Alkylphenols and Alkylphenol Ethoxylates

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MODERATE CONCERN

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Quick Summary

Alkylphenols, including nonylphenol and octylphenol, are key breakdown products of alkylphenol ethoxylate (APE) surfactants, once common in household detergents and other cleaning products and also used in a number of industrial applications. Alkylphenols and APEs have been detected in water, sediment, mussel, small fish, and cormorant egg samples from the Bay, sometimes at relatively high concentrations. Alkylphenols and some APEs are known endocrine disruptors. While concentrations measured in the Bay have mostly been below those known to cause chronic toxicity in marine organisms, there is new evidence that the existing levels of alkylphenols and APEs, in combination with pyrethroid pesticides, may be affecting Bay fish populations through endocrine disruption. A recent RMP report on APEs (Klosterhaus et al. 2012) presents additional information on use and production, fate in wastewater treatment plants and the environment, potential impacts, and information gaps.

What Are They?

- Alkylphenols are a family of synthetic organic compounds consisting of chains of carbon atoms, typically branched and consisting of eight or nine carbon atoms, attached to a six-carbon phenol ring.
- Alkylphenols are used to make APE surfactants, detergent-like compounds that have been widely used since the 1940s.
- Eighty to eighty-five percent of the APEs in use in the US are nonylphenol ethoxylates (USEPA 2010); octylphenol ethoxylates are the next most common APE (Chiu et al. 2010).
- Once released into the environment, APEs often break down into alkylphenols like nonylphenols and octylphenols
- The US Environmental Protection Agency (USEPA) has identified nonylphenol ethoxylates as priorities for voluntary phase-out.

What Are They Used For?

- APEs are commonly used as surfactants in detergents and cleaning products for industrial and institutional settings. They are now less common in products for the home.
- APEs have been added to pesticide formulations as "inert ingredients" to enhance performance.
- They are also used in paper production, leather and textile processing, metalworking, as oilfield chemicals and for dispersal of petroleum spills, and as ingredients in paints, adhesives, personal care products, and spermicidal lubricants.

How Are They Getting Into the Bay?

- Municipal wastewater treatment plant effluent is likely the major pathway to aquatic environments, although more information is needed on other potential pathways.
  - Long-chain APEs biodegrade during wastewater treatment to form nonylphenol and other compounds like short-chain APEs and oxidized APEs. Most studies have focused on nonylphenol and nonylphenol ethoxylates like nonylphenol monoethoxylates or diethoxylates.
  - Removal efficiencies in wastewater treatment through sorption to sludge are high, but APEs and their breakdown products are nevertheless commonly detected in wastewater effluent as a result of the high volume of use.
- Urban stormwater, septic system seepage, atmospheric deposition, and direct discharge, including application of pesticides to aquatic vegetation, are other important pathways.

TIER 3

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What Happens to Them in the Bay?

General Properties

- Alkylphenols and APEs entering the water column have a strong tendency to bind to sediment particles.
- APEs can be broken down by microbes or sunlight into alkylphenols and other compounds in the Bay, depending on environmental conditions. The environmental fate of these breakdown products is not well understood.
- Nonylphenol itself does not break down easily and is considered a persistent pollutant in aquatic environments.
- Alkylphenols and APEs are somewhat volatile, so a portion of these chemicals may be removed from the Bay by transfer into the air.
- Alkylphenols and APEs are known to accumulate in wildlife, especially invertebrates and fish. Most studies have focused on nonylphenol and octylphenol, as they are readily accumulated and stored in fat tissues and there is concern for toxicity, particularly endocrine disruption.

