Toxics Use Reduction Institute
Policy Analysis
February 2018

C1-C4 Halogenated Hydrocarbons/Halocarbons Not Otherwise Listed (C1-C4 NOL)

This document analyzes the implications of adding a category, *C1-C4 Halogenated Hydrocarbons/Halocarbons Not Otherwise Listed (C1-C4 NOL)*, to the TURA list of Toxic or Hazardous Substances (TURA List).

With this addition, businesses in TURA covered sectors with 10 or more full time employee equivalents (FTEs) would be subject to TURA program requirements if they manufacture or process 25,000 lb/year, or otherwise use 10,000 lb/year, of chemicals in this category. These businesses would be required to file annual toxics use reports, pay annual toxics use fees, and develop a toxics use reduction plan every two years.

This policy analysis explains the definition of the proposed category, summarizes key scientific information, reviews existing information about how the chemicals in this category are used, discusses opportunities for toxics use reduction, summarizes relevant regulatory information, and discusses the implications of this policy measure for the TURA program. The TURA Science Advisory Board (SAB) has recommended adding this category to the list. Based on all this information, the Toxics Use Reduction Institute recommends that this category be added to the TURA list.

1. Category Overview

This document discusses a proposed new category referred to as *C1-C4 Halogenated Hydrocarbons/Halocarbons Not Otherwise Listed (C1-C4 NOL)*. This category is defined as chemicals with 4 or fewer carbons, at least one halogen[1], and only hydrogen as the other constituent, that are not already individually listed on the TURA chemical list. This includes fully halogenated chemicals that contain no hydrogen.

Development of this category resulted originally from discussions surrounding the addition of n-propyl bromide (nPB) to the TURA list in 2009. During the Science Advisory Board (SAB) discussion of nPB, it was noted that regrettable substitutions can occur readily; small changes to chemicals currently on the market can result in the introduction of other, similarly toxic chemicals that are not regulated. The SAB has now evaluated a range of similar chemicals, in order to support an effort to avoid regrettable substitutions. Some chemicals that meet the criteria for this category are not currently manufactured or used, but are expected to pose health and environmental concerns if they were to be manufactured and used.

Universe of chemicals. As shown in Appendix 1, the chemicals in this category would include halogenated unbranched alkanes with 1 to 4 carbons, halogenated branched alkanes with 4 carbons, halogenated cyclic alkanes with 3 or 4 carbons, halogenated alkenes with 2 to 4 carbons, and potentially halogenated alkynes (this last is theoretically possible, but not commercially available).

The TURA program has created a working, non-comprehensive list of over 200 chemicals that meet the criteria for inclusion in this category. Forty-one of the chemicals on this working list are expected to be in commerce in the US according the the US EPA TSCA inventory. However, few of them are expected to be used in reportable quantities in Massachusetts. Thus, while the number of chemicals in the proposed category is large, the number of filers is expected to be low.

Relationship to chemicals already listed under TURA. The TURA program has identified 85 chemicals that meet the chemical structure criteria for this category and are already included on the TURA list. This includes trichloroethylene (TCE), perchloroethylene (PCE or "perc"), and 1-bromopropane (n-propyl bromide, or nPB), which are designated as Higher Hazard Substances (HHS). It also includes other chemicals, such as chloroform, 1,2-trans dichloroethylene and Freon 113, which are not designated as HHS. Reporting on these and other listed chemicals would not change with the addition of this category; the category would cover only those chemicals that are not already listed individually.

2. State of the science

Based on the SAB's review, central nervous system (CNS) effects are found consistently across the chemicals in this proposed category. Additional hazards noted for some of these chemicals include target organ toxicity; reproductive and developmental toxicity; carcinogenicity; and respiratory effects. In addition, most are persistent in air and/or sediment and many are ozone depleting chemicals and/or are greenhouse gases.

SAB approach. Initially, TURI created a list of 136 chemicals meeting the chemical structure criteria for inclusion in the group. Approximately half of these chemicals were already on the TURA list, making it possible to compare toxic effects. For the 136 chemicals, TURI collected a standard set of environmental health and safety (EH&S) data. The data set includes environmental/PBT information, human health information such as carcinogenicity, neurotoxicity and reproductive toxicity, and physical properties information such as vapor pressure, among other data points. The SAB also chose four sample chemicals – two pairs of chlorinated and brominated analogs -- for a review in greater depth: acetylene tetrachloride, acetylene tetrabromide, 1-bromopropane, and 1-chloropropane. Of these four, 1-bromopropane is listed on the TURA list and was useful for comparison since the SAB had recently reviewed it for listing.

