GENERAL FRAMEWORK FOR IDENTIFYING SUBSTANCES TO BE ADDRESSED IN THE GREAT LAKES BASIN

Test Case: Nonylphenol and its Ethoxylates (NPEs)

(Broader Organic Group: Alkylphenol Ethoxylates (APEs))

FEEDERS FOR SUBSTANCE IDENTIFICATION

Great Lakes Screening

NPEs are not involved in the Great Lakes Screening Project.[1]

National Chemical Management Programs

Canada

NPEs have been assessed CEPA toxic under the Second Priority List (PSL2) of the Canadian Environmental Protection Act (CEPA, 1999) and were added to CEPA 1999 Schedule 1- List of Toxic Substances in 2002.[2]

United States

APEs are High Production Volume (HPV) Chemicals.[3]

Other Sources of Information

United States

USEPA Region 5 actively investigated APEs and collaborated with EPA's Design for the Environment Program in outreach efforts to industry (i.e. developed low level analytical method and procured analytical standards for NP1EO and NP2EO, etc.). Additionally, USEPA Region 5 and the Great Lakes National Program Office (GLNPO) has supported several University and Federal Agency Studies through grants and participated in numerous collaborative sampling efforts to assess the presence of APEs in the region, demonstrate fate and transport of the chemicals, and assess toxicity of the chemicals.[4]

European Union

A risk assessment was completed by the European Union for 4-nonylphenol (branched) and nonylphenol in 2002 and the assessment was presented to the Organization for Economic Co-operation and Development (OECD) as a contribution to Chapter 19, Agenda 21 goals for evaluating chemicals.[5]

In 2003, the EU passed a Directive which restricts the marketing and use in Europe of products and product formulations that contain more than 0.1% of NPE or NP which came into force January 2005.[6]

OSPAR (The Convention for the Protection of the Marine Environment of the North-East Atlantic)

Nonylphenol Ethoxylate is on the OSPAR List of Chemicals for Priority Action (2007).[7]

CONSIDERATIONS FOR SUBSTANCE SELECTION

Monitoring and Surveillance

Numerous monitoring and surveillance data are available which demonstrates the presence of NPEs (APEs) in the Great Lakes Basin. For example:

- USEPA Region 5 & GLNPO are participating in numerous collaborative sampling efforts to assess the presence of APEs in the region.[4]

- Beenie *et al.* 1997, "Occurrence of alkylphenols and alkylphenol mono- and diethoxylates in natural waters of the Laurentian Great Lakes basin and the upper St. Lawrence River".[8]
  - Reports concentrations in surface water & sediments.
  - Of the surface water samples, 58% were found to contain NPE_1 and 32% contained NPE_2. Their concentrations ranged from <0.020 to 7.8 µg/L for NPE_1 and from <0.020 to 10 µg/L for NPE_2.
  - A total of 66% of sediments had detectable amounts of NPE_1 and concentrations ranged from <0.015 to 38 µg/g (dry weight), 66% of sediments had detectable amounts of NPE_2 and values ranged from <0.015 to 6.0 µg/g (dry weight)

- Beenie 1999, "Review of the environmental occurrence of alkylphenols and alkylphenol ethoxylates".[9]
  - Reports concentrations in Canadian and U.S. river, lake and harbour water & sediments.
  - Sites in the US indicate nonylphenol levels of less than 0.1 to 0.6 µg/L in river water and from less than 0.003 to 3.0 µg/g (dry weight) in sediments.
  - Nonylphenol levels in Canadian river water range from <0.01 to 0.9 µg/L.
  - Nonylphenol levels in Canadian river sediments similar to US sediments except samples (containing up to 72 µg/g dry weight) from Hamilton Harbor (Lake Ontario) near the discharge of the Burlington sewage treatment plant.
  - Levels of nonylphenol ethoxylates with 3 to 17 ethoxylate units range from less than 1.6 to 15 µg/L in US river water samples.

- Bennett *et al.* 2000, "Distribution of Degradation Products of Alkylphenol Ethoxylates Near Sewage Treatment Plants in the Lower Great Lakes, North America".[10]
  - Reports concentrations in sediment samples near sewage treatment plants (Hamilton Harbour & Detroit River).