Patterns of Occurrence in the Bay and in Other Aquatic Ecosystems

- There are RMP occurrence data for nonylphenol, octylphenol, and nonylphenol ethoxylates in the Bay (Klosterhaus et al. 2013a).
  - Only nonylphenol has been detected in Bay water samples, with concentrations less than 100 nanograms per liter (ng/L), compared to a USEPA saltwater chronic water criterion of 1,700 ng/L.
  - Nonylphenol, nonylphenol monoethoxylates, and nonylphenol diethoxylates were consistently detected at moderately high concentrations in RMP sediment samples, with a median of 35 ppb for nonylphenol.
  - Detection was sporadic in RMP mussel samples, but concentrations were sometimes high, with maximum measurements of nonylphenol, nonylphenol monoethoxylates, and nonylphenol diethoxylates of 1,290, 300, and 1,420 ppb, respectively.
  - High concentrations of nonylphenol (maximum 123 ppb) and nonylphenol ethoxylates (maximum 228 ppb) have also been found in Bay cormorant eggs.
  - Octylphenol was not detected in water, sediment, or mussel samples.
- The NOAA Mussel Watch California CEC Pilot Study (Mussel Watch) 2010 found lower concentrations in some cases than had been measured in RMP samples, but still higher concentrations than many other contaminants found in Bay mussels.
  - Concentrations of some compounds in Mussel Watch samples, for example 4-nonylphenol monoethoxylate, were high, at levels comparable to sites in Southern California (FIGURE 1). The maximum level of 4-nonylphenol monoethoxylate measured in the Bay was 300 ppb.
  - Bay mussel concentrations for other compounds, for example nonylphenol, were low in comparison to samples from Southern California (FIGURE 2).
- Overall, levels found in Bay samples were typically lower than those found in effluent-dominated systems, and similar to or lower than other marine and estuarine areas of the US.
- Diehl et al. (2012) found that concentrations of nonylphenol in mussels and small fish (gobies) from San Francisco Bay were lower than in Morro Bay and Tomales Bay, two undeveloped coastal areas. The maximum concentration of nonylphenol in Bay small fish was 420 ppb. Seepage from septic systems appeared to be one major pathway for nonylphenol to enter Morro Bay, with toilet paper a likely source (Diehl et al. 2012).

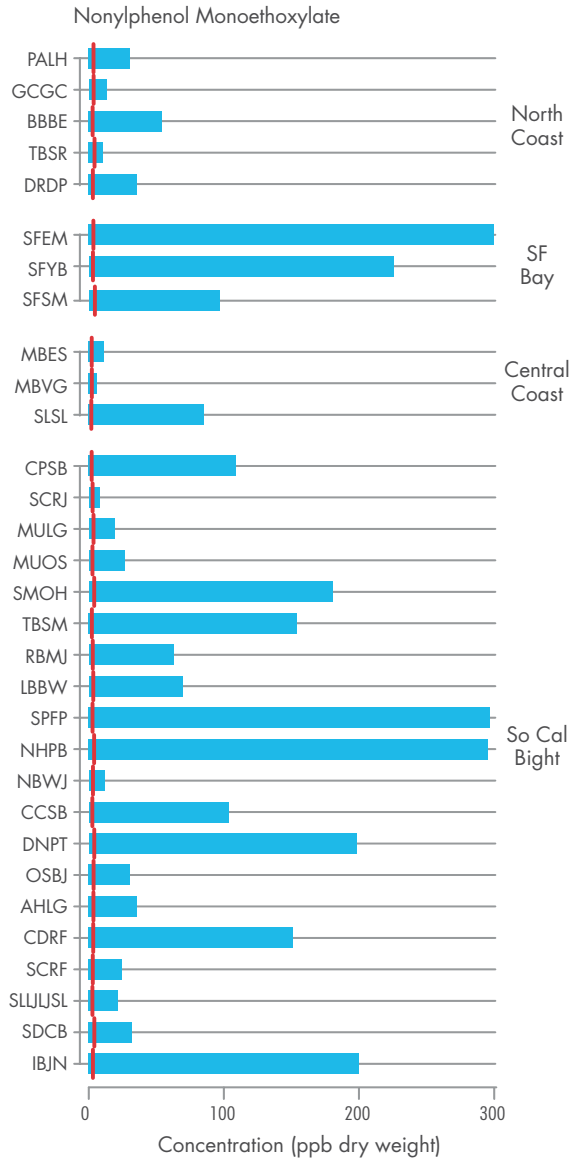

FIGURE 1
Of the three alkylphenol compounds that are detected frequently in the environment, 4-nonylphenol monoethoxylate is relatively abundant in San Francisco Bay as well as at stations in Southern California. It was detected in all 32 of the NOAA Mussel Watch stations sampled. Red lines indicate limit of detection.