The following summarizes some information considered by the SAB on the 136 chemicals:

> *Health effects.* The SAB found that there were data indicating neurotoxicity for 57 of the 136 chemicals. For the remaining chemicals on this list, no studies on neurotoxicity were found in the National Library of Medicine's HazMap database.[2] In California's Proposition 65 list, 26 of the chemicals on the list are listed as carcinogens, and 5 are listed as reproductive/developmental toxicants. Additional hazards noted for some of these chemicals include target organ toxicity (cardiovascular, liver, kidney, gastrointestinal, blood), and respiratory effects.
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> *Environmental Effects.* Environmental concerns include persistence in air and/or sediment, ozone depletion, and global warming potential. Most of the chemicals exhibited persistence and/or toxicity to aquatic organisms. Results from EPA's PBT profiler indicate that, of the 136 chemicals, 109 are persistent in air, 42 are persistent in sediment, and 81 are very persistent in sediment. Sixty-nine pose moderate chronic toxicity to fish, and 15 pose high chronic toxicity to fish.
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> *Physical properties.* Many of the 136 chemicals are liquids at room temperature; others are gases, and a few are solids. Twenty-six of the 136 chemicals are flammable liquids or gases. The SAB observed that in general, the chlorinated chemicals in the category have higher volatility than the brominated chemicals.

TURI review of additional chemicals. After the SAB's review of the data on the initial list of 136 chemicals, TURI obtained a more comprehensive list of refrigerants, and noted which of these refrigerants are in the C1-C4 NOL category and may be in commerce according to the TSCA Inventory. For those that had not already been reviewed by the SAB, TURI checked neurotoxicity data. TURI verified that nearly all have evidence of neurotoxicity, consistent with the findings of the SAB for the chemicals they had reviewed.

3. Use information

The chemicals in this proposed category may be used as solvents, propellants, refrigerants, blowing agents, fire extinguishing agents, chemical intermediates, and a variety of other uses.

Many of the chemicals in this category can be used for multiple uses. For example, a sample chemical in this category, trifluoromethane, is used as a fire suppressant and as a refrigerant, as well as a variety of other uses including as an electronic gas and in solvent cleaning.[3]

Massachusetts data available from Tier II. Tier II requires reporting of any chemical with an SDS if it is stored at 10,000 pounds or more at a facility (the threshold is 500 pounds for extremely hazardous substances). A review of the 2015 Tier II data shows approximately 76 records for chemicals in this proposed category stored at Massachusetts facilities. The majority of these records are for refrigerants, and fewer refer to solvents.

As shown in Table 1, 9 chemicals in the proposed C1-C4 NOL category were reported under Tier II in Massachusetts in 2015. Most are reported by only a handful of facilities, while others appear to be used more widely. The most commonly reported chemical in the category is 1,1,1,2-tetrafluoroethane (R134a).

TURI reviewed the Tier II data for those chemicals meeting the chemical criteria and not already listed under TURA. To develop an expected number of TURA filers, TURI limited the data set based on reportable SIC codes, employee numbers, and on-site quantity of chemical reported. Based on this analysis, the number of facilities that are likely to report on the category based upon Tier II is approximately 14.

Table 1: 2015 Tier II data

Chemical name	Tier II reports	Expected number of TURA filers
1,1,1-Trifluoroethane [HFC-143a]	1	1
1,1,1,2-Tetrafluoroethane [R134a]*	21	5
1,1-difluoroethane [HFC-152a]	1	1
Fluoroform [HFC-23]	2	0
Pentafluoroethane	1	1
Refrigerant (NOS**)	35	3
R-410	2	0
Solvent (NOS**)	10	3
Tetrafluoromethane [PFC-14]	3	0
Total	**76**	**14**

