Alkylphenols & Ethoxylates Research Council

Comments on US EPA Proposed Rule for Addition of Nonylphenol Category
To Community Right-to-Know Toxic Chemical Release Reporting
under Section 313 of the Emergency Planning and Community Right-to-Know Act


August 19, 2013

The Alkylphenols & Ethoxylates Research Council (APERC) provides the following comments in response to the EPA’s proposed rule to add a “Nonylphenol Category” to the Community Right-to-Know Toxic Chemical Release Reporting list under Section 313 of the Emergency Planning and Community Right-to-Know Act (EPCRA). (U.S.EPA, 2013, June20). APERC is a research organization and trade association that consists of North American manufacturers of alkylphenols, including nonylphenol, and their derivatives. ¹

EPA is proposing to add a nonylphenol category to the Toxics Release Inventory (TRI) because the Agency believes “the members of the nonylphenol category are expected to be manufactured, processed, or otherwise used in quantities that would exceed the EPCRA section 313 reporting thresholds” and nonylphenol “meets the criteria of EPCRA section 313(d)(2)(c)”, which is also known as the environmental effects criterion. EPA is proposing to add nonylphenol as a category that is defined by chemical structure rather than specific CAS Registration Numbers (CAS RNs) because the Agency believes “there is no one CASRN that adequately captures what is referred to as nonylphenol and because of the apparent confusion that has resulted from the use of multiple CASRNs.”

The comments below provide support for APERC’s view that:

¹ Members of the Alkylphenols & Ethoxylates Research Council are The Dow Chemical Company, Dover Chemical, SI Group Inc, and TPC Group.
Nonylphenol is a complex but predictable mixture of isomers that is described by existing CAS RNs; describing nonylphenol as a category will be a source of confusion and a greater reporting burden than simply referencing existing and suitably descriptive CAS RNs.

Nonylphenol is not persistent or bioaccumulative, which should be recognized in the hazard review under EPCRA for determining whether this compound represents a sufficiently serious hazard to warrant significant nation-wide reporting under the TRI.

EPA’s evaluation of the aquatic toxicity of nonylphenol is drawn from data in the Agency’s Water Quality Criteria (WQC) document for this compound; however it does not acknowledge that these WQC provide a reasonable basis for a probabilistic risk assessment of the extensive monitoring of nonylphenol in US waters, which indicates a low likelihood that this compound will exceed EPA’s own WQC; and

Considering that nonylphenol is not persistent and not bioaccumulative based on EPCRA criteria and not likely to exceed EPA’s WQC, which is protective of the aquatic environment, this compound does not sufficiently satisfy the criteria under EPCRA Section 313(c) as being “known to cause or can be reasonably anticipated to cause a significant adverse effect on the environment of sufficient seriousness” to warrant nationwide reporting under TRI.

1.0 Nonylphenol is a complex but predictable mixture of isomers that is described by existing CAS RNs; describing nonylphenol as a category will be a source of confusion and a greater reporting burden than simply referencing existing and suitably descriptive CAS RNs.
EPA is proposing a nonylphenol category defined by a structure because it believes “there is no one CASRN that adequately captures what is referred to as nonylphenol and because of the apparent confusion that has resulted from the use of multiple CASRNs”.

EPA is proposing to define the nonylphenol category using the structure and text below

![Chemical Structure](image)

Where $C_9H_{19}$ = Branched or straight alkyl chain

“The proposed category definition covers the chemicals that are included in CASRNs 84852–15–3 as well as those 4 position isomers covered by CASRN 25154–52–3. Any nonylphenol that meets the above category definition would be reportable regardless of its assigned CASRN”

Nonylphenol is the commercial description for a complex mixture of nine-carbon alkyl-chain substituted phenols. NP is produced through the Friedel-Crafts alkylation of phenol with nonene, which, in the presence of an acid catalyst, preferentially alkylates at the para position of phenol. Commercial nonene does not contain linear $C_9H_{18}$ alpha-olefin; rather it is a complex mixture of highly branched, predominantly nine-carbon olefins known as propylene trimers. Therefore, the NP formed by the alkylation of phenol with propylene trimers is also a complex mixture of branched isomers. (Bhatt, 1992; Kirk-Othmer, 1992; Wheeler, 1997; Thiele, 2004).
TABLE 1 Para Isomers of Nonylphenol

