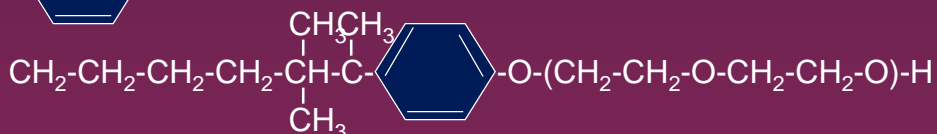
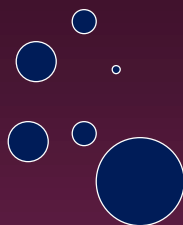


# Troubling Bubbles: Alkylphenol Ethoxylate Surfactants



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## Some Important Acronyms

- APE Alkylphenol ethoxylate
- AP Alkylphenol
- NPE Nonylphenol ethoxylate
- NP Nonylphenol
- OPE Octylphenol ethoxylate
- OP Octylphenol
- OBE Order of the British Empire
- IPO Initial public offering

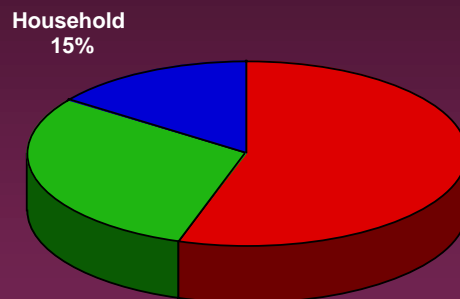


## Planet of the APES

- 450,000,000 pounds produced annually in US
- More than 1/2 goes “down the drain”
- Laboratory biodegradation is poor
- Removal efficiency in wastewater treatment is good (typically >90%)
- Removal is not biodegradation
- There are an estimated 170 metric tons of NPE in the sediment of the Strait of Georgia (Shang et al 1999)

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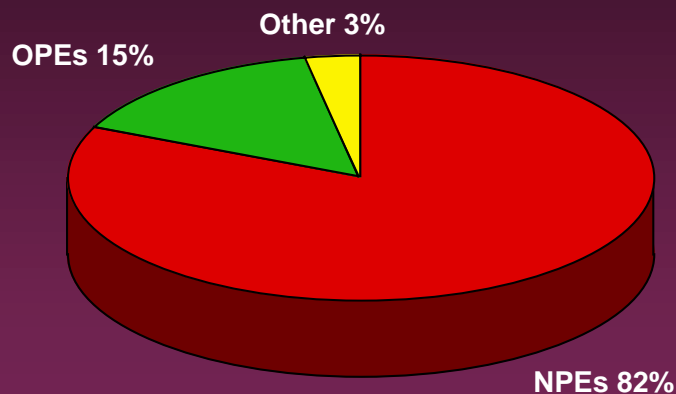
## Uses of APES by Sector



Naylor 1992

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## Types of APEs Used



Naylor 1992

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## Some Uses of APEs

- paints
- pesticides and adjuvants
- household cleaners (laundry, citrus cleaners, disinfecting cleaners, spot removers)
- I&I cleaners (vehicle, multi-purpose, laundry, floor, toilet, deodorizers)
- shampoos, conditioners, and hair colors
- contraceptives

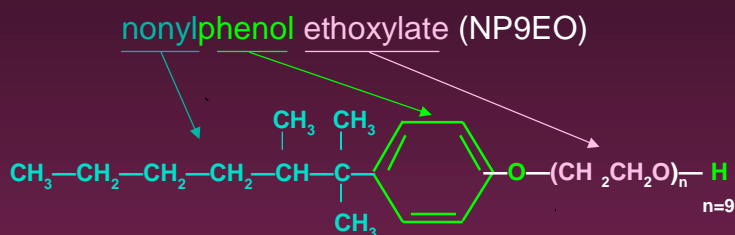
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## The Tells Seashells