This table shows Tier II reports for chemicals that meet the chemical structure criteria for the C1-C4 NOL category and are not already reportable individually under TURA. To develop an expected number of TURA filers, TURI limited the Tier II data set based on TURA reportable SIC codes, employee numbers, and quantity of chemical reported.
*Banned in the EU for use in specified automotive air conditioning systems.[4]
** Not otherwise specified

It is worth noting that there could be facilities that would be subject to TURA reporting requirements that may not appear under Tier II, either due to reporting errors or due to threshold considerations. For example, when n-propyl bromide (nPB) was added to the TURA list, there were no facilities filing under Tier II, but three facilities subsequently filed under TURA. (Additional facilities filed in subsequent years, after nPB was designated as a Higher Hazard

Substance, lowering the reporting threshold.) Thus, it is likely that a small number of additional filers are not captured in the data shown above. Conversely, facilities may report a significant amount as stored on site under Tier II, while still not exceeding the annual TURA use thresholds.

If a facility uses a chemical in the C1-C4 NOL category in a refrigeration system, the amount used initially to charge or to recharge the system would be counted towards the 10,000 pound use determination threshold. It is unlikely that chemical use will be consistently above reporting threshold from year to year. Most facilities with a good operations and maintenance program for their refrigeration system will not exceed the annual reporting threshold.

National trends in fluorocarbon use. National use trend information is available for fluorocarbons as a group. Fluorocarbons include all organic molecules that contain at least one fluorine. These include chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and hydrofluorocarbons (HFCs), among others. The broad category of fluorocarbons overlaps with the C1-C4 NOL category defined here, so it can be useful to consider these trends. Nationally, the largest use of fluorocarbons is in refrigeration and air conditioning, followed by polymer precursors. Other important uses are in foam blowing agents, aerosol propellants, and solvent cleaning.[5]

4. Opportunities for TUR: Selected Applications

A variety of opportunities for toxics use reduction exist for users of chemicals in the category. The alternatives available to users depend on the application for which the chemical is used. This section provides a brief discussion of alternatives for two categories of uses: solvent and refrigeration applications. For solvent applications, both drop-in substitutes and process change options are often available. For many refrigeration applications, drop-in substitutes may be identifiable in some cases, although adopting a safer alternative can require a large-scale equipment or process change. There are also important opportunities to reduce chemical use in refrigeration through operations and maintenance improvements, such as leak detection.

TUR options for solvent applications

The chemicals that meet the criteria for inclusion in the C1-C4 category and are not already listed under TURA do not appear to be used widely as solvents at this point. However, they are likely to have functional properties similar to those of solvents that are widely used, so they may be adopted for similar purposes in the future.

Safer alternatives to the use of these solvents are similar to the safer alternatives for other solvents with which the TURA program has experience, such as TCE, methylene chloride, nPB, toluene, hexane, and others. TUR options include process changes (e.g. aqueous cleaning solutions), improvements to existing processes (e.g. production unit modernization, improved operations and maintenance), and solvent substitutes (input substitution, product reformulation).

TURI is not aware of any widespread use of the chemicals in this category for metal degreasing applications. However, many of them could potentially be used in such applications, especially with increasing regulatory attention directed toward other, more commonly used solvents.

Solvent substitutes. Solvent alternatives may include hydrofluoroethers (HFE's), bio-based solvents and nonhalogenated hydrocarbons, although health, safety, and environmental concerns exist for each of these options. Some are considered "drop-in" substitutes, although they may require new equipment or equipment modification; for example, some solvents are flammable, and will require appropriate equipment.

Drop-in substitutes and blends may be identified by using the Hansen Solubility Parameters, a modeling approach that characterizes solvents and solutes based on three intermolecular forces: dispersion, dipolar intermolecular force, and hydrogen bonding. TURI has piloted the use of this approach to identify potential solvent blends that may serve as safer alternatives to solvents such as methylene chloride, toluene, methanol, and hexane.

Process change. Aqueous systems are a feasible alternative to many solvent-based vapor degreasing operations, although they require different process equipment, often making it necessary to make a 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 halogenated solvents for vapor degreasing include aqueous and semi-aqueous systems, ultrasonic immersion cleaning, and media blasting. In some cases it is possible to redesign the production process to eliminate the need for cleaning/degreasing. This may be accomplished by redefining cleanliness specifications, eliminating the process step that results in a dirty part, or changing the nature of the oils and other contaminants that must be cleaned off.[6]

For a facility that continues to use the solvent, adopting vacuum vapor degreasing or a similar technology helps to reduce chemical use, worker exposure, and release of the chemical.

