Response to Comments on the Draft Alternatives Assessment for Nonylphenol Ethoxylates
May 2012

On September 28, 2011, the US EPA Design for the Environment (DfE) Program issued a draft Alternatives Assessment for nonylphenol ethoxylates (NPEs) and posted it on its web site for public comment. DfE's Alternatives Assessment—*Alternatives for Nonylphenol Ethoxylates*—implements part of the EPA Nonylphenol/NPE Action Plan, which addresses concerns over potential ecological and other effects from the manufacturing, processing, distribution in commerce, and uses of NP and NPEs.

DfE's Alternatives Assessment Program helps industries choose safer chemicals and provides a basis for informed decision-making by developing a detailed comparison of potential human health and environmental effects of chemical alternatives. The Alternatives Assessment for NPEs highlights and builds on the EPA's and DfE Program's extensive work on surfactants and alternatives to NPEs, which has included substantial stakeholder involvement. As a result, this Alternatives Assessment process was able to proceed directly to the draft report stage and to focus on the comparison of a group of surfactants representative of those used in cleaning and detergent products.

DfE received nine comments on the draft *Alternatives for Nonylphenol Ethoxylates*, from a spectrum of interests—NPE manufacturers, product formulators, and an environmental organization—during the comment period, which ran from September 28 to November 30, 2011. DfE thanks everyone who took time to submit comments, including those who shared their support and ideas less formally.

Of the nine comments DfE received, most found the assessment very helpful and agreed with the approach used to compare alternatives. Two commenters raised potential issues with the draft assessment that DfE fully addresses in this document. The majority of commenters expressed appreciation for DfE's efforts in identifying and encouraging the use of safer surfactants. They felt, and we agree, that the *Alternatives for Nonylphenol Ethoxylates* should serve as a useful resource for those working on the manufacture of safer surfactants and cleaning products, as well as on advancement in the use of safer chemicals and products in general.

Below, DfE presents and discusses the comments received on the draft assessment and indicates planned changes to the proposed text. DfE has also made minor editorial and non-substantive technical corrections to the assessment. EPA received comments on 1) the assessment for NPEs, which are addressed first in this document, and 2) the assessment methodology, which are addressed briefly in this document because these issues were addressed in the Agency's 2011 responses to comments on the DfE Program. Please note that the comments have at times been paraphrased, summarized and combined, as appropriate, for efficiency and readability; full versions, as well as the final *Alternatives for Nonylphenol Ethoxylates*, are available on the DfE web site at www.epa.gov/dfe/pubs/projects/npe/index.htm.

Comments and DfE Responses

A. Comments on the Assessment for NPEs

Comment: The alternatives to NPEs in the assessment should include surfactants commonly used in cleaning products like all-purpose cleaners.

Response: DfE selected potential alternatives for the assessment that would illustrate the range of chemicals that function as surfactants and have been present in cleaning products that have been candidates for the DfE label. For each surfactant structural type, DfE sought a chemical that would be a good representative of its class and that had a complete set of data to address the surfactant criteria. To address the commenter's point that certain classes of surfactants are more commonly used in cleaning products than others and certain subclasses of surfactants are best suited to particular cleaning applications, DfE has included another safer alternative surfactant—a linear alcohol ethoxylate—often used in all-purpose cleaners and well-characterized for toxicity, to the assessment.

Comment: Use of the ten-day window criterion and corresponding designation of persistence status as "Very Low" is not appropriate for surfactant blends.

Response: As a general matter, DfE agrees with the commenter and only applies the 10-day window criterion to discrete surfactants, not blends (for which DfE assesses each ingredient in the blend). It is worth noting, however, that the Organization for Economic Cooperation and Development (OECD) indicates that there may be circumstances where a biodegradability test on a complex mixture of structurally similar chemicals, like oils and surfactants, might provide valuable information regarding the biodegradability of all the constituents. [1]

Comment: According to data on primary biodegradation (e.g., die-away tests), NPE, octylphenol ethoxylate (OPE) and their degradation intermediates should be designated as "Low" for environmental persistence as described in the recently published DfE Alternatives Assessment Criteria for Hazard Evaluation, which is not reflected in the current assessment.

