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Environmental Fate and Safety of Nonylphenol Ethoxylates

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Alkylphenol ethoxylates are nonionic surfactants widely used in many institutional and household cleaning products and industrial processes. They have been popular for their effectiveness, economy and ease of handling and formulating for more than 40 years. They function as emulsifiers, detergents, wetting agents and dispersants.

One of the largest application areas for alkylphenol ethoxylates (APEs) is textile wet processing. Nonylphenol ethoxylates (NPEs) are by far the most important APEs, accounting for about 80% of the total APE volume. Formulated products for fiber sizing, spinning, weaving, fabric dyeing, scouring and washing commonly contain NPEs. Water-based paints, inks and adhesives are also likely to contain NPEs.

ABSTRACT

Nonylphenol ethoxylates (NPEs), surfactants commonly used in textile manufacture as well as in industrial and household cleaning products, are perceived by some users as potentially hazardous to the environment. Producers have a great deal of information on the environmental fate and effects of NPEs to share with the textile industry.

NPEs, which have been tested thoroughly for effects toward mammals and aquatic life, exhibit toxicity patterns very similar to other widely used surfactants. They are highly treatable in aerobic biological treatment plants—studies in U.S. wastewater plants have shown up to 99.8% removal. Nationwide river monitoring has provided a statistically valid model of the distribution of nonylphenol (NP) and NPEs in U.S. surface waters. The treatability studies demonstrate their high degree of biodegradability under real-world conditions. The large body of data on NP and NPEs toxicity, combined with the environmental exposure data, allows very confident predictions of the risk they pose to the aquatic environment.

KEY TERMS

Nonylphenol Ethoxylates
River Studies
Surfactants
Wastewater

NPEs are manufactured by a base-catalyzed reaction of ethylene oxide with nonylphenol (NP). NP is produced from phenol and "nonene" using acid catalysis and consists almost entirely of the *para* positional isomer. Nonene is a branched C_9 olefin made by trimerizing propylene and consists of many isomers.[1,2] The generic NPE structure is depicted in Fig. 1. The average number of moles of ethylene oxide per mole of NP (n) ranges from 1 to 100. Relative amounts of the individual ethylene oxide (EO) oligomers follow a Poisson distribution with the peak at n.

NPEs have been controversial for many years because of the branching of the nonyl group and presence of the aromatic phenoxy ring. Numerous laboratory biodegradation studies indicated low NPEs biodegradability, while others showed high degradability.[3] Degradation intermediates identified included the lowest NPE oligomers NPE_1 and NPE_2 as well as NP. NP and low NPE concentrations were found in wastewater treatment plant sludges and downstream sediments in Switzerland.[4] NP was found to be much more toxic than NPE to aquatic organisms.[5]

All of these adverse reports have created doubts about the environmental safety of NPEs. Calls for restrictions and bans on their use started to be heard during the mid-1980s, particularly in Europe. About the same time producers of competitive surfactants used anti-NPE messages in their advertising. The U.S. Environmental Protection Agency (EPA) issued a Chemical Hazard Information Profile on NP and identified numerous environmental effect data gaps.[6]

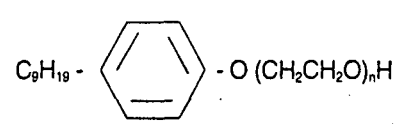


Fig. 1. Nonylphenol ethoxylate structure where n = the average number of moles of ethylene oxide per mole of NP and ranges from 1 to 100.

In response to this chorus of bad news the U.S. producers of NP and NPEs in 1987 formed a panel within the CHEMSTAR Division of the Chemical Manufacturers Association. The mission of the Alkylphenol and Ethoxylates Panel was to critically evaluate the published information on the environmental fate and effects of NPEs, start a cooperative dialogue with EPA and sponsor new studies needed for a formal risk assessment.