Advantages of these alternatives include reducing or eliminating worker exposure to solvents, hazardous waste generation, and the need for emissions controls. TURA program case studies can be used to generate ideas about safer alternatives, and the TURI lab can help facilities to evaluate cleaning options based on their specific surfaces, soils and cleaning needs.

Production unit modernization and improved operations and maintenance. Facilities using halogenated solvents for vapor degreasing applications may be able to minimize solvent losses through equipment upgrades. Equipment upgrades and improved housekeeping practices can also help to reduce solvent use. Finally, for those processes where there is no feasible alternative, solvent recovery systems such as distillation can help to reduce solvent use.

TUR options for refrigeration applications

TUR options for refrigeration applications include substituting safer chemicals, which generally requires a significant capital investment in new or modified equipment; or operations and maintenance improvements, such as improved leak detection.

Refrigerants: Background information

A number of technologies and chemicals have been used for refrigeration over time; they can be roughly divided into four generations. [7] The earliest generation of refrigerants included ammonia, methyl chloride, hydrocarbons, and sulfur dioxide. The next generation of refrigerants included chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). CFCs are potent ozone depleters; HCFCs, which are somewhat less potent ozone depleters, have been used as a transitional option. Both are being phased out globally under the Montreal Protocol. Many of these chemicals have high global warming potential as well.[8]

As businesses have shifted away from the refrigerants that pose the greatest concern with regard to ozone depletion, in some cases they have adopted refrigerants with very high global warming potential. The third generation refrigerants are hydrofluorocarbons (HFCs); these are not ozone depleters, but they have very high global warming potential. Some commonly used HFCs "have global warming potentials up to 12,000 times more potent than CO2." [9] Emissions of HFCs have grown substantially since the 1990s.[10]

Finally, hydrofluoroolefins (HFOs) are currently marketed as safer alternatives (non ozone depleting and with lower global warming potential than the other halogenated refrigerants), but they are persistent in the environment, and some pose flammability concerns, with potential generation of hydrofluoric acid at high temperatures.

The proposed C1-C4 NOL category includes some chemicals that fall into each of the categories of halogenated refrigerants noted above: CFCs, HCFCs, HFCs, and HFOs.

Substitutions

In general, identifying safer alternatives to refrigerants is a challenging task. However, some refrigerants pose greater concerns than others, so any facility using refrigerants may benefit from considering possible alternatives.

Under its Significant New Alternatives Policy (SNAP), the US EPA has identified refrigerants that it considers to be acceptable or unacceptable. Unacceptable alternatives include all flammable refrigerants; certain hydrocarbon blends; and a number of other products. EPA updates this list periodically based on new information.[11]

Of the halogenated refrigerants currently on the market, the HFOs are currently considered to be more preferable from an environmental standpoint. There is some renewed interest in ammonia refrigeration systems, although these present safety and toxicity concerns. There are also potentially promising opportunities related to safer alternatives such as carbon dioxide.

Carbon dioxide.[12] Carbon dioxide (CO_2) has been used as a refrigerant since the 19th century. Its use declined in the early part of the 20th century, but interest has increased in recent decades due to growing concerns about the environmental effects of widely used refrigerants. Advantages of CO_2 include the fact that it is readily available at low cost, has low toxicity, and is not flammable. Provided that the CO_2 for refrigeration applications is recovered from existing industrial processes, it does not pose additional concern related to generation of new greenhouse gases.

CO_2 used for refrigeration applications can pose safety concerns. Because CO_2 is colorless, odorless, and heavier than air, in enclosed spaces it can cause asphyxiation, and exposed individuals will not be aware of its presence unless detectors and alarms are in place. In this regard, it is similar to fluorocarbon refrigerants, which can pose a similar safety hazard.