Table 1. Concentrations of alkylphenol ethoxylate (APEO) degradation products and coefficient of variation (% CV) in mussels (lipid normalized; µg/g lipid) and semipermeable membrane devices (µg/g triolein) deployed at sites closest to discharges in the sewage treatment plant/(STP) Detroit River (sites 2 and 7) and in Hamilton Harbour

	4-tOP		4-NP		NP1EO		NP2EO	
	Mean	% CV	Mean	% CV	Mean	% CV	Mean	% CV
West Windsor STP Outflow Site 2								
Mussel data	3.19	40.3	91.02	11.3	73.4	40.3	21.3	19.7
SPMD data	2.96	*	117.2	*	NA	—	NA	—
Detroit River STP Outflow Site 8								
Mussel data	4.92	21.8	134.2	16.1	3.97	16.0	1.09	16.8
SPMD data	0.18	18.2	11.1	4.9	4.39	9.0	2.28	7.3
Burlington STP Outflow Site 13								
Mussel data	4.27	12.8	185.6	14.7	2.81	22.0	3.53	21.6
SPMD data	0.52	*	17.95	*	5.93	*	2.25	*

- Environment Canada & Health Canada 2001, "Priority Substance List Assessment Report-Nonylphenol and its Ethoxylates".[2]
  - Reports concentrations in Canadian freshwater, effluent and sludge from Canadian sewage treatment plants, surface waters & sediments.
  - Report available at: http://www.ec.gc.ca/substances/ese/eng/psap/final/npe.cfm.

- International Joint Commission, 2006, "Priorities 2003-2005: Priorities and Progress under the Great Lakes Water Quality Agreements".[11]
  - Reports concentrations in Great Lakes species (carp,1998-2000; carp and walleye, 1998-1999; 7 fish specieis, 1999; herring gull liver); sediments & water, 1998.

CHEMICAL	YEAR	SPECIES OR MEDIUM	LAKE OR LOCATION	CONCENTRATION in parts per billion unless indicated	CITATIONS
NP + NPEO[b]	98-00	Carp	Cuyahoga & Detroit R.	32 -920	Rice *et al.* 2003, Schmitz-Afonso *et al.* 2003
	98-99	Carp and walleye	Near WWTP outlet	4750	Schmitz-Afonso *et al.* 2003
	1999	7 fish species	Kalamazoo R.	< 3- 29	Keith *et al.* 2001
		Herring gull liver	Lower Great Lakes	225-464	Grasman *et al.* in preparation.
	1998	Sediments	Cuyahoga R.	250-1020	Rice *et al.* 2003
	1998	Sediments	Detroit and Rouge R.	<10-60000	Kannan *et al.* 2001b
	1998	Water	Cuyahoga R.	0.13 -5.1	Rice *et al.* 2003

- Lee *et al.* 2002, "Endocrine-disrupting chemical in industrial wastewater samples in Toronto, Ontario".[12]
  - Reports concentrations of NP & NPEO from <0.1 to 253 µg/L and <2 to 117,570 µg/L for NPEO in wastewater generated in Toronto. (From 97 samples from 40 facilities in 10 different industry classes.

Environmental Quality Benchmark Criteria

Yes, environmental quality benchmark criteria are available from both Canada and the United States.

Canada

Canadian Environmental Quality Guidelines for Nonylphenol and its Ethoxylates[13]

Environmental Media	Media Type	Guideline Type	Guideline Value *
Water	Freshwater	Full	1.0 $\mu g \cdot L^{-1}$
	Marine	Interim	0.7 $\mu g \cdot L^{-1}$
Sediment **	Freshwater	Provisional Interim	1.4 $mg \cdot kg^{-1}$
	Marine	Provisional Interim	1.0 $mg \cdot kg^{-1}$
Soil	Agricultural	SQG_E ***	5.7 $mg \cdot kg^{-1}$
	Residential/Parkland	SQG_E	5.7 $mg \cdot kg^{-1}$
	Commercial	SQG_E	14 $mg \cdot kg^{-1}$
	Industrial	SQG_E	14 $mg \cdot kg^{-1}$
	Groundwater	Check value	21 $mg \cdot kg^{-1}$

* all guidelines are expressed in nonylphenol toxic equivalent units

** these guideline values are for sediments containing 1% total organic carbon

*** environmental soil quality guideline; a full soil quality guideline would also consider protection for human health (CCME 1996)

United States

U.S. Water Quality Criteria for Nonylphenol in Fresh and Marine Water[14]

Environmental Media	Media Type	Guideline Value
Water	Fresh water	- A four day average of 6.6µg/L not exceeded more than once every three years - A one hour average of 28µg/L not exceeded more than once every three years
	Marine water	- A four day average of 1.7µg/L not exceeded more than once every three years - A one hour average of 7.0µg/L not exceeded more than once every three years

Note: The USEPA's WQC for nonylphenol does not consider toxicity related to the short chain nonylphenol ethoxylates, in particular the mono- and di- nonylphenol ethoxylates.

