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ALKYLPHENOLS & ETHOXYLATES RESEARCH COUNCIL COMMENTS ON EPA'S PROPOSED AMBIENT AQUATIC LIFE WATER QUALITY CRITERIA FOR NONYLPHENOL DOCUMENT

January 5, 2004; 69 Fed. Reg. 340; Docket ID No. OW-2003-0080

I. Introduction

The Alkylphenols & Ethoxylates Research Council (APERC) appreciates this opportunity to submit comments in response to the U.S. Environmental Protection Agency's (EPA) draft "Ambient Aquatic Life Water Quality Criteria for Nonylphenol," announced in the Federal Register on January 5, 2004 (69 Fed. Reg. 340). APERC's membership[1] is comprised of the major North American manufacturers and processors of alkylphenols, most notably nonylphenol (NP), as well as derivatives of NP including nonylphenol ethoxylates (NPEs). As such, APERC and its members have a unique interest in this proceeding.

The alkylphenol industry wholeheartedly endorses EPA's efforts to establish an aquatic life water quality criteria (WQC) for NP. APERC encourages EPA to proceed expeditiously to finalize these criteria so that they can be considered by states and tribes in setting their own state specific standards as well as regulatory and other public health agencies outside the U.S.

APERC believes that the Agency has considered most of the relevant studies on NP and that the aquatic life water quality criteria derived by EPA are generally supportable. At the same time, APERC's review reveals that EPA has not consistently applied its

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[1] Members of APERC include: Dover Chemical Corporation; Crompton Corporation; Great Lake Chemical Corporation; Huntsman LLC; Rhodia Inc.; Rohm and Haas Company; Schenectady International, Inc.; and, The Dow Chemical Company.

Guidelines in determining which test results to consider in the WQC derivation. Additionally, there are several places in the draft Criteria document, particularly in the important Introductory section, where EPA's characterization of the available science is not fully reflective of the most relevant information available on nonylphenol. APERC encourages EPA to revise this section to more accurately characterize the environmental fate and effects of NP.

II. EPA Should More Fully Reflect the Pathways for NP Entering the Environment

In the Introductory section of the draft Criteria document, EPA correctly notes that NP predominately enters the environment from the degradation of NPE (page 2, paragraph 2). However, the document as drafted gives the impression that most of the NPE that enters the environment will degrade to NP; this is simply not the case.

NP is not the predominant degradation product of NPE. As reflected on the attached chart, the two predominant degradation pathways for NPE are through the loss of ethylene oxide units to form low-mole ethoxylates or through the formation of carboxylated ethoxylates. As these degradation intermediates further degrade, they do not form NP, but they are broken down to ring-opened and other water soluble fragments, carbon dioxide and water, as well as become part of microbial biomass.

In fact, the formation of NP is the minor degradation pathway. The degradation of NPE to NP occurs under anoxic conditions as noted in Giger *et al.*, 1984. Such conditions may be found in:

- anoxic "dead spots" within sewer pipes and aeration basins;
- anaerobic digestion systems used to reduce the volume of sludge and the concentration of ammonia; and,
- in buried anoxic sediment and landfills.

While the degradation of NP is slow in these anoxic settings, the compound is not readily bioavailable. Furthermore, a significant percentage of the NP formed within anoxic waste treatment plants will be adsorbed onto dewatered sewage sludge and either incinerated, placed in landfills, or used as a soil amendment, where it will continue to degrade.

APERC encourages EPA to revise the Criteria document to reflect that NP is not the primary degradation product formed from NPE as this principally occurs in anoxic conditions. Once the NP enters an oxygenated environment, either in surface water, surficial sediment, or soil, it does not persist and will continue to degrade to mineralization.

III. Levels of NP in the Environment Are Typically Below the Proposed WQC

The draft Criteria document (page 2) presents several studies that report the presence of NP in water, sediment and fish. APERC believes that in revising this section, EPA should clarify that the important issue is not the detection of these compounds in the environment but the level at which they are found in relation to the WQC. Additionally, EPA should focus on levels of NP found in ambient waters of the United States and not in other parts of the world. For example, some of the results presented are 20 years old and include measurements for water bodies outside the U.S. Since the primary purpose of the document is to provide guidance to states and tribes for purposes of establishing their own criteria and discharge limitations, it is important to focus the document on the most recent comprehensive surveys of NP concentrations in U.S. waters.