There may also be safety concerns related to use of CO_2 under pressure. According to an industry source, the Australian Institute of Refrigeration, Air Conditioning and Heating, “when used as a refrigerant, carbon dioxide typically operates at a higher pressure than fluorocarbons and other refrigerants. While this presents some design challenges it can usually be overcome in systems designed specifically to use carbon dioxide – more issues may be encountered if carbon dioxide is to be retrofitted to a system designed for a different, lower-pressure refrigerant.”[13]

CO_2 is sometimes used in ‘cascade’ or ‘secondary loop’ systems, which use two types of refrigerants, each in a separate loop. Thus, for example, CO_2 may be used in one loop, with a fluorocarbon or ammonia refrigerant in the other loop.

According to the Australian industry report, CO_2 is currently used as a refrigerant in applications including vehicles, supermarkets, skating rinks, industrial freezers and cold storage units.[14] In 2002, Nestle UK converted a facility that produces freeze dried coffee to a cascade system using ammonia and carbon dioxide, providing evidence that such a technology can be used successfully by a large industrial facility.[15] The Australian report notes that in the past, refrigeration equipment suitable for the higher pressures needed for carbon dioxide refrigeration was unavailable; over time, such equipment has become increasingly readily available.[16] Several auto manufacturers, including Volkswagen, are also using CO_2 in some air conditioning systems.[17]

Refrigerant blends. In some cases, facilities have begun using blends of two or more refrigerants. A number of blends are commercially available. For example, the commercially available blend R404A consists of HFC-125 (44%), HFC-134a (4%), and HFC-143a (52%).[18] These blends can allow individual facilities to avoid high levels of impact in a specific area, such as ozone depletion or global warming, but they do not solve the larger problem of the collective impacts of all these facilities on the environment.

Improved O&M

Given the lack of safer alternatives, the most promising avenue for toxics use reduction for facilities using refrigerants is improved operations and maintenance. For example, facilities can reduce their total refrigerant use by ensuring they have good leak detection systems in place. Based on their professional experience, TURA program staff members have noted that it is not uncommon for a facility to recharge 1,000 lb/year of a refrigerant. This indicates that the facility has lost that quantity each year in leaks or other losses. Such losses pose serious environmental concerns. Both state and federal programs exist to encourage businesses to address and prevent leaks and other losses; these are discussed further in the section on regulations, below.[19]

5. Regulatory context

A variety of regulations apply to the chemicals in the proposed C1-C4 NOL category. These include regulations related to ozone depletion and greenhouse gas emissions, among other topics. Selected regulations are noted here.

International agreements

A number of chemicals in the proposed C1-C4 NOL category are ozone depleters and are subject to the Montreal Protocol on Substances that Deplete the Ozone Layer. Under the Montreal Protocol, production and consumption of chlorofluorocarbons (CFCs) has been eliminated globally, and hydrochlorofluorocarbons (HCFCs) are being phased out. Economically developed countries, including the US, are committed to having achieved a 99% reduction in HCFC production and consumption by 2015; a 99.5% reduction by 2020; and a 100% reduction by 2030.[20]

The Kigali Amendment to the Montreal Protocol, adopted in October 2016, expands the scope of the Protocol to address the production and use of HFCs, making it possible to address these greenhouse gases under the Protocol.[21]

Federal regulations

The US EPA regulates CFCs, halons, HCFCs and HFCs under the Clean Air Act and its amendments. EPA regulations include a market-based system for the phase-out of ozone depleters; controls on ozone depleters as used in refrigeration and automobile air conditioning; prohibitions on certain nonessential uses; labeling requirements; and procurement guidelines, among other elements.[22]

In December 2016, EPA finalized a rule under its Significant New Alternatives Policy (SNAP) program. This rule "expands the list of acceptable substitutes; lists unacceptable substitutes; and changes the status of a number of substitutes that were previously listed as acceptable, based on information showing that other substitutes are available for the same uses that pose lower risk overall to human health and/or the environment." Among other provisions, it identifies acceptable options for certain substances for refrigeration, air conditioning, and fire suppression; identifies specific unacceptable options for refrigeration and air conditioning; changes the status of some previously listed options; and adds propane as an acceptable option for refrigeration applications under certain conditions, in new equipment.[23]

In November 2016, EPA finalized a rule[24] updating the refrigerant management requirements under the Clean Air Act. Existing regulations required that "persons maintaining, servicing, repairing, or disposing of air-conditioning and refrigeration equipment containing more than 50 pounds of refrigerant observe certain service practices that reduce emissions of ozone-depleting refrigerant." The new rule updates and extends these requirements. The updates include "strengthened leak repair requirements, recordkeeping requirements for the disposal of appliances containing more than five and less than 50 pounds of refrigerant," and other requirements. The requirements are also extended to cover certain "non-ozone depleting substitute refrigerants, such as hydrofluorocarbons," in order to address the global warming impacts of these chemicals.

