California Environmental Protection Agency

Air Resources Board

ENVIRONMENTAL IMPACT ASSESSMENT OF SELECTED HALOGENATED CHEMICALS

STAFF REPORT

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California Environmental Protection Agency

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Disclaimer:

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Executive Summary

This document presents the Air Resources Board (ARB) staff's evaluation of the potential environmental impacts associated with granting volatile organic compound (VOC) exemptions in the ARB's Consumer Products Regulations for five types of halogenated chemicals (nine chemicals in total). The nine chemicals, which ARB has been petitioned to provide VOC exemptions for, are listed in Table ES-1, below.

Table ES-1. List of Compounds Requested for Exemption

Compound	Chemical Name	CAS Number
HCFC-225ca HCFC-225cb	3,3-Dichloro-1,1,1,2,2-pentafluoropropane 1,3-Dichloro-1,1,2,2,3-pentafluoropropane	422-56-0 507-55-1
HFC-245fa	1,1,1,3,3-Pentafluoropropane	690-39-1
HFC-365mfc	1,1,1,3,3-Pentafluorobutane	406-58-6
HFC-43-10mee	1,1,1,2,3,4,4,5,5,5-Decafluoropentane	138495-42-8
HFE-7100 HFE-7200	1,1,1,2,2,3,3,4,4-Nonafluoro-4-methoxybutane & 2-(Difluoromethoxymethyl)-1,1,1,2,3,3,3-hepta-fluoropropane 1-Ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane & 2-(Ethoxyfluoromethyl)-1,1,1,2,3,3,3-hepta-fluoropropane	163702-07-6 163702-08-7 163702-05-4 163702-06-5

As was the case with the environmental impact assessment prepared for tertiary-butyl acetate (TBAC) (ARB, 2006a), the environmental impact assessment of the chemicals listed in Table ES-1 was conducted in close coordination with several California Environmental Protection Agency (Cal/EPA) boards, departments, and offices with expertise in health, water quality, and hazardous waste issues. This document presents a brief summary of the relevant findings. The details of the assessment methodologies used in the evaluation can be found in the TBAC report, available online at http://www.arb.ca.gov/research/reactivity/reactivityexemption.htm.

This assessment relies on data available in the literature, as well as information submitted by the petitioners, to evaluate the possible impacts of increased usage of the above halogenated chemicals on the atmosphere, water, soil, economy, and public health, should VOC exemptions be recommended. Staff found that an exemption for these chemicals from the ARB's Consumer Products Regulations and the Districts' respective VOC definitions could be expected to have positive economic impacts on businesses by providing additional reformulation or substitution alternatives. Staff also determined that the potential risk to surface waters and soil is expected to be low, although the conclusion is uncertain due to the lack of multimedia impact data.

As to atmospheric impacts, a significant health concern in many areas of California is elevated ground-level ozone concentrations. For the Consumer Products Regulations, the primary goal of a VOC exemption is to provide alternatives that can replace VOC compounds which, in turn, leads to reductions in ground-level ozone concentrations. However, even though the substances evaluated in this assessment are unreactive, a significant reduction in ground-level ozone concentrations is not expected if VOC exemptions are recommended. This is because the substances evaluated are expected to replace substances that are similarly unreactive, such as HCFC-141b, for which production or import has been prohibited due to adverse impacts on stratospheric ozone.

In terms of other atmospheric impacts, increased use of the substances listed in Table ES-1 is not expected to increase the formation of secondary organic aerosols. However, two chemicals considered as part of this evaluation, HCFC-225ca and HCFC-225cb, are known to contribute to the depletion of stratospheric ozone. Further, all compounds evaluated in this report contribute to global warming to varying degrees. Specifically, their global warming potentials (GWPs) range from 59 to 1,500 times that of carbon dioxide for a time horizon of 100 years.

Based on the manner and amount of potential use, adverse health impacts are not anticipated for the substances evaluated with two exceptions. Specifically, increased use of HCFC-225ca and HCFC-225cb raises potential concern because, based on health conservative high exposure scenarios, the modeled concentration exceeded the estimated acute Reference Exposure Level by 75 percent (i.e., the Hazard Index is 1.75). A hazard index (HI) in excess of 1.0 indicates that exposures may result in adverse health effects in certain individuals. Using health-conservative assumptions, the HIs, both acute or chronic, for the other seven chemicals, i.e., HFC-245fa, HFC-365mfc, HFC-43-10mee, HFE-7100 (2 isomers), and HFE-7200 (2 isomers) are well under 1.0, indicating adverse health effects resulting from non-occupational exposures are unlikely.

Table ES-2 summarizes the adverse environmental impacts (i.e., ozone depleting potential, global warming potential, and health effects) associated with increased use of the chemicals evaluated, and staff's recommendation as to if a VOC exemption should be granted. As indicated in the table, both HCFC-225ca and HCFC-225cb are known ozone depleting chemicals and their production or import will be prohibited by 2015 in the U.S. in accordance with the Montreal Protocol. More recently, the Parties to Montreal Protocol agree to accelerate the phase-out of production and consumption of HCFCs. As previously indicated, all the chemicals evaluated in this report contribute to global warming to varying degrees with HFE-7200 being the least potent and HFC-43-10mee the most potent. Health effects in terms of the acute hazard index are also included in the summary table as it is an important indicator of potential concern for substances considered in this evaluation. As indicated, HCFC-225ca and HCFC-225cb have an acute HI of 1.75, suggesting the potential for adverse acute health effects (non-cancer).

As mentioned above, in accordance with the Montreal Protocol, as of January 2003, HCFC-141b can no longer be produced or imported to the United States, due to its stratospheric ozone depletion potential. The U.S. EPA (2007) is considering a limited exemption process for HCFC-141b users who can demonstrate that they have insufficient access to stockpiles of HCFC-141b and cannot transition to fully developed alternatives by the January 1, 2003 phase-out deadline. HCFC-141b, an exempt VOC, has been the solvent of choice for electrical and electronic cleaning applications, where there is need for a solvent with nonflammable properties. The ongoing depletion of HCFC-141b stockpiles has created a need for alternative solvents that can serve as a sole replacement, or a replacement when used in combination with other available solvents. The halogenated chemicals evaluated in this report are potential replacements for HCFC-141b. This is relevant because ARB has established VOC content limits for electrical and electronic cleaners. Therefore, in evaluating whether an exemption for one or more of the chemicals evaluated in this report is appropriate, staff included in its analysis possible reformulation pathways for products in the electrical and electronic cleaning categories.