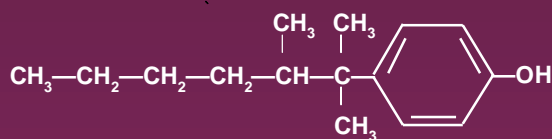
- nonoxynol
- nonylphenol ethoxylate
- nonylphenol polyethylene oxide
- nonylphenol polyethylene glycol ether
- nonylphenoxy poly(ethyleneoxy)ethanol
- alpha-(p-nonylphenyl)-ω-hydroxypoly(oxyethylene)

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## Structure of NP9EO and NP

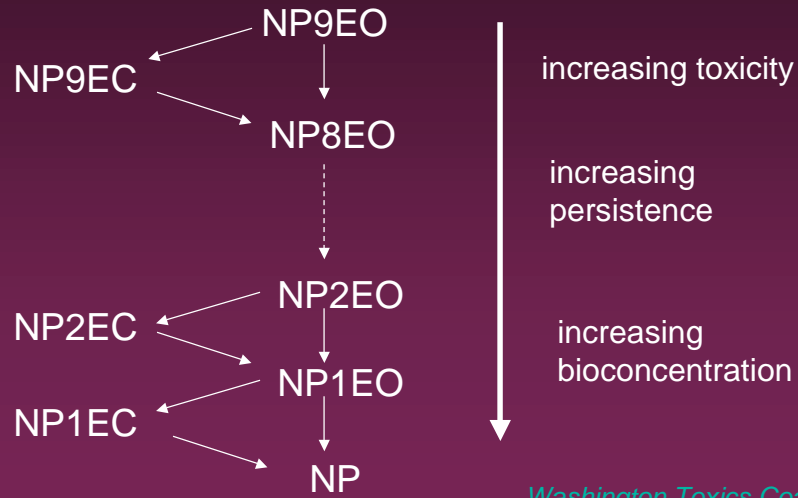


p-nonylphenol (NP or 4-NP)



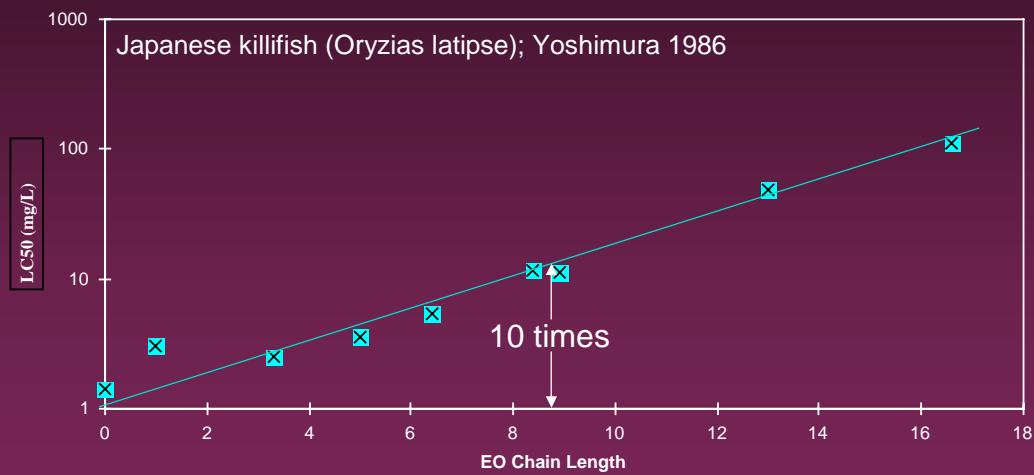
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## Breakdown Metabolites of a Typical NPE



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## Aquatic Toxicity vs Ethoxylate Chain Length



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## Effects of Alkylphenolics: Fish