Footnote: SFEM-San Francisco Bay, Emeryville; SFYB-San Francisco Bay, Yerba Buena; SFSM-San Francisco Bay, San Mateo Bridge

Alkylphenols and Alkylphenol Ethoxylates

TIER 3

Endocrine disruption caused by mixtures of pyrethroid insecticides, alkylphenols, and akylphenol ethoxylates could be contributing to the pelagic organism decline (POD)

Trends in the Bay and Nationally

- No trend data are available.

Is There a Risk of Harm in the Bay?

- Alkylphenols and some APEs are known endocrine disruptors.
- Concentrations of nonylphenol and nonylphenol ethoxylates in the Bay are generally well below concentrations shown to be toxic to aquatic organisms, such as the USEPA saltwater chronic water criterion of 1,700 ng/L.
- An exception is a study suggesting the potential for impacts on barnacle settlement due to exposure to nonylphenol concentrations of 60 ng/L in water (Billinghurst et al. 1998).
- Sites near wastewater or stormwater outfalls may have higher concentrations of these contaminants and be at greater risk.
- Schlenk et al. (2012) found estrogenic activity in laboratory fish exposed to mixtures of pyrethroid pesticides, alkylphenols, and APEs. Pesticides alone did not cause estrogenic activity. Their results suggested that endocrine disruption, caused by these mixtures, could be partially responsible for the observed declines of pelagic fish populations in the San Francisco Bay-Delta.

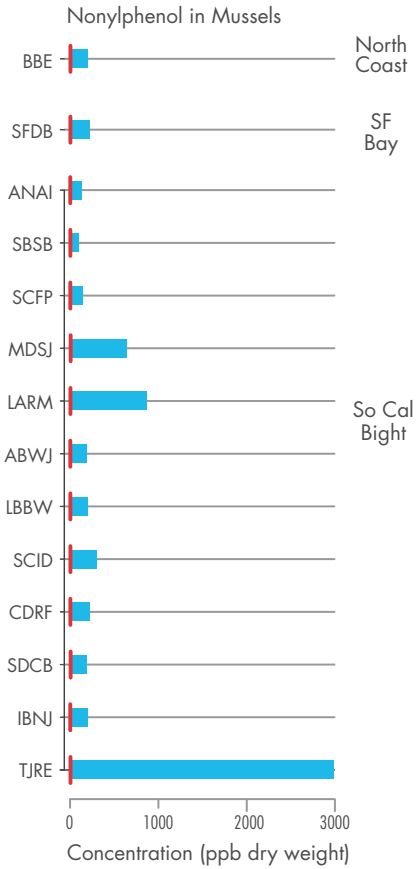

FIGURE 2
4-Nonylphenol was found at the highest concentration, 3,000 ppb, in a NOAA Mussel Watch sample from the Tijuana River in Southern California. The concentration in the Bay sample from near the Dumbarton Bridge (SFDB) was not high relative to other stations. Red lines indicate limit of detection.

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Key Information Gaps

- Although APEs and alkylphenols are widely used and ubiquitous in the environment, even in remote areas, there is a need for basic information.
  - More complete characterization of concentrations of alkylphenols and APEs throughout the Bay and particularly near outfalls, including monitoring for a full range of long-chain APEs and a greater variety of important degradation products.
  - Information on potential long-term effects on Bay wildlife.
  - Information on combined effects of multiple endocrine disruptors in mixture exposures.
  - Information on combined biological effects of APEs and alkylphenols with pesticides like pyrethroids.
  - Better sampling and analytical methods for alkylphenols and APEs.

Management Timeline