low or sub- μg/L range in water and ng/g dw in sediment. In 2010, the Regional Monitoring program detected <0.01 to 0.073μg/L from nearshore surface water sites in San Francisco Bay and 22 – 86 ng NP/g dw in sediment from nearshore sites in San Francisco Bay. [45,46] SCCWRP points out that high concentrations of NP and NPE reported in an outfall in Southern California Bight by Schlenk *et al.*, (2005) were found to be an order of magnitude lower in more recent studies. [47,48]

SCCWRP also cites an abstract by Bay *et al.*, 2008 that reports measures of chemical exposure and biological response at the tissue and individual level for *Pleuronichthys verticalis* for over 600 individuals that concluded "the local population trends for *P. verticalis* based on trawl surveys at these outfalls have not shown any indication of steady or continuous decline." SCCWRP concluded "the results of this study coupled with the apparent absence of obvious effects on the biology in other California receiving waters suggests that we cannot attribute effects that are likely to be associated with APEs at their current environmental levels directly to this class of contaminants. [49, 50]

[45] SCCWRP. (2010, July 15).
[46] Hoenicke, R..San Francisco Estuary Institute (SFEI). (2010, July 13). Letter to State Water Resources Control Board – Occurrence of Alkylphenol Ethoxylates in San Francisco Bay and Potential Impacts on Water Quality.
[47] SCCWRP. (2010, July 15)
[48] Schlenk, D. et al.(2005). In vivo bioassay buided fractionation of marine sediment extracts from the Southern California Bight, USA for estrogenic activity. Environ. Toxicol. Chem. 24:2820-2826
[49] SCCWRP. (2010, July 15)
[50] Bay, S. et al. (2008). Effects of emerging contaminants on Southern California flatfish: synthesis and next steps. Abstract for the Society of Environmental Toxicology and Chemistry National Meeting, Tampa, FL (as cited by SCCWRP, 2010, July 15)

3.0 AP/APES ARE NOT A MAJOR SOURCE OF ESTROGENIC ACTIVITY IN WASTEWATER TREATMENT EFFLUENT

ARB and SWRCB have expressed concerns about the estrogenicity of AP/APEs and the potential effects that an increase in the use of APEs might have on receiving waters.

Scientists determine whether a compound is estrogenic by testing the substance in a system that is known to respond to estrogen in a specific way. NP is approximately 10^3 - 10^6 fold less potent than the endogenous estrogen, 17β-estradiol, depending on the species and endpoint investigated, and the short chain NPE are orders of magnitude less estrogenic than NP [51, 52, 53, 54, 55, 56] Depending on the test system, NPEC and the longer chain ethoxylates (NPEn>4) appear to have little or no estrogenic activity *in vivo*. [57, 58, 59]

Estrogenic activity measures the tendency of a molecule to interact with the estrogen receptor; it is a mechanism rather than an effect. Adverse effects to aquatic organisms due to all mechanisms of toxicity from NP/NPE are addressed in the development of the WQC and PNECs described above.

The Water Environment Federation recently noted "alkylphenols, alkylphenol ethoxylates, bisphenol A, and other non-steroidal estrogenic compounds are typically present in treated effluents at µg/L levels (compared to ng/L for hormones). However, their relative activity is such that outside of a few well-documented special cases (e.g., Sheahan *et al*. 2002) their contribution to total estrogenicity of effluents is considered minimal. [60]

4.0 THE ARB AND THE SWRCB SHOULD RELY ON ONGOING ENVIRONMENTAL MONITORING PROGRAMS TO DETERMINE WHETHER THE OCCURRENCE OF AP/APE WILL INCREASE IN

[51] Jobling S and Sumpter JP. 1993. Detergent components in sewage effluent are weakly oestrogenic to fish: an *in vitro* study using rainbow trout (*Oncorhynchus mykiss*). Aquat Toxicol 27: 661-672