Major accomplishments of the panel include:[7-10]

- Negotiation of a consent order with EPA under TSCA Section 4
- Completion of all environmental effect tests required under the consent order
- A voluntary nationwide river monitoring study, designed with assistance from EPA
- Development and validation of analytical methods capable of measuring NP and NPEs at the sub-part-per-billion level
- Treatability evaluation of NPEs in a variety of wastewater treatment plants
- Additional aquatic toxicity testing

This paper reviews previously reported results, presents new information and begins to assemble all the data into an assessment of NPEs' environmental risk. Risk is the product of exposure of a substance to the environment times its effects on target organisms, and its calculation is done according to accepted EPA protocol.[11,12]

Results

Aquatic Toxicity of NP and NPEs

There is a large and growing body of data on the acute and chronic toxicity of NP and NPEs toward aquatic organisms.[13] Selected values are given in

Table I. Aquatic Toxicity of NP and NPEs

Water Assay	NP, µg/L	NPE_9, µg/L
All fish, LC50 acute range	130-1400	1300-1,000,000
Fathead minnow, LC50 96hr acute	300	4600
Fathead minnow, MATC[a] 7 day chronic	-	1400
Fathead minnow, MATC 28 day chronic	10	
All invertebrates, LC50 acute range	20-1590	2900-100,000
Daphnia magna, LC50 48hr acute	190	14000
Daphnia magna, MATC 7 day chronic	-	14000
Daphnia magna, MATC 28 day chronic	30	
All algae, EC50 acute range	25-750	210-5,000,000
Selenastrum capricornutum, EC50 96 hr acute	400	12000
Sediment Assay	NP, µg/kg	
Midge, MATC 14 day sub-chronic, dosed sediment	26,100	
Tadpole, LC50 10-30 day acute, dosed sediment	260,000	

[a]Maximum acceptable toxicant concentration

Table I for commonly tested organisms. A number of patterns are apparent:

- Fish, invertebrates and algae all vary widely, by orders of magnitude, in their sensitivity as measured by acute toxicity. The ranges of LC50 values for the three classes of organisms are similar.
- NPE_9 is much, at least about 10-fold, less acutely toxic than NP.
- The representative species, fathead minnow *Pimephales promelas*, water flea *Daphnia magna* and green algae *Selenastrum capricornutum*, have quite similar acute toxicities toward both NP (LC5O's or EC50's 190 to 400 ppb) and NPE_9 (4600 to 14000).
- The ratio of acute to chronic toxicity values for the minnow and water flea range from 6 to 30 with NP, from 1 to 3 with NPE_9.
- Exposure of sediment-dwelling or feeding organisms to NP dosed into the sediment does not appear to allow NP to express its high toxicity. Much higher levels of NP are required in sediment than in water to cause adverse effects (26,100 ppb with midge *Chironomus tentans* larva; 260,000 with tadpoles).

Much of the data of Table II were obtained from testing on nonylphenol required under the TSCA Section 4 Consent Order agreement between the EPA and the panel.[7] These tests were performed according to the EPA Good Laboratory Practices protocols.[14] From this new information three especially sensitive organisms were identified. The mysid shrimp, fathead minnow and marine alga *Skelatonema costatum* show chronic toxic effects with NP concentrations at or below 20 ppb. The maximum acceptable concentration (MATC) of NP for the mysid is 5.1 ppb, that for the fathead minnow is 10.2 ppb.