Response: Primary biodegradation studies in surfactants measure degradation processes that chemically alter the parent compound, often causing a chemical to lose its surfactant properties. These studies do not measure the degree of ultimate biodegradation or mineralization, i.e., degradation of the compound to CO_2 and water, a more complete and accurate measure of environmental preferability and indicator that a chemical no longer poses a concern for environmental health. The DfE surfactant review criteria, which were used for this assessment, are based on the rate of ultimate biodegradation, not primary biodegradation. The die-away tests that the commenter cites measure primary biodegradation and thus are not applicable to the DfE criteria. In addition, nonylphenol, a potential NPE degradate, has been characterized as moderately persistent based on several biodegradation studies submitted to EPA under the High Production Volume Challenge Program.

[1] OECD Guidelines for the Testing of Chemicals, Section 3, paragraph 43, adopted March 23, 2006.

Comment: DfE defines "degradates of concern" in the Criteria for Safer Surfactants as meeting both specific acute toxicity thresholds and "slow" biodegradation. Based on a number of biodegradation studies, NPE and OPE degradation intermediates should be designated as "Low" for persistence and thus not "degradates of concern."

Response: DfE has reviewed the studies that the commenter cited in support of the rapid biodegradation of NPE and OPE degradation products and finds they do not meet the requirements in the DfE Criteria for Surfactants, which call for data on ultimate biodegradation, measured according to accepted guidelines. The studies are not valid evidence of low persistence; therefore, the NPE and OPE degradates remain properly characterized as "degradates of concern" under DfE's Criteria.

Specifically addressing the studies, the OECD 301B test data generated for octylphenol ethoxycarboxylates (OPECs) and nonylphenol ethoxycarboxylates (NPECs) in Staples, et al. (1999) (and repeated in Staples, et al. (2001) and Klecka, et al. (2008)) were measured using an inoculum that was presumed by the authors to be acclimated to APEs. According to OECD guidelines for the 301-series ready biodegradability tests[2], the inoculum may be pre-conditioned to the experimental conditions but not pre-adapted to the test substance. Likewise, the key data generated in Staples, et al. (2001) employed inocula that were either presumed to be acclimated to APEs (OECD 301B tests) or were intentionally pre-acclimated to NPE-9 (ISO Headspace test). Even if the microbial populations in typical POTWs are acclimated to APEs, as some of the cited studies indicate, using a pre-acclimated inoculum is not consistent with the stated test guidelines, referenced in the DfE criteria. Furthermore, the biodegradation data reported for the other surfactant types reviewed in this document were measured using non-acclimated inocula, and a valid comparison would demand the same test conditions.

Also, the cited river die-away study for NPE1-3, Ahel, et al. (1994), is a primary biodegradability study that reported the rate of conversion of the NPEs to the corresponding NPECs. As stated in the previous response, primary biodegradability studies are not applicable to DfE's criteria.

Regarding NP and OP degradates, Klecka, et al. (2008) reported that both fail the OECD 301C (MITI) test. In addition, the biodegradation data reported for NP and OP in the HPV Hazard Characterization Document (EPA, 2009) indicate that these substances are not readily biodegradable. Klecka, et al. (2008) characterize most of the results from Staples et al. (1999) and Staples, et al. (2001) as evidence of inherent biodegradability, noting that the substances did not meet the 10-day window criterion. DfE agrees that the studies indicate that NPE and OPE degradates may be inherently biodegradable, but the weight of evidence does not support their classification as readily biodegradable. As such, a persistence rating of "Low" for any of these compounds is inappropriate.

Comment: Regardless of the classification for degradates of NPE and OPE surfactants, similar data should be required for the degradates of the alternative surfactants in the NPE Alternatives

[2] OECD (1992),*Test No. 301: Ready Biodegradability*, OECD Guidelines for the Testing of Chemicals, Section 3, OECD Publishing.

Assessment document since their use will likely result in chronic exposure of aquatic species to their degradates. More rapid biodegradation of the alternative surfactants is not an adequate reason to disregard the chronic ecotoxicity of the degradates since the use and disposal patterns for the primary uses under discussion (i.e., cleaning, detergent and other consumer products) result in ongoing chronic exposure of aquatic species to the degradates.