[52] Dussault, E.B., Sherry, J.P., Lee, H.-B., Burnison, B.K., Bennie, D.T., and Servos, M.R. 2005. *In vivo* estrogenicity of nonylphenol and its ethoxylates in the Canadian environment. Hum Ecol Risk Assess 11: 353-364

[53] Lee PC and Lee W. 1996. *In vivo* estrogenic action of nonylphenol in immature female rats. Bull Environ Contam Toxicol 57: 341-348

[54] Islinger M, Pawlowski S, Hollert H, Volkl A, Braunbeck T. 1999. Measurement of vitellogenin-mRNA expression in primary cultures of rainbow trout hepatocytes in a non-radioactive dot blot/RNAse protection-assay. Sci Total Environ 233: 109-122

[55] Metcalfe CD, Metcalfe TL, Kiparissis Y, et al. 2001. Estrogenic potency of chemicals detected in sewage treatment plant effluents as determined by in vivo assays with Japanese medaka (*Oryzias latipes*). Environ Toxicol Chem 20: 297-308

[56] Balch G, Metcalfe C. 2006. Developmental effects in Japanese medaka (*Oryzias latipes*) exposed to nonylphenol ethoxylates and their degradation products. Chemosphere 62: 1214-1223

[57] Dussault. (2005).

[58] Metcalfe (2001).

[59] Balch and Metcalfe (2006).

[60] Higgins, C.P., Sharp, J.O., Sepulvado, J.G., Littrell, B.J., O'Connor,G., Snyder, E. (2010) Final Report- Trace Organic Chemicals in Biosolids-Amended Soils: State-of-the-Science Review. Water Environment Research Foundation, Alexandria, VA.

CALIFORNIA SURFACE WATERS AS A RESULT OF EFFORTS TO REFORMULATE VOC CONTAINING CONSUMER PRODUCTS

The use of APEs is neither necessary, nor is it likely the preferred reformulation approach to develop low VOC cleaning products. However, to prohibit the use of APEs in heavy duty cleaning product categories may unnecessarily restrict reformulation options for formulators. APEs are highly effective surfactants and current monitoring data in California do not indicate a need for concern about risk from the presence of trace levels of APEs or their degradants in the environment. California has ongoing programs to monitor contaminants in surface water and sediment. The state also has other regulatory mechanisms available under the Clean Water Act to assess and regulate locations that might be found to exceed the US EPA WQC for NP and sources that contribute to them.

The fact that alternative surfactants are available, or that other jurisdictions have taken risk management actions related to APE surfactants, is not a sufficient basis to justify regulation to prohibit the use of these compounds in cleaning and degreasing products in California. This is particularly relevant to the currently proposed prohibition of the use of APEs, which is based entirely on a hypothetical scenario that foresees an unrealistic increase in the use of APEs in consumer cleaning products resulting in an unrealistic increase exposure and risk to the aquatic environment in California.

ATTACHMENT TO APERC COMMENTS
TABLES AND FIGURES

Table 1a **Chronic Population-Level Effects of NPE, NPEC, and NP to Aquatic Organisms (attached as separate document due to size)**

Table 1b **Secondary and Supplemental Endpoints (attached as separate document due to size)**

Table 2. Short-term acute and sub-chronic toxicity data for nonylphenol and sediment dwelling organisms (Staples *et al.*, 2010)

Species	Duration	Endpoints	Results	Reference
Clam (F) *Anadonta Cataractae*	144-h	Survival	LC50: 1,700 µg/L	McLeese *et al*. (1980)
Amphipod (F) *Hyallela azteca*	96-h	Survival	LC50: 150 µg/L	England and Bussard (1994)
Amphipod (F) *Hyallela azteca*	96-h	Survival	EC50: 20.7 µg/L LC50: 20.7 µg/L	Brooke (1993)
Dragonfly (F) *Ophiogomphus sp.*	96-h	Survival	EC50: 596 µg/L LC50: >768 µg/L	Brooke (1993)
Snail (F) *Physalia virgata*	96-h	Survival	EC50: 378 µg/L LC50: 774 µg/L	Brooke (1993)
Annelid (F) Lumbriculus variegatus	96-h	Survival	EC50: 268 µg/L LC50: 342 µg/L	Brooke (1993)
Midge fly (F) *Chironomus tentans*	96-h	Survival	LC50: 160 µg/L	England and Bussard (1993)
Midge fly (F) *Chironomus tentans*	14-d, dosed sediment (OC 1.27%)	Larval weight -	NOEC (LOEC): 20,000 (34,000) ng/g-dw	England and Bussard (1993)