Massachusetts regulations and refrigerant policy

Massachusetts requires reporting on greenhouse gas emissions that exceed 5000 CO_2 equivalents per year.

In addition, Massachusetts has a Stationary Equipment Refrigerant Policy. As described in the Massachusetts Clean Energy and Climate Plan[25] for 2020, the goal is to "reduce emissions of HFCs by requiring actions that will reduce the amount of refrigerant that leaks from refrigeration systems, buying time while less harmful replacement compounds are developed."[26] The policy focuses on "leak detection and monitoring, leak repair, system retrofit and retirement, required service practices, and recordkeeping and reporting" and encourages "eventual replacement of non-residential refrigeration equipment at the end of its life by equipment using no-GWP [Global

Warming Potential] or lower GWP substances, where such alternatives are available and practicable."[27]

California

In 2010, the California Air Resources Board (CARB) adopted a regulation that phases in requirements related to leak detection and repair.[28] The rule applies to "refrigeration units containing a charge of 50 pounds of refrigerant or greater." [29] Adoption of a similar rule has been proposed as an option for Massachusetts.[30]

European Union

The European Union has adopted two important pieces of legislation addressing fluorinated greenhouse gases: the Mobile Air Conditioning (MAC) Directive and the F-gas Regulation.

The MAC Directive provides for the elimination of fluorinated greenhouse gases with GWP's greater than 150 in the air conditioning systems of passenger cars and light commercial vehicles. It was designed to address the widespread use in these vehicles of the refrigerant R134a, which has a Global Warming Potential (GWP) of 1300.[31] Under this regulation, effective as of 2011, the EU has prohibited new vehicle models from using air conditioning systems with "fluorinated greenhouse gases having GWPs greater than 150."[32] As of January 1, 2017, this prohibition applies to all new vehicles regardless of model.[33]

The F-gas Regulation deals with all other important uses of fluorinated greenhouse gases. It includes provisions related to both leak prevention and substitution with safer alternatives. The leak prevention provisions include measures related to training and certification, equipment labeling, gas containment, and gas recovery.[34] The substitution provisions focus on "[a]voiding the use of F-gases where environmentally superior alternatives are cost-effective." An updated F-gas regulation adopted in 2015 limits the amount of key F-gases that can be sold in the EU, "phasing them down in steps to one-fifth of 2014 sales in 2030." It also prohibits the use of F-gases "in many new types of equipment where less harmful alternatives are widely available, such as fridges in homes or supermarkets, air conditioning and foams and aerosols."[35]

Industry standards

Industry standards can also have an important effect on businesses' choices of refrigerant options. For example, according to an industry publication, Underwriters Laboratories, Inc. (UL) updated its pressure standard for refrigerants in air conditioning and refrigeration systems, making it possible to accommodate alternative refrigerants.[36] UL has also recently published a white paper that discusses issues related to flammable refrigerants, as use of these chemicals is likely to increase as part of the effort to phase out refrigerants of particularly high concern.[37]

6. Implications for the TURA program

Implications of category designation

Chemical categories are used in the TURA list in a number of cases. In many cases, a category is defined using a chemical structure and text description, with a non-exhaustive list of CAS numbers provided as guidance to assist the regulated community. The TURA program's approach to categories has generally been based on the approach used under the federal Emergency Planning and Community Right-to-Know Act (EPCRA).

Defining a chemical category is appropriate in a number of circumstances, and can provide several advantages compared with listing chemicals individually. Advantages to use of categories include avoiding adverse substitutions; providing clear information to users in the absence of a defined list of CAS numbers; and addressing a set of chemicals with similar health or environmental effects together.

