
# Nonylphenol Ethoxylates:

## A Safer Alternative Exists to This Toxic Cleaning Agent

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## Executive Summary

The Sierra Club urges the Environmental Protection Agency (EPA), state agencies and corporations to eliminate the use of the cleaning agent, nonylphenol ethoxylates (NPEs), in the industrial and domestic laundry detergent used in the United States. NPE metabolites often pass through wastewater treatment plants at a concentration that has been shown to cause harmful effects to aquatic biota in laboratory studies. Unlike any other cleaning agent, NPEs metabolize into more toxic, less biodegradable metabolites that display estrogenic properties. [1-4]

NPE metabolites enter the aquatic environment through wastewater treatment effluent. These cleaning agents are used in homes and industries across America, where wastewater from washing clothes and cleaning goes down the drain and into a sewer. Most of the time, this water is then transported to a wastewater treatment plant, where it undergoes treatment before it is discharged into our waterways. Unfortunately, wastewater treatment plants are not equipped to treat all of the chemicals that flow into sewers – most plants are unable to fully degrade NPEs. Consequently, aquatic organisms are exposed to NPE metabolites daily, as some of these chemical compounds pass through wastewater treatment plants and enter our waterways.[1-4, 6]

NPEs take longer to degrade than any other cleaning agent. Their persistence in the aquatic ecosystem increases the amount of time organisms are exposed to these toxic chemicals. NPEs are the only high-volume cleaning agents that become *more* toxic as they degrade. [7]

Even at levels often found in America's waterways, NPEs may hinder the reproduction, growth, and survival of organisms such as the winter flounder, salmon and oysters. [1-4, 8-12, a] Extensive research indicates that NPE metabolites disrupt the endocrine system and interfere with the hormones of fish and shellfish. Exposure to NPE metabolites causes organisms to develop both male and female sex organs; increases mortality and damage to the liver and kidney; decreases testicular growth and sperm counts in male fish; and disrupts normal male to female sex-ratios, metabolism, development, growth, and reproduction.[1-4, 8-11, 13-18]

Nonylphenol (NP), the chemical used to make the cleaning agent NPEs, is used in many industries. In 2004 alone, more than 260 million pounds of NP was used in the U.S. Over 80% of NP is used in cleaning products, most notably laundry detergents. Metabolites of NPEs are present in over 61% of tested U.S. streams. [1-2, 19]

Canada and the European Union have banned the use of NPEs in detergents, as NP compounds are toxic and their use "may have an immediate or long-term harmful effect on the environment or its biological diversity." [1-3] Meanwhile, NPE sales have increased in the U.S.[19] Fortunately, some U.S. corporations have recognized the dangers of NPEs and voluntarily eliminated NPEs in their products. Procter & Gamble (P&G) voluntarily stopped using NP compounds in their high-volume applications. P&G recognizes that NPE use "might create long-term concerns

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[a] This paper does not address the toxicity of NPE compounds in humans, as human exposure to NP compounds has not been adequately studied. However, it should be noted that a recent study measuring NP levels in humans found that 95% of those tested contained a detectable level of NP in their urine.[13, 20]

for the environment."[5] Other U.S. companies continue to use NPEs in detergent. [1-4]

In the interest of protecting water quality and commercial and sportsfishing industries, industrial users and producers of detergents should switch to an alternative cleaning agent in detergent. The EPA, state environmental agencies and corporations should take rapid action to eliminate the use of NPEs in industrial and domestic detergent formulations. Safer alternatives to NPEs are readily available and technically feasible for industrial and domestic laundry detergents.

Alcohol ethoxylates (AEs) are the main replacement option. These alternatives are less toxic and degrade more quickly in the environment.

Furthermore, the EPA should strengthen its draft water quality criteria, which are too weak to protect aquatic organisms. It must fully address the toxicity and prevalence of NPEs, account for all NPE metabolites, and implement final water quality criteria for NPE metabolites. Until final water quality criteria are implemented, NPEs will continue to threaten the reproduction, growth and survival of aquatic organisms.

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## What Are Nonylphenol Ethoxylates?

