TURI
TOXICS USE REDUCTION INSTITUTE
University of Massachusetts Lowell

Toxics Use Reduction Institute

Summary of Policy Analysis

Higher Hazard Substance Designation Recommendation:
1-Bromopropane (n-Propyl Bromide)
CAS 106-94-5

1. State of the Science

N-propyl bromide has both acute and chronic adverse health effects. Acute effects can include eye, nose, throat and lung irritation, headache, dizziness, and nausea. The National Toxicology Program (NTP) has proposed classification of n-propyl bromide as reasonably anticipated to be a human carcinogen; Proposition 65 lists n-propyl bromide as a developmental toxin; other chronic effects include central nervous system damage.

2. Number of facilities affected

The TURA program estimates that the 1,000 pound reporting threshold that would apply to a Higher Hazard Substance would affect between 6 and 17 facilities.

3. Opportunities for New Filers

Practical alternatives to n-propyl bromide are available for most uses. For metal degreasing, options include both drop-in substitutes (alternative solvents) and process changes (including aqueous systems and mechanical removal). For adhesives there are several alternative solvents that can be used. For dry cleaning, there are alternative solvent options and process changes (wet cleaning) available.

4. Regulatory context

Compared with other chemicals that have been designated as Higher Hazard Substances under TURA, nPB is subject to relatively few regulatory restrictions at the federal level. For this reason, it has gained popularity as a substitute for other, more strictly regulated HHS solvents. While it is not regulated as a carcinogen by OSHA or USEPA, nPB has recently been proposed for classification as Reasonably Anticipated to be a Human Carcinogen by NTP. To date, OSHA has not issued a regulatory Permissible Exposure Limit (PEL), however ACGIH has proposed lowering its current recommended TLV of 10 ppm to 0.1ppm. California regulates n-propyl bromide as a developmental toxicant under Proposition 65. nPB is a VOC and there has been a recent petition to regulate nPB as a Hazardous Air Pollutant (HAP).

5. Implications for the TURA program

The TURA program is in a good position to offer services to new filers interested in reducing or eliminating their use of nPB. The program has substantial expertise on safer alternatives to halogenated solvents, including nPB.

Designating nPB as a Higher Hazard Substance would complement the programs past decisions on other halogenated solvents. Trichloroethylene, perchloroethylene, and methylene chloride were designated as Higher Hazard Substances in 2007, 2009, and 2013, respectively (decisions effective for reporting years 2008, 2010, and 2014, respectively). Designating nPB as a Higher Hazard Substance would ensure that the program does not inadvertently motivate facilities to shift from TCE, PCE, or methylene chloride to n-propyl bromide in those applications where that is feasible.

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This policy analysis summarizes key scientific information on n-propyl bromide; estimates the number of facilities that are likely to enter the program as a result of the lower reporting threshold; analyzes opportunities and challenges that new filers are likely to experience; and discusses the implications of this policy measure for the TURA program. Based on this analysis, the Toxics Use Reduction Institute, in consultation with the Science Advisory Board, recommends that n-propyl bromide be designated as a Higher Hazard Substance (HHS).

If nPB is designated as a HHS, the reporting threshold for nPB use would be lowered to 1,000 lb/year for companies in TURA-covered industry sectors with ten or more full-time employee equivalents (FTEs). Facilities subject to TURA are required to file an annual toxics use report, pay an annual toxics use fee, and develop a toxics use reduction plan every two years.

1. **State of the Science**

N-propyl bromide (nPB) has serious adverse effects on human health, including both acute and chronic health effects. nPB most often enters the environment through fugitive emissions and by spills or accidental releases to air, soil or water. For a list of specific data points considered by the SAB, see Appendix A.