<table>
<thead>
<tr>
<th>Group #</th>
<th>Isomer Type</th>
<th>Number of Isomers</th>
<th>Para Isomers, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Alpha-dimethyl</td>
<td>10</td>
<td>48.6%</td>
</tr>
<tr>
<td>2</td>
<td>Alpha-methyl, alpha-ethyl, beta-primary</td>
<td>3</td>
<td>8.9%</td>
</tr>
<tr>
<td>3</td>
<td>Alpha-methyl, beta-methyl</td>
<td>4</td>
<td>24.7%</td>
</tr>
<tr>
<td>4</td>
<td>Alpha-methyl</td>
<td>2</td>
<td>6.6%</td>
</tr>
<tr>
<td>5</td>
<td>Alpha-methyl, alpha-propyl</td>
<td>3</td>
<td>11.2%</td>
</tr>
<tr>
<td></td>
<td><strong>Total Isomers</strong></td>
<td><strong>22</strong></td>
<td><strong>100%</strong></td>
</tr>
</tbody>
</table>


The complexity of the chemistry and nomenclature that relates to NP has been recognized in governmental risk assessments. The EU Risk Assessment on NP simultaneously addressed CAS RN 84852-15-3 (EINECS No. 284-325-5) “4-Nonylphenol (branched)” and CAS RN 25154-52-3 (EINECS No. 246-672-0) “Nonylphenol” as equivalent commercially-relevant compounds. Furthermore, the EU Assessment recognized the following additional synonyms for nonylphenol: isononylphenol (CAS RN 11066-49-2); Phenol, nonyl-, branched (CAS RN 90481-04-2); and, monoalkyl (C3-C9) phenol.

As explained in the EU Risk Assessment for nonylphenol, changes relating to nomenclature practice within the U.S. EPA and Chemical Abstract Service (CAS) were behind the varied nomenclatures for this compound. NP, CAS RN 25154-52-3 was originally defined by CAS to cover all nonylphenols. However, subsequent revisions in nomenclature practice and CAS RN assignments redefined this CAS RN to cover only straight chain NP. Given the method of manufacture for nonylphenols, the production of straight chain NP is essentially impossible; as such, this isomer is considered
commercially irrelevant. However, straight chain NP (CAS RN 104-40-5) can be synthesized on a laboratory scale and is available as a research chemical.

In the development of WQC for NP, US EPA utilized data from CAS RNs 84852-15-3 and 25154-52-3 (US EPA, 2005). In its RM1 document for para-NP US EPA accepted the view that CAS RN 84852-15-3 is the most descriptive of the commercially relevant branched p-NP, while noting that CAS RN 25154-52-3 (nonylphenol, mixed isomers) and CAS RN 104-40-5 (4-nonylphenol) have been also reported by manufacturers to represent this compound (US EPA, 1996).

Following is a table that summarizes CAS numbers for nonylphenol and their associated nomenclatures, which can be used to more clearly identify this compound and its mixture of isomers.

**TABLE 2 Nonylphenol CAS Numbers and Nomenclature**

*(Sources: CAS, NIST, APERC)*

<table>
<thead>
<tr>
<th>CAS RN</th>
<th>Description</th>
<th>Assessments</th>
<th>Structure (Source CAS, NIST)</th>
</tr>
</thead>
<tbody>
<tr>
<td>84852-15-3</td>
<td>Phenol, 4-nonyl-, branched</td>
<td>EU (2001)</td>
<td>Unspecified, mixed isomers</td>
</tr>
<tr>
<td></td>
<td><strong>Other Names</strong></td>
<td>ECB (2003)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4-Nonylphenol;</td>
<td>US EPA (1996)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>p-Nonylphenol, branched;</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Branched 4-nonylphenol (mixed isomers)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CAS RNs</td>
<td>Other Names</td>
<td>Other Names</td>
<td>Sources</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
<td>-------------</td>
<td>---------</td>
</tr>
<tr>
<td>1300-16-9; 56459-00-4</td>
<td>Former CAS RNs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11066-49-2</td>
<td>Isononylphenol</td>
<td>EU (2001)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Phenol, isononyl; Isononylphenol (mixed isomers)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4-Nonylphenol; Phenol, p-nonyl; 4-n-Nonyl phenol; Phenol, 4-n-nonyl</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Sources: Chemical Abstract Services, National Institutes for Standards and Technology

In summary, based on current understanding of the various CAS RNs used to describe nonylphenol, there are in principle two forms of the material, i.e., linear NP as described by CAS RN 104-40-5 and branched NP, as best described by CAS RN 84852-15-3. However, CAS RNs 25154-52-3 and 11066-49-2 could also be considered as equivalent synonyms for branched NP for the purpose of identifying emissions.