NPEs are cleaning agents that belong to the larger group of compounds called alkylphenol ethoxylates (APEs). There are different types of APEs, such as NPEs and octylphenol ethoxylates (OPEs). To use an analogy, if APEs are fruit, then NPEs and OPEs are an apple and an orange – they are a type of fruit. Because OPEs and NPEs are in the same family, they have similar chemical properties. NPEs are used more than OPEs – both are toxic, estrogenic, and more difficult to degrade than other cleaning agents. [1-4]

Nonylphenol (NP) is used in the production of NPE cleaning agents, also known as surface active agents or surfactants. NPEs are known as surfactants because they decrease surface tension and clean by concentrating between non-mixable interfaces, such as oil and water. NPEs have been commercially synthesized for almost 50 years.[1-4]

## Uses of Nonylphenol Ethoxylates

NPEs are produced for high-volume use in many industrial sectors, including industrial laundering, textile processing, pulp and paper processing, paint and resin formulation, oil and gas recovery, steel manufacturing, pest control and power generation. NPEs are also utilized in the production and formulation of many commercially sold products: as an industrial and commercial detergent, as an emulsifier in wax for fruit and vegetables, as a polymer resin in plastic food packaging and polyethylene plastic, in cosmetic products (such as skin cream, deodorant, makeup, hair dye, and shampoo), and even in spermicides.[1-3]

The largest quantity of NPEs is used in cleaning products, especially detergents.[1-2] Of the 260 million pounds of NP used in 2004, 80% was used as a surfactant. In general, 37% of NPE metabolites enter the aquatic ecosystem.[1-2, 19] Based on this data, nearly 77 million pounds of NPE-based cleaning agents entered U.S. waterways in 2004.

## Toxicity of Nonylphenol Ethoxylate Metabolites

Many countries, large corporations and scientific entities have classified NPE metabolites as toxic. Canada classified NPE metabolites as toxic, as they are "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."[1-2] The European Union classifies NP as "very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment."[3] Procter & Gamble voluntarily stopped using NPEs in its high-volume applications as they also recognize that their use "might create long-term concerns for the environment."[5]

NPE metabolites are toxic in three ways. First, NPE metabolites can cause an organism to become stupefied and lose consciousness. Second, NPE metabolites can cover organisms with a soap-like coating that inhibits them from moving. Third, and perhaps most importantly, NPE metabolites disrupt normal hormonal functioning in the body and thus are considered endocrine-disrupting chemicals.[2]

The endocrine system is comprised of glands and hormones in the body. Different endocrine glands release small, specific amounts of hormones into the bloodstream. These hormones mediate many bodily functions, including reproduction, growth, development, maturation, immune system functioning and metabolism. Endocrine disrupting chemicals (EDCs) interrupt normal bodily functioning by blocking, interfering with, or

mimicking natural hormones in the body. [2, 10] Even infinitesimal amounts of certain synthetic chemicals can cause endocrine disruption.[10] It may be more difficult for organisms exposed to EDCs to reproduce and survive in the long term.[1-4, 13]

Extensive research indicates that NPE metabolites substantially interfere with the endocrine system and, in turn, reproduction, growth and survival. These NPE metabolites mimic the natural hormone estradiol and bind to the estrogen receptor in living organisms. Studies show that endocrine disruption causes organisms to develop both male and female sex organs; increases mortality and damage to the liver and kidney; decreases testicular growth, the formation of sperm, and testosterone levels in male fish; and disrupts normal male to female sex-ratios, metabolism, development, growth and reproduction.[1-4, 8-11, 13-18]

Additional studies also confirm that exposure to NPE metabolites changes the reproductive organs of aquatic organisms. One study found that during a three month exposure to NP, 50% of the Japanese medaka male fish developed both male and female sex organs when exposed to 50 parts per billion of NP, and 85% of the fish developed both sex organs when exposed to 100 parts per billion of NP. No fish within the control group developed the hermaphroditic (both sex organs) condition. Furthermore, there was an abnormal female-male sex ratio – more female fish were formed when compared to the control group.[4, 9]