Acute toxicity

- Exposure to nPB can cause symptoms including eye, nose and throat irritation, headache, dizziness, nausea, and fatigue.
- ACGIH lists the TWA-TLV as 10 PPM and has published an intended change to 0.1PPM, in order to "provide protection against the potential for neurotoxicity, hepatotoxicity, and reproductive and developmental toxicity in 1-bromopropane-exposed workers". The basis for the TLV is Central Nervous System impairment, peripheral neuropathy, hematological effects, reproductive toxicity (both male and female), and developmental toxicity.[1]

Chronic toxicity

- The US National Toxicology Program proposes classifying n-propyl bromide as "Reasonably anticipated to be a human carcinogen." NTP states that overall, the available experimental studies demonstrate (1) that 1-bromopropane is carcinogenic in experimental animals causing tumors at multiple tissue sites in two rodent species and (2) that 1-bromopropane causes molecular alterations that are relevant for human carcinogenicity.

Although the data in humans are limited, they are consistent with the conclusion that 1-bromopropane is *reasonably anticipated to be a human carcinogen.* [2]

- N-propyl bromide is listed as a male and female developmental toxicant on California's Proposition 65 list.
- Peripheral and central nervous system toxicity have been observed in workers exposed to nPB, and in animals. [3,4,5]

Uncertainty

Substantial information is available regarding both the acute and the chronic health effects of n-propyl bromide. Uncertainty does not play a significant role in the development of our recommendations for this substance.

2. Number of facilities affected

N-propyl bromide is a solvent used in Massachusetts and nationally. Use of nPB is increasing as an alternative for other solvents that have become more strictly regulated, such as methylene chloride, perchloroethylene (perc), and trichloroethylene (TCE).[6,7] nPB is used in vapor degreasing, metal cleaning, and dry cleaning; as a solvent carrier in adhesives; and as a chemical intermediate.

An investigative journalism article published in the New York Times in March 2013 uncovered information about nPB use and its effects on occupational health among workers in the furniture manufacturing sector. The article describes severe damage to workers' health at furniture manufacturing facilities in South Carolina and other states. Many of these workers have developed crippling neuropathies as a result of exposure to large amounts of nPB in glues. [8]

a. Trends in n-propyl bromide use

N-propyl bromide use reported under TURA has decreased since reporting began in 2010, but releases have increased. In 2010, 3 TURA filers reported n-propyl bromide use; in 2011, 2 filers reported n-propyl bromide use. There has been a 27% reduction in reported n-propyl bromide use from 2010 to 2011, and a 2% increase in reported n-propyl bromide releases from 2010 to 2011 (figures not adjusted for changes in production levels). More than half of the n-propyl bromide used is released to the environment, making it the chemical with the 17th largest releases reported under TURA, despite the fact that both use and the number of filers is small. This trend is a source of particular concern.

Table 1. Massachusetts TURA n-Propyl Bromide Use and Release Data: 2010 and 2011 (figures not adjusted for production)

	Year		Change In lbs	% Change
	2010	2011		
N-Propyl Bromide used (lbs)	47,209	34,209	-13,000	-27%
N-propyl Bromide released (lbs)	25,961	26,415	+454	+2%

b. Historical data on sectors using n-propyl bromide in Massachusetts

N-propyl bromide was added to the TURA list in 2009, with the first reporting year being 2010. In 2010 and 2011, n-propyl bromide was reported under TURA by the sectors listed below.

3449	Miscellaneous metal products
3674	Semiconductors and related devices
3675	Electronic capacitors

c. Current data on n-propyl bromide use in Massachusetts

Since reporting began in 2010, 3 companies reported use of n-propyl bromide.

- In SIC Code 3449, "miscellaneous metal products", 1 company otherwise used n-propyl bromide.
- In SIC code 3674, "semiconductors and related devices" 1 company otherwise used n-propyl bromide.
- In SIC code 3675, "electronic capacitors", 1 company otherwise used n-propyl bromide.

d. Estimated number of companies that would be affected by a lower reporting threshold

To develop an estimate of the number and type of companies likely to be affected by a 1,000 lb reporting threshold for n-propyl bromide, the Institute consulted sources including the TURA data, the Environmental Results Program (ERP) data and EPCRA Tier II data. In addition, staff at the Office of Technical Assistance (OTA) and the TURI Laboratory developed estimates based on their experience working with industry. Based on these sources, TURA program staff estimate the following impact:

- 34xx (fabricated metal products), is expected to result in 3 to 5 filers
- The following sectors are expected to generate between one and three filers each: 2891 (adhesives and sealants), 3675 (electronic capacitors), 5169 (wholesale trade - chemicals and allied products), 7216 (dry cleaning).

