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 of 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 **P**redicted **N**o **E**ffect **C**oncentrations (PNECs) for NP for sediment dwelling organism.
- Conduct an assessment of risk to sediment dwelling organisms potentially exposed to NP.

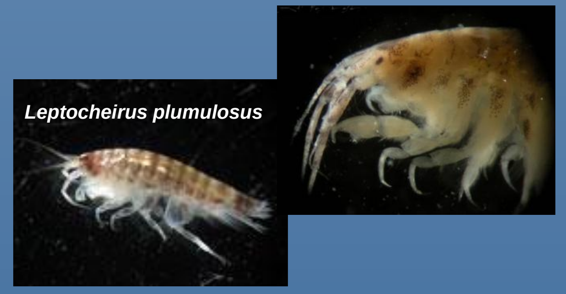
Table 1. Physical properties, biodegradation and bioaccumulation potential of NP in sediments

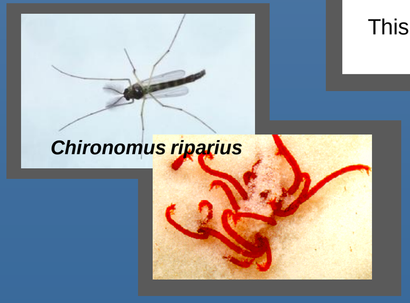
CAS RN Aqueous Solubility Log Kow Vapor Pressure	25154-52-3, 84852-15-3 6 mg/L 3.0 to 4.48 0.07 Pa Data indicate: - Moderate hydrophobicity, - Some partitioning to solids - low volatility	Staples et al. (2008)
Biodegradation in freshwater and marine sediment	T ½ ranges from 14 to 99 days (oxic conditions) 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





ACKNOWLEDGMENTS

This work was sponsored by the Alkylphenols and Ethoxylates Research Council, Washington, D.C., USA.

Table 3. Short-term acute and sub-chronic toxicity data for nonylphenol and sediment dwelling organisms

Species	Duration	Endpoints	Results	Reference
Clam (F) *Anadonta Cataractae*	144-h	Survival	LC50: 1,700 µg/L	McLeese et al. (1980)
Amphipod (F) *Hyallela azteca*	96-h	Survival	LC50: 150 µg/L	England and Bussard (1994)
Amphipod (F) *Hyallela azteca*	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 (OC 1.64 to 3.2%)	Survival Head capsule length Larval wet weight	NOEC: 440,000 to 2,000,000 ng/g-dw NOEC: 440,000 to 2,000,000 ng/g-dw NOEC: 77,000 to 2,000,000 ng/g-dw	Maenpaa and Kukkonen (2006)
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) *Mya arenaria*	96-h	Survival	LC50: >700 µg/L	McLeese et al. (1980)
Soft shell clam (F) *Mya arenaria*	360-h	Survival	LC50: 1,000 µg/L	McLeese et al. (1980)
Mussel (M) *Mytilus edulis*	96-h	Survival	LC50: 3000 µg/L	Granmo et al. (1989)
Mussel (M) *Mytilus edulis* 	35-d	Fertilization success Larval development	Fertilization success: NOEC: 200 µg/L, no effects Larval development: NOEC: 200 µg/L, no effects	Granmo et al. (1989)
Mussel (M) *Mytilus edulis*	15-d 35-d	Survival Survival	LC50: 500 µg/L LC50: 140 µg/L	Granmo et al. (1989)
Coot Clam (F) *Mulinia lateralis*	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) *Eohaustorius estuarius*	96-h	Survival – Re-burrowing 48-h Post-exposure	LC50: 227 µg/L EC50: 138 µg/L	Hecht and Boese (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) *Rana catesbiana*	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)

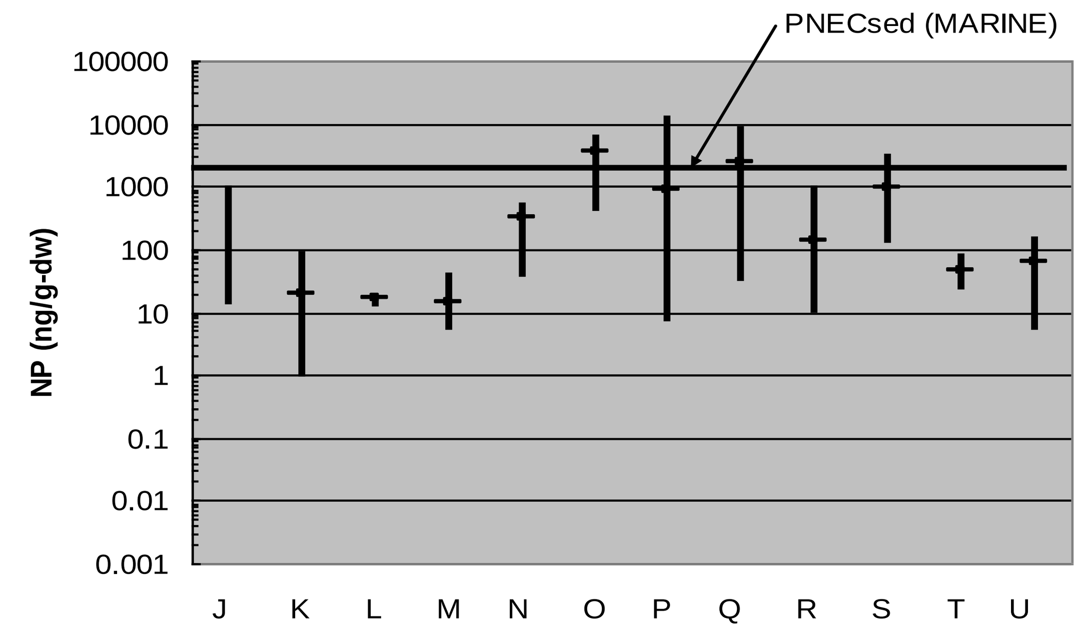
(F) or (M) designates freshwater or marine species, respectively; OC is organic carbon content of dosed sediment

