Alkylphenols & Ethoxylates Research Council

Attached are comments of the Alkylphenols & Ethoxylates Research Council on the Draft Report to the Legislature on Priority Consumer Products (Jan. 2020). Due to limits on the number of files allowed for submission via this public online comment form supplemental data files will be submitted to Ecology via email. Barbara Losey, Director, Alkylphenols & Ethoxylates Research Council



March 2, 2020

Safer Products for Washington Team Hazardous Waste and Toxics Reduction Program Department of Ecology Olympia, Washington

Submitted via: Safer Products for Washington Public Online Comment Form

Subject: Comments on Priority Consumer Products Draft Report to the Legislature: Safer Products for Washington Implementation Phase 2, January 2020, Publication 20-04-004

The Alkylphenols & Ethoxylates Research Council (APERC) appreciates this opportunity to provide comments on the "Priority Consumer Products Draft Report to the Legislature: Safer Products for Washington Implementation Phase 2" (Draft Report). ¹

The Draft Report identifies priority consumer products, which are being proposed for the first five "priority chemical" classes that were indentified in the Revised Code of Washington (RCW) for the Safer Products for Washington law (Chapter 70.365 RCW). APERC's comments focus on alkylphenol ethoxylates (APEs), a subgroup of the priority chemical category "phenolic compounds" identified in the Safer Products for Washington law. The Draft Report correctly notes that the most common APEs are nonylphenol ethoxylates (NPE) and octylphenol ethoxylates (OPE).²

APERC is a North American research-based trade association representing manufacturers of nonylphenol (NP), 4-tert-octylphenol (OP) and their derivatives, including NPE and OPE. For more than twenty years, APERC and its member companies have been actively engaged in the conduct and review of the toxicity, ecotoxicity, environmental fate, occurrence and risk assessment of NPEs, OPEs and their degradation intermediates.³

The Draft Report proposes priority consumer products that are in the view of the Department of Ecology (DoE) and the Department of Health (DoH) a "significant source or use" of priority chemicals that were specifically identified in the Safer Products for Washington Act.⁴

¹ Department of Ecology, State of Washington (DoE) (2020, January). Priority Consumer Products Draft Report to the Legislature: Safer Products for Washington Implementation Phase 2. <u>https://fortress.wa.gov/ecy/publications/summarypages/2004004.html</u>

² DoE. (2020, January). Pg. 48

³ Members of APERC are The Dow Chemical Company, SI Group, Inc., and Dover Chemical Corporation.

⁴ Washington State Pollution Prevention for Healthy People and Puget Sound Act, May 2019.

Alkylphenols & Ethoxylates Research Council Comments on Draft Report on Priority Products March 2, 2020 Page 2 of 9 At this time there is no guidance provided to inform the determination of "significant source or use" under the new Safer Products for Washington regulatory process. DoE reasoning to support "significant sources" appears to be developed on a case-by-case basis in the Draft Report.

With this in mind, APERC offers the following comments regarding the Draft Report and the proposal to make APEs in laundry detergent a Priority Product under the "phenolics" chemical class in the Safer Chemicals for Washington law. One comment also addresses an inaccurate characterization of APEs as persistent and bioaccumulative in webinar slides from the February 19, 2020 webinar on implementation of phase 2 of Safer Products for Washington.⁵

1. The process to identify "significant sources or uses" of Priority Chemicals should consider risk and prioritize products that actually pose risk to human health or the environment in the state of Washington; in the case of APEs, screening level risk assessments do not indicate risk in the State of Washington from any use of APEs.

Since regulation of a Priority Product under the Safer Products regulations will potentially set into motion regulations that will be significant and burdensome to implement for both affected businesses and the Departments of Ecology and Health, APERC recommends that the Safer Products for Washington process for determining "significant sources or uses" focus on uses of priority chemicals that have been demonstrated to pose a risk and/or represent the greatest potential for human or environmental exposure. This approach would be consistent with the apparent intention of the "significant sources or uses" criteria in the Safer Products for Washington law. In the case of APEs, screening level occupational and environmental risk evaluations presented in Attachments I and II to these comments do not suggest any source or use of NPE or OPE that poses significant exposure or risk in Washington State.

2. Although screening assessments do not find risk to the environment or human health from the use of NPE in laundry detergent, this use does represent a potentially high volume use with a high percentage of this surfactant in a product category that is intentionally discharged to wastewater treatment plants.

As discussed in these comments, there is no indication that any use of NPEs (or APEs generally) results in releases or exposures that are sufficiently significant to pose a risk to human health or the environment in the State of Washington; nevertheless this new law directs the DoH to identify "significant sources or uses" of the priority chemical class "phenolics", which has been defined to include APEs. The Draft Report identifies laundry detergent as a significant source of APEs and references a study conducted by the California Department of Toxic Substances Control (DTSC), which found that institutional cleaners, including laundry detergent, are the largest use of NPE surfactants. In addition, the Draft Report notes that laundry detergents that are "discarded down-the-drain make their way through wastewater treatment plants to bodies of water". ⁶ These findings regarding NPE are consistent with APERC's understanding of the

⁵ DoE and DoH. (2020, February 19). Safer Products for Washington Implementation Phase 2: Draft Report on Priority Consumer Product. Webinar slides.

⁶ DoE and DoH. 2020, January, pg. 5

Alkylphenols & Ethoxylates Research Council Comments on Draft Report on Priority Products March 2, 2020 Page 3 of 9 relative use of NPE surfactants as well as their intentional disposal to wastewater treatment plant when used at significant percent concentrations of up to 28% NPE in laundry detergents.⁷

3. A recent Canadian screening assessment found that uses of OPE do not result in releases to the environment in a quantity or concentration or under conditions that constitute or may constitute a danger in to human life, health or the environment; since use patterns of OPE in the State of Washington are not expected to differ substantially from Canada, significant sources or uses of OPE that are relevant to the Safer Products for Washington regulations are unlikely.

Regarding OPEs, APERC understands that these surfactants are used primarily in industrial applications with minor use in laundry detergent and that the volume of OPEs used in North America is approximately one-third that of NPEs. In addition, Environment and Climate Change Canada and Health Canada (ECCC) recently released a draft screening risk assessment on OPEs, which concluded that OPEs are not toxic under the Canadian Environmental Protection Act (CEPA) because they are "not entering the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity or that constitute or may constitute a danger to the environment on which life depends" and "are not entering the environment in a quantity or concentration or under conditions that constitute or may constitute a danger in Canada to human life or health." ⁸ Since use patterns of OPE in Canada are not expected to differ significantly from those in the United States or the State of Washington, based on the Canadian draft screening assessment there does not appear to be any significant exposure or risk to human health or the environment or any significant sources or uses of OPE that are relevant to the Safer Products for Washington regulations.

4. The European Union (EU) Environmental Quality Standards (EQS) values for NP are scientifically unacceptable benchmarks for comparison to environmental concentrations of AP/APE in Washington State; United States Environmental Protection Agency (US EPA) Water Quality Criteria (WQC) for NP provide more scientifically robust benchmarks for assessment of the environmental risk of AP/APE in the State of Washington.

In a discussion of potential environmental exposure to AP and APEs in the State of Washington the Draft Report notes that "globally there are there is widespread detection of APEs and APs in water, air, and sediment" and "detection is often at levels well above the probable no effect

⁷ Cheng, C.y and Ding, W.H. (2002). Determination of nonylphenol polyethoxylates in household detergents by high-performance liquid chromatography. *Journal of Chromatography A*, Vol. 968, Issues 1-2, pgs. 143-150

⁸ Environment and Climate Change Canada and Health Canada (2019, December). Draft Screening Risk Assessment – Polyethers/polyalkoxylates. <u>https://www.canada.ca/content/dam/eccc/documents/pdf/pded/poly(alkoxylates-ethers)/DSAR-Poly(alkoxylates_ethers)-EN.pdf</u>

Alkylphenols & Ethoxylates Research Council Comments on Draft Report on Priority Products March 2, 2020 Page 4 of 9 concentration for NP- determined by the EU to protect aquatic health – of 0.33 ug/L in water and 0.039 mg/kg in sediment." ⁹