Midge (F) *Chironomus riparius*	10-d, dosed sediment (OC 1.64 to 3.2%)	Survival Head capsule length Larval wet weight	NOEC: 440,000 to 2,000,000 ng/g-dw NOEC: 440,000 to 2,000,000 ng/g-dw NOEC: 77,000 to 2,000,000 ng/g-dw	Maenpaa and Kukkonen (2006)
Amphipod (M) *Leptochierus plumulosus*	96-h	Survival	LC50: 62 µg/L	Lussier *et al*. (2000)
Mudcrab (M) *Dyspanopeus sayi*	96-h	Survival	LC50: >195 µg/L	Lussier *et al*. (2000)
Soft shell clam (F) *Mya arenaria*	96-h	Survival	LC50: >700 µg/L	McLeese *et al*. (1980)
Soft shell clam (F) *Mya arenaria*	360-h	Survival	LC50: 1,000 µg/L	McLeese *et al*. (1980)
Mussel (M) *Mytilus edulis*	96-h	Survival	LC50: 3000 µg/L	Granmo et al. (1989)
Mussel (M) *Mytilus edulis*	35-d	Fertilization success Larval development	Fertilization success: NOEC: 200 µg/L, no effects Larval development: NOEC: 200 µg/L, no effects	Granmo *et al*. (1989)
Mussel (M) *Mytilus edulis*	15-d 35-d	Survival Survival	LC50: 500 µg/L LC50: 140 µg/L	Granmo *et al*. (1989)
Coot Clam (F) *Mulinia lateralis*	96-h	Survival	LC50: 38 µg/L	Lussier *et al*. (2000)
Estuarine mysid (M) *Neomysis integer*	96-h	Survival	LC50: 590 µg/L	Verslycke *et al*. (2004)
Clam (F) *Tapes philippinarum*	7-d	Re-burrowing 24-h post-exposure	NOEC (LOEC): 50 (100) µg/L	Matozzo *et al*. (2004)
Amphipod (F) *Eohaustorius*	96-h	Survival – Re-burrowing	LC50: 227 µg/L EC50: 138 µg/L	Hecht and Boese (2002a)