- Increased vitellogenin in male rainbow trout *in vitro* and *in vivo* (Jobling and Sumpter 1993)
- Decrease in size of testes (Jobling et al. 1996)
- Clear dose-response relationship
- Apparent thresholds (rainbow trout): 10 µg/L (NP); 3 µg/L (OP)
- OP caused reduced % fertilized eggs, reduced embryo survival, abnormal embryos (Japanese Medaka) (Gronen et al. 1999)

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## Effects of Alkylphenolics: Frogs & Turtles

- OP at “environmentally relevant doses” altered expression of certain proteins in the snapping turtle (Trudeau et al. 2002)
- Exposure of Leopard frog tadpoles to OP plus UV light disrupted normal premetamorphic development. Neither agent alone caused the effects. (Crump et al., 2002)

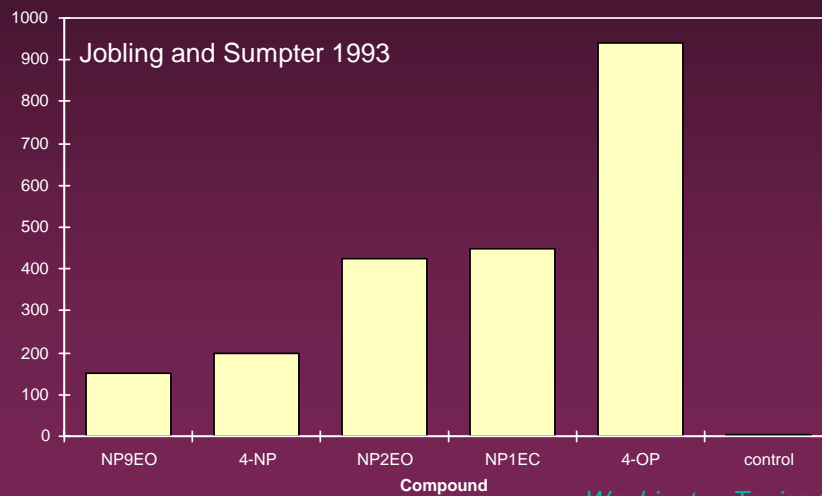
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## Concentrations of NP Producing Effects in Aquatic Organisms

Species	Effect	Lowest conc.
Mysid shrimp	length @ 21 d	6.7 µg/L
	survival @ 29d	9.1 µg/L
	number young	9.1 µg/L
Rainbow trout	vitellogenesis	~10 µg/L
Rainbow trout	weight of juvenile females	1 µg/L
Fathead minnow	vitellogenesis	0.1 µg/L

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## Vitellogenin Production Induced by Various APEs



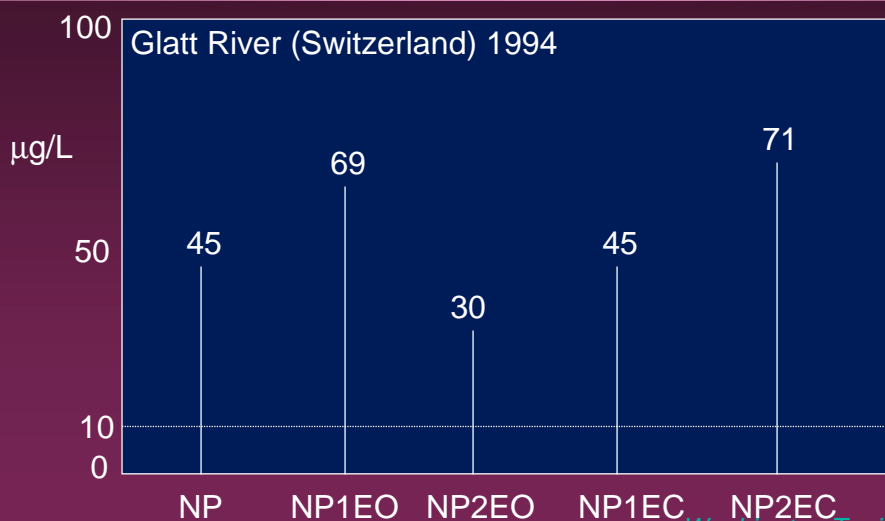
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## Effects of Alkylphenolics: Mammals