Based on this information, we estimate that a 1,000 lb reporting threshold would affect between 6 and 17 filers. These would include some facilities that are already reporting on their use of toxic chemicals and now have to include n-propyl bromide in their annual reporting, as well as some that could be new to the program.

3. Opportunities for New Filers

Feasible alternatives are available for most uses of n-propyl bromide. In the discussion below, we briefly review trends in n-propyl bromide use among existing TURA filers. We then consider the known alternatives for some of the most common uses of n-propyl bromide.

a. Opportunities to reduce n- Propyl Bromide use

i. Metal Degreasing

N-propyl bromide is used as a metal degreaser in a variety of applications. It is used in vapor degreasing and sometimes in wipe cleaning. Alternatives to n-propyl bromide for vapor degreasing include either drop-in substitute solvents, or a process change (conversion to ultrasonics using alternative solvents, media blasting or aqueous cleaning).

Drop-in substitutes: Many alternative solvents have been tested for performance in TURI's Lab and elsewhere. Effective drop-in replacement solvent alternatives include n-methyl-pyrollidone (NMP), HFE's, HCFC's, biobased solvents and hydrocarbon solvents, although health, safety, and environmental concerns exist for each of these options. Depending on the substance, concerns include reproductive toxicity, central nervous system effects, flammability, and ozone depleting and global warming potential. These drop-in substitutes may have purchase costs that are greater than that of n-propyl bromide on a per gallon basis. NMP is a TURA listed substance.

Process change: Aqueous systems are a feasible alternative to many solvent-based vapor degreasing operations, although they may involve additional process time and capital investment. Each company's cleaning needs are unique and cleaning processes should be specifically tailored for those needs.

From a health and environmental standpoint, the best alternatives to n-propyl bromide for vapor degreasing are:

- Switching to an aqueous or semi-aqueous system;
- Ultrasonic immersion cleaning;
- Mediablasting;
- Working within the supply chain to change the contaminant on the part that requires cleaning; or
- Investigating a materials change to prevent contamination and cleaning altogether.
- Adopting vacuum vapor degreasing, or similar technology to reduce chemical use, worker exposure, and release of the chemical.

ii. Adhesives

N-propyl bromide can be used as the solvent carrier in adhesives. For applications where the use of flammables is acceptable, acetone, methyl acetate and ethyl acetate are viable alternatives. Acetone and ethyl acetate are TURA listed substances, however they are both categorized by the SAB as relatively less hazardous chemicals. Acetone is extremely volatile, so appropriate controls and precautions should be used if this chemical is substituted. For applications where non-flammable materials are required, water-based systems (with drying systems) are a viable alternative. In addition, hot melt adhesives are an alternative that is suitable for some applications.

iii. Dry Cleaning[9]

The least toxic alternatives to nPB for both environmental and public health in dry cleaning applications are carbon dioxide (CO_2) and professional wet cleaning systems. CO_2 systems clean garments by using pressurized CO_2 as either a liquid or as a supercritical fluid in specialized equipment. These systems need to be evaluated for cost effectiveness. Professional wet cleaning is an aqueous process that uses computer-controlled washers and dryers, specifically formulated detergents and specialized tensioning equipment to clean and finish garments.

While detergents may cause skin and eye irritation, TURI research and analysis has determined that professional wet cleaning is a safer, cost-effective, and technically feasible alternative to solvent-based dry cleaning.[10] TURI has worked with garment cleaning facilities in Massachusetts helping them to convert from perc to professional wet cleaning. Results show good cleaning quality, fewer health hazards, and resource savings in water and energy.[11]

Hydrocarbon-based solvents, siloxanes, and other solvents are also popular replacements for dry cleaning operations. These solvents require process changes and some present health and safety hazards such as fire hazards. For others, health and environmental information is emerging and beginning to show concern.

b. Implementation: Opportunities and challenges

The services of the Office of Technical Assistance and the TURI Lab can facilitate the transition from n-propyl bromide to safer alternatives. Both OTA and the TURI Lab have extensive experience providing assistance to facilities working to replace hazardous solvents with safer alternatives, and are engaged in on-going projects to help users identify alternatives that are appropriate to their specific needs.