Environmental Levels and Trends

Beenie *et al.* 1997 reported NPE concentration ranges for surface water and sediment samples from the Laurentian Great Lakes Basin. Of the surface water samples, 58% were found to contain NPE_1 and 32% contained NPE_2. Their concentrations ranged from <0.020 to 7.8 µg/L for NPE_1 and from <0.020 to 10 µg/L for NPE_2. A total of 66% of sediments had detectable amounts of NPE_1 and concentrations ranged from <0.015 to 38 µg/g (dry weight), 66% of sediments had detectable amounts of NPE_2 and values ranged from <0.015 to 6.0 µg/g (dry weight).[8]

The highest range of NPE (NPE_1 & NPE_2) surface water concentrations exceeds both the Canadian freshwater guideline value of 1.0 µg/L and the United States fresh water four day average of 6.6µg/L.

Source/Use/Release/Exposure Information

Source/use/release/exposure information available primarily from Environment Canada & Health Canada's Priority Substance List Assessment Report- Nonylphenol and its Ethoxylates.[2]

Source/Use

Nonylphenol polyethoxylate-containing products are used in many sectors, including textile processing, pulp and paper processing, paints, resins and protective coatings, oil and gas recovery, steel manufacturing, pest control products and power generation. A variety of cleaning products, degreasers and detergents are also available for institutional and domestic use. These products have numerous applications, including controlling deposits on machinery, cleaning equipment, scouring fibres, as wetting and de-wetting agents, in dyeing, in machine felt cleaning and conditioning and in product finishing. NPEs are also used in a wide range of consumer products, including cosmetics, cleaners and paints, and in a variety of applications.

The amount of NP/NPE available for use in Canada was 23 800 tonnes in 1995 and 19 000 in 1996.

In the United States NP production was 147.2 million pounds (66.8 million kg) in 1980 (USITC 1981), 201.2 million pounds (91.3 million kg) in 1988 (USITC 1989), 230 million pounds (104 million kg) in 1998 (Harvilicz 1999), and demand is increasing about 2 percent annually.[4]

Release
The major route for the release of NP and NPEs to the Canadian environment is through discharge of effluents. The composition of the mixture can differ considerably among the various effluents, depending on the source and the degree and type of treatment. Textile mill effluents represent a major source of NPEs to the environment. Municipal effluents are a significant source of NPEs and are widespread across Canada.

Exposure:
In Canada, these chemicals have been found in fresh water, sediment, fish and beluga whale tissue, textile mill effluents, pulp and paper mill effluents, MWWTP influents, effluents and sludges, and soil to which municipal sludges had been applied.

Environmental and Health Data
Environmental and health information available primarily from Environment Canada & Health Canada's Priority Substance List Assessment Report- Nonylphenol and its Ethoxylates.[2]

CEPA 1999 64(a): Based on the available data, it is concluded that nonylphenol and its ethoxylates 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. Therefore, nonylphenol and its ethoxylates are considered to be "toxic" as defined in CEPA 1999 Paragraph 64(a).

CEPA 1999 64(b): Based on the available data, it is concluded that nonylphenol and its ethoxylates are not entering the environment in a quantity or concentration or under conditions that constitute or may constitute a danger to the environment on which life depends. Therefore, nonylphenol and its ethoxylates are not considered to be "toxic" as defined in CEPA 1999 Paragraph 64(b).

CEPA 1999 64(c): On the basis of consideration of the margin of exposure between effect levels and reasonable worst-case estimates of intake from environmental media, nonylphenol and its ethoxylates are not considered a priority for investigation of options to reduce public exposure through control of sources that are addressed under CEPA 1999.

Other Reasons for Concern
Evidence from scientific journals suggests NPEs have endocrine disrupting properties. [4,12,15]

PRESENT MANAGEMENT STATUS

Canada
The risk management objective for products containing NPEs is to achieve a 50% reduction of NPEs by 2007 and a 95% reduction of NPEs by 2010 in soap and cleaning products, processing aids used in textile wet processing and pulp and paper processing aids (baseline year 1998).[16]

There are 2 Pollution Prevention (P2) Planning notices under CEPA developed to manage risks associated with NPEs (both effective December 04, 2004):

- Notice Requiring the Preparation and Implementation of Pollution Prevention Plans in Respect of Nonylphenol and its Ethoxylates Contained in Products.

- Notice Requiring the Preparation and Implementation of Pollution Prevention Plans in Respect of Nonylphenol and its Ethoxylates Used in the Wet Processing Textile Industry and Effluents From Textile Mills that Use Wet Processing.[16]

United States

OPPT, Design for the Environment Program (DfE) through its Formulator Program, has partnered with cleaning product manufacturers and others in the design of products with a more positive health and environmental profile. Building on its Formulator work, DfE is developing the Safer Detergents Stewardship Initiative SDSI, a high-level recognition program for companies (manufacturers, formulations, end users, and sellers) who switch completely to safer surfactants. For example, NPEs are a surfactant class that does not meet the definition of a safer surfactant.[4]

REFERENCES

[1] Muir, D.C., Howard, P.H. and Meylan, W. 2007. Project: Screening Chemicals in Commerce to Identify Possible Persistent and Bioaccumulative (P&B) Chemicals in the Great Lakes.