Response: DfE has not disregarded the chronic ecotoxicity of alternative surfactant degradates. The rapid and complete ultimate biodegradation exhibited for the featured alternatives under standard test protocols attests to the lack of formation of persistent biodegradation intermediates, and the high probability of mineralization during sewage treatment and before environmental release. Unlike the degradates of NPE and OPE surfactants, the degradates of the safer alternatives will degrade before and during wastewater treatment and thus never enter an aquatic environment. In addition, while not all of the degradation products of the alternatives are known, their biodegradation pathways have been described and examined. These pathways do not lead to formation of intermediates that are known or suspected to be persistent.[3] If any of these intermediates had raised concerns, they would have been subjected to the same scrutiny as NP and OP.

The use and continual release pattern for cleaning products has important environmental implications, especially if their ingredients and degradates persist in the environment, posing a concern for aquatic organisms and adding to the cumulative environmental toxicant load. A similar use pattern for surfactants that rapidly and fully degrade would not present a concern. A study by Dorn, et al. (1993) compared the acute and chronic toxicities of separate CAS biotreater effluents from NPE-9 and an LAE (C12-15 alcohol ethoxylate EO-9) to fish and daphnia. The effluents from the NPE biotreater were significantly more toxic, both acutely and chronically, than the effluents from the LAE unit. In fact, both fish and daphnia exhibited no ill effects when tested in undiluted LAE effluent for 7 days (LC_0 and chronic NOEC = 100% effluent), whereas NPE effluent was lethal (LC_{50}) to fish at 21% dilution, and to daphnia at 40% dilution.[4] (Specific metabolites within the two effluent streams were not identified.)[5]

Comment: DfE should view the surfactant replacement package as the alternative, not just the surfactant, and should assess the hazards and risks of all the ingredients in the package to the same degree that NPEs have been assessed.

Response: Formulators have successfully replaced alkylphenol ethoxylates (APEs) with individual surfactants and blends of surfactants in many products. Specific blends are tailored to specific formulations, and DfE cannot know with certainty which blends may be optimal for

---

[3] For discussions of the biodegradation pathways of ethoxylated and propoxylated alcohols, see Talmage (1994), pp. 35-50 and Balston and Felix (1995); for alkyl polyglucoside surfactants, see Willing, et al. (2004); for linear alkylbenzene sulfonates, alkyl sulfate esters and alcohol ether sulfates, see Seber and Berger (1995). The biodegradation pathway of sorbitan esters is expected to be analogous to that described for sucrose esters in Baker, et al. (1995).

[4] Dorn, P.B.; Salanitro, J.P.; Evans, S.H.; Kravetz, L.1993. Assessing the Aquatic Hazard of Some Branched and Linear Nonionic Surfactants by Biodegradation and Toxicity. Environ. Toxicol. Chem., 12, pp. 1751-1762.

[5] While a 21-day study would be the preferred testing protocol, the 7-day test results are indicative of the increased toxicity of NPE over LAE degradates.

specific products and applications. The alternatives document highlights surfactant types that have been used to replace NPEs in products. Surfactants designed to biodegrade readily to low concern degradates present an optimal profile for protection of environmental health. NPE surfactants do not meet this profile. The safer alternatives featured in the assessment are preferred replacements for NPE, whether used individually or in combination.

Comment: Alternative surfactants with less data, and therefore subject to modeling and expert judgment, should not be viewed as being assessed in a manner that is either comparable to NPEs or adequate for determining their relative hazards.

Response: DfE relied on modeled data only twice in this assessment: for the chronic aquatic toxicity endpoint for OPE10 and Ecosurf EH-9. In both cases, DfE used experimental data for acute aquatic toxicity and, as a result, has high confidence in the estimated chronic values. Further, acute aquatic toxicity is the key endpoint for designating a safer surfactant, in part because it is more generally available as a measured value and can reliably be used to estimate chronic toxicity. Although the sizes of the datasets for the various surfactant types vary, and APEs (including NPEs) are more data-rich than many surfactants, adequate measured data were available for the assessment of each chemical presented in the document.

Comment: The NPE Alternatives Assessment relied primarily on Talmage (1994)[6] as the basis of most of the biodegradation data for NPE, OPE and their degradation intermediates and ignored many newer, more reliable studies that should be used to assess the persistence of these compounds.