It is APERC's view that the EU EQS developed for NP under the EU Water Framework Directive are not appropriate benchmarks for use in the context of assessing the environmental occurrence of AP/APE in the State of Washington or elsewhere. The EU developed EQS Predicted No Effect Concentrations (PNECs) for NP based on the most sensitive endpoint in the dataset reviewed. The basis of the EU EQS PNEC was a toxicity study by Kopf, 1997 in the freshwater algae *Scenedesmus subspicatus*.¹⁰ The PNEC (surface water) in the Kopf, 1997 study was calculated by dividing the EC_{10(Biomass}) by an assessment factor of 10. This assessment factor was justified by the fact that long-term No Observed Effect Concentrations (NOECs) from at least three species representing three trophic levels were available. Therefore, the NOEC for this freshwater alga provided the basis of the PNEC (water) value of 0.33 µg/L. The EU PNEC(sediment) was calculated as 0.039 mg/kg wet wt using an equilibrium partitioning method, which assumes that sediment-dwelling organisms are equally sensitive to NP and is based on the PNEC(water) value of 0.33 µg/L.¹¹

It is important to note that the Kopf, 1997 study was rejected for use by U.S. EPA in deriving WQC for NP because it did not meet the study quality criteria necessary to include it in a WQC derivation.¹² Environment Canada (now called Environment and Climate Change Canada) and the Canadian Council of Ministers of the Environment (CCME) also did not rely on the Kopf, 1997 study in their risk assessment of NP/NPE.^{13,14} In addition, the EU EQS is based on an algal biomass endpoint, which according to current EU guidance on Information Requirements and Chemical Safety Assessment, is not the preferred algal endpoint, particularly for development of an EQS.¹⁵

In summary, the current EU EQS for NP was developed based on an endpoint that would not be acceptable to the EU today from a study that does not meet the study quality requirements of the U.S. EPA or ECCC. Therefore, it is APERC's view that the EU EQS for NP is not sufficient from a scientific perspective for use in the context of the discussion of AP/APEs in the Draft Report.

⁹ DoE and DoH. (2020, January). pg. 52

¹⁰ Kopf, W. (1997). The action of endocrine substances in biological tests with aquatic organisms. <u>Papers on</u> <u>Wastewater, Fisheries and River Biology.</u> Volume 50. R. Oldenbourg Verlag, Munich

¹¹ European Commission. (EC). (2005, July 31). Environmental Quality Standards Substance Data Sheet: Nonylphenol. Final Version, Brussels

¹² 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.

¹³ Environment Canada and Health Canada (EC and HC). (2001). Priority substances list assessment report for nonylphenol and its ethoxylates. ISBN: 0-662-29248-0.

¹⁴ Canadian Council of Ministers of the Environment (CCME). (2002). Canadian water quality guidelines for the protection of aquatic life: Nonylphenol and its ethoxylates. <u>Environment Canada Publication Number 12999</u>. ISBN 10896997-34-1.

¹⁵ European Chemicals Agency (ECHA). (2017.June). Guidance on Information Requirements and Chemical Safety Assessment. Chapter R.7b Endpoint Specific Guidance. Version 4.0

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U.S. EPA developed Water Quality Criteria (WQC) for NP based on a robust aquatic toxicity database for NP that included adverse effects observed in *in vivo* toxicity studies that characterize population level effects in the environment (*i.e.* effects on survival, growth and development, and reproduction) and consideration of acute to chronic ratios. ¹⁶ NP has been the subject of attention due to its toxicity to aquatic organisms and because some studies have indicated that NP exhibits weakly estrogenic properties. In its final WQC document, EPA noted "the ability of nonylphenol to induce estrogenic effects has seldom been reported at concentrations below the freshwater final chronic value of 6.5965 μ g/L." ¹⁷

A review of more recent aquatic toxicity studies (17 freshwater species and 13 marine species) on NP, nonylphenol monoethoxylate (NP1EO) and nonylphenol diethoxylate (NP2EO) that were available after US EPA developed the WQC for NP was conducted by Coady *et al*, 2010, which confirmed that these newer data also support that the US EPA chronic WQC for NP in freshwater and saltwater are protective of aquatic species.¹⁸

U.S. EPA WQC for NP are appropriate from both a regulatory policy and scientific perspective for evaluating whether environmental exposure patterns indicate an environmental risk in the State of Washington. APERC provides a screening assessment of environmental concentrations of NP/NPE and OP/OPE in surface waters in the State of Washington relative to the EPA WQC for NP in comment number 5 below and in more detail in Attachment II to these comments. Since US EPA has not yet developed sediment quality criteria, toxicity-based PNECs for benthic organisms based on studies with sediment concentrations of NP and derived according to methods similar to US EPA guidance are provided in Attachment III and used for comparison to sediment concentrations in the State of Washington in Attachment II.

5. Available data on the environmental occurrence and concentrations of NPE, OPE and their degradants NP and OP in the State of Washington over a twenty-one year period between 1997 and 2018 indicate that these compounds are predominantly undetected, and when they are detected their concentrations are well below US EPA WQC for NP in fresh and marine water and relevant PNECs for NP in sediment.

Attachment II to these comments provides a review of the environmental occurrence and exposures of NPE, OPE and their environmental degradation intermediates NP and OP in the State of Washington. The dataset was drawn primarily from The DoE Environmental Information Management System (EIM) and the National Water Quality Monitoring Council Water Quality Portal.^{19, 20} The available data show that these compounds are undetected in most

¹⁶ 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.
¹⁷ US EPA (2005)

¹⁸ Coady, K., Staples, C. Losey, B., and 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 Assessment*. Volume 16, Issue 5, pgs 1066-1094

¹⁹ Department of Ecology (DoE), The State of Washington, Environmental Information Management System (EIM) <u>https://ecology.wa.gov/Research-Data/Data-resources/Environmental-Information-Management-database</u>

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samples, and where they are detected concentrations are well below US EPA WQC for NP in fresh and marine water and relevant PNECs for NP in sediment. In fact, *none* of the valid detected OP, NP or Total NP Equivalent (TNPEQ) values reported for the twenty-one year period between 1997 and 2018 exceed US EPA WQC for NP in fresh surface water ($6.6 \mu g/L$ NP) or marine surface water ($1.7 \mu g/L$ NP). Also, *none* of the detected values for OP, NP or TNPEQ in sediment exceed toxicity-based PNECs for NP in freshwater sediment (6,150 ng/g-dw) or marine sediment (1,230 ng/g-dw). These findings do not indicate *any* uses or sources of NPE or OPE as being a significant source or posing a risk to the environment in the State of Washington.²¹

There were two cases in the dataset where reported concentrations of NP and/or TNPEQ exceeded these WQC and PNEC. The first case was related to proxy data reported for **non-detected** samples of NP and/or TNPEQ due to the fact that ½ the Reporting Limit (RL) or Minimum Detection Limit (MDL) for the analytical method exceeded the relevant WQC or PNEC. The second case was related to questionable data reported under a Lummi Nation monitoring program using a method that is not relevant to or validated for NP/NPE. Details for both of these cases are provided in Attachment II.

Unfortunately, sampling locations in the dataset were not selected for direct temporal comparison and there are an insufficient number of sample locations with actual measured detections both before and after 2005/2006, when retail driven deselection of NPE in consumer detergents began with a Wal-Mart initiative²²; therefore there are insufficient data to provide a useful temporal comparison. However, the overall data do not suggest any uses of NPE or OPE over the twenty-one year sample period resulted in environmental exposures sufficient to result in risk to the environment in the State of Washington.

6. US EPA and other screening assessments find high Margins of Exposure (MoE) and low potential for risk to laundry workers and consumers from the use of NPE in Laundry Detergent.

The Draft Report raises exposure to laundry detergent as being particularly relevant for workers, who have a higher potential for exposure compared to the general population.²³

US EPA calculated worst-case laundry worker exposures to NPE based on a generic scenario for water-based washing operations at industrial and institutional laundries and with existing exposure estimation models available from US EPA and the Occupational Safety and Health Administration (OSHA) with results that indicate - even based on worst-case exposure estimates

²⁰ National Water Quality Monitoring Counci, Water Quality Portal. <u>https://www.waterqualitydata.us/</u>

²¹ Alkylphenols & Ethoxylates Research Council (2019, Nov 25.) Analysis of Environmental Monitoring for Nonylphenol, Octylphenol and their Ethoxylates in the State of Washington (Attachment II)

²² Wal-Mart. (2006).Chemical Intensive Products Preferred Principles Fact Sheet. October .