Table II. Nonylphenol Aquatic Toxicity

Species	Type	LC50 (96 hr) ppb, or Chronic Effect	No Observable Effect, ppb	Lowest Observable Effect, ppb	Maximum Acceptable Toxicant, ppb
Mysidopsis bahia[a]	Acute	43			
marine shrimp	Chronic	Length at 28 days	3.9	6.7	5.1
		Reproduction	6.7	9.1	7.8
		Survival	6.7	9.1	7.8
Pimephales promelas	Acute	300			
Fathead minnow, fresh water	Chronic[a]	135 Hatch rate	23	>23	>23
		Length, 28 days	23	>23	>23
		Survival, 33 days	7.4	14	10.2
Cyprinodon variegatus[a]	Acute	310			
Sheepshead minnow, marine					
Salmo gairdneri	Acute	230			
trout, fresh water		480 (24 hr)			
Daphnia magna	Acute	190 (48 hr)	77	160	111
flea, fresh water		440 (48 hr)			
	Chronic	Reproduction rate	24	39	31
Selenastrum capricornutum[a]	Acute	EC50 410	92	190	132
fresh water green alga					
Skelatonema costatum[a]	Acute	EC50 27	10	20	14.1
marine algae					
Rana Catesbiana[a]	Acute, 10 day	260mg/kg			
tadpole, fresh water	NP in Sediment				
Chironomus tentans[a]	Subacute, 14 day				26.1mg/kg
midge larva, fresh water	NP in Sediment				
Mytilus edulis	Acute	2600			
mussel, marine	Chronic	Growth and strength 32 days		56	

[a]Alkylphenol and Ethoxylates Panel data

Table III. NPEs in Thirty Rivers

Data Summary	NP in Sediment µg/kg (ppb)	NPE_1 in Sediment	NP in Water, ppb	NPE_1 in Water	NPE_2 in Water	NPE_{3-17} in Water
Method Detection Level	2.9	2.3	0.11	0.07	0.06	1.6
Overall average	162	18	0.12	0.09	0.10	2.0
95%-ile value	695	100	0.35	0.31	0.40	6.6
Average of highest 10%	1117	104	0.43	0.36	0.66	8.8
Highest value	2960	175	0.64	0.60	1.20	14.9

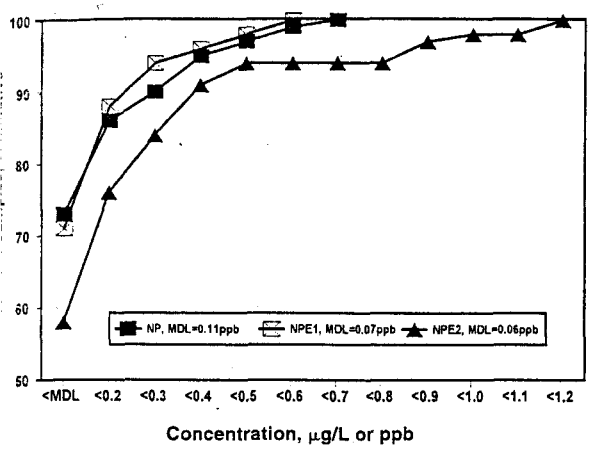
Bioaccumulation of NP

Also performed under the consent order was a nonylphenol bioaccumulation study of the fathead minnow. The fish were exposed to NP at concentrations of 5 ppb and 25 ppb—levels that could occur in wastewater treatment plant effluents (Table VI). After four days the bioconcentration factor reached about 350—factors less than 1000 are evidence of low risk for bioaccumulation. Within two days after exposure to NP was stopped NP was no longer detectable in the fish, indicating that NP uptake is readily reversible.

Rivers Study

The nationwide survey to determine the concentrations of NP and NPEs in rivers was a voluntary project not part of the EPA consent order. The EPA assisted the panel in designing the survey and provided access to its River Reach File database. The panel used the database to randomly select 30 sites for sampling. This number was sufficient to give the survey results the statistical power to be representative of the entire U.S.[8]

The sites were chosen from those river reaches considered likely to have been exposed to NPEs, that is, immediately downstream from industrial or wastewater treatment plant discharges. Each river was sampled across a transect perpendicular to the direction of flow. Three or four water samples and two or three sediment samples were collected and analyzed. All the



ig. 2. NP and NPE levels in river water from the 30 river study.