Use of existing CAS RNs, which among them include all the various isomers of this compound, would simplify any efforts to indentify nonylphenol for purposes of TRI
reporting, including threshold determinations and air, water and waste emissions reporting. Often, reporting sites rely on Material Safety Data Sheet (MSDS) composition information to determine if components of products contain TRI chemicals. The use of CAS RNs provides clarity in the identification of TRI chemicals for both product suppliers and customers. Use of a structurally based category for TRI reporting purposes will likely create confusion - and a greater reporting burden - as individuals responsible for TRI reporting are not necessarily chemical nomenclature experts.

2.0 Nonylphenol is not persistent or bioaccumulative, which should be recognized in the hazard review under EPCRA for determining whether this compound represents a sufficiently serious hazard to warrant significant nation-wide reporting under the TRI.

The criteria listed under EPCRA Section 313(c) allow EPA to propose listing of a chemical on the TRI if the chemical “is known to cause or can be reasonably anticipate to cause a significant adverse effect on the environment of sufficient seriousness, in the judgment of the Administrator to warrant reporting under this section because of:

(i) its toxicity
(ii) its toxicity and persistence in the environment, or
(iii) its toxicity and tendency to bioaccumulate in the environment.”

EPA proposes the addition of NP to the TRI on the basis of EPCRA Section 313(c) (iii) primarily based on its ecotoxicity hazard.

The Proposed Rule does not propose listing nonylphenol because it is persistent; however nonylphenol is mischaracterized in the Proposed Rule as persistent based on statements previously made in the EPA Action Plan for this compound (U.S. EPA, 2010, August 18). Therefore, EPA should correct the record for this proposed rule as well as the Action Plan document for this compound to reflect that nonylphenol is not persistent or bioaccumulative. APERC previously submitted comments requesting that EPA correct
the casual use of the term “persistent” in the Action Plan document for Nonylphenol and Nonylphenol Ethoxylates (APERC, 2011, October 31). The same reasoning applies to the current proposed rule.

The characterization of nonylphenol as “persistent” is particularly troubling since it is not consistent with the data for these compounds and it overlooks robust governmental assessments conducted by the European Union, Environment Canada, Washington State and the state of Oregon (ECB, 2003, EC, 2006, WA DOE, 2006, OR DEQ, 2009). These assessments, which were specific to the properties of persistence and bioaccumulation, concluded nonylphenol is not persistent or bioaccumulative. In light of the available data and the conclusions of these assessments, the use of the terms “persistent” or “bioaccumulative” to describe nonylphenol is both factually incorrect and misleading.

EPA should rely on definitions for “persistence” and “bioaccumulative”, which are consistent with those described under EPCRA. (US EPA, 1999, October 29). In addition, the numerous laboratory and field studies, which are available on the persistence and bioaccumulative properties of nonylphenol, should be recognized. Companion papers by Staples et al. (2008) and Klecka et al. (2008) summarize the available data on the environmental fate, persistence and bioaccumulative properties of NP and NPE. Specific data for nonylphenol, which were utilized by Environment Canada in that Agency’s determination that nonylphenol is not persistent or bioaccumulative, are provided in below in Table 3 (EC, 2006). The data clearly show that nonylphenol does not meet the EPCRA persistence and bioaccumulation criteria (US EPA, 1999, October 29). Therefore, EPA should not make references as such, even in a casual manner.

**Table 3: Nonylphenol Properties vs. EPA EPCRA Persistence and Bioaccumulation Criteria**

<table>
<thead>
<tr>
<th>EPCRA Persistence and Bioaccumulation Criteria</th>
<th>NP Properties</th>
</tr>
</thead>
</table>
The fact that nonylphenol is neither persistent nor bioaccumulative according to EPCRA criteria should be considered in assessing whether this compound warrants the priority of nation-wide TRI reporting under EPCRA.