Table 4. Long-term chronic sediment toxicity data for nonylphenol using aqueous exposure and dosed sediments.

Species	Duration (Org. C)	Endpoints	Results NOEC (LOEC) or ECx	Reference
Aqueous Exposure				
Midge (F) Chironomus tentans	Full Life cycle, aqueous exposure	Survival (0-20 d) Survival (20+d) Growth – Sex Ratio – Fecundity – Viability – Emergence –	Survival (0-20 d): 42 (91) µg/L Survival (20+ d): 91µg/L, no effects Growth: (91µg/L, no effects Sex Ratio: 91 µg/L, no effects Fecundity: 91 µg/L, no effects Viability: 91 µg/L, no effects Emergence: 91 µg/L, no effects	Kahl et al. (1997)
Dosed Sediment Exposure				
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) *Tubifex tubifex*	28-d (2.3%)	Emergence -	EC10: 203,000 to 259,000 ng/g-dw	Bettinetti et al. (2002b

(F) or (M) designates freshwater or marine species, respectively;
Org. C is sediment organic carbon content (%)

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



RESULTS

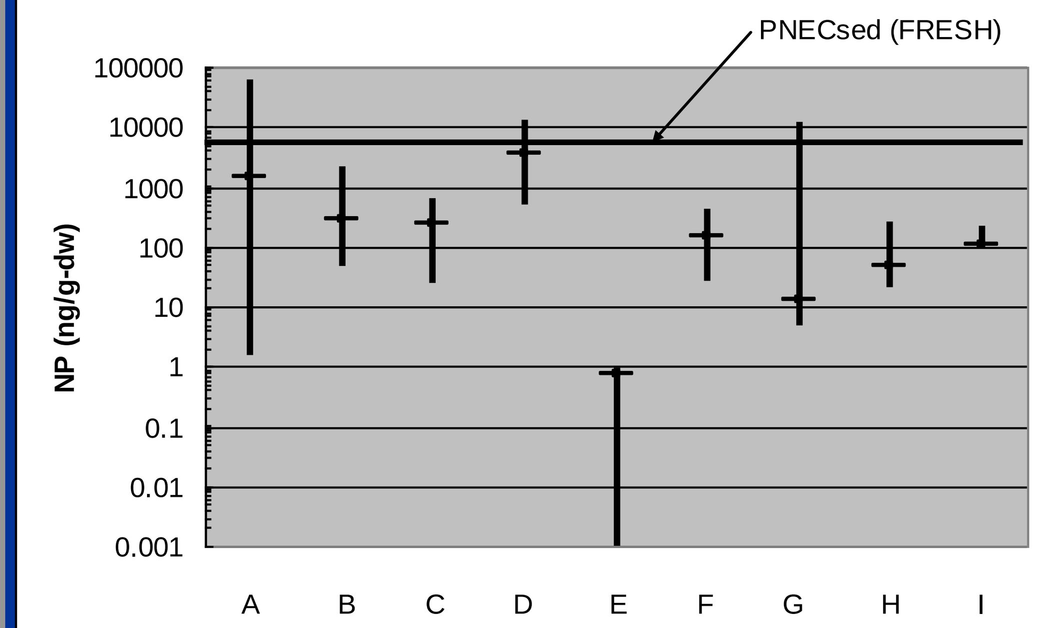
- From 9 studies, 327 sediment samples were collected from fresh surface water systems in North America and Europe.
- From 12 studies, 132 sediment samples were collected from estuarine and coastal marine sites.
- Most freshwater (~93%) and marine (~96%) data are below their respective PNECsediment.
  - 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):
    - Study A: 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).
    - Study D: Sediments taken from the heavily polluted Glatt River basin in Switzerland in the early 1990s (n=1).
    - Study G: 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)
    - Study P: Heavily urbanized harbor area, NY, USA (n=2)
    - Study Q: Heavily polluted and urbanized Tees R, UK (n=1)
    - Study S: Coastal site near outfall, CA, USA (n=1)

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

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