Another study found sexual deformities in oyster larvae exposed to levels of NP that are often present in the aquatic environment. At levels of even 0.1 part per billion, the oyster embryos and larvae showed delays in development, abnormalities in the shell hinge and increased death rates. [11, 17]

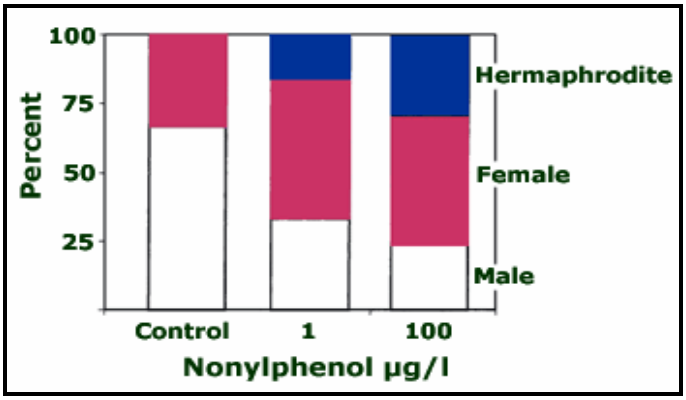


**Figure 1. Percentage of Oysters Developing into Males, Females and Hermaphrodites after Single Exposure to NP (in ppb)** [17]

Furthermore, exposure to NP also increased the number of oysters with both male and female sex organs (hermaphrodites) and female oysters when compared to the control. As Figure 1 above indicates, 17% of oyster larvae exposed to 1 part per billion of NP became hermaphroditic, and there was a disproportionate female-male sex ratio. When oyster larvae were exposed to 100 parts per billion of NP, 30 % of the adult oysters were hermaphroditic, and again, there was a disproportionate female-male sex ratio. This study indicates that NP can seriously harm oysters -- even a one-time exposure to NP at levels present in our waterways may be a threat to the survival of the oyster industry.[11, 17]

NP was first shown to cause endocrine disrupting effects in 1991 when researchers studying breast cancer cells bought a new brand of plastic tubes and subsequently witnessed abnormal cell proliferation. The researchers ultimately determined that the chemical causing cell proliferation was NP. They also found that NP increased mitotic activity in rat endometrium and induced progesterone receptors. [14] A 2005 study also found that exposure to NP increases the inci-

dence of breast cancer in lab mice. William Baldwin, co-author of the study, stated that "environmental estrogens are a cause or part of the cause for breast cancer." Researchers have already noted that 70% of women who develop breast cancer have no known risk factors, which indicates that environmental conditions play a predominant role in the development of breast cancer.[21-23]

## Biodegradation of Nonylphenol Ethoxylates

Treatment at wastewater treatment plants produces NPE metabolites that are more toxic, more estrogenic, and more persistent when compared to the original parent compounds. When compared to other surfactants, NPEs take substantially longer to biodegrade. The intermediary chemicals formed from initial degradation are much more persistent than the original compounds of NPE – ultimate biodegradation occurs slowly. Overall, wastewater treatment decreases the concentration of NPEs that enter the environment but increases the concentrations of the NPE metabolites. [2]

Environment Canada, Canada's environmental protection agency, estimates that "at least 63% of the total mass of all NP compounds entering wastewater treatment plants is released into the environment."[2] Additionally, the *highest* concentrations of certain NPE metabolites entering the environment come from wastewater treatment plants with *more* treatment. [1]

A number of factors can influence the biodegradation of NPEs. First, NPEs degrade more quickly when there are higher temperatures.[1-4] Second, ultimate degradation takes longer in seawater.[4, 24] Third, biodegradation occurs more quickly when water is moving.[25]

## Bioaccumulation of Nonylphenol Ethoxylate Metabolites

Most studies suggest that aquatic species bioconcentrate and bioaccumulate NPE metabolites to a low or moderate degree. Aquatic organisms take in NP compounds faster than they can eliminate them, so NP compounds can bioaccumulate in the body. [1-4]