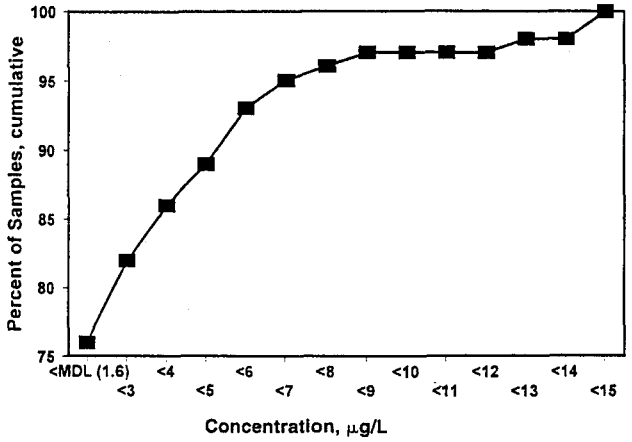


Fig. 3. NPE_{3-17} levels in river water from the 30 river study.

amples, about 100 of water and 80 of ediment, were given equal weight in ie data analysis.

The concentration ranges of key PE species in river water and sediient are shown graphically in Figs. 2-. The first gives the cumulative perentage distribution of values in water or NP, NPE_1 and NPE_2 from below eir method detection levels (MDL) p to the highest values found. More an half of the samples were below DL. The highest levels for NP, NPE_1, id NPE_2 were all about 1 ppb (µg/L). he composite totals of NPE_{3-17} oligoers were mostly below the MDL of 6 ppb (Fig. 3) with the highest value out 15 ppb.

Levels of NP and NPE_1 in river sedients are profiled in Fig. 3. Less than alf (28%) of the samples had non-

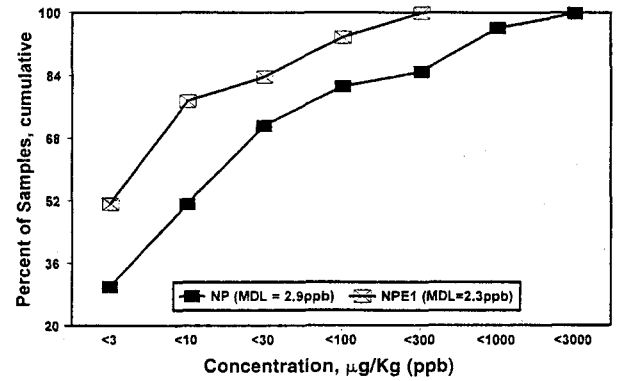


Fig. 4. NP and NPE_1 levels in river sediment from the 30 river study.

detectable (< MDL) NP, while close to half of the NPE_1 measurements were below MDL. The highest levels were about 3000 ppb NP and 175 ppb NPE_1 (Table III).

Consideration of each river separately, rather than each sample, allows a qualitative "exposure rating" for each river from zero to low, medium and high. Table IV lists the rivers by name and their ratings.

Grouping rivers having the same exposure rating emphasizes that a minority of them account for a majority of the highest NP and NPE concentrations (Table V). The "high" group of four rivers had two-thirds of all the highest NPE analyte levels. They thus comprise the "worst-case" category for the risk assessment exposure model.[15] The two lowest exposure ratings apply to 20 of the 30 rivers. They had the large majority of "non-detectable" results (90% were below MDL). The pro-

Table IV. Relative Contamination by Nonylphenol Species

ver Name	State	Exposure Rating
ohawk	N.Y.	Medium
iattahoochee	Ala.	Zero
iattooga	Ga.	Low
rnard Bayou	Miss.	High
d	Ark.	Medium
and Calumet	Ind.	High
agoon Creek	Wash.	Low
andywine Creek	Pa.	Low
Cr., W. Branch	N.Y.	Low
eat Egg Harbor	N.J.	High
nnebec	Maine	Low
cos	N.M.	Zero
louse, S.Fork	Wash.	Medium
yahoga	Ohio	Low
nneuf	Idaho	Medium
rry Creek	Ga.	Low
ames	Conn.	Medium
tawba	N.C.	Low
rkey Creek	La.	Medium
laware	N.J./Pa.	High
enandoah, N.Fork	Va.	Low
llahaga Creek	Miss.	Low
uth Anna	Va.	Zero
tomac	Md.	Low
nite	Vt.	Low
ughiogheny	Pa.	Low
Clair	Mich.	Low
llowstone	Mont.	Zero
chias	Maine	Low
skegon	Mich.	Zero