²³ DoE and DoH. (2020, January). page 51

Alkylphenols & Ethoxylates Research Council Comments on Draft Report on Priority Products March 2, 2020 Page 7 of 9 – that risk to laundry workers is extremely low. ^{24, 25} In addition, US EPA noted that due to "the low volatility and negligible dermal absorption of NP and NPE, EPA does not expect that, where liquid detergents are used, NPE will present a significant exposure potential to workers."^{26,27}

While the exposure estimates developed in the EPA Engineering Report are useful to demonstrate low worker exposures to NPE during the use of laundry detergents, they are extremely conservative and can be further refined using other available data and models.²⁸ Therefore, APERC conducted an exposure screening assessment to calculate potential exposure and MoE, or margins of safety, of industrial and institutional laundry workers to NPE, which is presented in Attachment I. The MoEs are based on multiple, conservative assumptions regarding exposure and therefore represent an upper bound estimate of laundry worker occupational exposure - not actual exposure. All MoEs indicate a low potential for risk to laundry workers. MoEs for the risk to consumers are expected to be even lower based on their lower exposures.

7. Assessment of source-specific human exposure and aggregate human exposure, as measured by human biomonitoring, to NP and OP studies indicates reasonable certainty of no harm.

The Draft Report discusses the potential for exposure to sensitive populations and references findings related to AP in human biomonitoring, noting that APs are more often measured in studies than APEs and can serve as an indicator of APE exposure.²⁹ In fact, human biomonitoring studies can provide reliable estimates of aggregate exposure to NP and or OP from all sources and uses, including of their ethoxylates.

The Draft Report correctly references human biomonitoring conducted by the US Centers for Disease Control (CDC) that found concentrations of OP in human urine that were so negligible and declining in the United States between 2005 and 2010 that CDC stopped reporting monitoring for this compound in human urine after 2010.

The Draft Report also cites several human biomonitoring studies that measured NP in human tissues, blood and urine. Osimitz et al (2015) conducted a critical review of papers published between 1998 and 2003 on human exposure to NP from both source-specific environmental monitoring (i.e., food, drinking water, air and dust) and human biomonitoring (blood, urine, breast milk) and calculated MOEs.³⁰ The MOEs were based on the use of a No-Observed-Adverse-Effect-Level (NOAEL) for sensitive toxicological endpoints of interest, that is, systemic

²⁴ US EPA. (2007, July 18). Draft: Engineering report of nonylphenol (NP) and nonylphenol ethoxylates (NPEs) Exposure to Laundry Workers :Response to section 21 petition.

²⁵ US EPA. (2006, October 24).). Chemicals used in water-based washing operations at industrial and institutional laundries - generic scenario for estimating occupational exposures and environmental releases - draft. US Environmental Protection Agency, Washington, DC, USA.

²⁶ US EPA. (2007, July 18).

²⁷ US EPA. (2006, October 24).

²⁸ US EPA. (2007, July 18).

²⁹ DoE and DoH.(2020, January). pg. 50

³⁰ Osimitz, T.O., Droege, W., Driver, J. (2015). Human Risk Assessment for Nonylphenol. *Human and Ecological Risk Assessment*, 21: 1903-1919

Alkylphenols & Ethoxylates Research Council Comments on Draft Report on Priority Products March 2, 2020 Page 8 of 9 and reproductive toxicity from continuous-feeding more than 3.5 generations (13 mg/kg/day). The MOEs were all greater than 1000, ranging from 2.9×10^3 to 8.4×10^7 , indicating reasonable certainty of no harm to humans for source-specific and aggregate (based on biomonitoring) exposures to NP. ³¹

8. AP/APEs are not persistent or bioaccumulative according to any governmental criteria, including those in Washington State.

While these comments are primarily directed at issues raised in the Draft Report, APERC would like to take this opportunity to provide corrections to a webinar presentation broadcast by DoE and DoH on February 19, 2020 on "Implementation Phase 2: Draft Report on Priority Consumer Products".³²

While the Draft Report does not represent AP/APEs as persistent or bioaccumulative, the webinar presentation (slide 9) lists "persistent" and "bioaccumulative" as environmental hazards from chemicals within the "phenolic compounds" class.

Klecka et al, 2007 examined the persistence and bioaccumulation potential of C8- and C9alkylphenols and their ethoxylates and concluded that the commercial APE products and their degradation intermediates do not meet any national or international criteria for identifying these compounds as PBT substances.³³ Environment Canada performed an assessment of all commercially relevant APE and AP and concluded that none of the substances met the CEPA criterion for either persistence or bioaccumulation.^{34, 35} Further, the European Commission Subgroup for the Identification of PBT and vPvB Substances concluded that the persistence and bioaccumulation criterion were not fulfilled by NP.^{36, 37} Also, NP is listed in the European Chemical Substances Information System (ESIS) as not fulfilling PBT and vPvB criteria.³⁸

Most relevant is that Washington DoE selected NP as one of 65 candidate chemicals for PBT screening and prioritization as part of a proposed PBT strategy in 2000 and decided not to include this compound on the PBT Working List because it does not meet the state's criteria for

Council Comments. Gatineau, Quebec. November 21, 2005

³¹ Osimitz *et al.* (2015).

³²Department of Ecology and Department of Health. (2020, February 19). Implementation Phase 2: Draft Report on Priority Consumer Products. Webinar Slides.

https://www.ezview.wa.gov/Portals/ 1962/Documents/saferproducts/February 2020 Webinar Presentation.pdf ³³ Klecka, G. *et al*. (2008). C8- and C9-Alkylphenols and Ethoxylates: II. Assessment of Environmental Persistence and Bioaccumulation Potential. Human and Ecological Risk Assessment, 14:1025-1055

³⁴ Environment Canada (EC). 2005. Decision on Categorization of Nonylphenol, Octylphenol and their Ethoxylates: Letter in Response to Alkylphenols & Ethoxylates Research

³⁵ Environmental Canada (EC). 2007. Ecological categorization of substances on the Domestic Substance List; Categorization Decisions (Completed in September 2006).

³⁶ European Commission (EC). (2002, August 30). Identification of Potential PBTs or vPvBs among the IUCLID High Production Volume Chemicals. European Chemicals Bureau Doc. ECB. Ispra, Italy.

³⁷ European Commission (EC). (2003, October 27-28). Minutes of Third Meeting of TM Subgroup on Identification of PBT and vPvB Substances. Arona, Italy. October 27–28, 2003

³⁸ European Chemicals Bureau European Substances Information System. ECB-ESIS. (2007). ESIS Version 5 Existing Substances PBT Module.

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persistence and bioaccumulative. ^{39,40} The DoE Response to Public Comments document stated "Ecology has reviewed the comments received on this issue and has decided not to include nonylphenol on the PBT Working List. The two main reasons why Ecology has elected not to include this substance on the PBT Working List are (1) the regional half-life values is below the criterion used to assess persistence; and (2) the bioconcentration factor is below the criterion used to assess bioaccumulation potential." 41

If vou have any questions regarding these comments or the attachments please contact me at blosey@regnet.com or (202) 419-1506.

Respectfully,

Barbarc 5. Losey

Barbara Losey Director

Attachments

Attachment I. Laundry Worker Exposure and Margin of Exposure Attachment II. Summary of Environmental Monitoring for Nonylphenol and Nonylphenol Ethoxylates in the State of Washington Attach II Fig.1 NP FW SW OBG 11.25.2019 Attach II Fig. 2_NP_Mar_SW_OBG_11.25.2019 Attach II Fig. 3_NP_FW_Sed_OBG_11.25.2019 Attach II Fig. 4 NP Mar Sed OBG 11.25.2019 Attach II Fig. 5_TNPEQ_FW_SW_OBG_11.25.2019 Attach II Fig. 6_TNPEQ_Mar_SW_OBG_11.25.2019 Attach II Fig. 7_TNPEQ_FW_Sed_OBG_11.25.2019 Attach II Fig 8_TNPEQ_Mar_Sed_OBG_11.25.2019 Attach II Fig. 9 OP FW SW OBG 12.05.2019 Attach II Fig 10 OP Mar SW OBG 12.05.2019 Attach II Fig. 11 OP FW Sed OBG 12.05.2019 Attach II Fig. 12_OP_Mar_Sed_OBG_12.05.2019

Attachment III. Staples, C. et al(2010, Nov.) Assessing the Effects and Potential Risks of Branched para-Nonylphenol to Sediment Dwelling Organisms. Poster at Society of Environmental Toxicology & Chemistry Annual Meeting, North America

³⁹ Washington Department of Ecology (DoE). (2000, December). Proposed Strategy to Continually Reduce Persistent, Bioaccumulative Toxins (PBTs) in Washington State. Publication 00-03-0054

⁴⁰ Washington Department of Ecology.(DoE) (2002, June). Ecology PBT Working List: Responses to Public Comments on Appendix E. Publication No. 02-03-030 ⁴¹ DoE. (2002, June).