## Where Nonylphenol Ethoxylate Metabolites Go

NPEs which are not degraded and do not stick to sewage sludge often enter our waterways. From there, aquatic organisms are primarily exposed to NPE metabolites either through the skin or by ingesting water, sediment, and other contaminated organisms.[1-4] Studies show that releases of NP compounds into rivers and streams can carry the compounds into estuaries (waters where fresh water and salt water mix). Aquatic organisms are even more likely to be exposed to NPE metabolites in estuaries because they are areas of high biological activity. [1-2]

NPE metabolites that stick to sewage sludge can enter the terrestrial environment by agricultural spreading. Large quantities of wastewater treatment plant sludge are spread on agricultural land as fertilizer for crops. Although NP metabolites entering the terrestrial environment will most likely stick to soil, there is potential for NPE metabolites to leach into groundwater. Terrestrial organisms can be exposed to NP compounds either through skin to soil contact or by ingesting plants, soil, and water. [1-2]

## Nonylphenol Ethoxylate Metabolites in U.S. Waters

In a landmark study, United States Geological Survey (USGS) tested 139 streams for organic wastewater contaminants, including three NPE metabolites and OPE metabolites. These metabolites were detected in 85 streams, or 61% of tested streams. In streams where NPE metabolites were found, concentrations ranged from 0.2 parts per billion to 40 parts per billion. [6, 26]

NP was one of the seven most frequently detected organic wastewater contaminants detected in the USGS study. Furthermore, NPE metabolites, identified as detergent metabolites in the USGS study, "were generally measured at higher concentrations than the other chemical groups." Detergent metabolites represented the largest percentage of the total measured concentration of contaminants in the USGS study. This study indicates that there is an ongoing presence of NP in ambient waters. [6, 26]

An EPA analysis of drinking water samples in the U.S. found an overall average concentration of alkylphenolic compounds of 1 part per billion. [28]

## What Is the Alternative to Using Nonylphenol Ethoxylates?

Reports suggest and industry figures confirm that alcohol ethoxylates (AEs) are a feasible, technically effective and environmentally friendlier alternative to NPEs. [7]

### *Environmental Profiles – AEs versus NPEs*

All cleaning agents are somewhat toxic to aquatic organisms and can cause skin and eye irritation in humans. However, there are certain key factors that make AEs more desirable than NPEs (Table I.). First, a safer cleaning agent readily degrades into intermediary metabolites and ultimately degrades in a short time period. AEs are readily and ultimately biodegradable, while NPEs will ultimately biodegrade but it takes more time.[2, 7] Second, it is desirable for the original cleaning agent to be less toxic – AEs are less toxic than NPEs.[1-3]

| | NPEs | AEs |
|---|---|---|
| **Degrades Easily?** | N | Y |
| **Eventually Degrades?** | Y | Y |
| **Toxicity** | More | Less |
| **Metabolites More Toxic?** | Y | N |
| **Endocrine Disruptor?** | Y | N |

**Table I. Environmental Profile: NPEs versus AEs**

Third, it is important that the metabolites of a cleaning agent are less toxic than the original parent compound. The metabolites of AEs are much less toxic than the original AE compound, while the metabolites of NPEs are much more toxic than the original NPE compound. As a result, AEs pose significantly less danger to aquatic organisms. Fourth, it is important that an alternative cleaning agent does not cause endocrine disruption in aquatic organisms. Unlike the APE family (NPEs and OPEs), AEs do not pose an endocrine disruption threat.[7]

### *Substitution feasibility*

When compared to NPEs, AEs foam little, are less sensitive to hard water, remove oil residue and clean synthetic fibers very effectively, work better than NPEs in cold water, and can be used in powdered and liquid detergent. Since AEs work as well as NPEs and in some cases are superior to NPEs, AE usage in laundry detergent is quickly increasing. [7]

### *Cost and Availability of AEs*

In 1994, AEs were produced more than any other nonionic surfactant, by volume, with NPE production second worldwide. It is important to note that the price of both AEs and NPEs fluctuates with the price of the raw materials. Based on data from 1999-2000, alternative surfactants are 20-40% more expensive than APEs. However, two new production plants have increased the supply of AEs, so the prices of AEs and NPEs should become more comparable.[7]