Our analysis concluded that, without additional VOC exempt solvent alternatives, reformulations to comply with the VOC limits may result in products posing greater environmental concerns such as toxicity or climate change. For example, this is because substances such as VOC-exempt HFC-134a (GWP 1300) are likely to be used more extensively in reformulations.

Table ES-2. Summary of Adverse Environmental Impacts of Selected Halogenated Chemicals and Exemption Recommendation

Compound	Stratospheric Ozone Depleting Potential[1]	Global Warming Potential (100 years)[2]	Health Effects (Acute Hazard Index)[3]	Exemption Recommendation
HCFC-225ca & HCFC-225cb	0.02[4] 0.03	122 595	1.75	No No
HFC-245fa	0.00	1,056	0.08	No
HFC-365mfc	0.00	794	0.01	No
HFC-43-10mee	0.00	1,640	0.47	No
HFE-7100 & HFE-7200	0.00	297 59	0.01	No Yes

1) Ozone depleting potential is defined as the total ozone destruction that results per unit mass of a species emitted per year relative to that for a unit mass emission of CFC-11.
2) Global warming potential is an index for estimating relative global warming contribution due to atmospheric emission of one kilogram of a particular greenhouse gas compared to the emission of one kilogram of carbon dioxide for a certain time horizon (IPCC, 2007).
3) Hazard index is the ratio of a hazardous air pollutant concentration divided by its Reference Exposure Level, or safe exposure level. A hazard index in excess of 1.0 indicates that exposure may result in adverse health effects in certain individuals.
4) In accordance with the Montreal Protocol, production or import of any HCFCs, including HCFC-225ca and HCFC-225cb, will be prohibited in the U.S. by 2015.

To minimize increases in emissions of high-GWP substances, while providing an alternative for HCFC-141b, staff is recommending that a VOC exemption for HFE-7200 (two isomers) be granted. As presented in this report, HFE-7200 has a relatively low GWP of 59, compared to other replacements for HCFC-141b, with no other adverse environmental or health impacts having been identified. Thus, staff believes that the exemption of this compound as a VOC in the Consumer Products Regulations provides an important alternative which minimizes climate change impacts while providing an additional reformulation option for electrical and electronic cleaning products. In addition to opening pathways to reduce the use of high-GWP electronic and electrical cleaners, granting a VOC exemption for HFE-7200 potentially provides the opportunity for other consumer products to be formulated at a lower VOC content.

Based on its assessment, staff does not recommend excluding HCFC-225ca or HCFC-225cb from the definition of VOC from the California Consumer Products Regulations for several reasons. First, there is a concern about the potential adverse health effects from use of HCFC-225ca and HCFC-225cb because exposure scenarios indicate that a HI of 1.0 could be exceeded. Second, these two substances are being phased out due to concerns over stratospheric ozone depletion. Finally, HCFC-225ca and HCFC-225cb are potent greenhouse gases. Thus, staff believes providing a VOC exemption for HCFC-225ca and HCFC-225cb would result in adverse environmental impacts.

Exemptions are also not recommended for HFC-245fa, HFC-365mfc, HFC-43-10mee, and HFE-7100 (two isomers). The basis for our recommendation is that these substances are potent greenhouse gases. Further, products for use on energized electrical and electronic equipment are not subject to VOC limits. Thus, in these niche applications, the substances evaluated in this report could be used whether or not a VOC exemption is granted. By granting an exemption for HFE-7200, an alternative to HCFC-141b is provided that minimizes potential adverse environmental impacts. Finally, providing an exemption for HFC-245fa, HFC-365mfc, HFC-43-10mee, and HFE-7100 (two isomers) could have the effect of increasing their use in categories where there are more desirable alternatives with respect to environmental impacts. Therefore, staff believes that providing a VOC exemption for HFC-245fa, HFC-365mfc, HFC-43-10mee, or HFE-7100 (two isomers) is not warranted.

We encourage the air pollution control districts in California, as they update their applicable rules, to consider this evaluation and the associated concerns. Specifically, prior to providing a VOC exemption or continuing a previously granted exemption for the substances considered in this evaluation, it is recommended that districts consider the potential health impacts, as well as global warming and ozone depleting potential of the candidate chemicals, relative to the alternatives that are currently available.

1. Introduction

This document is an assessment of the potential environmental impacts that could be expected if one or more halogenated compounds were exempted from the definition of volatile organic compound (VOC) in Air Resources Board (ARB or Board)'s and local air pollution control and air quality management districts (Districts)' regulations. It was developed in response to petitions that the ARB exclude these compounds from its definition of VOC for certain source categories. Before amending an existing regulation to include an exemption, the ARB is required by the California Environmental Quality Act (CEQA) to conduct an assessment of the environmental impacts. The purpose of this assessment is to provide the basis for an ARB staff recommendation regarding the granting of an exemption for all or a subset of the substances evaluated. As part of this assessment, impacts on the State's atmosphere, water, and soil were considered, as well as possible impacts on the health of Californians.

The United States Environmental Protection Agency (U.S. EPA), ARB, and the South Coast Air Quality Management District (SCAQMD) have all been petitioned to exempt these chemicals from their respective VOC definitions. In the mid-1990s, the U.S. EPA granted the exemptions by excluding these chemicals from its definition of VOC for purposes of federal regulations related to attaining the national ambient air quality standards (NAAQS) for ozone under Title I of the Clean Air Act (Appendix A & B). The U.S. EPA has indicated that adding these chemicals to the list of compounds excluded from its definition of VOCs is based on their negligible contribution to tropospheric ozone formation. U.S. EPA VOC exemptions are based on a comparison of the reactivity of the chemicals to that of ethane, the "benchmark" species chosen by the U.S. EPA. Data presented by petitioners in support of the petition include rate constants for their reaction with hydroxyl radicals (K_{OH} values). Shortly after the federal exemption, the SCAQMD also exempted these chemicals from its definition of VOCs in Rule 102. Rule 102 provides a blanket exemption because it is applicable to numerous categories rather than a category-by-category exemption.