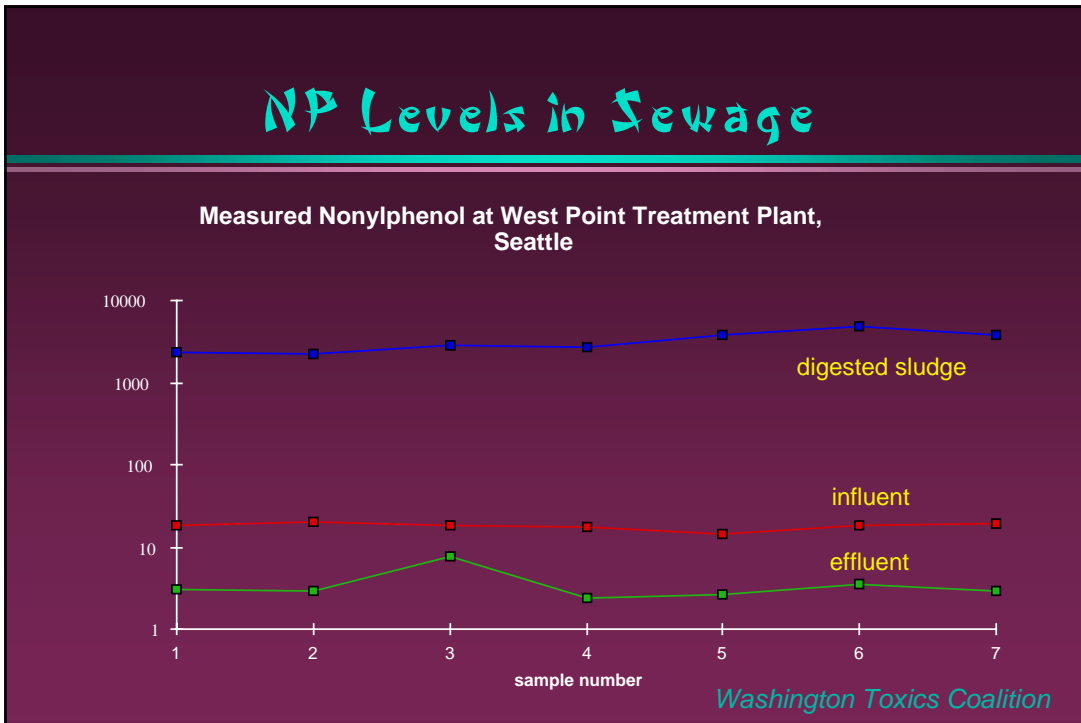
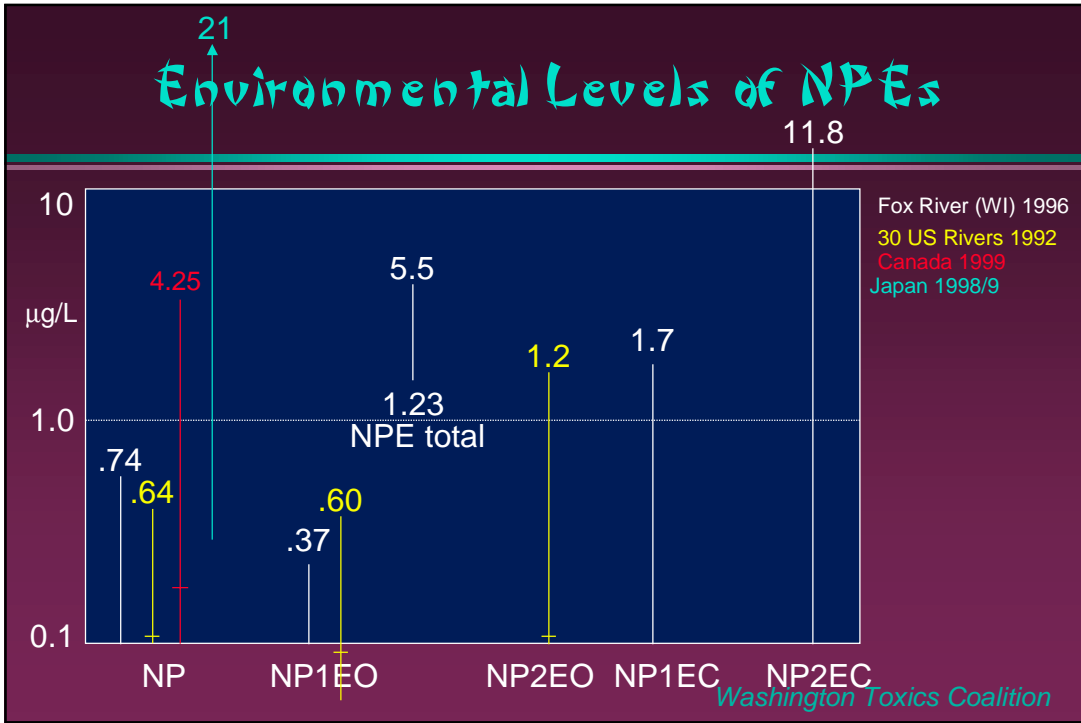
- NP and OP induced growth of human estrogen-sensitive breast cancer cells. (Soto et al. 1991)
- OP was ten times more potent than NP
- OP and OPE produced decreases in testicular size and sperm production in rats when admin. during gestation or first 21 days of postnatal life (Sharp et al. 1996)
- OP stimulated estrogen-dependent uterine growth in prepubertal rats (Bicknell et al. 1995)