Adverse substitutions:
One important reason to create a chemical category is to address concerns related to adverse substitutions. If a large group of chemicals that are structurally similar may potentially be used as substitutes for one another, regulating them one at a time can create unintended consequences, in which a more-regulated chemical may be replaced by an equally hazardous, less-regulated chemical. Creating a category provides clear guidance to chemical users, and helps to avoid such adverse substitutions.

Incomplete set of CAS numbers:
A chemical category is also helpful when specific CAS numbers do not adequately capture the chemicals of concern. For example, if there are a number of theoretical compounds in a category, and many of them do not yet have CAS numbers, then a category defined through chemical structure and descriptive text is more informative than a list of specific chemicals.

Similar hazards across a group:
A category is also useful when a number of structurally similar chemicals have, or are reasonably anticipated to have, similar health or environmental impacts. This makes it possible to proactively address these hazards by addressing the group of chemicals together.

The proposed C1-C4 NOL category meets all the criteria described above. A number of the chemicals may be reasonably anticipated to be used as substitutes for one another; for example, solvents may be used as substitutes for other solvents, and refrigerants may be substituted for one another or used together in mixtures. A number of possible compounds exist for which CAS numbers have not been generated. Across the group of chemicals, specific health and environmental impacts (e.g. neurotoxicity) appear frequently.

By defining and listing a C1-C4 NOL category, the TURA program can efficiently address this group of chemicals. The TURA program can provide clear, proactive guidance to businesses that may be considering newly adopting chemicals in this category that are not yet on the market or not yet widely used.

A TURA Advisory Committee member asked about the feasibility of narrowing the proposed category to cover a single end use. For example, a category could be created only for those chemicals used as solvents or only for those used as refrigerants. TURA program staff investigated this possibility, but found that because many of the chemicals are used for multiple applications, it would not be possible to categorize them by end use. A number of chemicals have both solvent and refrigerant applications, as well as other applications, such as use as blowing agents or as intermediates.

Avoiding adverse substitutions

A number of chemicals in the C1-C4 NOL category are likely to have functional properties similar to those of solvents currently on the market. In the absence of a category designation, this could lead to adverse substitutions.

During its evaluation of n-propyl bromide (1-bromopropane or nPB), the SAB observed that its isomer, 2-bromopropane, was present as a contaminant. 2-bromopropane is more toxic, but is not listed under TURA. The SAB was concerned that businesses could begin using unlisted short-chain halogenated hydrocarbons with similar functional properties, such as 2-bromopropane. This concern about substitution was the original impetus for the SAB to examine other halogenated hydrocarbons and propose creation of this category.

Another example is 1,2-trans-dichloroethylene. Both the trans isomer of this chemical, and a mixture of the trans and cis isomers are listed under TURA. However, the cis isomer on its own is not listed. This could be an example of a future adverse substitution, if the cis isomer were to be marketed individually.

Clarity for filers

The TURA program designated TCE, PCE, methylene chloride and nPB as Higher Hazard Substances in 2007, 2009, 2013, and 2015, respectively (effective 2008, 2010, 2014, and 2016, respectively). Since some chemicals in the C1-C4 NOL category may be used interchangeably with or developed to replace these solvents in some applications, listing the category will communicate a consistent message to users of TCE, PCE, methylene chloride, and n-propyl bromide.

TURA program services

For businesses using chemicals in the C1-C4 NOL category for solvent applications, the TURA program can draw on its broader experience with solvent alternatives, providing assistance to any businesses interested in testing and adopting safer alternatives. Several on-going program activities would help meet the demand for services.

Both the Office of Technical Assistance and the TURI Laboratory have significant experience helping large and small users identify safer solvent alternatives 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 chemicals in the C1-C4 NOL category presents an on-going challenge for companies with respect to shifting to safer alternatives, TURI could support R&D to find feasible solutions.

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 chemicals in the C1-C4 NOL category.

Fees and planning-related costs. Although the proposed category includes a potentially large number of chemicals, the total number of expected filers (10-20) is relatively small.
There would be some additional cost to companies that would begin reporting C1-C4 Halogenated Hydrocarbons, including preparing annual toxics use reports and biennial toxics use reduction plans, and paying toxics use fees. All current Tier II filers are already filing under TURA for other chemicals, so they would not incur a base fee due to this listing. They 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 the C1-C4 NOL category, 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 who is knowledgeable about methods for reducing the costs and liabilities of toxics use. Additionally, through the process of planning and reducing or eliminating use of chemicals in the category, companies may be able to expand their markets, better comply with other regulations and reduce their overall regulatory burden.