After a federal VOC exemption is granted, the ARB and Districts can decide whether to grant a VOC exemption for the source categories under their respective jurisdictions. If exempted from State and local air regulations that restrict VOC content, use of these halogenated chemicals is expected to increase. Increased use is predicted in industrial and commercial/institutional applications such as aerosol applications (precision cleaning of electrical and electronic components) where the ARB has authority, and possibly other source categories that are under Districts' jurisdiction, such as selected industrial cleaning applications.

The ARB received five petitions from various companies requesting that a total of nine halogenated chemicals be exempted from the ARB's VOC definition (Appendix C through G). Table 1-1 is a list of halogenated chemicals for which exemptions have been requested. Upon receipt of these petitions, the ARB requested that the California Office of Environmental Health Hazard Assessment (OEHHA) evaluate the possible adverse health effects associated with exposure to these chemicals. In addition, the State Water Resources Control Board (SWRCB) and the Department of Toxic Substances Control (DTSC) were asked to evaluate the potential impacts on ecosystems such as surface water, ground water, and soil if such an exemption were granted.

Table 1-1. List of Halogenated Chemicals under Review

Petitioner	Compound	Chemical Name	CAS No.
AGC Chemical Americas, Inc.	HCFC-225ca	3,3-Dichloro-1,1,1,2,2-pentafluoropropane	422-56-0
	HCFC-225cb	1,3-Dichloro-1,1,2,2,3-pentafluoropropane	507-55-1
Honeywell Specialty Chemicals	HFC-245fa	1,1,1,3,3-Pentafluoropropane	690-39-1
Solvay Company	HFC-365mfc	1,1,1,3,3-Pentafluorobutane	406-58-6
DuPont Fluoroproducts	HFC-43-10mee	1,1,1,2,3,4,4,5,5,5-Decafluoropentane	138495-42-8
3M Chemicals	HFE-7100	1,1,1,2,2,3,3,4,4-Nonafluoro-4-methoxybutane & 2-(Difluoromethoxymethyl)-1,1,1,2,3,3,3-hepta-fluoropropane	163702-07-6 163702-08-7
	HFE-7200	1-Ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane & 2-(Ethoxyfluoromethyl)-1,1,1,2,3,3,3-hepta-fluoropropane	163702-05-4 163702-06-5

The purpose of this assessment is to provide the ARB with a technical evaluation of the potential impact of increased usage of these halogenated chemicals in consumer products and possibly other categories. This assessment is also intended to inform the Districts and interested parties of potential environmental impacts associated with the increased use of these halogenated chemicals. This report includes an assessment of possible environmental impacts (i.e., air, water, soil, and health) of the halogenated chemicals, an analysis of possible substitutions and exposure scenarios, and the associated potential health risks.

This assessment was conducted in a very similar manner to the environmental impact assessment of tertiary-butyl acetate (TBAC), which is the ARB's most recent comprehensive impact assessment for a VOC exemption request. Specifically, the detailed description of methodologies and assumptions that formed the basis for this report is the same as those presented in the TBAC report, which is posted at http://www.arb.ca.gov/research/reactivity/reactivityexemption.htm. Therefore, this report presents a summary of the methodology that was used, as well as the associated conclusions and recommendations.

2. Environmental and Economic Impacts

This report presents staff's analysis of the potential impacts associated with increased usage of several halogenated chemicals if exemptions from the VOC definition were recommended. The analysis considers potential impacts on the atmosphere, water, and soil, and was conducted based on information supplied by petitioners, as well as information available in the literature. In addition, the potential economic impacts associated with VOC exemptions are discussed. However, it should be noted that information regarding potential environmental impacts for the chemicals evaluated in this document is limited due to lack of data.

2.1 *Physical Properties*

Because of the recognition that CFCs are a threat to stratospheric ozone, their use in various applications has been banned or limited at the national or international level. HCFCs and HFCs have been suggested as substitute compounds. The term "HCFC" refers to hydrochlorofluorocarbons that are compounds containing hydrogen, chlorine, and fluorine; whereas "HFC" refers to hydrofluorocarbons that are compounds containing hydrogen and fluorine but no chlorine. Finally, "HFE" refers to hydrofluoroethers which are ethers containing hydrogen and fluorine.

All of these chemicals contain abstractable hydrogen atoms, and hence, they are removed to varying extents by reaction with hydroxyl radicals in the troposphere before reaching the stratosphere. In general, they react too slowly to contribute to elevated ozone levels in populated areas, but react too fast to contribute to stratospheric ozone depletion. However, there are exceptions, depending on the nature of the chemicals.

In general, halogenated chemicals offer superior non-flammability and low residual characteristics. Hence, they can be found in many different applications such as refrigeration and solvent cleaning. The nine compounds addressed in this report are expected to be predominately used in precision cleaning applications such as electrical and electronic cleaners.

2.2 *Atmospheric Impacts*

When released to the atmosphere, halogenated chemicals undergo chemical and physical transformations. The impacts of both the parent compound and its products on the formation of ground-level ozone and secondary organic aerosol, depletion of stratospheric ozone, and climate change, are discussed in the following sections.

2.2.1 Atmospheric Chemistry and Reactivity

In the atmosphere, gas-phase VOCs undergo a series of physical loss processes (wet and dry deposition), photolysis, and a series of chemical reactions, mainly with hydroxyl radicals (OH), nitrate radicals (NO_3), and ozone (O_3) (Atkinson, 1988). In the atmosphere, halogenated chemicals are expected to react primarily with hydroxyl radicals because of their abstractable hydrogen atoms and are not expected to react with ozone and nitrate radicals or to photolyze to a significant extent (Finlayson-Pitts and Pitts, 1999). Table 2-1 gives rate constants for the reaction of OH with the chemicals reviewed in the report and the atmospheric lifetimes based on the reaction rate and ambient concentration of OH (12-hour daytime average concentration of 5.0×10^6 molecule/cm^3). These data are compared to those of ethane, the reference compound used by the U.S. EPA in its VOC exemption process.