## Governmental Actions Related to Nonylphenol Ethoxylates

The European Union and Canada have effectively banned the use of NPEs. In 1987, the U.S. EPA placed NP on its Inerts List 1 for pesticides due to "toxicological concern because human health and/or ecological considerations."[1]

NP compounds are not currently regulated under the federal Clean Water Act, but in 2004 the EPA proposed draft water quality criteria for NP "designed to protect aquatic organisms." [4]

The EPA's draft criteria are divided into freshwater and saltwater criteria, as NP is more toxic to organisms in saltwater. For freshwater, the draft criterion for short-term exposure to NP is 27.9 parts per billion, and the criterion for long-term exposure is 5.9 parts per billion. For saltwater, the draft criterion for short-term exposure is 6.7 parts per billion, and the criterion for long-term exposure is 1.5 parts per billion.[4] Canada has set regulations for NPEs that are much more protective of aquatic organisms. First of all, Canada is regulating all NPE metabolites, while the U.S. draft criteria proposes to only regulate NP. Secondly, Canada's freshwater regulation is 1 part per billion, while their saltwater regulation is 0.7 parts per billion.[1-2]

The EPA has not yet produced final water quality criteria for NP or any other metabolites of NPEs, but the draft criteria are not stringent enough. The EPA states that the draft criteria are "designed to protect aquatic organisms and their uses." However, the critical studies chosen to reach the draft water quality standard do not take into account more sensitive aquatic organisms, endocrine disrupting effects, or the cumulative effects of NPE metabolites.[1-4]

The EPA's draft water quality criteria are inadequate, as the EPA proposes criteria only for one of the NPE metabolites, NP. Under the draft water quality criteria, as long as NP is below the water quality standard, aquatic organisms are considered "protected" – even though organisms are also exposed to other NPE metabolites, which are also toxic and estrogenic. When NPE metabolites are considered together, organisms that are considered to be protected, according to the draft criteria, may actually be harmed. It does not make logical sense to establish water quality criteria for NP only and set the criteria at a level that may harm certain organisms. The water quality criteria are supposed to protect aquatic organisms. [1-4]

The final water quality criteria must include all NPE metabolites in order to fully protect aquatic organisms. The EPA needs to implement final water quality criteria before NPEs can be regulated.

## Procter & Gamble's Elimination of Nonylphenol Ethoxylates

Procter & Gamble (P&G) is an industrial giant based in the U.S. that produces items ranging from laundry detergent to mascara. P&G recognizes that NPE metabolites are more toxic and degrade more slowly than other cleaning agents. P&G states that NP compounds "might create long-term concerns for the environment," and furthermore, that alternatives are both available and feasible. P&G acknowledges that "for most products, there are available substitutes, and indirect uses can be avoided." P&G also noted that the European Union has revised its risk assessment for NP compounds, and prohibited the use of NP compounds in consumer products. P&G then stated that "based on these scientific assessments and actions, P&G has eliminated the intentional use of NP and NPEs in our products," including laundry detergent and other cleaning products. [5]

## Conclusion

Eliminating NPEs in laundry detergent will significantly reduce the threat that NPE metabolites pose to our environment. [27] Phasing out the use of the cleaning agents, NPEs (and OPEs), has both economic and environmental benefits. The toxicity and estrogenicity of NPE metabolites is well-documented. Laboratory studies show that exposure to NPE metabolites harms aquatic organisms. [1-3, 7] The use of NPEs is a threat to the fishing economy along the U.S. coastline, the Great Lakes and other waterways.

The EPA, state environmental agencies and corporations should take rapid action to eliminate the use of NPEs in industrial and domestic detergent formulations. Safer alternatives to NPEs are readily available and technically feasible for industrial users and consumers of NPEs. Alcohol ethoxylates (AEs) are less toxic, readily biodegradable, and they do not display estrogenic properties.[7] AEs are a much better alternative to utilizing NPEs or OPEs, as both are more persistent, more toxic, and more estrogenic.[1]

The Sierra Club strongly urges state and federal environmental agencies, as well as corporations, to embrace a feasible pollution prevention strategy by eliminating NPEs and substituting AEs in detergent formulations.

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