If a facility exceeds the reporting threshold for the C1-C4 NOL category due to a one-time charging of a refrigeration system, this is unlikely to occur in consecutive years, so it is possible they would not need to complete a TUR Plan.

The total additional cost in fees to filers (and revenue to the program) could be $11,000 to $22,000 in per-chemical fees (10-20 filers for C1-C4 NOL). No new base fees are estimated at this time.

Appendix 1: C1-C4 Halogenated Hydrocarbons/Halocarbons: Theoretical Universe

Halogens

Any combination of Cl, Br, F, I

Hydrocarbons | **Examples of halogenated compounds**

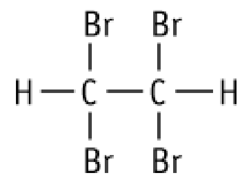
Simple unbranched alkanes (Single carbon bonds)

C1: - methane

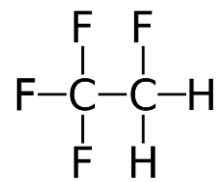
C2: - ethane

C3: - propane

C4: - butane



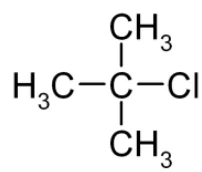
tetrabromoethane



1,1,1,2-Tetrafluoroethane (R-134a)

Branched alkanes

Add methyl or ethyl groups

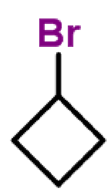


2-chloro-2-methyl propane

Cyclic alkanes (Single carbon bonds)

C3: cyclopropane

C4: cyclobutane



bromocyclobutane

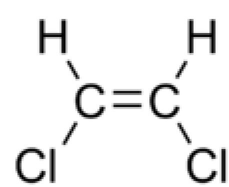
Alkenes (Double C bonds) (olefins)

C2: Ethylene

C3: propene or propylene (one double bond, 1 single bond)

C4: butene or butylenes (with one double bond, 2 single bonds)

C4: butadiene (2 double bonds, 1 single bond)



cis-1,2-dichloroethylene

Alkynes (triple C bond) (not commercially available)

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[4] Jebens A et al. 2014. *Chemical Economics Handbook: Fluorocarbons.* IHS Chemical, p. 26.
[5] Jebens A et al. 2014. *Chemical Economics Handbook: Fluorocarbons.* IHS Chemical.
[6] Massachusetts Toxics Use Reduction Institute, "Massachusetts Chemical Fact Sheet: Trichloroethylene (TCE).
[7] Will, Ray. "Refrigerants ain't what they used to be." *IHS Chemical Week* September 19/26, 2016, p. 31.
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[9] Massachusetts Clean Energy and Climate Plan for 2020: An Integrated Porfolio of Policies. New Policy: Stationary Equipment Refrigerant Management. Accessed at http://www.mass.gov/eea/docs/dep/air/climate/refpolicy.pdf, September 20, 2017.
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[12] Unless otherwise noted, information on carbon dioxide systems is drawn from Australian Institute of Refrigeration, Air Conditioning and Heating. 2007. *Natural Refrigerants: Case Studies.*
[13] Australian Institute of Refrigeration, Air Conditioning and Heating. 2007. *Natural Refrigerants: Case Studies.*
[14] Australian Institute of Refrigeration, Air Conditioning and Heating. 2007. *Natural Refrigerants: Case Studies.*
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[17] Environmental Leader. March 23, 2015. "VW Using CO2 in Air Conditioning Systems" https://www.environmentalleader.com/2015/03/vw-using-co2-in-air-conditioning-systems/
[18] German Environment Agency. "Global Warming Potential (GWP) of certain substances and mixtures that contain such substances, based on the Fourth Assessment Report of the Intergovernmental Panel on Climate Change and a hundred years time period." May 2017.
[19] For more information, see: https://www.epa.gov/sites/production/files/documents/RealZeroDesigningOutLeaks.pdf
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