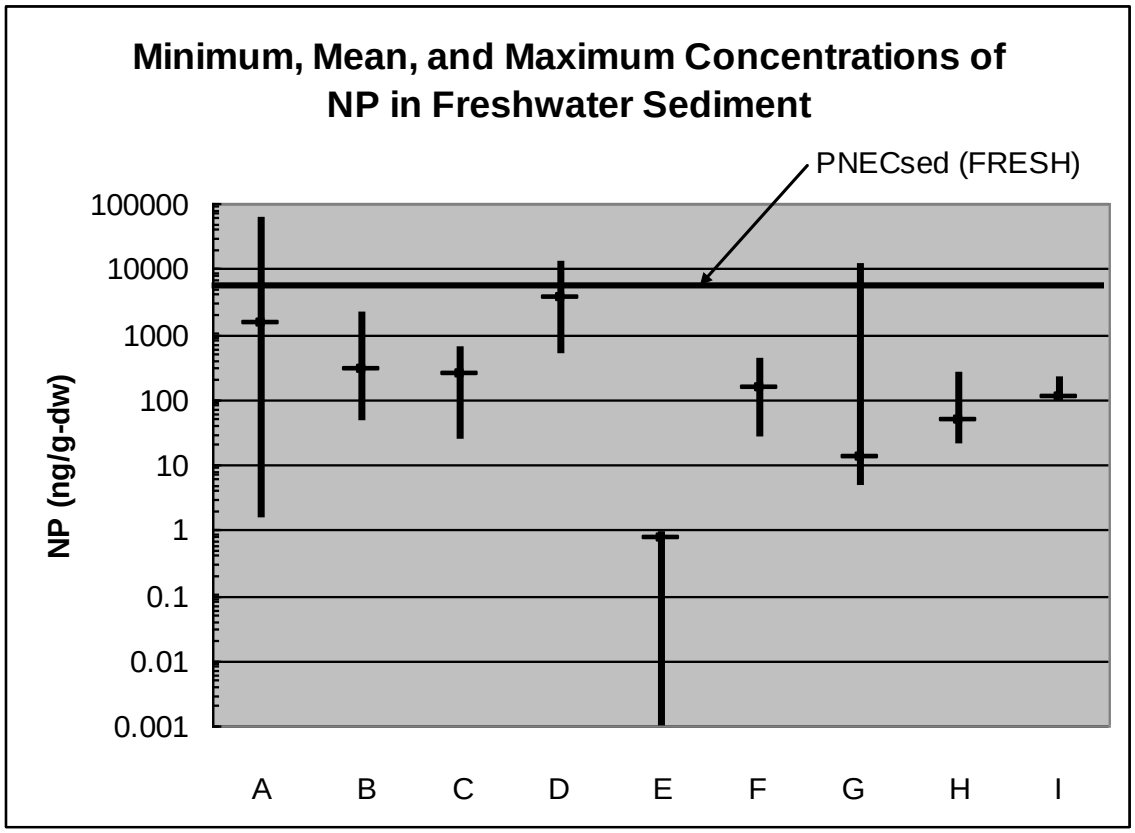
estuarius		48-h Post-exposure		
Midge (F) *Chironomus riparius*	10-d, dosed sediment (OC 2.3%)	Survival – (culture A from polluted river, clean lab cultures B,C)	A: LC50: 603,000 to 674,000 ng/g-dw B: LC50: 314,000 to 350,000 ng/g-dw C: LC50: 315,000 to 465,000 ng/g-dw	Bettinetti *et al*. (2002a)
Tadpole (F) *Rana catesbiana*	30-d, dosed sediment (OC 0.052%)	Survival, Sublethal effects, Wet Weight	NOEC (LOEC): 155,000 (390,000) ng/g-dw 155,000 (390,000) ng/g-dw 155,000 (390,000) ng/g-dw	Ward and Boeri (1992)
Amphipod (M) *Ampelisca abdita*	10-d, dosed sediment (OC 2.6%)	Survival	LC50: 160,000 ng/g-dw	Fay *et al*. (2000)
Benthic macro invertebrates communities	20-d exposure benthos evaluated for 2 y, littoral enclosures	Abundance (Oligochaeta, Mollusca, Chironomidae)	NOEC (LOEC): Oligochaeta - Naididae 23 (76) µg/L - Tubificidae 243 µg/L, no effects Mollusca - Bivalvia 23 (76) µg/L - Gastropoda 76 (243) µg/L Chironomidae - Tanytarsini 76 (243) µg/L - Chironomini 243 µg/L, no effects	Schmude *et al* (1999)
(F) or (M) designates freshwater or marine species, respectively; OC is organic carbon content of dosed sediment				