Alkylphenols & Ethoxylates Research Council Comments for Washington Ecology on APEs December 19, 2019 ATTACHMENT I TABLES IA and IB Laundry Worker Exposure and Margin of Exposure

While the exposure estimates developed in an EPA Engineering Report are useful to demonstrate low exposures to NPE in laundry detergent, they are extremely conservative and can be further refined using other available data and models.¹ The Alkylphenols & Ethoxylates Research Council (APERC) conducted exposure screening assessments to calculate potential exposure of industrial laundry workers to NPE. They are based on multiple, conservative assumptions regarding exposure and therefore represent an upper bound estimate of laundry worker occupational exposure - not actual exposure.

Table IA. Calculated Upper-Bound Laundry Worker Inhalation Exposure to NPE9 from Respirable Dust in Granular Laundry Detergent						
	Value	Units				
			Basis			
Exposure scenario	Double pouring granular detergent. No personal protection equipment		Hendricks (1970)			
Dust exposure factor	0.27	μg	Hendricks (1970) measured 0.27 µg exposure per 0.2 kg handled			

¹ US EPA. (2007, July 18). Draft: Engineering report of nonylphenol (NP) and nonylphenol ethoxylates (NPEs) in response to section 21 petition

Calculated Upper-Bo	Table IA ound Laundry Worker Inhalation Ex Laundry Det	posure to N	IPE9 from Respirable Dust in Granular
	Value	Units	
			Basis
Exposure scenario	Double pouring granular detergent. No personal protection equipment		Hendricks (1970)
NPE percentage in detergent	28%	%	EPA (2007) assumes powdered detergents used in smaller laundries formulated similar to consumer detergents
Respirable dust fraction in granular laundry detergent	0.2%	%	Hendricks (1970)
Detergent handled daily	154	kg	EPA (2007) Assumes one worker handles all detergent for site in 8 hour shift
Inhalation dose	0.116	µg/day	Calculated
Convert units	1.2E-04	mg/day	Calculated. Inhalation Dose/1000
Body weight	71.8	kg	EPA (1999) Table 7-2. Mean body weight (males and females age 18<75)
Estimated daily dose	1.6E-06	mg/kg- bw/day	Calculated

Table IA. Calculated Upper-Bound Laundry Worker Inhalation Exposure to NPE9 from Respirable Dust in Granular Laundry Detergent						
	Value	Units				
			Basis			
Exposure scenario	Double pouring granular detergent. No personal protection equipment		Hendricks (1970)			
No Observed Effect Level (NOEL) for NPE9	50	mg/kg/day	EPA (2006, July 31)			
Margin of Exposure (MOE)	30,835,567	none	Calculated MOE = NOEL ÷ Est. Daily Dose (inhalation)			

	Table IB. Calculated Upper-Bound Laundry Worker Dermal Exposure to NPE9 from Laundry Detergents (Liquid and Granular)							
	A *	B *	C	D	Units	Basis		
	Single layer clothing, no gloves	Single layer clothing, no gloves	Single layer clothing, using gloves	Single layer clothing, using gloves		EPA PHED (1998)		
Exposure scenario	Granular, open loading and washing	Liquid, open loading and washing	Liquids, open loading and washing	Liquids, closed loading and washing		EPA PHED (1998).		
Dermal unit exposure value	0.0084	2.9	0.023	0.0086	mg NPE / lb detergent handled	Derived from EPA PHED (1998) active ingredient exposure based on lbs handled		
NPE fraction of detergent	28%	100%	100%	100%	fraction	EPA (2007) 28% for powder and 100% for liquid.		
Detergent handled daily by one worker in 8 hour shift	154	154	154	154	kg			
NPE handled daily	95.1	339.6	339.6	339.6	lb	Calculated		
External dermal dose	0.80	984.75	7.81	2.92	mg/day	Calculated		
Relative dermal absorption	1%	1%	1%	1%	%	Monteiro-Riviere et al., 2000		

Table IB. Calculated Upper-Bound Laundry Worker Dermal Exposure to NPE9							
				(Liquid and G			
	A *	B *	С	D	Units	Basis	
Exposure scenario	Single layer clothing, no gloves	Single layer clothing, no gloves	Single layer clothing, using gloves	Single layer clothing, using gloves		EPA PHED (1998)	
	Granular, open loading and washing	Liquid, open loading and washing	Liquids, open loading and washing	Liquids, closed loading and washing		EPA PHED (1998).	
Dermal dose	0.008	9.848	0.078	0.029	mg/day	Calculated	
Mean body weight	71.8	71.8	71.8	71.8	kg	EPA (1999) Table 7-2. Mean body weight (males and females age 18<75)	
Absorbed dose	1.11E-04	1.37E-01	1.09E-03	4.07E-04	mg/kg/day	Calculated	
NOEL for NPE9	50	50	50	50	mg/kg/day	EPA (2006, July 31)	
MOE	449,498	365	45,966	122,932	none	Calculated	

* Note EPA PHED (1998) did not have an exposure estimate value for a scenario for loading powders or liquids with single layer clothing and no gloves with closed loading and mixing or washing. Scenarios A and B are provided as a worst case alternatives.

Discussion

While the exposure estimates developed in an EPA Engineering Report are useful to demonstrate low exposures to NPE in laundry detergent, they are extremely conservative and can be further refined using other available data and models.²

1. Refinements to respiratory exposure to NPE and MOE for powdered laundry detergent

EPA relies on the OSHA Particulate Not Otherwise Regulated (PNOR) Permissible Exposure Limit (PEL) for nuisance dust (15 mg/m³) to calculate inhalation exposure to NPE. Another approach is to consider data regarding the actual characteristics of dust in granular laundry detergent.

Assumptions regarding the inhalation exposure of NPE from granular detergents can be refined based on data presented in a paper by Hendricks, 1970, which examined dust levels and characteristics in powdered laundry detergents.³ While the focus of this paper was on enzyme exposure, it provides the following useful data regarding the characteristics of dust in laundry detergent. First, on average 0.27 μ g detergent dust exposure per cup of product was found for double-pour machine loading with powdered detergent. "Double-pour" indicates pouring from a large container to a measuring container and then pouring from that measuring container into the washing machine; this is similar to the worst-case work practice assumptions in EPA's Engineering Report. Also, Hendrix reported a maximum of only 0.2% of the dust from granular detergent was found to be less than 5 μ for consumer powdered laundry detergents. The author notes that particles larger than 5 μ are generally considered to be too large to be respirable.

Based on these data provided in the Hendrick, 1970 paper and other assumptions provided in the EPA Engineering Report (i.e., an average laundry site handles 154 kg detergent per day), APERC calculated an inhalation dose of 0.00012 mg NPE /day from granular detergent as shown in Table 8a. APERC assumed one worker handles all 154 kg of laundry detergent during the course of a single 8 hour work shift; the worker double pours the powdered laundry detergent, and no personal protection equipment is worn. Dividing the estimated daily inhalation dose of 0.00012 mg/day by a mean body weight of 71.8 kg results in an average daily dose of 0.000016 mg/kg-bw/day. When the lowest NOEL for NPE9 (50 mg/kg-bw/day) is divided by this calculated exposure an MOE of 30,835,567 is calculated.

² US EPA. (2007, July 18). Draft: Engineering report of nonylphenol (NP) and nonylphenol ethoxylates (NPEs) in response to section 21 petition ³ Hendricks, M.H. (1970). Measurement of enzyme laundry product dust levels and characteristics in consumer use. <u>Journal of the American Oil Chemists'</u> <u>Society</u>, <u>47</u>, 207-211.

2. Refinements to dermal exposures to NPE and MOE for powdered and liquid laundry detergent

For dermal exposure calculations EPA assumed that both hands of the worker (840 cm²) were completely exposed to a quantity of detergent (as defined by the EPA Generic Scenario document) without being wiped off and that there was 100% relative dermal absorption.^{4,5} APERC used an alternate approach to refine the dermal exposure calculations that relied on surrogate dermal unit exposure values from the 1998 EPA Pesticide Handler Exposure Database (PHED)⁶ to estimate exposures for manual loading of solid and liquid detergents. EPA commonly uses PHED data, which is based on actual monitoring in occupational settings, for screening level exposure analyses in the absence of monitoring data for other occupational settings as described below.