Table 2-1. Rate Constants for the Reaction of OH with Selected Halogenated Chemicals

Compound	***k*** **(298 K) ($cm^3 molecule^{-1} s^{-1}$)**	**Atmospheric Lifetime (days)**
HCFC-225ca[1] HCFC-225cb[1]	2.5×10^{-14} 8.9×10^{-15}	90 260
HFC-245fa[1]	7.0×10^{-15}	330
HFC-365mfc[1]	6.9×10^{-15}	330
HFC-43-10mee[1]	3.4×10^{-15}	680
HFE-7100[2] HFE-7200[3]	1.2×10^{-14} 6.4×10^{-14}	190 40
Ethane[4)]	2.4×10^{-13}	10
HCFC-141b	5.8×10^{-15}	400

1) Sander S.P. et al. (2006); 2) Wallington T.J. et al. (1997); 3) Christensen L.K. (1998); and 4) Atkinson R. et al. (2005).

As can be seen from Table 2-1, the rate constants for the selected halogenated chemicals are much lower than that of ethane. Thus, it is expected that these chemicals will not contribute to tropospheric ozone formation to any significant extent once emitted into the atmosphere.

The actual impact on ground-level ozone concentrations of increased usage of the halogenated chemicals as a result of a VOC exemption will depend on the amounts and identities of the chemicals that are replaced with them. If the halogenated chemicals are substituted for more reactive compounds such as toluene and xylenes, less ground-level ozone will be formed. If the halogenated chemicals are substituted for similarly unreactive compounds, such as methylene chloride, HCFC-141b, and perchloro-ethylene, no ozone reduction will occur.

2.2.2 Impacts on Secondary Organic Aerosol

Like ozone, secondary organic aerosol (SOA) results from the atmospheric oxidation of VOCs. While the oxidation of most VOCs results in ozone formation, SOA is generally formed only from the oxidation of compounds comprised of six or more carbon atoms (Seinfeld and Pandis, 1997). This is because the oxidation products must have vapor pressures that are sufficiently low to enable them to partition into the aerosol phase. Since the halogenated chemicals have no more than six carbon atoms and very low photochemical reactivity, they are not expected to generate SOA.

2.2.3 Impacts on Stratospheric Ozone Depletion

The stratospheric ozone layer shields the earth from harmful ultraviolet (UV) radiation. Depletion of the Earth's ozone layer allows a higher penetration of UV radiation to the earth's surface. The increase in UV radiation leads to greater incidence of skin cancer, cataracts, and impaired immune systems, as well as reduced crop yields and diminished ocean productivity. Because chemical reactions that form tropospheric ozone are driven by UV radiation, it is conceivable that a reduction in stratospheric ozone can also result in an increase in photochemical smog, due to the increased UV radiation.

Certain chemicals such as CFCs, which do not have tropospheric sinks and persist in the atmosphere, will diffuse high into the stratosphere where they are photolyzed by UV radiation. The photolysis reactions release chlorine or bromine atoms, which are highly reactive with ozone and establish a rapid cycle of ozone depletion (Seinfeld and Pandis, 1997). All nine of the halogenated chemicals evaluated in this report have relatively long atmospheric lifetimes so they are expected to diffuse into the stratosphere. However, some of the chemicals, i.e., HFC-245fa, HFC-365mfc, HFC 43-10mee, HFE-7100, and HFE-7200 do not have any chlorine or bromine atoms so they are not expected to contribute to stratospheric ozone depletion. However, two chemicals (i.e., HCFC-225ca and HCFC-225cb) do contain chlorine atoms so they are expected to contribute to stratospheric ozone depletion although they are not as potent as CFCs. In accordance with the Montreal Protocol, the U.S. will prohibit production and importing of any HCFCs, including HCFC-225, in the U.S. by 2015, except for use as refrigerants in equipment manufactured before January 1, 2020. No production or importing of any HCFC is allowed by 2030. In September 2007, the Parties to Montreal Protocol agree to accelerate the phase-out of production and consumption of HCFCs (U.S. EPA, 2007).

The stratospheric ozone-depleting potential of a compound emitted at the Earth's surface depends on how much of it gets to the stratosphere, its dissociation, and subsequent chemistry. The ozone depletion potential (ODP) of a compound is defined as the total ozone destruction that results per unit mass of a species emitted per year relative to that for a unit mass emission of CFC-11 ($CFCl_3$). Table 2-2 compares the ODPs for the substances evaluated in this report with the ODP of CFC-11.

Table 2-2. Ozone Depletion Potential (ODP) Derived from Two-Dimensional Models (WMO and UNEP, 2002)

Chemical	Ozone Depletion Potential
CFC-11	1.00
HCFC-225ca HCFC-225cb	0.02 0.03
HFC-245fa	0.00
HFC-365mfc	0.00
HFC-43-10mee	0.00
HFE-7100 HFE-7200	0.00 0.00
HCFC-141b	0.12

Both HCFC-225ca and HCFC-225cb are ozone-depleting compounds although their ODPs are relatively low. As mentioned above, in accordance with the Montreal Protocol, production of HCFC-225ca and HCFC-225cb will be prohibited before 2015. In California's Consumer Products Regulation, use of more than a dozen ozone-depleting compounds, including both CFCs and HCFCs, have been prohibited because of concerns regarding increased harmful UV radiation due to stratospheric ozone depletion.

2.2.4 Impacts on Climate Change

Climate change refers to a change in climate due to human activity or natural variability observed over comparable time periods. The global average surface temperature has increased over the 20th century due to increased anthropogenic emissions that absorb infrared radiation in the atmosphere (IPCC, 2001). Important emissions, known as greenhouse gases, include carbon dioxide, methane, nitrous oxide, halogenated VOCs, and tropospheric ozone. Other VOCs are minor contributors to global warming. Thus, the halogenated compounds evaluated in this report are expected to contribute to global warming since they are greenhouse gases.

As is the case for the ozone depletion potential, the effects of greenhouse gases are partly dependent on their lifetimes in the atmosphere. Global warming potentials (GWP) are an index for estimating relative global warming contribution due to atmospheric emission of a kg of a particular greenhouse gas compared to the emission of a kg of carbon dioxide. GWPs are calculated for different time horizons and show the effects of atmospheric lifetimes of the different gases. Table 2-3 summarizes direct radiative forcings calculated for these compounds, as well as relative GWPs in two different time horizons. Direct radiative forcing refers to the direct effects on the radiation balance of the atmosphere of the greenhouse gases.