### 3.0 EPA’s evaluation of the aquatic toxicity of nonylphenol is drawn from data in the Agency’s WQC document for this compound; however it does not acknowledge that these WQC provide a reasonable basis for a probabilistic risk assessment of the extensive monitoring of nonylphenol in US waters, which indicates a low likelihood that this compound will exceed EPA’s own WQC.

EPA is proposing nonylphenol for listing on the TRI based on the following reasoning. “Nonylphenol is toxic to aquatic organisms and has been found in ambient waters. Because of nonylphenol’s toxicity, chemical properties, and widespread use as a chemical intermediate, concerns have been raised over the potential risks to aquatic organisms from exposure to nonylphenol. All of the hazard information presented here has been adapted from EPA’s 2005 Criteria document for nonylphenol, which was previously peer reviewed (Ref. 3). Water Quality” (U.S. EPA, 2013, June 20).
EPA acknowledges its own WQC document for nonylphenol in the Proposed Rule to add nonylphenol to the TRI and draws all of the aquatic toxicity data from the EPA WQC document (U.S. EPA, 2005). However, there is no discussion of the numeric WQC developed for nonylphenol in that document, the validity of which stand up to more recent studies (Coady, 2010). In addition, the Agency does not consider whether concentrations in US waters represent a risk relative to those WQC. This approach provides that best method to assess whether a compound can be reasonably anticipated to cause significant adverse effects in aquatic organisms.

3.1 The EPA WQC provide a reasonable basis to assess the hazard and risk of nonylphenol in the aquatic environment.

The proposal to add nonylphenol to the TRI speculates that a study by Giesy et al, 2000 “may suggest a possible hormetric response of fish fecundity to nonylphenol (U.S. EPA, 2013, June 20). This finding was also considered in the derivation of the WQC for nonylphenol (U.S. EPA, 2005). In the first experiment in this study, there were no statistically significant differences in fecundity up to and including the highest concentrations of nonylphenol (3.4 µg/L) in comparison to the control groups, and in the second experiment, the lowest apparent effect (based on an increase in egg production per female) should be disregarded because the solvent controls had no reproduction after eleven days, which suggests significant problems with the test (Giesy et al., 2000). The authors conclude that a NOEC and a LOEC could not be determined based on fecundity from either of the experiments individually (Giesy et al., 2000).

More relevant studies with NOEC and LOEC values based on apical endpoints related to reproduction, growth and development during exposure to nonylphenol at critical life stages have been conducted in fathead minnows, Japanese medaka, zebrafish, and rainbow trout. These reproductive, growth, and development endpoints include sex ratio,
egg production, hatching success, length and weight, and gonad weights. In studies with fathead minnows ranging from 28 to 42 days (early life stage growth and development and short term reproduction tests), effects were observed at 14 to 77.5 µg/L, with NOEC ranging from 7.4 to 38.1 µg/L (Ward and Boeri, 1991b; Brooke 1993b; Harries et al., 2000). In studies with Japanese medaka ranging in exposure from 14 days to 1.5 generations, effects on reproduction, growth, and development endpoints were reported at 8.2 to 183 µg/L, while NOEC ranged from 6 to 183 µg/L (Shioda et al., 2000; Yokota et al., 2003; Balch and Metcalfe, 2006); Seki et al., 2003). In studies with zebrafish ranging from 21 to 58 days that examined reproduction following direct exposures and cross-breeding unexposed and exposed fish, no effects on reproduction were reported with NOEC of 100 and 500 µg/L (Lin and Janz, 2006; Yang 2006). In studies with rainbow trout ranging from 21 to 90 days (early life stage growth and male gonad growth), effects at 10.3 to 54.3 µg/L were reported with NOEC of 6 to 20.3 µg/L (Brooke 1993a; Jobling et al., 1996). Thus, the effects on reproduction, growth and development in various fish species shows an overall range of effect concentrations of 8.2 to 183 µg/L, which clearly does not agree with the suggestion of reproductive effects below 1 µg/L or the suggestion of hormetic dose response in the Proposed Rule to add nonylphenol to the TRI.