PHED provides generic pesticide worker (i.e., mixer/loader and applicator) exposure estimates. The dermal and inhalation exposure estimates generated by PHED are based on actual field monitoring data, which are reported generically (i.e., chemical specific names not reported) in PHED. It has been the Agency's policy to use a surrogate or generic exposure data for pesticide applicators in certain circumstances because it is believed that the physical parameters or application technique, not the chemical properties of the pesticide, attribute to exposure levels. [Note: Vapor pressures for the chemicals in PHED are in the range of E-5 to E-7 mm Hg.] Chemical specific properties are accounted for by correcting the exposure data for study specific field and laboratory recovery values as specified by the PHED grading criteria. PHED handler exposure data are generally provided on a normalized basis for use in exposure assessments. The most common method for normalizing exposure is by pounds of active ingredient (ai) handled per replicate (i.e., exposure in mg per replicate is divided by the amount of ai handled in that particular replicate). These unit exposures are linear based on the amount of active ingredient handled.⁷

⁴ US EPA. (2006, October 24)

⁵ US EPA. (2007, July 18).

⁶ US EPA. (1998).

⁷ US Environmental Protection Agency (US EPA). (2008, January 9). Occupational and residential exposure chapter for diiodomethyl p-tolyl sulfone.

Commonalities between the process used for loading pesticide into a mixing tank and that used for loading laundry detergent into a washing machine further supports the usefulness of this approach to estimating laundry worker exposure to NPE in detergents. The potential dermal exposure of a laundry worker to NPE from laundry detergent was calculated using data from PHED and the following assumptions during various scenarios of loading detergent:

- Unit exposure factor for **open** mixing and loading of **granular** products, with a single layer of clothing without gloves is 0.0084 mg /lb handled.⁸
- Unit exposure value of 2.9 mg /lb handled for all **liquids**, **open** mixing and loading based on a single layer of clothing without gloves and 0.023 2.9 mg/lb handled using gloves.⁹
- Unit exposure value of 0.0086 mg /lb handled for all **liquids**, **closed** mixing and loading based on a single layer of clothing using gloves (Note the EPA PHED did not have a value for a closed system loading not wearing gloves).¹⁰
- An average of 154 kg (340 lb) of solid powder detergent was used per site per day.¹¹
- An average of 154 kg (340 lb) of liquid detergent is used per site per day.
- The NPE represents 28% of the granular detergent and 100% of the liquid detergent formulations.¹²
- One worker manually does all the detergent loading for the site (154 kg) during an 8-hour shift and cleans his/her skin at the end of the shift.
- The relative dermal absorption of NPE was less than 1% of the applied dose in solution after 8 hours of exposure based on Monteiro-Riviere et al. (2000).¹³
- The mean body weight was 71.8 kg for an adult male or female from age 18 to 75.¹⁴

Table Ib provides estimated dermal exposures to NPE for various scenarios (*i.e.*, with and without gloves; open or closed loading; open or closed mixing /washing) based on ingredient exposures measured in the EPA PHED. Assumptions and calculations to derive daily exposures (mg/kg-bw/day) and MOEs are also provided in Table 8b. For workers using granular laundry detergent with no

⁸ US EPA. (1998).

⁹ US EPA. (1998).

¹⁰ US EPA. (1998).

¹¹ US EPA. (2007, July 18).

¹² US EPA. (2007, July 18).

¹³ Monteiro-Riviere et al. (2000).

¹⁴ US EPA. (1998).

gloves and open loading and mixing/washing, a daily absorbed dose of 0.000111mg/kg-bw/day was estimated. The MOE for this exposure based on the same lowest NOEL for NPE9 (50 mg/kg-bw.day) is calculated as approximately 450,000. For workers using liquid laundry detergent with no gloves, open loading /mixing/washing, a daily absorbed dose of 0.137 mg/kg-bw/day was estimated and a corresponding MOE was calculated as approximately 365. For workers using liquid laundry detergent with gloves and open loading /washing/mixing a daily absorbed dose of 0.0011mg/kg-bw/day was estimated and a corresponding MOE of approximately 46,000 was calculated. Finally, for workers using liquid laundry detergent with gloves and closed loading/washing/mixing, a daily absorbed dose of 0.00041mg/kg-bw/day was estimated and a corresponding MOE of approximately 23,000 was calculated.

References for Table IA and IB:

Hendricks, M.H. (1970). Measurement of enzyme laundry product dust levels and characteristics in consumer use. Journal of the American Oil Chemists' Society, <u>47</u>, 207-211.

Monteiro-Riviere, N.A., Van Miller, J.P., Simon, G., Joiner, R.L., Brooks, J.D., & Riviere, J.E. (2000). Comparative in vitro percutaneous absorption of nonylphenol and nonylphenol ethoxylates (NPE-4 and NPE-9) through human, porcine and rat skin. <u>Toxicology and Industrial Health</u>, 16, 49-57.

US Environmental Protection Agency (US EPA). (1998). Surrogate Exposure Guide - Estimates of Worker Exposure from the Pesticide Handler Exposure Database (PHED) Version 1.1. Washington, DC, USA.

US Environmental Protection Agency (US EPA). (1999). Exposure Factors Handbook. EPA/600/C-99/001. Office of Research and Development, Washington, DC, USA.

US Environmental Protection Agency (US EPA). (2006, July 31) Action memo by Wagner, P., Chief, Inert Ingredient Assessment Branch, US EPA. Inert reassessments: Four exemptions from the requirement of a tolerance for nonylphenol ethoxylates. US Environmental Protection Agency, Washington, DC, USA. US Environmental Protection Agency (US EPA). (2006, October 24). Chemicals used in water-based washing operations at industrial and institutional laundries - generic scenario for estimating occupational exposures and environmental releases - draft. US Environmental Protection Agency, Washington, DC, USA.

US Environmental Protection Agency (US EPA). (2007, July 18) Draft: Engineering report of nonylphenol (NP) and nonylphenol ethoxylates (NPEs) in response to section 21 petition.

Alkylphenols & Ethoxylates Research Council Comments for Washington Ecology on APEs December 19, 2019

Attachment II Summary of Environmental Monitoring for Nonylphenol and Nonylphenol Ethoxylates in the State of Washington

In an effort to better understand the environmental occurrence for 4-nonylphenol (NP), nonylphenol ethoxylates (NPE), octylphenol (OP) and octylphenol ethoxylates (OPE) in the environment in the State of Washington, the Alkylphenols & Ethoxylates Research Council (APERC) sponsored an analysis of available environmental monitoring data in the state.^{1, 2} Results are discussed below and presented in Attachment II Figures 1 though 12.

Environmental monitoring data from the State of Washington were queried from publicly available governmental monitoring programs and were compiled into a statewide database. Monitoring programs included the Department of Ecology, State of Washington, Environmental Information Management System (EIM) and the National Water Quality Monitoring Council (NWQMC), Water Quality Portal (WQP). The EIM contains environmental monitoring data collected by Department of Ecology scientists and their partners, including the Department of Natural Resources and Parks, the University of Washington, the US Army Corps of Engineers, and consultants of the Department of Ecology. The WQP is a cooperative service sponsored by the NWQMC, the Environmental Protection Agency (EPA), and United States Geological Survey (USGS). Nationwide, the WQP serves data collected by over 400 state, federal, tribal, and local agencies. A literature search was also conducted that identified one additional environmental monitoring data resource in the State of Washington by Meador, J.P. et al, 2016, which was included in the database.³

The environmental monitoring database contains historical and current data generated by multiple sources using a variety of standards and quality assurance programs. Historical data are generally less robust in study detail than current data. The NWQMC addressed this matter in 2006 with the publication of *Data Elements for Reporting Water Quality Monitoring Results for Chemical, Biological, Toxicological, and Microbiological Analytes.*⁴ With that report, the

¹ Tazelaar, D. and Stolz, S. (O'Brien & Gere Engineers, Inc, Ramboll Group) (2019, November 25) Summary of NP and TNPEQ Environmental Monitoring Data in the State of Washington Figures 1-8.