Table V. NPEs Exposure of Thirty Rivers

River Exposure Rating	No. of of Rivers	No. of Samples	No. in highest 10% of values	No. <MDL	Percent in top 10%	Percent <MDL
High	4	78	40	1	51.3	1.3
Medium	6	112	17	29	15.2	25.9
Low	15	302	2	210	0.7	69.5
Zero	5	90	0	87	0.0	96.7
Total	30	582	59	327	10.1	56.2

River Exposure Rating	Percentage of rivers	Percentage of samples	Percentage of highest 10%	Percentage <MDL
High	13.3	13.4	67.8	0.3
Medium	20.0	19.2	28.8	8.9
Low	50.0	51.9	3.4	64.2
Zero	16.7	15.5	0.0	26.6

River Exposure Rating	Rating Criteria
High	General contamination, most of the highest values of NP and NPE in water and sediment
Medium	Spotty contamination, a few of the highest values
Low	Low-level contamination, most values <MDL (method detection level), no values >>MDL
Zero	All samples </~MDL

Table VI. Wastewater Treatment Plants' Treatability of Nonylphenol Ethoxylates

Plant and Location	Date	Removal Rate wt % Influent - Effluent[a]	Influent NP	Conc.ppb NPE_{1-17}	Effluent NP	Conc. ppb NPE_{1-17}	Portion in digested sludge %
Burlington, N.C.							
East Plant	May 1992	94.6	384	903	14.4	54	
South Plant	May 1992	98.2	359	2619	15.3	39	
High Point, N.C.							
East Plant	Jan. 1993	96.5	44	289	<1	<5	
West Plant	Jan. 1993	97.7	124	487	1	<5	
East Plant	April 1993	98.3	14	274	<0.2	<5	
West Plant	April 1993	99.2	12	631	<0.2	<5	
East Plant	July 1993	99.3	234	640	<1	<5	
West Plant	July 1993	99.8	978	3140	0.2	<5	
East Plant	May 1988	95.6	-	1780	1.3	79	
West Plant	May 1988	95.6	-	2395	2.3	95	
Small City, Midwest USA	Aug. 1990	97.2	121	1390	3.5	39	
Small City, Midwest USA	Mar. 1991	92.5	28	1110	4.9	80	0.1
Wood Pulp Mill, USA	June 1990	97.6	24	8450	3.3	201	
Paper Mill, USA avg. of 4 assays	April 1993	99.3	516	33700	8.4	261	1.7

[a][Influent conc.-effluent conc.]/[Influent conc.] x 100%

file of NPEs exposure which emerges from the study of 30 rivers is a small proportion of rivers containing most of the NPE contamination and a majority (2/3) of rivers having virtually no contamination.

Treatability Studies

Many test methods are available for measuring biodegradability. Different methods attempt to simulate different environmental conditions, and a given test substance can give widely varying results depending on the method and test conditions. NPEs are a prominent example; extent of degradation has been reported from 0% to 100%.[3] All laboratory methods have the limitations of being artificial and lacking "real world" dynamics. Therefore, it was important to determine the biological treatability of NPEs in conventional wastewater plants. This became possible through the use of improved and streamlined analytical methods developed for the Thirty Rivers Study.[9]

The full distribution of NPE oligomers were monitored in raw sewage, activated sludge basins, digested sludge and treated effluents. Removal rates and material balances were obtained at a number of locations in the U.S. Table VI lists results from nine sampling projects at seven different treatment plants. Influent and effluent concentrations of NPEs are given, as are removal rates and in two cases, the portion of influent NPEs sorbing into the digested sludge.