[2] Environment Canada and Health Canada. April 2001. Priority Substances List Assessment Report Nonylphenol and its Ethoxylates. Available from Environment Canada's Web site at http://www.ec.gc.ca/substances/ese/eng/psap/final/npe.cfm.

[3] *Document Provided by Ted Smith:* Emerging Chemicals (2005), EC list April 2005.

[4] *Document Provided by Ted Smith:* Toxic Chemicals of National Concern (TCNC) DOSSIER. Alkylphenol Ethoxylates (nonyl and octyl phenol ethoxylates). 2006.

[5] European Chemicals Bureau, European Commission- Joint Research Centre. (July 2002). *European Union Risk Assessment Report: 4-Nonylphenol (branched) and Nonylphenol- Final Report, 2002*. Available online from: http://ecb.jrc.it/DOCUMENTS/Existing-Chemicals/RISK_ASSESSMENT/REPORT/4-nonylphenol_nonylphenolreport017.pdf.

[6] European Parliament legislative resolution on the proposal for a directive of the European Parliament and of the Council relating to restrictions on the marketing and use of nonylphenol, nonylphenol ethoxylate and cement (twenty-sixth amendment of Council Directive 76/769/EEC) (COM(2002) 459 - C5-0382/2002 - 2002/0206(COD)). Available online from: http://www.europarl.europa.eu/omk/omnsapir.so/pv2?PRG=CALDOC&TPV=PROV&FILE=030327&TXTLST=1&POS=1&LASTCHAP=24&SDOCTA=16&Type_Doc=FIRST&LANGUE=EN

[7] OSPAR Commission. *Hazardous Substances Series- Nonylphenol/Nonylphenolethoxylates.* (2001 (2004 Update)). Available online from: http://www.ospar.org/documents/dbase/publications/p00136_BD%20on%20nonylphenol.pdf.

[8] D.T. Bennie, C.A. Sullivan, H.B. Lee, T.E. Peart and R.J. Maguire, "Occurrence of alkylphenols and alkylphenol mono- and diethoxylates in natural waters of the Laurentian Great Lakes basin and the upper St. Lawrence River," *The Science of the Total Environment*, volume 193, pages 263-275, 1997.

[9] D.T. Bennie, "Review of the environmental occurrence of alkylphenols and alkylphenol ethoxylates," *Water Quality Research Journal of Canada,* vol. 34, pages 79-122, 1999.

[10] Bennett ER, Metcalfe CD, "Distribution of Degradation Products of Alkylphenol Ethoxylates Near Sewage Treatment Plants in the Lower Great Lakes, North America. Environmental Toxicology and Chemistry," Vol. 19, No. 4 pp. 784–7, 2000.

[11] International Joint Commission, Canada and United States. *Priorities 2003-2005: Priorities and Progress under the Great Lakes Water Quality Agreements*. (June 2006). Available online from: http://www.glc.org/bridges/documents/prioritiesfullreport-ch4.pdf.

[12] Lee, H-B., Peart, T.E., Gris, G., Chan, J., "Endocrine-disrupting chemical in industrial wastewater samples in Toronto, Ontario," Water Qual. Research J. Canada, 37(2), 459-472, 2000.

[13] Environment Canada. 2002. *Canadian Environmental Quality Guidelines for Nonylphenol and its Ethoxylates (Water, Sediment, and Soil)*. Scientific Supporting Document. Ecosystem Health: Science-based Solution Report No. 1-3. National Guidelines and Standards Office, Environmental Quality Branch, Environment Canada. Ottawa. Available online at: http://dsp-psd.pwgsc.gc.ca/Collection/En1-34-4-2002E.pdf.

[14] United States Environmental Protection Agency- Office of Water & Office of Science and Technology. (December 2005). *Aquatic Life Ambient Water Quality Criteria- Nonylphenol (EPA-822-R-05-005)*. Available online from: http://www.epa.gov/waterscience/criteria/nonylphenol/final-doc.pdf.

[15] M.R. Servos, Review of the aquatic toxicity, estrogenic responses and bioaccumulation of alkylphenols and alkylphenol ethoxylates. *Water Qual Res J Can* 34, pp. 123–177, 1999.

[16] Environment Canada. (2004). *Management of Toxic Substances- Substance Detail: Nonylphenol and its ethoxylates.* Available online from: http://www.ec.gc.ca/TOXICS/EN/detail.cfm?par_substanceID=72&par_actn=s1.