² Tazelaar, D. and Stolz, S. (O'Brien & Gere Engineers, Inc, Ramboll Group) (2019, December 5) Summary of OP Environmental Monitoring Data in the State of Washington Figures 9-15.

³ Meador, J. P., Yeh, A., Young, G., & Gallagher, E. P. (2016). Contaminants of emerging concern in a large temperate estuary. *Environmental pollution*, *213*, 254-267.

⁴ National Water Quality Monitoring Council(2006, April) Technical Report No. 3 Data Elements for Reporting Water Quality Monitoring Results for Chemical, Biological, Toxicological, and Microbiological Analytes. <u>https://acwi.gov/methods/pubs/wdqe_pubs/wqde_trno3.pdf</u>

NWQMC developed sets of data elements which they believe are the minimum elements necessary to foster the comparability and exchange of data. In spite of the potential variability in data reliability among the available resources, the entire breadth of data queried was considered and included in the environmental database. Highly variable data were assessed on a study-specific basis and clearly delineated in the summaries herein. Marine and freshwater sediment and surface water data were summarized in both maps and tables in the attached Figures 1 through 12. Efforts to omit replicate and duplicate samples were made after identifying records with duplicative sample detail. When sample-specific detail lacked the distinction of either freshwater or marine, the waterbody detail was used derive that information. Data queried and compiled in the environmental database were subjected to internal quality control checks for accuracy of transposition at a frequency of 10%. For undetected sample results, half the reporting limit (RL) was assigned as a proxy value. For samples that had no reported RL, half the method detection limit (MDL) was assigned as the proxy value. Results reported as estimated values (J flags) were treated as detected results.

Presentation of Environmental Monitoring Data

Results are presented in Figures 1 though 12 that represent detected and non-detected results of NP, Total NP Equivalents (TNPEQ) and OP collected in fresh surface water, marine surface water, freshwater sediment, and marine sediment in Washington between 1997 and 2018. Available monitoring data for NP and are presented in Figures 1 through 4. Aggregate TNPEQ concentrations for NP and NP ethoxylates are presented in Figures 5 through 8. TNPEQ concentrations were calculated according to the Toxicity Equivalence Factors (TEF) relative to NP in Table 1 below, which were originally developed by Environment Canada and later corroborated by Coady et al, 2010. ^{5, 6} Available monitoring data for OP are presented in Figures 9 through 12 and are presented according to the TEF for OP relative to NP, which was also developed by Environment Canada. There were no results for OPE available.

Compound	TEF
NP	1
NP1,2EO	0.5
NP3-17EO	0.005
OP	1
OP1,2EO	0.5
OP3-17EO	0.005

TABLE 1 Toxicity Equivalence Factors for NP, NPEs, OP and OPEs (Environment Canada, National Guidelines and Standards Office, 2001, April)

⁵ Environment Canada, National Guidelines and Standards Office (2001, April). Canadian Environmental Quality Guidelines for Nonylphenol and Its Ethoxylates. Scientific Supporting Document

⁶ Coady, K., Staples, C. Losey, B., and 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 Assessment: An International Journal.* Volume 16, Issue 5, pgs 1066-1094

Data are reported in accordance with US EPA Guidance on Environmental Data Verification and Data Validation. ⁷ Detected results were presented as reported. Tabular results in Figures 1 though 12 present detected samples in the top row. The bottom row of each table presents all samples in the date range including detected and non-detected samples, which are reported as proxy values of ¹/₂ RL or ¹/₂ MDL. The number of samples (n), average, standard deviation (StDev), and maximum (Max) values are also reported in the tabular results.

Comparison of Environmental Monitoring to Toxicity-Based Water Quality Criteria and Predicted No Effect Concentrations

All results for NP, TNPEQ, and OP including detected values and proxy non-detected values (1/2 RL or MDL) are presented relative to US EPA Water Quality Criteria (WQC) for NP for media where WQC are available, or to toxicity-based Predicted No Effect Concentrations (PNECs) for NP.^{8,9,10} US EPA WQC "represent the concentration in water at which aquatic life are protected from acute and chronic adverse effects".¹¹

U.S. EPA developed WQC for NP based on a robust aquatic toxicity database for NP that included adverse effects observed in *in vivo* toxicity studies that characterize population level effects in the environment (*i.e.* effects on survival, growth and development, and reproduction) and consideration of acute to chronic ratios. ^{12,13} NP has been the subject of attention due to its toxicity to aquatic organisms and because some studies have indicated that NP exhibits weakly estrogenic properties. In its final WQC document, EPA noted "the ability of nonylphenol to induce estrogenic effects has seldom been reported at concentrations below the freshwater final chronic value of 6.5965 μ g/L."¹⁴

A review of more recent aquatic toxicity studies (17 freshwater species and 13 marine species) on NP, NP1EO and NP2EO that were available after US EPA developed the WQC for NP was conducted by Coady et al, 2010, which confirmed that these newer data also support that the US EPA chronic WQC for NP in freshwater and saltwater are protective of aquatic species.¹⁵

⁷ US EPA (2002, Nov. 20) Guidance on Environmental Data Verification and Data Validation. EPA QA/G-8 https://www.epa.gov/sites/production/files/2015-06/documents/g8-final.pdf

⁸ 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.

⁹ US Environmental Protection Agency (US EPA). (2006, February 23). Notice of availability of final aquatic life ambient water quality criteria for nonylphenol. <u>Federal Register</u>, <u>71</u> (36), 9337-9339.

¹⁰ Staples, C.A., Coady, K. and Losey, B. (2010, Nov). Assessing the Effects and Potential Risk of Branched para-Nonylphenol to Sediment Dwelling Organisms. Poster Presentation at Society of Environmental Toxicology and Chemistry, North American Annual Meeting, Portland, OR, USA

¹¹ US Environmental Protection Agency (US EPA). (2005).

¹² US Environmental Protection Agency (US EPA). (2005).

¹³ US Environmental Protection Agency (US EPA). (2006, February 23).

¹⁴ US Environmental Protection Agency (US EPA). (2005).

¹⁵ Coady, K., Staples, C. Losey, B., and Klecka, G. (2010).

U.S. EPA WQC are appropriate from both a regulatory policy and scientific perspective for evaluating whether environmental exposure patterns indicate a significant environmental source or use of a priority chemical under the Safer Products for Washington. Since US EPA has not yet developed sediment WQC, toxicity-based Predicted No Effect Concentrations (PNECs) for benthic organisms based on studies with sediment concentrations of NP and derived according to methods similar to US EPA guidance are used for comparison.¹⁶

Table 2 presents the WQC and PNECs used is this evaluation of environmental monitoring data for NP, TNPEQ and OP in the State of Washington.

Media	Туре	WQC (µg/L)	Source
Water	Freshwater, acute	28.0	US EPA (2005,2006)
	Freshwater, chronic	6.6	US EPA (2005,2006)
	Saltwater, acute	7.0	US EPA (2005,2006)
	Saltwater, chronic	1.7	US EPA (2005,2006)
Media	Туре	PNEC (ng/g-dw)	Source
Sediment	Freshwater	6,150	Staples (2010, Nov)
	Marine	1,230	Staples (2010,Nov)

TABLE 2 NP WQCs(aq) and PNEC(sed)

Analytical Methods

Analytical methods were not consistent across the dataset due to the fact that the data are drawn from different monitoring programs. Consequently RLs and MDLs vary in sensitivity, accuracy and precision across the dataset. However, most analytical methods used in this dataset are sufficiently sensitive to allow comparison to WQC and PNEC values.

In one case, monitoring data conducted in the Lummi Nation, a self-governing nation of the third largest tribe in Washington State, reports values for "NP, total" using an analytical method that is not suitable for the detection of NP or NPE. The Lummi Nation data for "NP, total" was collected using National Environmental Methods Index (NEMI) Standard Method No. 5540C "Anionic Surfactants in Water as MBAS". ¹⁷ NPE is a *nonionic* surfactant. NEMI Standard Method No. 5540C is a method for anionic surfactants and has not been validated for the detection of 4-NP, 4-t-OP and their ethoxylates; therefore is not suitable for use in monitoring these substances. Since the Lummi Nation fresh surface water data for "NP, Total" are questionable, they are presented separately in Figure 1 "NP Sample Results in Fresh Water, Surface Water" and Figure 5 "Total NP Equivalent Sample Results in Freshwater, Surface

¹⁶ Staples, C.A., Coady, K. and Losey, B. (2010, Nov).