Extent of NPE removal, as measured by the decrease of NP/NPE concentrations in effluents compared to influents, was consistently well above 90% (range 92.5-99.8%). Many of the influents had high levels of NP (up to 978 ppb) and NPEs (up to 33700 ppb). Effluent concentrations of NP ranged from 15 ppb to less than 1 ppb, while those of NPEs varied from 260 ppb to less than 5 ppb.

Seasonal effects were minor. The two winter samplings (High Point, N.C., January 1993 and the midwestern city, 1991) had removal rates 2-5% less than those of corresponding summer samplings.

The two measurements of NP in digested sludge indicate that sludge is not a major sink for NP, in contrast to earlier reports.[4,5]

Changes in the NPE oligomer distribution during biological treatment provide a sensitive probe for following the degradation of NPEs. It was shown during analytical method development that preservation of oligomer distribution of fresh NPEs must be maintained during sample extraction and LC analysis.[9] Distortion of the distribution or loss of total NPEs is an indication of matrix effects during sample work-up. The analytical protocol therefore ensures that the oligomer distributions of NPEs in wastewater are due to biological action and are no artifacts of the methods.

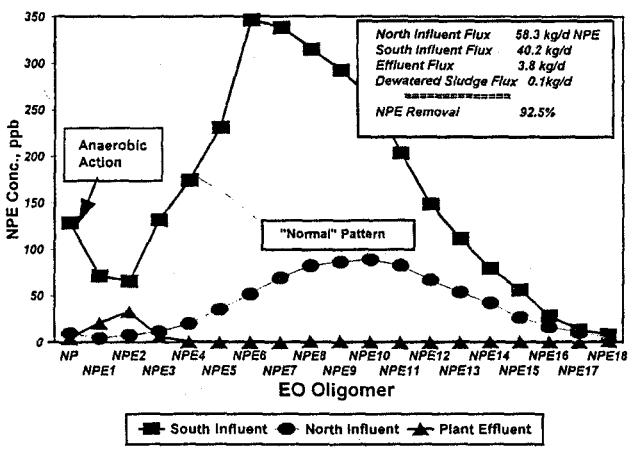


Fig. 5. Oligimer distributions of influent and effluent streams from a midwestern city's wastewater facility, March 1991.

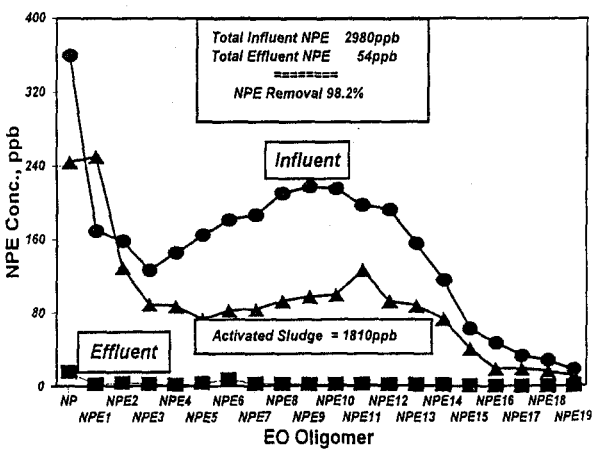


Fig. 6. Oligimer distributions of influent and effluent streams fro Burlington, N.C.'s South Plant, May 1992.

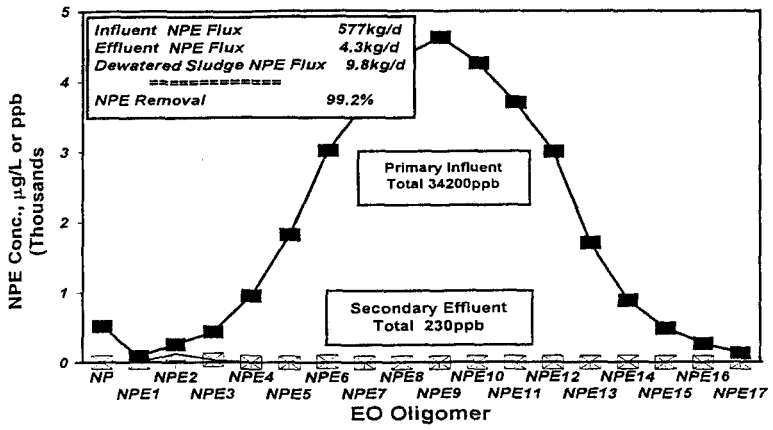


Fig. 7. Oligimer distributions of influent and effluent streams from a paper mill's wastewater, April 1993.