4. Regulatory context

N-propyl bromide is subject to less extensive regulation at the federal, state, and international level than the majority of substances that it is used to replace. For a glossary of regulations referred to in this section, see Appendix B.

EPCRA	• Not reportable to US EPA under TRI • Subject to US EPA Tier II reporting requirements[12]
CAA	• Not regulated as a hazardous air pollutant under the Clean Air Act. Pending petition for nPB to be added.[13] • nPB is a VOC
CWA	• Not identified as either an EPA Clean Water Act Priority Pollutant or an EPA Clean Water Act 311 List Hazardous Substance.
RCRA	• Not listed as a hazardous constituent under the Resource Conservation and Recovery Act (RCRA).
SARA	• Not found on the EPA Superfund Amendments and Reauthorization Act (SARA) 302A Extremely Hazardous Substances List.
EPA SNAP	• EPA has approved use of nPB as an alternative to ozone depleting substances TCA and CFC113 in solvent cleaning. • EPA issued a proposed rule in 2007 to prohibit use of nPB as a substitute for certain ozone depleting substances in adhesives and aerosol solvents, and to

	restrict its use in coating applications. This rule is still pending.
TSCA	• On 2013-2014 TSCA Workplan
OSHA PEL	• None
ACGIH TLV (TWA)	• 10 ppm (current) [14]; 0.1 ppm (proposed)[15]
SDWA	▪ No maximum contaminant levels (MCLs) under the Safe Drinking Water Act

Other state regulations (selected)

- California regulates n-propyl bromide under the Safe Drinking Water and Toxics Enforcement Act of 1986 (Proposition 65) as a developmental toxicant.[16]
- In 2009, California Occupational Safety & Health Standards Board adopted a PEL (8-hour time weighted average) for workplace exposures of 5 ppm.
- Pennsylvania lists nPB on its hazardous substances list.

International:

- Substance is listed on the Canadian Domestic Substances list and indicated as 'Persistent.'

Other information:

- EU hazard classification: The European Union classifies nPB as R60 (may impair fertility) and R63 (possible risk of harm to the unborn child).[17]
- Substance is listed on the NGO International Chemical Secretariat (ChemSec) "Substitute It Now" list due to CMR classification.
- Substance is listed as a Low Production Volume chemical by OECD (Organization for Economic Co-operation and Development).

5. Implications for the TURA program

The TURA program is in a good position to offer services to new filers interested in reducing or eliminating their use of n-propyl bromide. The program has substantial experience with and expertise on n-propyl bromide alternatives, and has a history of working successfully with users on these issues.

Activities of both OTA and TURI already provide infrastructure which could help smaller users to reduce their use of n-propyl bromide. Several on-going program activities would help meet the demand for services.

- The TURA program designated TCE, PCE, and methylene chloride as Higher Hazard Substances in 2007, 2009, and 2013, respectively (effective 2008, 2010, and 2014, respectively). Since n-propyl bromide may be used interchangeably with TCE, PCE, or methylene chloride in some applications, designating n-propyl bromide as a Higher Hazard Substance will communicate a consistent message to users of TCE, PCE, methylene chloride, and n-propyl bromide. Failure to designate nPB as a HHS could lead to unintended

consequences, motivating the remaining users of TCE, PCE, and methylene chloride to shift to n-propyl bromide in those applications where feasible.