¹⁷ National Environmental Methods Index Standard Method No. 5540C "Anionic Surfactants in Water as MBAS" <u>https://www.nemi.gov/methods/method_summary/7612/</u>

Water". The only detected results in the entire dataset for NP that exceeded benchmark WQC and PNECs were from this Lummi Nation dataset.

An equally important issue that should be recognized is uncertainty more generally with the analytical methodology for measuring NP in water samples, which is related to a high occurrence of false positive detection of this compound even with validated analytical methods. The high degree of analytical bias for false positive detections of NP in surface waters indicates that available monitoring data overstate the actual occurrence and concentrations of this compound in the environment. A published paper by Vanderford et al, 2014 presented the results of a largescale interlaboratory comparison study of 25 chemicals of concern (CECs), including NP to assess the accuracy and precision of available analytical methods with spiked samples of drinking water and source water.¹⁸ The paper presents the results of two single-blind interlaboratory comparisons conducted at 25 research and commercial labs located in the EU, the United States, Canada and Australia. The study evaluated 10 different analytical methods for measuring NP in drinking water and 11 different methods for measuring NP in source water. The authors state that NP is difficult to analyze accurately at the low concentrations expected to be found in the environment and 69% of all unspiked samples were reported to have detectable NP, indicating an extremely high percentage of false positives. The rate of false negative results for NP was only 9%, suggesting only a low degree of concern for generating false negative results. The overall results for NP precluded the authors from recommending specific analytical methods for this compound. The authors concluded: "Perhaps most importantly, results from this work likely suggest that some studies in the literature have very high degrees of analytical bias and/or large numbers of false positives. Further, the use of occurrence data from unsuitable analytical procedures may have resulted in inappropriate risk assessments and prioritization for regulation. Thus, it is important that the consequences these data potentially have had on past decisions is recognized and critical that analytical quality and reliability be considered in future assessments." 19

Discussion of Results

In Figure No. 1 when the questionable samples from the Lummi Nation monitoring program, which were measured with an analytical method that is not suitable or validated for NP/NPE, are removed from the data set none of the detected or proxy non-detected sampling results for NP taken in fresh surface water between 1997 and 2018 exceeded the EPA WQC (freshwater, chronic) of 6.6 μ g/L NP.

¹⁸ Vanderford, B.J., Drewes, J.E., Eaton, A., Guo, Y.C., Haghani, A., Hoppe-Jones, C., Schluesener, M.P., Snyder, S.A., Ternes, A. and Wood, C.J. (2014). Results of an Interlaboratory Comparison of Analytical Methods for Contaminants of Emerging Concern in Water. *Anal. Chem.*, *86* (1), pp 774–782

¹⁹ Vanderford, B. J., et al. (2014).

In Figure No. 2 none of the detected or proxy non-detected NP results in marine surface water taken between 2006 and 2018 exceeded the US EPA WQC (chronic, marine) of $1.7 \mu g/L$. No sampling results were available before 2006.

In Figure No. 3 none of the detected or proxy non-detected NP results taken in freshwater sediment between 1997 and 2018 exceeded the toxicity-based PNEC (freshwater, sediment) of 6,150 ng/g dw.

In Figure No. 4 none of the detected NP results in marine sediment in samples taken between 1997 and 2018 exceeded the toxicity-based PNEC (marine, sediment) of 1,230 ng/g dw. Proxy values for 2 of 1139 non-detected samples exceeded the PNEC (marine, sediment) due to the fact that ¹/₂ the RLs in the analytical method exceeded the PNEC (marine, sediment). The actual measured maximum value in marine sediment was 350 ng/g dw, which is almost four times less than the PNEC.

In Figure No. 5 when the questionable samples from the Lummi Nation monitoring program, which were measured with an analytical method that is not suitable or validated for NP/NPE, are removed from the data set, none of the detected or proxy non-detected sampling results for aggregated TNPEQ samples taken in fresh surface water between 1997 and 2018 exceeded the EPA WQC (freshwater, chronic) of 6.6 μ g/L NP.

In Figure No. 6 none of the aggregate detected or proxy non-detected TNPEQ results in marine surface water taken between 2006 and 2018 exceeded the US EPA WQC (chronic, marine) of $1.7 \mu g/L$. No sampling results were available before 2006.

In Figure No. 7 none of the detected or proxy non-detected aggregate TNPEQ results taken in freshwater sediment between 1997 and 2018 exceeded the toxicity-based PNEC (freshwater, sediment) of 6,150 ng/g dw.

In Figure No. 8 none of the detected aggregate TNPEQ results in marine sediment in samples taken between 1997 and 2018 exceeded the toxicity-based PNEC (marine, sediment) of 1,230 ng/g dw. Proxy values for 3 of 1139 non-detected samples exceeded the PNEC (marine, sediment), due to the fact that ¹/₂ the RL in an analytical method exceeded the PNEC (marine, sediment). The actual measured aggregate maximum values in marine sediment was 350 ng/g dw, which is almost four times less than the PNEC.

In Figure 9 none of the detected or proxy non-detected OP results in fresh surface water taken between 1997 and 2018 exceeded the EPA WQC (freshwater, chronic) of 6.6 μ g/L NP.

In Figure 10 none of the detected or proxy non-detected OP results in marine surface water taken between 2006 and 2018 exceeded the US EPA WQC (chronic, marine) of 1.7 μ g/L. No sampling results were available before 2006

In Figure 11 none of the detected or proxy non-detected OP results for freshwater sediment taken between 2006 and 2018 exceeded the exceeded the toxicity-based PNEC (freshwater, sediment) of 6,150 ng/g dw. No sampling results were available before 2006.

In Figure 12 non of the detected or proxy non-detected OP results for marine sediment taken between 2006 and 2018 exceeded the toxicity-based PNEC (marine, sediment) of 1,230 ng/g dw. No sampling results were available before 2006.

In summary, none of the detected NP, TNPEQ, or OP values from validated analytical methods reported for the 21-year period between 1997 and 2018 exceeded EPA WQC for NP in fresh surface water ($6.6 \mu g/L$ NP) or marine surface water ($1.7 \mu g/L$ NP). Also, none of the detected values exceeded toxicity based PNECs in freshwater or marine sediment. There were two cases where exceedances of these WQC and PNEC were reported in the dataset. The first was proxy data reported for **non-detected** samples due to the fact that the RL or MDL for the analytical method exceeded the relevant WQC or PNEC. The second source was questionable data reported under a Lummi Nation monitoring program using a method that is not relevant to or validated for NP, or NPEs, which is discussed under the Analytical Methods section above.

It should be noted that the paper by Meador et al, 2006, which was used as a source to for this environmental monitoring dataset, misreported the US EPA WQC (marine) as 1.7 ng/L, which is one thousand fold less than the actual US EPA WQC (marine) of $1.7 \mu g/L$.²⁰ Therefore, the authors erroneously concluded that the concentrations they reported (14 – 41 ng/L) in estuaries in the State of Washington exceeded the US EPA WQC.

Temporal Comparison of Monitoring Data

Data in Figures 1 through 12 were presented in two time frames (1997-2005 and 2006-2018) to allow comparison of monitoring results before and after a Wal-Mart initiative that began in 2006 to promote reductions in the use of NPEs in consumer laundry and cleaning products.²¹ As summarized above, the data indicate that measured concentrations of NP and TNPEQ are well below EPA WQC for fresh and marine surface water and toxicity-based PNECs for freshwater and marine sediment both before and after NPE reduction initiatives, which began in 2006. In addition, non-detects for NP and TNPEQ represent approximately 97% of the samples reported between 1997 and 2018.

Unfortunately, sampling locations were not selected by the monitoring programs for direct temporal comparison and there are an insufficient number of samples with actual measured detections both before and after the cutoff in 2005/2006 to provide a useful temporal comparison. However, the overall data do not suggest any uses or use patterns either before or

²⁰ Meador, J.P., Yeh, A., Young, G. and Gallagher, E.P.(2016). Contaminants of emerging concern in a large termperate estuary. *Environmental Pollution*, 213, 254-267.

²¹ Wal-Mart. Preferred Chemical Principles . October 2006.

after market reductions in the use of NPEs that represent a significant source, exposure or risk to the environment in the State of Washington.