The chemicals evaluated as part of this assessment contain hydrogen (shortening their tropospheric lifetimes, hence decreasing the amounts that reach the stratosphere) and/or fluorine (which does not participate in stratospheric ozone destruction. However, these chemicals are potent greenhouse gases and as such contribute to global warming. Table 2-3 indicates the atmospheric lifetimes as well as the 20 and 100-year GWP for each of the substances evaluated. The 100-year GWPs are usually the standard for comparison.

Global warming poses a serious threat to the economic well-being, public health, natural resources, and the environment of California. The potential adverse impacts of global warming include the exacerbation of air quality problems, a reduction in the quality and supply of water to the State from reduced snowpack, a rise in sea level, damage to marine ecosystems and the natural environment, and an increase in the incidences of infectious diseases, and other human health-related problems. To address the issue of global warming, on September 27, 2006, Governor Schwarzenegger signed Assembly Bill 32, known as the California Global Warming Solution Act of 2006 (Assembly Bill, 2006). This landmark bill establishes a first-in-the-world comprehensive program of regulatory and market mechanisms to achieve real, quantifiable, cost-effective reductions of greenhouse gases, including carbon dioxide, methane, nitrous oxide, hydrofluorocarbons, perfluorocarbons, and sulfur hexafluoride in an effort to reduce greenhouse gas emissions to 1990 levels by 2020.

Table 2-3. Global Warming Potentials[1] (Mass Basis) Relative to Carbon Dioxide

Chemical	Radiative Efficiency ($Wm^{-2}ppb^{-1}$)	Lifetime (years)	GWP Time Horizons	
			20 years	100 years
CO_2	1.64	~150[2]	1	1
HCFC-225ca	0.22	1.9	429	122
HCFC-225cb	0.32	5.8	2,030	595
HFC-245fa	0.28	7.6	3,380	1,056
HFC-365mfc	0.21	8.6	2,520	794
HFC-43-10mee	0.40	15.9	4,140	1,640
HFE-7100	0.31	3.8	1,040	297
HFE-7200	0.30	0.77	207	59
HCFC-141b	0.14	9.3	2,250	725

1) Data source: IPCC (2007); 2) no single lifetime can be defined for CO_2 due to different rates of uptake by different removal processes.

As part of the bill and subsequent Executive Orders issued by the Governor, the ARB is required to adopt rules and regulations to achieve the maximum technologically feasible and cost-effective greenhouse gas emission reductions for sources or categories of sources. Excluding these halogenated chemicals, with high global warming potentials, from the definition of VOC for source categories under ARB's or Districts' jurisdiction would likely result in increased use of the chemicals in California and subsequently increasing their contribution to global warming.

2.3. Multimedia Impacts

The potential environmental effects associated with the increased use of these halogenated chemicals were evaluated with respect to water and soil impacts based on their intended use, data provided by petitioners, and via a search of the literature. The available information indicates that these halogenated chemicals will likely be used as cleaning solvents in electronic and precision devices, but are not expected to be used in water-based paints or stored in underground storage tanks. These halogenated chemicals are volatile, so most emissions are probably to air and have little tendency to partition from air to soil, water, or sediment.

Based on this information and assuming the material is stored, used, and disposed in accordance with hazardous materials regulations, the potential risk to the surface waters and soil of the State is expected to be low. However, the uncertainty associated with this conclusion is large since little directly applicable information exists with respect to potential impacts on the water and soil environment.

2.4 *Economic Impacts*

As described in the TBAC report (ARB, 2006a), a regulation that exempts organic chemicals from the ARB's VOC definition could be expected to have positive impacts on California businesses that use VOCs in the production of their products. VOC exemptions would provide these businesses with alternative compounds to reformulate their products to meet VOC content requirements. Greater choices for reformulation would likely result in cost savings. If the exemptions were granted, it is not expected to cause a noticeable change in the cost or savings to any State, local agency, or school district. It also is not expected to create a cost or savings in federal funding to the State.

2.5 *Summary*

This chapter has evaluated, based on currently available data, the possible impacts of increased usage of these halogenated chemicals on the atmosphere, water, soil, and economy should VOC exemptions be recommended. Increased use of the compounds is not expected to increase the formation of secondary aerosols. The potential risk to surface waters and soil is expected to be low although the conclusion is very uncertain due to the lack of multimedia impact data. Even though the candidate substances evaluated in this assessment are unreactive, a significant reduction in ground-level ozone, a significant health concern in many areas of California, is not expected. That is because the substances evaluated in this assessment are expected to replace substances that are similarly unreactive such as HCFC-141b. Further, two chemicals considered as part of this evaluation, HCFC-225ca and HCFC-225cb contribute to the depletion of stratospheric ozone since they contain chlorine atoms. All five types of chemicals (nine individual chemical species in total) considered in this report for exemption contribute to global warming to varying degrees. Their global warming potentials are typically on the order of 59 to 1640 times that of carbon dioxide for a time horizon of 100 years. An exemption of these chemicals from the ARB's and the Districts' respective VOC definitions could be expected to have positive economic impacts on businesses.

3. Substitution and Scenario Analyses

Increased emissions of the halogenated chemicals are expected if VOC exemptions are granted. Per requirements under the California Environmental Quality Act, it is necessary to assess if significant environmental impacts could result from increased emissions. To assess their impacts, emission estimates of these chemicals that potentially could be used in California are needed. This chapter presents an analysis of possible substitutions and potential exposure scenarios.

3.1 Substitution Analysis

The categories examined in this analysis are consumer products and most of the categories where the petitioned compounds could be used are relatively small VOC emission sources such as precision cleaning of electrical and electronic components. Emission data used in this analysis were obtained from manufacturer surveys for consumer products (ARB, 2006b). Note that the survey emissions are reported data only and are not adjusted for market coverage or to reflect growth to the current year.

Emissions inventory analysis was conducted on a category-by-category basis to identify VOCs for which the nine chemicals evaluated could be substituted. The compounds considered for substitution include methylene chloride (MC), perchloroethylene (perc), trichloroethylene (TCE), and HCFC-141b. The choice of these chemicals was based on information provided by the petitioners and review of the literature. MC, perc, and TCE are potential candidates for replacement since they are toxic chemicals which are currently prohibited from use in several categories of consumer products. HCFC-141b was included because it is an ozone-depleting substance and its production has been banned in the U.S. since 2004. The compounds analyzed in this report as potential candidates for replacement by these halogenated chemicals, together with their associated Maximum Incremental Reactivity (MIR) value, are listed in Table 3-1.