- Both the Office of Technical Assistance and the TURI Lab have significant experience helping large and small users identify safer alternatives to n-propyl bromide and both are available as a resource for new filers entering the program. The TURI Lab has conducted solvent cleaning alternative testing since 1993, assisting businesses in making the transition to less toxic alternatives without compromising performance.
- TURI has an academic research grant program that can target seed funding to researchers who are developing safer alternatives to toxic chemicals for specific applications. When specific industry needs are identified, along with companies willing to share performance criteria, materials and/or other forms of expertise, TURI can identify university researchers interested in focusing their R&D efforts for solutions. If a specific application of the use of n-propyl bromide presents an on-going challenge for companies with respect to shifting to safer alternatives, TURI could support R&D to find feasible solutions.
- TURI has been providing wet cleaning grants for several years for conversion from perchloroethylene dry cleaning to wet cleaning. This grant solicitation could be broadened to include switching from nPB to wet cleaning.
- TURI's incentive grants for businesses can help businesses to defray the costs of safer technologies. TURI's demonstration site grants can help businesses that have already made a change to showcase their innovations to other businesses in related sectors. Both of these categories of grants can be used as a resource in helping Massachusetts businesses adopt safer alternatives to nPB.
- The TURA program does not currently know whether any Massachusetts facilities are using nPB-based adhesives. A HHS designation would help to obtain this information and support the TURA program's efforts to work with adhesive manufacturers and users to identify safer alternatives to HHS in adhesives.

There would be some additional cost to companies that would begin reporting n-propyl bromide based on a lower reporting threshold, including preparing annual toxics use reports and biennial toxics use reduction plans, and paying toxics use fees. The average base fee paid by TURA filers in 2010 was $3,425. However, most new filers for n-propyl bromide are likely to be facilities with fewer than 50 employees. The base fee for this size facility is $1,850. Some filers would not be new to the program and already pay a base fee, but would begin to pay an additional per-chemical fee of $1,100.

After two years of reporting toxics use, companies are required to engage in TUR planning. For companies that only need to report n-propyl bromide the cost of hiring a planner will likely be in the range of $1,000 - $3,000. Companies that want to have their own in-house TUR planner can qualify either by relying on past work experience in toxics use reduction or by having a staff member take the TUR Planners' training course. Those companies with experienced staff can become certified for as little as $100. For those that want staff to take a course the cost will be between $650- $2000 depending on whether the company has previously filed a TURA report. Companies with in-house toxics use reduction planners are likely to reap ancillary benefits from having an employee on staff that is knowledgeable about methods for reducing the costs and liabilities of toxics use. Additionally, through the process of planning and reducing or eliminating n-propyl bromide use, companies may be able to expand their markets, better comply with other regulations and reduce their overall regulatory burden.

The total additional cost in fees to filers (and revenue to the program) could be $6,600 to $18,700 in per-chemical fees (6-17 filers for n-propyl bromide) plus an estimated $5,550-$14,800 (base fee for 3-8 small sized [less than 50 employees] companies reporting n-propyl bromide only).

6. Summary

N-propyl bromide is less regulated than other TURA Higher Hazard Substances, has similar health effects, and is known to be a substitute for these chemicals in some applications. Initial TURA reporting shows that over 50% of the n-propyl bromide used is released to the environment, likely in part due to lack of regulation. Designating n-propyl bromide as a higher hazard substance will make it a less attractive alternative to other Higher Hazard Substances as well as make it possible to extend the benefits of the TURA program and TURA planning to a wider community of users. The TURA program is very experienced in providing assistance to the sectors that are most likely to be using nPB. A range of services would be available to the regulated community; these include training in TUR planning methods, assistance in identifying safer alternatives for specific uses, and in some cases potentially, direct grants for capital investments in new equipment.

Appendix A: Data the SAB considered for N-Propyl Bromide as a Higher Hazard Substance

National Toxicology Program (NTP)	2-year animal studies showed clear evidence of carcinogenicity. Reasonably Anticipated to be a human carcinogen (proposed)
PBT Profiler:	
Half life in water	15 days
Half life in soil	30 days
Half life in sediment	140 days
Half life in air	14 days
Bioconcentration factor	11
Reproductive Toxicity	Male and Female Reproductive Toxin
Developmental Toxicity	Developmental Toxin; on California's Prop 65 list
Neurotoxicity	Central Nervous System Depressant; Causes Peripheral Neuropathy in Workers [3,4,5]
Chronic fish ChV (mg/l)	7.2
OSHA PEL (TWA)	None
ACGIH TLV (TWA)	10 ppm (0.1 proposed 2012)
LD50 (mg/kg) – oral rat	2,950
LC50 (ppm/4H) – mouse	7,000
Vapor Pressure	110.8 mm Hg at 20 deg C; Vapors are heavier than air and collect in low lying areas