The Proposed Rule to add nonylphenol to the TRI also lists secondary effects, such as observations of increased vitellogenin (VTG) in male fish and the occurrence of altered gonadal histopathology, which can provide information about the estrogenic mechanism of action nonylphenol. However, these biochemical and histopathological endpoints are not traditionally used as indicators of adverse effects in ecological risk assessments. More relevant to understanding the aquatic hazard and risk of nonylphenol are the acute and chronic numeric criteria, which are based on adverse effects for population-level parameters and were developed by EPA in the WQC document for nonylphenol (U.S. EPA, 2005).
EPA utilizes a statistical extrapolation procedure that draws upon both acute and chronic toxicity data from a wide 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” (US EPA, 2005). In the case of nonylphenol, EPA used results from acute studies to statistically calculate a Final Acute Value (FAV) along with results for apical endpoints (e.g., reproduction and growth) from chronic tests to calculate acute-to-chronic ratios. Since the chronic endpoints used to derive the chronic nonylphenol WQC reflect the culmination of molecular, biochemical and tissue-level effects at the whole organism level, the nonylphenol WQC in turn addresses all mechanisms of action - including estrogenic effects - that result in measurable alterations in these apical endpoints. Although nonylphenol has been shown to have weak estrogenic activity, EPA noted in the nonylphenol 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. (US EPA, 2005).

3.2 Probabilistic risk assessment of the extensive monitoring of nonylphenol in US waters indicates a low likelihood that this compound will exceed EPA’s own WQC. Extensive monitoring data on the occurrence and concentrations of nonylphenol in U.S. surface water is available, much of it conducted by EPA and the US Geological Survey. In a statistical assessment of surface water and/or sediment monitoring studies available in the published or publicly available literature, Klecka et al. (2007) found that the likelihood that concentrations of nonylphenol and other metabolites of nonylphenol ethoxylates in US surface waters will exceed EPA’s chronic WQC (6.6 µg/L) for nonylphenol is low – even when considered in aggregate on a toxic-equivalent basis. 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 alkylphenol ethoxylates (APEs) and their 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 APEs and their 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 for NP reported, which is below the chronic WQC for nonylphenol in freshwater. The study also found that 99% of nonylphenol concentrations in fresh surface waters were below the EPA Chronic WQC for NP (6.6 µg/L) during the time period of the assessment.

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 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, including nonylphenol 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, including nonylphenol, in US surface waters have not increased since this study was conducted.

4.0 **Considering that nonylphenol is not persistent and not bioaccumulative based on EPCRA criteria and not likely to exceed EPA’s WQC, which is protective of the aquatic environment, this compound does not sufficiently satisfy the criteria under EPCRA Section 313(c) as being “known to cause or can be reasonably anticipated to cause a significant adverse effect on the**
environment of sufficient seriousness” to warrant nationwide reporting under TRI.

The statute under EPCRA does not specify how serious or significant an effect must be in order for a chemical to meet the criteria under EPCRA Section 313(c) and leaves determination of whether a chemical “can be reasonably anticipated to cause significant adverse effects in aquatic organisms” up to the EPA Administrator’s discretion. In addition, EPA has stated it does not believe that it is appropriate to consider exposure for chemicals that are highly toxic based on a hazard assessment when determining whether the compound meets the criteria of EPCRA section 313(d)(2)(c) (EPA, 2013, June 20). Recognizing this, it is important to note that nonylphenol does not meet the persistence and bioaccumulation criteria defined under EPCRA. Furthermore, based on environmental monitoring conducted primarily by US government Agencies, nonylphenol is not likely to occur in the aquatic environment at concentrations exceeding WQC, which were developed according to rigorous methodology by EPA and confirmed in a later paper published in the peer-reviewed literature (EPA, 2005, Coady, 2010).

Considering this, APERC contends that EPA should acknowledge its own numeric criteria for persistence, bioaccumulation and WQC and recognize that nonylphenol does not sufficiently satisfy the criteria under EPCRA Section 313(c) as being “known to cause or can be reasonably anticipated to cause a significant adverse effect on the environment of sufficient seriousness” to warrant nationwide reporting under TRI.

REFERENCES


U.S. EPA (2010, August 18) Nonylphenol (NP) and Nonylphenol Ethoxylates (NPEs) Action Plan (August 18, 2010) RIN 2070-ZA09