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## Environmental Levels of NPEs



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## Some Endocrine Disruptors in Aquatic Environments

- nonylphenol
- nonylphenol ethoxylates
- octylphenol
- octylphenol ethoxylates
- 17β estradiol
- estrone
- DDT, DDE, DDD
- dioxins and furans
- PCBs
- phthalates
- pesticides
- mercury
- arsenic
- PAHs?

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## The Incredible Shrinking Margin of Safety

APE	Range	Assume	Potency	Effect
NP	.08-.74	.24	1	.24
NP1EO	.04-.37	.12	(0.67)	.08
NP2EO	no data	(.12)	0.67	.08
NP1EC	ND-1.7	.57	0.68	.40
NP2EC	ND-11.8	4	(0.68)	2.7
Subtotal				3.5
OP	no data	(.05)	4.1	(.20)
Subtotal				(.20)

Range from  
Fox River

Potency  
from Jobling  
& Sumpter  
1993

Effective NP Concentration ~ 3.7 µg/L  
(15-fold increase)

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## Alternatives to APEs

Name	Aq. Concern	Ult. Biodeg.	Metabolites	Env. Profile
NP9.5EO	.001 ppm	months/longer	more toxic	reference
LAE (9EO)	.02 ppm	weeks/months	less toxic	more pos
Coco fatty acids, ethoxy	.04 ppm	weeks	less toxic	more pos
Dodecanamide, N-(2-hydroxyethyl)	.04 ppm	weeks	less toxic	more pos
D-Glucopyranose, decyl octyl glycosides	.47 ppm	days/weeks	less toxic	more pos
t-Dodecanol, ethoxy	.04 ppm	weeks/months	less toxic	more pos

Source: US EPA Design for the Environment  
Formulator Initiative

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## Conclusions

- **Breakdown products** of NPE and OPE are endocrine disruptors
- Effects on some aquatic species are expected at current levels in some rivers
- VTG in male fish causes reproductive effects
- Human exposure is largely to APEs rather than APs
- Safety should not be assessed by looking at single compounds
- Effective products are being made without APEs
- APEs do not belong in “green” products

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