Data of particular relevance that should be more comprehensively discussed include measurements of NP in the Great Lakes (as reported by Bennie, 1999), a comprehensive study of a small watershed in Michigan (Keith *et al*., 2001 and Kannan *et al*., 2003[2]), a survey of 30 rivers that was designed with the assistance of the EPA (Weeks *et al*., 1996[3]) and a survey of approximately 140 streams known to receive effluents from

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[2] Kannan, K., T.L. Keith, C.G. Naylor, C.A. Staples, S.A. Snyder and J.P. Giesy. 2003. Nonylphenol and Nonylphenol Ethoxylates in Fish, Sediment, and Water from the Kalamazoo River, Michigan. Arch. Environ. Contam. Toxicol. 44:77-82.

[3] Weeks, J.A., W.J. Adams, P.D. Guiney, J.F. Hall and C.G. Naylor. 1996. Risk Assessment of Nonylphenol and its Ethoxylates in U.S. River Water and Sediment. The Alkylphenols & Alkylphenol Ethoxylates Review. 1:64-74.

sewage treatment plants (Kolpin *et al.*, 2002[4]). These studies are more relevant to discuss because they are representative of the waters of the U.S. and they show that NP is typically found in surface waters at levels below the proposed WQC – in fact the concentration of NP is typically less than 1 microgram per liter.

EPA should consider referencing the conclusions the Agency previously reached in its RM-1 document prepared as part of the evaluation under the Toxic Substances Control Act (Rodier, 1996). The RM-1 document concluded that on a national basis, NP does not pose a significant risk to aquatic organisms.

In the limited cases where NP has been reported at concentrations higher than the proposed WQC, it is generally associated with inefficient wastewater treatment plants and effluent dominated streams. These environments often suffer from general contamination problems that could be best remedied not by focusing on controlling any specific compound, but rather through a more comprehensive program that likely involves upgrading wastewater treatment capabilities.

IV. EPA Mischaracterizes the Fate of NP in the Environment

In the discussion on the environmental fate of NP/NPE found on pages 2-4, information on the biodegradation of NP and NPE is intertwined with reports of ambient monitoring data. APERC recommends that EPA clearly separate the discussions on the fate of NP in wastewater treatment plants (arguably this is not the "ambient environment") from the characterization of NP's biodegradation in environmental waters and sediments. As noted in the criteria document, detailed studies on the fate of NP (and NPEs) in wastewater treatment plants have been conducted. Maguire (1999) documents that secondary sewage treatment plants can easily and extensively remove these compounds from aqueous waste streams through both degradation and sorption to solids.

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[4] Kolpin, D.W., E.T. Furlong, M.T. Meyer, E.M. Thurman, S.D. Zaugg, L.B. Barber and H.T. Buxton. 2002. Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in US Streams, 1999-2000: A National Reconnaissance. Environ. Sci. Technol. 36:1202-1211.

In the discussion of the degradation of NP in aqueous media, there are several studies referenced in the Criteria document that are not adequately utilized to describe the extent to which the degradation of NP occurs. Of particular significance are the reports by Staples *et al*., 1999 and 2001,[5] Sundaram and Szeto, 1981 and Ahel *et al*., 1994c. Collectively, these studies show that NP released into surface waters is subjected to biodegradation, photolysis and some deposition to sediment. They reported that NP degrades (biodegradation and photolysis) in freshwater with half-lives of less than 30 days and in saltwater with half-lives of 58 days. Also, NP continues to biodegrade in surficial sediments. Ekelund *et al.* (1993) reported similar half-lives in a study with saltwater and sediment. The study by Heinis *et al*. (1999) shows a half-life (dissipation time) of 66 days from sediment.

NP also degrades, but at slower rates, in buried anoxic sediments. As already noted, the presence of NP in buried anoxic sediments should be of limited concern as the compound is generally not bioavailable in this environment. Thus, EPA should divide the current section on environmental fate, located on pages 2-4 of the Criteria document, into three separate sections: a) characterization of the fate of NP in the aquatic environment; b) description of NP formation and fate within sewage treatment plants, and; c) description of processes that remove NP from being bioavailable to aquatic wildlife (*i.e*., deep burial in anoxic zones). APERC suggests that EPA consider drawing on the conclusions from EPA's RM-1 document and Maguire (1999). The RM-1 noted that while NP was not readily biodegradable it should not be considered persistent. Additionally, the RM-1 highlights that "POTWs in the U.S. seem to have a very high efficiency in removing 4-NP".