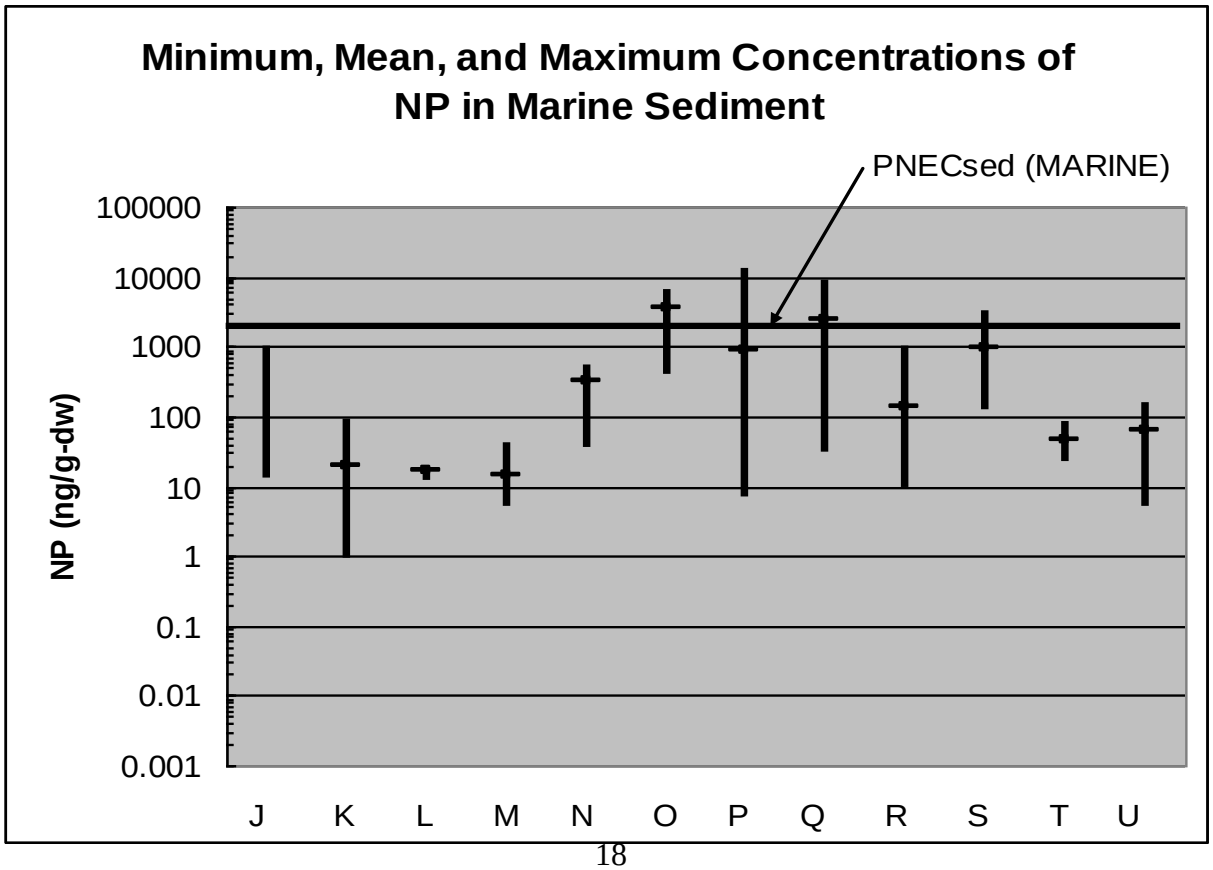
Table 3. Long-term chronic sediment toxicity data for nonylphenol using aqueous exposure and dosed sediments. (Staples *et al*., 2010)				
Species	Duration (Org. C)	Endpoints	Results NOEC (LOEC) or ECx	Reference
Aqueous Exposure				
Midge (F) Chironomus tentans	Full Life cycle, aqueous exposure	Survival (0-20 d) Survival (20+d) Growth – Sex Ratio – Fecundity – Viability – Emergence –	Survival (0-20 d): 42 (91) µg/L Survival (20+ d): 91µg/L, no effects Growth: (91µg/L, no effects Sex Ratio: 91 µg/L, no effects Fecundity: 91 µg/L, no effects Viability: 91 µg/L, no effects Emergence: 91 µg/L, no effects	Kahl *et al*. (1997)
Dosed Sediment Exposure				
Amphipod (M) *Leptocheirus plumulosus*	28-d (2.6%)	Survival – Reproduction (young/female)	61,500 (>61,500) ng/g-dw 61,500 (>61,500) ng/g-dw	Zulkowsky *et al*. (2002)
Midge (F) *Chironomus riparius*	28-d (2.3%)	Cocoons/adult No. young/adult	EC10: 337,000 to 383,000 ng/g-dw EC10: 335,000 to 383,000 ng/g-dw	Bettinetti *et al*. (2002b)
Oligochaete (F) *Tubifex tubifex*	28-d (2.3%)	Emergence -	EC10: 203,000 to 259,000 ng/g-dw	Bettinetti *et al*. (2002b
(F) or (M) designates freshwater or marine species, respectively; Org. C is sediment organic carbon content (%)				