Table 3-1 also shows the maximum amount, in tons per day (TPD), of MC, perc, TCE and HCFC-141b that could be replaced. This assumes “drop-in” replacement. Most of the chemicals that could be replaced by the petitioned compounds are less reactive than ethane (0.31 g O_3/g VOC) except TCE whose MIR value (0.60 g O_3/g VOC) is higher. Thus, a slight ozone benefit would be expected if TCE is replaced by any of the nine substances evaluated. However, the overall impact on reduced ozone formation is not expected to be significant.

Table 3-1. Compounds Selected as Having Potential for Replacement with the Halogenated Chemicals and their Associated MIR Values

Compounds	MIR Value ($g\ O_3/g\ VOC$)	Potential Use for Substitution (TPD)
Compounds Considered for Replacement		
Methylene Chloride (MC)	0.07[1]	0.27
Perchloroethylene (perc)	0.04[1]	1.29
Trichloroethylene (TCE)	0.60[1]	0.64
HCFC-141b	<0.01[2]	0.29
Chemicals Petitioned for Exemption		
HCFC-225ca HCFC-225cb	<0.01[2] <0.02[2]	NA
HFC-245fa	<0.01[2]	NA
HFC-365mfc	<0.01[2]	NA
HFC-43-10mee	<0.01[2]	NA
HFE-7100 HFE-7200	0.02[3] 0.10[3]	NA
Total		**2.49**

1) ARB (2003), 2) Carter (2006), and 3) 3M (1999).

As shown in Table 3-1, the total usage of these halogenated chemicals would increase by 2.49 TPD if all of the MC, perc, TCE, and HCFC-141b were replaced by the petitioned chemicals. Note that a large fraction of MC, perc, and TCE exist in the 2003 survey due to the “sell-through” period although their use is now prohibited. Nevertheless, their 2003 usage provides useful upper-bound should an exemption be granted to the substances considered in this evaluation. Table 3-2 lists the top four consumer products categories where the substitution is expected with the general purpose degreasers and electrical cleaners being the highest, followed by electronic cleaners and energized electrical cleaners (Appendix H). Adhesives and sealants contain these halogenated chemicals considered for replacement but the substitution is not likely expected in these two categories based on the substitution information provided by the petitioners. The most likely categories where the halogenated chemicals petitioned for exemption will be used to replace the four chemicals (i.e., MC, perc, TCE, and HCFC-141b) are electrical cleaners, electronic cleaners, and energized electrical cleaners. These three categories contain approximately 30 percent of the potential total substitution. For these reasons, exposure scenarios were developed for these categories, as presented in the following section.

Table 3-2. Summary of Substitution Analysis for Perchloroethylene (Perc), Methylene Chloride (MC), Trichloroethylene (TCE), and HCFC-141b in Selected Categories

Category	Chemical	Potential Use for Substitution (TPD)
General Purpose Degreasers	Perc	0.47
	MC	0.02
	TCE	0.36
	HCFC-141b	0.00
	Total	**0.85**
Electrical Cleaners	Perc	0.20
	MC	0.02
	TCE	0.20
	HCFC-141b	0.04
	Total	**0.46**
Electronic Cleaners	Perc	0.00
	MC	0.00
	TCE	0.00
	HCFC-141b	0.16
	Total	**0.16**
Energized Electrical Cleaners	Perc	0.01
	MC	0.00
	TCE	0.03
	HCFC-141b	0.10
	Total	**0.14**
Total		**1.61**

3.2 Exposure Analysis

Exposure scenarios were developed for electronic/electrical repair shops where the halogenated chemicals requested for exemption would likely be used in products to replace compounds listed in Table 3-2 if VOC exemptions were granted. The approach adopted in the analysis is similar to the TBAC near-source impact analysis for “brake shops” (ARB, 2006a) and assumes that the halogenated chemicals have similar characteristics to TBAC in terms of facility emission characteristics, usage, emission rate, and other inputs. The objective of the scenarios is to identify upper-bound or worst-case exposure scenarios. Table 3-3 lists several possible formulations using the halogenated chemicals. In addition to the halogenated chemicals requested for exemption, we expect other chemicals such as 1,1,1,2-tetrafluoroethane (i.e., HFC-134a or 134a), dichloroethylene (DCE), and perc to be used in the substitution.

Table 3-3. Possible Scenarios with the Use of the Halogenated Solvents

	Worst-case scenario			**Mid Scenario**	
Most Likely Category	Non-Aerosol	Aerosol		Non-Aerosol	Aerosol
Electronic Cleaners	100% HFC*	80% HFC		100% HFC	80% HFC
		20% 134a			20% 134a
Electrical Cleaners	85% HFC	70% HFC		75% HFC	50% HFC
	15% DCE	20% 134a		25% DCE	20% 134a
		10% DCE			30% DCE
Energized Electrical Cleaners	85% HFC	70% HFC		75% HFC	50% HFC
	15% Perc	20% 134a		25% Perc	20% 134a
		10% Perc			30% Perc

* This includes any of the nine chemicals petitioned for exemption, including HFC, HCFC, and HFE.

For the "worst case" scenarios, the electronic/electrical repair shops were assumed to use 6-8 cans per day of cleaning solvent that contains 100% HFC (e.g., HFC-245fa). The maximum annual emission rate is estimated to be approximately 2,100 lbs (i.e., 950 kg) assuming the annual operation time is approximately 3,000 hours. Therefore, an annual emission rate of 950 kg for a single facility is anticipated to represent a conservative scenario to ensure potential near-source exposures are not underestimated.

The Industrial Source Complex-Short Term3 (ISCST3), a U.S. EPA-approved regulatory model, was used in the TBAC dispersion modeling analysis (ARB, 2006a). It uses actual region-specific meteorological data with receptors placed beyond the facility fenceline. These results were derived at the nearest off-site receptor which may be either at the property line or approximately 20-30 meters from the source. Using the annual emission rate of 950 kg, the maximum annual concentration near a high use facility is estimated to be as high as 10 $\mu g/m^3$ and the maximum one-hour concentration is estimated to be approximately 2,800 $\mu g/m^3$ (ARB, 2006a).