December 17, 2019

ASSESSING THE EFFECTS AND POTENTIAL RISKS OF BRANCHED PARA-NONYLPHENOL TO SEDIMENT DWELLING ORGANISMS

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BACKGROUND

- Nonylphenol (NP) enters the environment primarily via wastewater treatment plant effluent discharges.
- Based on physical/chemical properties, NP is expected to partition from the water column to sediment (Table 1).
- NP has been detected in North American and European surface water and sediment (Table 2).
- NP has been shown to have low to moderate bioaccumulative properties in organisms inhabiting sediment (Table 1).
- Biodegradation of NP in sediment has been measured with half-lives of 14 to 100 days reported under oxic conditions. Slower degradation expected under anoxic conditions (Table 1).
- Since NP toxicity data in benthic species were limited, risk assessments for NP in sediments have been conducted in North America and Europe using Equilibrium Partitioning (EqP) methods.
- PNECsediment calculated using Equilibrium Partitioning methods, while useful in the absence ecotoxicity data in benthic organism, are subject to shortcomings.
- Rely on PNECwater to predict effects in sediment dwelling organisms
- · Require an estimated sediment-water partition coefficient and sediment organic carbon content that are applicable to all waters worldwide.

STUDY OBJECTIVES

- Identify valid toxicity studies with NP in benthic organisms that used dosed sediment from the literature.
- Calculate Freshwater and Marine Predicted No Effect **<u>C</u>**oncentrations (PNECs) for NP for sediment dwelling organism
- Conduct an assessment of risk to sediment dwelling organisms potentially exposed to NP.

Table 1. Physical properties, biodegradation and bioaccumulation potential of NP in sediments

CAS RN Aqueous Solubility Log Kow Vapor Pressure	25154-52-3, 84852-15-3 6 mg/L 3.0 to 4.48 0.07 Pa Data indicate: - Moderate hydrophobicity, - Some partitioning to solids - Iow volatility	Staples et al. (2008)
Biodegradation in freshwater and marine sediment	T ½ ranges from 14 to 99 days (oxic conditions) T ½ 287 days (anoxic conditions)	Ferguson & Brownawell (2003) Yuan et al. (2004) Ekelund et al. (1993)
Bioaccumulation in sediment dwelling organisms	BSAF 24 to 55 g C/g lipid (earthworms) Accumulation in bivalves: 1 to 54 ng/g-wet weight	Croce et al. (2005) David et al. (2009)

Table 2. Environmental Monitoring Data for NP in Freshwater Sediment (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						



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Table 3. Sho			onic toxicity data for n ing organisms	onylphenol		
Species	Duration	Endpoints	Results	Reference		
Clam (F) <i>Anadonta Cataractae</i>	144-h	Survival	LC50: 1,700 μg/L	McLeese et al. (1980)		
Amphipod (F) <i>Hyallela azteca</i>	96-h	Survival	LC50: 150 µg/L	England and Bussard (1994)		
Amphipod (F) <i>Hyallela azteca</i>	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	Survival	NOEC: 440,000 to 2,000,000 ng/g-dw	Maenpaa and Kukkonen (2006)		
	(OC 1.64 to 3.2%)	Head capsule length	NOEC: 440,000 to 2,000,000 ng/g-dw			
and the second s		Larval wet weight	NOEC: 77,000 to 2,000,000 ng/g-dw			
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) <i>Mya arenaria</i>	96-h	Survival	LC50: >700 µg/L	McLeese et al. (1980)		
Soft shell clam (F) <i>Mya arenaria</i>	360-h	Survival	LC50: 1,000 μg/L	McLeese et al. (1980)		
Mussel (M) <i>Mytilus edulis</i>	96-h	Survival	LC50: 3000 µg/L	Granmo et al. (1989)		
Mussel (M) Mytilus edulis		Fertilization success	Fertilization success: NOEC: 200 µg/L, no effects	Granmo et al. (1989)		
	35-d	Larval development	Larval development: NOEC: 200 µg/L, no effects			
Mussel (M) <i>Mytilus edulis</i>	15-d 35-d	Survival Survival	LC50: 500 μg/L LC50: 140 μg/L	Granmo et al. (1989)		
Coot Clam (F) <i>Mulinia lateralis</i>	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) <i>Eohaustorius estuarius</i>	96-h	Survival – Re-burrowing 48-h	LC50: 227 µg/L	Hecht and Boese (2002a)		
		Post-exposure	EC50: 138 µg/L	(2002a)		
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) <i>Rana catesbiana</i>	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 fres	hwater or marine	species, respectively	CC is organic carbon content c	of dosed sediment		

Table 4. Long-term chronic sediment toxicity data for nonylphenolusing aqueous exposure and dosed sediments.						
Species	Duration (Org. C)	Endpoints	Results NOEC (LOEC) or ECx	Reference		
Aqueous Expo	osure					
Midge (F) Chironomus tentansFull Life cycle, aqueous exposureSurvival (0-20 d) Survival (20+d)Survival (0-20 d): 42 (91) µg/L 						
Dosed Sedime	ent Exposur	e				
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) <i>Tubifex tubifex</i>	28-d (2.3%)	Emergence -	EC10: 203,000 to 259,000 ng/g-dw	Bettinetti et al. (2002b		
(F) or (M) design Org. C is sedime		ter or marine species, rbon content (%)	respectively;			





- and coastal marine sites. PNECsediment.
- Applies to Studies B, C, E, F, H, I, J, K, L, M, N, R, T, U. For studies A, D, G, O, P, Q, S some data points exceed their PNECsediment. - Freshwater (n=number of samples >PNEC):
 - <u>Study A</u>: The highest concentrations were observed for rivers in heavily urbanized or industrial locations (Detroit and Rouge rivers, MI (n=11), the Grand Calumet canal in Indiana (n=2
 - est.), and the Schuylkill river in Pennsylvania (n=1).

 - <u>Study D</u>: Sediments taken from the heavily polluted Glatt River basin in Switzerland in the early 1990s (n=1).
- <u>Study G</u>: All samples taken at WWTP outfalls (n=5 est.) - Marine (n= number of samples >PNEC):
 - Study O: Samples taken from a tidal area in the Chesapeake Bay, MD, USA as part of an analytical method development effort. Further details of the site are unknown. (n=1)
 - <u>Study P</u>: Heavily urbanized harbor area, NY, USA (n=2)
 - <u>Study Q</u>: Heavily polluted and urbanized Tees R, UK (n=1)
 - <u>Study S</u>: Coastal site near outfall, CA, USA (n=1)

Minimum, Mean, and Maximum Concentrations of **NP in Marine Sediment**

PNECsed (MARINE) J K L M N O P Q R S T U

RESULTS

From 9 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

Most freshwater (~93%) and marine (~96%) data are below their respective

PREDICTED NO EFFECT CONCENTRATIONS FOR SEDIMENT (PNEC)

Followed currently applicable EU guidance and is generally similar to US and Canada methods.

- Short-term studies (Table 3) focused on mortality or short-term growth.
- Long-term studies using dosed sediment (Table 4) with three benthic species having different feeding and living conditions - basis of PNECsediment.
- Freshwater
 - Lowest chronic NOEC obtained: 61,500 ng/g-dw
- Assessment factor (AF) of 10 justified as three chronic tests with species with different feeding and living conditions.

- PNECsediment (fresh) = 6,150 ng/g-dw.

- Marine
- Lowest NOEC obtained: 61,500 ng/g-dw.
- AF of 50 justified as only one marine species along with two freshwater sediment species are available.
- PNECsediment (marine) = 1,230 ng/g-dw.

Minimum, Mean, and Maximum Concentrations of **NP in Freshwater Sediment**



DISCUSSION AND CONCLUSIONS

- The occurrence of NP in freshwater and marine sediment has been studied in North American and European surface waters, estuaries, and coastal marine sites.
- Concentrations of NP in freshwater and marine sediment vary widely, spanning almost eight orders of magnitude, with mean concentrations ranging from approximately 1 to 3,500 ng/g-dw.
- PNECsediment for freshwater organisms (6,150 ng/g-dw) and for marine organisms (1,230 ng/g-dw) have been determined following current EU guidance.
- About 93% and 96% of all sediment measurements of NP are below these PNECsediment.
- Concentrations exceeding PNECsediment were collected at wastewater treatment plant outfalls or were taken from sites known to be polluted from extensive industrial and urban activities.

REFERENCES

A list of cited references will be provided with a copy of the poster on request. Please leave your card and email address.