Response: DfE does not agree that the assessment relied primarily on Talmage (1994). DfE cites Kravetz, et al. (1991) for the biodegradation rate data on NPE, not Talmage (1994). The data in Kravetz, et al. were measured according to OECD Guidelines (OECD BOD test and modified Sturm test) and the authors reported 31% ThBOD in an OECD BOD test and 14-34% $ThCO_2$ in a modified Sturm test, both measured for NPE-9. The data also indicate that the BOD measurement for NPE-9 had reached a plateau at 30-31% by day 15, remaining essentially unchanged up to day 30. Likewise, CO_2 evolution reached a plateau between days 5-10, with no significant increase up to day 28. These results are not inconsistent with data reported by Salanitro, et al. (1995), who reported 50% biodegradation of NPE-9 as CO_2 evolution, using a modification of the Sturm test. In addition, a recent biodegradation test in river water using ring-labeled NPE-9 (Naylor, et al., 2006) reported that attack of the phenolic ring did not begin until day 28 of the study, reaching 40% of maximum CO_2 (based on ring C only) at approximately day 112. This test demonstrates that, while the ultimate degradability of NPE's phenyl ring is possible, the complete degradation of NPE can be expected to occur relatively slowly.

As explained in an earlier response, primary biodegradation tests, and tests run using acclimated inocula, are not appropriate for evaluation using DfE's Criteria for Surfactants, and therefore were not included in the assessment. DfE used Talmage (and other sources as cited in the report) for information on biodegradation pathways for APEs; DfE also cited Talmage for aquatic

[6] Talmage S.S. (1994). Environmental and Human Safety of Major Surfactants—Alcohol and Alkylphenol Ethoxylates. Lewis Publishers, Boca Raton, FL, USA.

toxicity data. No biodegradation rate data were reported for APE degradation products in DfE's report.

Comment: Many of the old studies on NPEs, which were conducted to assess treatability in wastewater treatment plants, relied on indirect measures of quantification of NPE (e.g., colorimetric methods) and should not be used in the assessment.

Response: To assess biodegradation, DfE did not use any data based on colorimetric methods (e.g., MBAS, BIAS, CTAS) or any other method indicating primary loss of the parent compound or the destruction of surfactancy. The colorimetric analyses indicate changes in the ability to form solvent-extractible salts or complexes with surfactant molecules. Other test protocols measure destruction of surfactant properties by monitoring surface tension or foaming ability. These analyses can indicate that primary biodegradation (change of the chemical identity of the parent) has occurred. DfE built its evaluation on data for rates of ultimate biodegradability, developed using OECD or equivalent test methods, which measure O_2 uptake or CO_2 evolution. Although oxygen uptake and CO2 evaluation are indirect measurements that do not quantify NPE concentrations, they are accepted protocols for determining the degree of ultimate biodegradation of a test substance. Direct quantification of NPE in the test medium would only indicate loss of parent compound, indicating primary biodegradation, unless the analysis also measured every degradate formed, including CO2.

Comment: DfE selected only one study out of many listed in Talmage (1994) to reflect the biodegradation of NPEs, namely, Kravetz et al. 1978, which showed 10 to 53% degradation of NPE in 28 days.

Response: This comment is not accurate and needs clarification. The Kravetz (1978) study is not the citation DfE used for the biodegradation rate data for NPE-9. Talmage reported data for OPE-10, cited to Kravetz (1978). Importantly, most of the data reported in Talmage for OPEs—and for NPEs as well—were from primary biodegradation studies. As described in earlier responses, these data are not applicable to DfE's Critera for Surfactants and were thus not evaluated. Regarding OPE-10, Kravetz reported shake-flask assays that generated 10% $ThCO_2$ and achieved 53% ThBOD in 28 days. Although the Kravetz (1978) results are old, they are consistent with more recent MITI test data for OPE. Octylphenol ethoxylate achieved 22% BOD in 28 days, as measured in the OECD 301C (MITI) test (NITE, 2002).[7]

Comment: DfE should have included in its assessment three river die-away studies that showed OPE10 degrading 78 to 95% in 11 days, 94 to 95% in 5 days, and NPE9 degrading 75 to 95% in 10 to 20 days, respectively. [8] [9] [10]

---

[7] National Institute of Technology and Evaluation (NITE) 2002. Biodegradation and Bioconcentration of Existing Chemical Substances under the Chemical Substances Control Law. http://www.safe.nite.go.jp/data/hazkizon/pk_e_kizon_input_second.home_object

[8] Ruiz Cruz J, Dobarganes Garcia MC. 1976. Pollution of natural waters by synthetic detergents. X. Biodegradation of nonionic surfactants in river water Grasas y Aceitas 27: 309-322.