4. Health Effects and Impacts

The preliminary evaluation by the OEHHA of the potential human health effects associated with exposure to the halogenated chemicals evaluated in this report includes a review of health impacts materials submitted by the petitioners and an update to a previous review of HFE-7100 and 7200 prepared by the OEHHA (2003). In addition, the potential health impacts associated with the estimated near-source exposures for “worst case use” facilities are briefly described.

This review indicates that the most serious data gap for all the halogenated chemicals requested for exemption was the absence of a chronic or lifetime study of the chemical’s effects. The longest studies based on OEHHA's review of the data were subchronic inhalation studies lasting 13 weeks or 90 days. Lack of a long-term chronic study is a serious data gap and prior experience shows that a chronic study in animals is needed as a predictor of the potential effects of long-term exposure in humans. Additional data gaps were the use of only one strain of one species (rat) and the small group sizes (10/sex/dose) in some studies. There were no data on neonatal rats for most of the chemicals. In the subchronic studies, rats were exposed beginning at approximately 4 to 6 weeks of age. The materials submitted for some chemicals include a developmental toxicology study.

Using the available toxicological studies, OEHHA has estimated interim health-protective acute and chronic Reference Exposure Levels (RELs) for each of the halogenated chemicals. Due to the lack of data, rather large uncertainty factors were used, particularly for HCFC-225ca and HCFC-225cb. Use of uncertainty factors complicates the interpretation of the Hazard Index (HI) but is necessary for this screening level risk assessment. The hazard index is the ratio of a hazardous air pollutant concentration divided by its Reference Exposure Level, or safe exposure level. A hazard index value that is equal to or less than 1.0 indicates that no adverse human health effects (non-cancer) are expected to occur. On the other hand, a hazard index of more than 1.0 suggests the potential for adverse health effects.

Our findings indicate that, amongst the chemicals evaluated, HCFC-225ca and HCFC-225cb are of greatest concern in that the modeled one-hour concentration exceeds the estimated acute REL (Hazard Index = 1.75). For the others, none of the modeled concentrations exceeded the interim RELs, either acute or chronic, and thus exposures to these chemicals are not likely to lead to adverse health effects. The derivation of the interim acute and chronic RELs and the calculation of acute and chronic HIs are described in Appendix I and J, and summarized in Table 4-1. The air quality modeling data were provided in Chapter 3 for one-hour maximum and annual off-site concentrations of HCFC-141b, a surrogate chemical for HFC emissions (e.g., HFC-245fa), which is being phased out and which one or more of the chemicals may replace.

Table 4-1. Estimation of Acute and Chronic Hazard Indices (HI) from Draft Interim Reference Exposure Levels (RELs)

Chemical	1 hour Conc. µg/m³	Draft Acute REL µg/m³	"Acute HI"	Annual Conc. µg/m³	Draft Chronic REL, µg/m³	"Chronic HI"
HCFC-141b	2800	-		10	-	
HCFC-225ca & HCFC-225cb	2800	1600	**1.75**	10	80	0.13
HFC-245fa	2800	33,000	0.08	10	250	0.04
HFC-365mfc	2800	370,000	0.01	10	27,000	0.00
HFC-43-10mee	2800	6000	0.47	10	1500	0.007
HFE-7100 & HFE-7200	2800	380,000	0.01	10	3000	0.003

The OEHHA's earlier assessment on HFE-7100 and HFE-7200 states that both chemicals are possible carcinogens (OEHHA, 2001). The further analysis indicates that HFE-7100 and 7200 are peroxisome proliferators. However, peroxisome proliferation in and of itself is not sufficient evidence to consider a chemical carcinogenic to humans.

5. Conclusions and Recommendations

This document presents the ARB's technical evaluation of the potential impacts associated with the increased use of nine halogenated chemicals for which VOC exemptions in the California Consumer Products Regulations have been requested. The evaluation includes an assessment of possible environmental impacts (air, water, soil, and health) from use of the halogenated chemicals, an analysis of possible substitution and exposure scenarios, and estimates of the potential associated health benefits and risks. The environmental impact assessment of the halogenated chemicals was conducted in a similar manner to the TBAC assessment, in close coordination with several California Environmental Protection Agency (Cal/EPA) organizations with expertise on health, water quality, and hazardous waste issues. The resulting conclusions are summarized below.

This assessment relies on data available in the literature, as well as information submitted by the petitioners, to evaluate the possible impacts of increased usage of these halogenated chemicals on the atmosphere, water, soil, economy, and public health, should VOC exemptions be recommended. Staff found that an exemption for these chemicals from the ARB's Consumer Products Regulations and the Districts' respective VOC definitions could be expected to have positive economic impacts on businesses by providing additional reformulation or substitution alternatives. We also determined that the potential risk to surface waters and soil is expected to be low, although the conclusion is uncertain due to the lack of multimedia impact data.

As to atmospheric impacts, a significant health concern in many areas of California is elevated ground-level ozone concentrations. In the Consumer Products Regulations, the primary goal of a VOC exemption is to provide alternatives that can replace VOC compounds which, in turn, leads to reductions in ground-level ozone concentrations. Related to this, even though the substances evaluated in this assessment are unreactive, a significant reduction in ground-level ozone concentrations is not expected. This is because the substances evaluated are expected to replace substances that are similarly unreactive, such as HCFC-141b, for which production or import has been prohibited due to adverse impacts on stratospheric ozone. In terms of other atmospheric impacts, increased use of these compounds is not expected to increase the formation of secondary organic aerosols. Two chemicals considered as part of this evaluation, HCFC-225ca and HCFC-225cb, are known to contribute to the depletion of stratospheric ozone. Further, all compounds evaluated in this report contribute to global warming to varying degrees. Specifically, their global warming potentials (GWP) range from 59 to 1500 times that of carbon dioxide for a time horizon of 100 years.