V. Field Studies Should Be Given Greater Consideration in Assessing Bioaccumulation Potential

The draft Criteria document summarizes much of the available information on the ability of NP to bioconcentrate and biomagnify in the food chain. Overall, EPA concludes that

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[5] Staples, C.A., C.G. Naylor, J.B. Williams and W.E. Gledhill. 2001. Ultimate Biodegradation of Alkylphenol Ethoxylate Surfactants and Their Biodegradation Intermediates. Environ. Toxicol. Chem. 20:2450-2455.

NP has a low potential to bioaccumulate in aquatic organisms. While APERC does not disagree with EPA's characterization, this conclusion can be strengthened by making greater utilization of the available field studies (presented in Staples *et al.*, 1998) which show that field bioaccumulation factors (BAFs) are much lower than laboratory-derived lipid-normalized bioconcentration factors (BCFs).

It is also relevant to note that the laboratory BCFs and field BAFs are considerably lower than would be predicted due to strict partitioning. Since the measured log Kow of NP is 4.3 (Kow=20,000), the potential bioaccumulation factors are predicted to be higher, absent consideration of metabolism of the NP within the organisms. The results from the laboratory BCFs and field BAFs show that NP is extensively metabolized in aquatic organisms and only accumulates to a limited degree.

A. EPA Should Correct the Reported Bioconcentration Factor for Algae

On page 4, paragraph 2, EPA cites a study by Ahel *et al.* (1993) as suggesting that NP bioconcentrates in algae 10,000 times. EPA needs to be careful in its use of this result since it is reported on a dry weight basis rather than the more traditional wet weight basis. Assuming that the macrophyte algae is 95% water, Staples *et al*. (1999) determined that the dry weight value of 10,000 L/kg can be converted on a wet weight basis to 487 L/kg.

VI. EPA Should Consistently Apply the EPA Guidance for Determining the Acceptability of Studies Used in the Development of Criteria

There are several instances in the EPA draft Criteria document where the Agency appears to have inconsistently applied its guidance for determining the appropriateness of using certain studies in deriving the aquatic life criteria.

In a study by England (1995), *Ceriodaphnia dubia* were exposed to NP for 7 days, enabling effects to be discerned from both acute (48 hour) and chronic (7 day) exposures. While EPA relied on the chronic data, the Agency excluded the acute data since the organisms were fed. As such, this study was not used in deriving the acute to chronic ratio (see Table 2b).

APERC questions the appropriateness of excluding the results from this study as the data were generated from a study that followed standard protocols as well as EPA and international standards of Good Laboratory Practices (GLP). The study also included comprehensive analysis of the test substance.

EPA's exclusion of the acute results from England 1995 is in contrast with the Agency's decision to include, for purposes of deriving the salt water WQC, studies involving feeding. In the case of salt water, EPA justified the use of results from feeding studies, noting that there was not a consistent difference in LC50 values from fed and non-fed studies. EPA noted that for mysids, feeding increased the LC50 value slightly, while for sheepshead minnow, feeding reduced the LC50 value.

It is APERC's view that EPA should consistently apply the guidance for selection of studies for consideration in deriving a WQC. Since there are not very many comparative acute and chronic values from which to derive the WQCs, APERC believes that EPA should reconsider its dismissal of the England acute results. This is particularly relevant since, in contrast with England 1995, the feeding studies that EPA used in deriving the saltwater values do not appear to have been conducted following GLP nor did the studies measure NP concentrations.

VII. The Section on Endocrine Response Should Be Revised

APERC suggests that EPA consider modifying the "endocrine" section (pages 4-5) since it includes various statements that are not grounded with the same degree of scientific support as the rest of the document; as such, their inclusion detracts from the scientific credibility of the document. APERC has developed several specific suggestions for EPA's consideration.

A. General Studies Not on NP Should Be Removed

There are numerous studies documenting so called endocrine responses from exposure to wastewater treatment plant effluents. As EPA is well aware, natural and synthetic estrogens are considered the dominant compounds in waste treatment effluents capable of triggering endocrine responses in fish. The fact that NP may be one of many compounds in the effluent is not adequate to associate an estrogenic response with NP; therefore, such studies should not be included in a formal Criteria document. To include studies on general wastewater treatment merely because NP has been shown or is even conjectured to be present in the effluent, is inappropriate.