Table 4. Environmental Monitoring Data for NP in Freshwater Sediment (Staples *et al.*, 2010) (ng/g-dry weight).				
Study Area Location	**Mean (SD)**	**Range**	**No. Samples**	**Reference**
FRESHWATER				
A – Rivers, USA	1,474 (5337)	1.5 to 60,000	196	Klecka *et al*. (2007)
B – Great Lakes, Canada	290 (480) (excluding sites at STP outfalls)	<46 to 2,250 16,180 to 37,800 (at STP outfalls)	25 3	Bennett and Metcalfe (1998)
C – Rivers, Spain	237 (160)	25 to 650	24	Petrovic *et al*. (2002a)
D – Glatt R. basin, Switzerland	3,520 (4,610)	510 to 13,100	7	Ahel *et al*. (1994)
E – River basins, Europe	0.712 (0.315)	0.001 to 0.91	8	Schmitt *et al*. (2010)
F – Elbe R., Germany	151 (142)	27 to 430	12	Stachel *et al*. (2003)
G – Near STP outfalls, VA, USA	12.4 (median)	<5 to 12, 400	24	Hale *et al*. (2000)
H – Streams, MN, USA	48 (72)	<20 to 260	11	Lee *et al*. (2008)
I – Lakes and rivers, MN, USA	108 (28)	<100 (n = 16) 102 to 224 (n=4)	20	Ferrey *et al*. (2008)
MARINE				
J – Coastal sites, Italy, Germany	Not calculable	13 to 192	10 (est.)	Cited in David *et al*. (2009)
K – Estuarine sites, The Netherlands	19.52 (23.63) (excluding site at river source)	0.9 to 92.2 1,080 (at river source)	17 1	Jonkers *et al*. (2003)
L – Salt marsh, GA, USA	16.7 (2.8)	11.88 to 18.67	6	Sajwani *et al*. (2003)
M – Venice Lagoon, Italy	14.2 (8.7)	5 to 42	20	Marcomini *et al*. (1990)
N – Vancouver area, BC, Canada	317 (198)	35 to 550	5	Shang *et al*. (1999)

O – Tidal area, USA	3,555 (4,448)	410 to 6,700	2	Loyo-Rosales *et al*. (2003)
P – NY harbor sites, USA	875 (1,624)	7 to 13,700	10	Ferguson *et al*. (2001a,b)
Q – Rivers, UK	2,384 (3,243)	30 to 9,050	8	Lye *et al*. (1999)
R – Estuarine coastal sites, Spain	140 (225)	<10 to 1,050	34	Petrovic *et al*. (2002b)
S – Coastal sites at STP outfalls, CA, USA	913 (1,525)	122 to 3,200 <10 to 380	4 5 (est.)	Schlenk *et al*. (2005) SCCWRP (2010)
T – San Francisco Bay coastal sites, CA, USA	45 (11)	22 to 86	5	California Regional Monitoring Pgm. (2010)
U – Morro Bay coastal sites, CA, USA	60 (13) (detected values only)	<0.5 to 158	5 (est.)	San Francisco Estuarine Institute (2010)
STP = Sewage Treatment Plant; est. = estimated number of samples				

FIGURE 1: CONCENTRATIONS OF NP IN FRESHWATER AND MARINE SEDIMENT (Staples *et al.*, 2010)





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