Related to potential health impacts, based on the manner and amount of potential use, adverse health impacts are not anticipated for the substances evaluated with two exceptions. Specifically, increased use of HCFC-225 isomers raises potential concern because, based on high exposure scenarios, the modeled concentration exceeded the estimated acute Reference Exposure Level (Hazard Index = 1.75). A hazard index (HI) in excess of 1.0 indicates that exposures may result in adverse health effects in certain individuals. Using very conservative assumptions, the HIs, either acute or chronic, for the other seven chemicals, i.e., HFC-245fa, HFC-365mfc, HFC-43-10mee, HFE-7100 (2 isomers), and HFE-7200 (2 isomers) are well under 1.0, indicating adverse health effects resulting from non-occupational exposures are unlikely.

Table 5-1 summarizes the adverse environmental impacts (i.e., ozone depleting potential, global warming potential, and health effects) associated with increased use of the chemicals evaluated, and staff's recommendation as to if a VOC exemption should be granted. As indicated in the table, both HCFC-225ca and HCFC-225cb are known ozone depleting chemicals and their production or import will be prohibited by 2015 in the U.S. in accordance with the Montreal Protocol. All the chemicals evaluated in this report contribute to global warming to varying degrees with HFE-7200 being the least potent and HFC-43-10mee the most potent. Health effects in terms of acute hazard index are also included in the summary table. As indicated, HCFC-225ca and HCFC-225cb have an HI of 1.75, suggesting the potential for adverse acute health effects (non-cancer).

Table 5-1. Summary of Adverse Environmental Impacts of Selected Halogenated Chemicals and Exemption Recommendation

Compound	Stratospheric Ozone Depleting Potential[1]	Global Warming Potential (100 years)[2]	Health Effects (Acute Hazard Index)[3]	Exemption Recommendation
HCFC-225ca & HCFC-225cb[4]	0.02 0.03	122 595	1.75	No No
HFC-245fa	0.00	1,056	0.08	No
HFC-365mfc	0.00	794	0.01	No
HFC-43-10mee	0.00	1,640	0.47	No
HFE-7100 & HFE-7200	0.00	297 59	0.01	No Yes

1. Ozone depleting potential is defined as the total ozone destruction that results per unit mass of a species emitted per year relative to that for a unit mass emission of CFC-11.
2. Global warming potential is an index for estimating relative global warming contribution due to atmospheric emission of one kilogram of a particular greenhouse gas compared to the emission of one kilogram of carbon dioxide for a certain time horizon (IPCC, 2007)
3. Hazard index is the ratio of a hazardous air pollutant concentration divided by its Reference Exposure Level, or safe exposure level. A hazard index in excess of 1.0 indicates that exposure may result in adverse health effects in certain individuals.
4. In accordance with the Montreal Protocol, production or import of any HCFCs, including HCFC-225ca and cb, will be prohibited in the U.S. by 2015.

As mentioned above, in accordance with the Montreal Protocol, as of January 2003, HCFC-141b can no longer be produced or imported to the United States, due to its stratospheric ozone depletion potential. More recently, the Parties to Montreal Protocol agree to accelerate the phase-out of production and consumption of HCFCs. HCFC-141b, an exempt VOC, has been the solvent of choice for electrical and electronic cleaning applications, where there is need for a solvent with nonflammable properties. This prohibition has created a need for alternative solvents that can serve as a sole replacement, or a replacement when used in combination with other available solvents. The halogenated chemicals evaluated in this report are potential replacements for HCFC-141b. This is relevant because ARB has established VOC content limits for electrical and electronic cleaners. Therefore, in evaluating whether an exemption for one or more of these replacements is appropriate, staff analyzed possible reformulation pathways for products in the electrical and electronic cleaning categories with, and without, these chemicals being exempt VOCs. Our analysis concluded that, without additional VOC exempt solvent alternatives, reformulations to comply with the VOC limits may result in products posing greater environmental concerns such as toxicity and climate change. For example, with the phase-out of HCFC-141b, substances such as VOC-exempt HFC-134a (GWP 1300) are likely to be used more extensively in reformulations.

To minimize GWP increases, while providing an alternative for HCFC-141b, staff is recommending that a VOC exemption for HFE-7200 (two isomers) be granted. As presented in this report, HFE-7200 has a relatively low GWP of 59, and no other adverse environmental or health impacts have been identified. Thus, staff believes that the exemption of this compound as a VOC in the Consumer Products Regulations provides an important alternative which minimizes climate change impacts and provides an additional reformulation option for electrical and electronic cleaning products. In addition to opening pathways to reduce the GWP of electronic and electrical cleaners, granting a VOC exemption for HFE-7200 potentially provides the opportunity for other consumer products to be formulated at a lower VOC content.

Based on its assessment, staff does not recommend excluding HCFC-225ca or HCFC-225cb from the definition of VOC from the California Consumer Products Regulations for several reasons. First, there is a concern about the potential adverse health effects from use of HCFC-225ca and/or HCFC-225cb because exposure scenarios indicate that a HI of 1.0 could be exceeded. Second, these two substances are being phased out due to concerns over stratospheric ozone depletion. Finally, HCFC-225ca and HCFC-225cb are fairly potent greenhouse gases. Thus, staff believes providing a VOC exemption for HCFC-225ca and HCFC-225cb would result in adverse environmental impacts.

Exemptions are also not recommended for HFC-245fa, HFC-365mfc, HFC-43-10mee, and HFE-7100 (two isomers). The basis for our recommendation is that these substances are potent greenhouse gases. Further, products for use on energized electrical and electronic equipment (a target application for the substance evaluated) are not subject to VOC limits. Thus, in these specialized, niche applications these compounds could be used whether or not a VOC exemption is granted. Further, by granting an exemption for HFE-7200, an alternative to HCFC-141b is provided that minimizes potential adverse environmental impacts. Finally, providing an exemption for HFC-245fa, HFC-365mfc, HFC-43-10mee, and HFE-7100 (two isomers) could have the effect of increasing their use in categories where there are more desirable alternatives with respect to the environment. Therefore, staff believes providing a VOC exemption for HFC-245fa, HFC-365mfc, HFC-43-10mee, or HFE-7100 (two isomers) is not warranted.

We encourage the air pollution control districts in California, as they update their applicable rules, to consider this evaluation and the associated concerns. Specifically, prior to providing a VOC exemption or continuing a previously granted exemption for the substances considered in this evaluation, it is recommended that districts consider the potential health impacts, as well as global warming and ozone depleting potential of the candidate chemicals, relative to the alternatives that are currently available.

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