The draft Criteria document cites several studies that fall into this category that should be excluded from the final report. For example, the draft document cites Purdom *et al.* (1994) who reported that rainbow trout exposed to outfalls of sewage treatment plants had increased vitellogen concentrations. The authors speculated that the response could be associated with estrogenic substances present in the effluents including ethynylestradiol and nonylphenol. As this study did not directly associate NP with the increased vitellogen, it should not be included in the dossier.

Similarly the studies by Allen *et al.*, 1999, Harries *et al.*, 1997, Lye *et al.*, 1999 and Tanghe *et al*., 1999 cited in the Criteria document involved demonstrating that the waters from rivers and estuaries below sewage treatment plants have the ability to induce estrogenic effects in a yeast assay and in fish. These authors speculated that the observed effects could be due to mixtures of xenoestrogens, human estrogens, and other compounds, including perhaps NP in the effluent. The inference that NP may be responsible for the observed estrogenic effects is pure speculation and is unlikely given the mixture of potent hormonally active products in the effluents.

B. EPA Should Carefully Distinguish Between *In Vitro* From *In Vivo* Studies

APERC further believes EPA should more carefully distinguish between endocrine responses that are found from *in vitro* assays from those associated with whole animal, *in vivo* studies. As the Agency is well aware, the ability of a compound to trigger a response in an *in vitro* assay is not necessarily indicative of the compounds ability to generate an apical, biologically significant response *in vivo*. It is particularly important to make this distinction when addressing biomarkers such as increased vitellogen, which have uncertain physiological significance.

VIII. Clarification Regarding the Description of NP and Associated CAS Registration Numbers

Commercial nonylphenol is a complex mixture of isomers, which results from the natural variation in the starting materials. Several CAS Registration Numbers have been used to describe these products. Since manufacturers of NP use essentially the same starting materials and synthesis process, commercially available NP products have a comparable isomeric content.

The draft Criteria Document is directed at two CAS Numbers: 84852-15-3 and 25154-52-3. While these are the two dominant numbers used in the marketplace, CAS Number 104-40-5 should also be specified as it is also used to represent commercial NP. Additionally, there are several statements in the introductory section of the document that should be clarified. APERC offers the following edits to clarify the introductory description of NP as well as the CAS Numbers to which the Criteria document applies. Deletions are indicated by strikeouts and additions are indicated by underlines.

> Recommended Revisions to Introduction of Proposed WQC Document for NP
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> Nonylphenol ($C_{15}H_{24}O$) is produced from cyclic intermediates in the refinement of petroleum and coal-tar crudes. It is manufactured by alkylating phenol with mixed isomeric nonenes in the presence of an acid catalyst. The resulting product is a mixture of various isomers of nonylphenol ~~alkylphenols~~, predominantly *para*-substituted nonylphenol, (Phenol, 4-nonyl-, branched, CAS No., 84852-15-3; 4-

nonylphenol, ~~;~~ CAS No. 104-40-5; and Phenol, nonyl , CAS No. 25154-52-3) ~~and occasionally~~ with small amounts of *ortho*-substituted (2-nonylphenol; CAS No. 136-83-4), and trace amounts of 2,4 dinonylphenol (phenol, dinonyl, branched; CAS No. 84962-08-3). Additional isomers, which represent the numerous branched structures that occur within the nonyl (nine carbon) group, add to the complexity of the compound. ~~with various isomeric, branched-chain nonyl (nine carbon) groups. (~~ Commercial nonylphenol is most accurately described by CAS No. 84852-15-3 (Phenol, 4-nonyl-branched), but ~~mixtures~~ ~~containing specified amounts of nonylphenol isomers and 2,4-dinonylphenol~~ ~~are given specific~~ CAS Numbers~~, either~~ 104-40-5 (Phenol, 4-nonyl-) and 25154-52-3 (Phenol, nonyl) have also been used to describe these compounds commercially~~ or 84852-15-3~~. ~~These products were used for deriving the water criteria for nonylphenol.)~~ This criteria document was derived to address these three commercially relevant CAS numbers, essentially representing one compound.