[9] Dobarganes Garcia MC, Ruiz Cruz J. 1977. Pollution of natural waters by synthetic detergents. XI. Influence of experimental variables in the biodegradation of nonionic surfactants in river water Grasas y Aceitas 28: 161-172.

Response: The papers the commenter cites are examples of studies using indirect colorimetric methods (based on cobalt thiocyanate active substance), which, as measures of primary rather than ultimate biodegradation, are not appropriate for the DfE assessment. These studies measured changes in the ability to form solvent-extractible complexes between the parent surfactant and cobalt thiocyanate, which can indicate primary biodegradation (destruction of the parent compound) but do not address the ultimate biodegradation of the substance. DfE's analysis is based on the rate of ultimate biodegradation and whether persistent and toxic degradates form.

B. Comments on the Assessment Methodology

Comment: Hazard-based assessment is inconsistent with EPA's statutory responsibility to consider risk under the Toxic Substances Control Act (TSCA) and the NPE Alternatives Assessment should be expanded to include consideration of other factors, like exposure, risk and performance, which are part of informed decision-making.

Response: Exposure and risk assessment have an important place in risk management, particularly for regulatory action. Risk assessments are not, however, the only tools for guiding the transition to safer and more environmentally sustainable chemicals. DfE Alternatives Assessments are hazard-focused tools that evaluate chemicals and potential alternatives with the goal of informing substitution to safer, highly functioning alternatives. The NPE Alternatives Assessment was not conducted to support a regulatory activity under TSCA; EPA expects it will inform decisions made in voluntary programs such as the Safer Product Labeling Program.

Comment: Hazard-based assessments are not a measure of safety and incorrectly assume drop-in replacement with alternatives.

Response: Hazard is a key component in assessing chemical safety and hazard-based assessments, like the alternatives assessment for NPEs, are part of an informed substitution process that considers a range of factors, including technical feasibility and performance. The assessment for NPEs states that the ability of an alternative surfactant to replace an NPE surfactant will depend on a formulation's performance demands. It is possible that a formulator will replace an NPE surfactant with a blend of surfactants. When NPE replacement surfactants are selected from among DfE-designated safer alternatives, each will have the characteristic of a safer surfactant, i.e., the chemical will biodegrade more readily to degradates of low concern, thereby improving the hazard profile of the whole detergent system.

Comment: The NPE alternatives assessment should consider additional human health and environmental endpoints.

Response: The methodology in the NPE alternatives assessment is tailored to the toxicological profile of surfactants and focuses on the evaluation of NPE and its alternatives from an environmental health perspective. The potential for toxicity to aquatic organisms—from the parent

[10] Ruiz Cruz J, Dobarganes Garcia MC. 1977. Pollution of natural waters by synthetic detergents. XII. Relation between structure and biodegradation of nonionic surfactants in river water Grasas y Aceitas 28: 325-331

surfactant and its degradation byproducts—and environmental persistence have been important areas of toxicological research and are endpoints that allow assessors to distinguish between chemicals with effects of concern and safer alternatives. The Action Plan for NP and NPEs highlights Agency concerns for the toxicity posed by these compounds to aquatic organisms.

Comment: The biodegradation criteria in the NPE Alternative Assessment have not been subject to adequate public review and comment; instead, DfE should use the biodegradation criteria in the more general DfE Alternatives Assessment Criteria for Hazard Evaluation, which have been subject to public comment.

Response: The DfE Criteria for Surfactants were developed in collaboration with the Green Blue Institute as the selection criteria for surfactants that would populate the CleanGredients database of safer cleaning product ingredients. Green Blue convened a diverse group of interested parties and subject matter experts to develop the criteria, which followed an open, consensus-based process. In addition, DfE requested public comment on its draft Standard for Safer Cleaning Products, which incorporates the DfE Criteria for Surfactants, in 2009, and again when it issued enhancements to its Standard in 2010 and 2011.