Oligomer distributions of influent and effluent streams from three of the wastewater treatment plants of Table VI are shown in Figs. 5-7.

The profiles of two influent streams and the effluent at a small city municipal wastewater treatment plant in March 1991 are shown in Fig. 5. The "North" influent was of mainly domestic household origin. Its NPE oligomer distribution had a "normal" pattern, peaking at 9-10 EO, an indication that NPE_{9-10} was being used in detergents and cleaning products. The "South" influent stream carried wastewater from a detergent manufacturing plant. The NPE oligomer distribution, although somewhat distorted, apparently reflected the use of NPE_{6-7} at the plant. The enhanced levels of NP and NPE_1 probably were an indication that anaerobic biodegradation was occurring in the sewer line. The NPE concentration in the South stream was much higher than in the North stream but accounted for about 40% of the NPEs entering the treatment plant. The effluent had only traces of all oligomers but NPE_1 and NPE_2. These two species accounted for 65% of the total. Flux of NPEs was estimated from the flow data. Total influent flux was 98.5 kg/day, effluent flux 3.8 kg/day and flux to dewatered sludge was 0.1 kg/day.

Fig. 6 shows the streams at the South Plant in Burlington, N.C. as the NPE concentration was reduced from 3000 ppb to 54 ppb. The plant received wastewater from domestic sources and textile mills and was experiencing chronic aeration basin foaming and effluent toxicity. NPEs were thought to be responsible.

Evidence for anaerobic degradation in the sewer lines was even stronger than in Fig. 5; NP was the dominant influent species. The pattern was similar in the activated sludge, although now NPE_1 and NPE_2 were very significant also. The effluent had only low levels of all oligomers. This picture of high treatability and low residual concentrations of NPEs provided strong evidence that NPEs were most probably not involved with the foaming and toxicity. Textile wastes typically are very complex and can contain a wide variety of surface active materials.

The high treatability of NPEs under conditions of extremely high loadings on the wastewater plant is shown in Fig. 7. It was an industrial activated sludge unit handling wastewater generated by a newsprint recycling mill which used NPE_9 as a deinking agent. NPE flux in the influent averaged 577 kg/day and 4.3 kg/day in the effluent mostly as NPE_2. Another 9.8 kg/day sorbed into the dewatered sludge, also mostly as NPE_2. Effluent NP flux was very low (0.1 kg/day).

Conclusion

Three major aspects of NPE environmental impact—exposure, degradability and toxicity—have been studied extensively. While the formal assessment of risk to the environment has been presented elsewhere, the most important elements were given here.[15] Nonylphenol (NP) is the NPE metabolite of highest toxicity. NP is not a significant metabolite except under anaerobic conditions. NPEs are extensively biodegraded (92.5 to 99.8% removal rate) in secondary treatment. The nationwide survey of NPEs in rivers provides a statistically valid model for environmental exposure. The highest NP level found in river water was 0.64 ppb. The highest NP level in river sediment was 2960 ppb. The most sensitive aquatic organisms have thresholds of observable toxic effects in the NP concentration range of 6.7 to 14 ppb. The threshold of toxic effects for one sediment-dwelling organism was 34,200 ppb. Estimated minimum safety margins for NP in both water and sediment, that is, the ratio of toxic effects threshold and worst case observed concentrations, are at least 10-fold.

This evidence provides a strong basis for the conclusion that NPEs are highly biodegradable, do not accumulate in water, sediment or aquatic organisms and do not pose a credible threat to the environment.

Acknowledgements

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