Note: The SAB also considered key endpoints compared to other Higher Hazard Substances

Appendix B: Glossary of Regulatory Terms & Acronyms

ACGIH	American Conference of Governmental Industrial Hygienists
CAA	Clean Air Act
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CWA	Clean Water Act
EPCRA	Emergency Planning and Community Right to Know Act
ERP	Environmental Results Program
FDA	Food and Drug Administration
MACT	Maximum Achievable Control Technology
MCL	Maximum Contaminant Level
NESHAP	National Emissions Standards for Hazardous Air Pollutants
NIOSH	National Institutes of Occupational Safety and Health
OSHA	Occupational Safety and Health Administration
RfD	Reference Dose
RCRA	Resource Conservation and Recovery Act
SARA	Superfund Amendments and Reauthorization Act
SDWA	Safe Drinking Water Act
STEL	Short Term Exposure Limit
Tier II	Chemical inventory reporting requirements for facilities subject to EPCRA
TRI	Toxic Release Inventory
TWA-PEL	Time-weighted average - Permissible Exposure Limit
TWA-REL	Time-weighted average – Recommended Exposure Limit
TWA-TLV	Time-weighted average - Threshold Limit Value

[1] Draft ACGIH Intended Change Document for 1-bromopropane, 2012.
[2] Draft RoC Monograph on 1-Bromopropane, Available at http://ntp.niehs.nih.gov/NTP/About_NTP/MonoPeerRvw/2013/March/DraftRoC1BPMonograph_508.pdf viewed January 2014.
[3] Li W, et al. Dose-dependent neurologic abnormalities in workers exposed to 1-bromopropane, J Occup Environ Med. 2010;52:769-77.
[4] Perrone J, et al. Neurologic illness associated with occupational exposure to the solvent 1-bromopropane—New Jersey and Pennsylvania, 2007-2008, Morbid Mortal Week Report. 2008;57:1300-1302.
[5] Ichihara G. Neuro-reproductive toxicities of 1-bromopropane and 2-bromopropane. International Archives of Occupational and Environmental Health. 2005;78(2):79-96.
[6] Ian Urbina, "As OSHA Emphasizes Safety, Long-Term Health Risks Fester" *New York Times* March 30, 2013
[7] Draft RoC Monograph on 1-Bromopropane, Available at http://ntp.niehs.nih.gov/NTP/About_NTP/MonoPeerRvw/2013/March/DraftRoC1BPMonograph_508.pdf viewed January 2014.
[8] Ian Urbina, "As OSHA Emphasizes Safety, Long-Term Health Risks Fester" *New York Times* March 30, 2013
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[11] Onasch, J. A feasibility and cost comparison of perchloroethylene dry cleaning to professional wet cleaning: case study of Silver Hanger Cleaners, Bellingham, Massachusetts. Journal of Cleaner Production. 2011;477-482.
[12] US EPA, Emergency Planning and Community Right-to-Know Act (EPCRA) Hazardous Chemical Storage Reporting Requirements, available at http://www.epa.gov/emergencies/content/epcra/epcra_storage.htm#msds.
[13] HSIA Files Petition with the Environmental Protection Agency to Add n-Propyl Bromide (nPB) to the List Of Hazardous Air Pollutants. Oct 28, 2010. Accessed 1/25/2011, at: http://www.hsia.org/news/HSIAnPBPressRelease.pdf.
[14] Hazardous Substances Data Bank (HSDB), a database of the National Library of Medicine's TOXNET system, http://toxnet.nlm.nih.gov
[15] 1-Bromopropane ACGIH Intended Change Document 2012
[16] Proposition 65 list available at: http://www.oehha.ca.gov/prop65/prop65_list/files/060107LST.pdf
[17] European Commission Joint Research Center, Institute for Health and Consumer Protection, European chemical Substances Information System. CAS# 106-94-5. Accessed 1/25/2011, at: http://ecb.jrc.ec.europa.eu/esis/index.php?GENRE=CASNO&ENTREE=106-94-5.