

California Environmental Protection Agency



Air Resources Board

**ENVIRONMENTAL IMPACT ASSESSMENT
OF *TERTIARY-BUTYL ACETATE***

STAFF REPORT

January 2006

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California Environmental Protection Agency

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Appendix J. Air Resources Board, "Initial Statement of Reasons for Proposed Rulemaking Executive Summary/Staff Report: Airborne Toxic Control Measure for Emissions of the Hexavalent Chromium and Cadmium from Motor Vehicle and Mobile Equipment Coatings," Appendix C, Stationary Source Division, August 2001.

Executive Summary

This document presents the Air Resources Board (ARB)'s evaluation of the potential environmental impacts associated with granting an exemption to *tertiary*-butyl acetate from the ARB's volatile organic compound (VOC) definition. This document was developed in close coordination with several California Environmental Protection Agency (Cal/EPA) organizations with expertise on health, water quality, and hazardous waste issues and to serve as the basis for a recommendation concerning granting such an exemption.

1. What is *tertiary*-butyl acetate?

tertiary-Butyl acetate ($\text{CH}_3\text{COOC}(\text{CH}_3)_3$) is the common name for acetic acid, 1,1-dimethylethyl ester. Other names include *t*-butyl acetate, *tert*-butyl acetate, and, informally, TBAC or TBACTM. It is a colorless, flammable liquid with a camphor-like odor and an effective viscosity reducer with an intermediate flash point and vapor pressure. It is often used in organic chemistry laboratories as a solvent. Industrially, it can be used in a variety of coatings and cleaners.

2. What is the background on the VOC exemption request for TBAC?

On January 17, 1997, ARCO Chemical Company (predecessor of Lyondell Chemical Company) submitted a petition to the United States Environmental Protection Agency (U.S. EPA) requesting that the U.S. EPA add TBAC to the list of exempted compounds under its definition of VOC. The exemption was proposed on September 20, 1999 and granted on November 29, 2004 by the U.S. EPA. The final rule became effective on December 29, 2004. On February 28, 2000, Lyondell Chemical Company (Lyondell) submitted a request to the ARB that TBAC be exempted from its definition of VOC. If granted, this exemption would only apply to the ARB's consumer products source category. In California, local air pollution control and air quality management districts (Districts) have regulatory authority over most of the stationary source categories. As such, the South Coast Air Quality Management District (SCAQMD) has also been requested by Lyondell to exempt TBAC.

The rationale for a VOC exemption is based on a comparison of the reactivity of the substance in question to that of ethane, which has been considered as negligibly reactive by the U.S. EPA since 1977. Several studies have shown that under various ambient conditions, TBAC forms, on average, less than one-half as much ozone as ethane on a per-gram basis.

3. What is the process for determining whether an organic compound should be exempted from the VOC definition?

The first step in the VOC exemption process is a petition to the U.S. EPA whose decision on whether to exempt a compound from its VOC definition is based on the

tropospheric ozone formation potential of the compound relative to that of ethane, the “benchmark” VOC chosen by the U.S. EPA. A comparison of reactivity can be on either a per-gram or per-mole basis. All compounds exempted before 1994 were less reactive than ethane on both bases. Acetone was the first compound to be exempted which is less reactive than ethane on a per-gram basis, but more reactive on a per-mole basis. TBAC is similar to acetone in that it is less reactive than ethane on a per-gram, but not a per-mole basis.

In the final rule for the TBAC exemption, the U.S. EPA indicates that comparing reactivities on a per-mole basis is more appropriate than comparing them on a per-gram basis since it is more consistent with the historical use of K_{OH} values as a basis of comparison, and is arguably more environmentally protective. However, the U.S. EPA believes that the issues of comparison basis warrant a more extensive review of the overall exemption policy and its scientific bases. To address these issues, the U.S. EPA is working with the State of California and the Reactivity Research Working Group, a government/industry/academic working group established under NARSTO to identify research priorities related to VOC reactivity. Consequently, the U.S. EPA is not revising its current VOC exemption policy with the final rule for TBAC exemption.

After a federal exemption is granted, state and local agencies can decide whether or not to follow the federal recommendation. As of today, the ARB's decisions on VOC exemptions have been consistent with the U.S. EPA's recommendations. Further, several Districts have also accepted the U.S. EPA's recommendations in the past and exempted VOCs that the U.S. EPA and the ARB have exempted.

4. Why did we perform this assessment?

Under the California Environmental Quality Act (CEQA), the ARB is required to evaluate the potential adverse environmental impacts of proposed regulations. In addition to possible atmospheric impacts, such as the formation of tropospheric ozone and secondary organic aerosol, the depletion of stratospheric ozone and climate change, health, multimedia, and economic impacts need to be considered. Because this document may serve as the basis for regulatory changes concerning exempting TBAC, an integrated team was formed within the Cal/EPA to perform a comprehensive evaluation. The team included staff from the ARB, the Office of Environmental Health Hazard Assessment (OEHHA), the State Water Resources Control Board (SWRCB), and the Department of Toxic Substances Control (DTSC).

The goal of this assessment is to consider the best scientific information currently available to serve as the basis for recommending whether the ARB should exempt TBAC from its VOC definition.

5. What categories might be reformulated with TBAC if exempted?

If the ARB grants TBAC an exemption from its VOC definition, a substantial increase in the use of TBAC in California is expected. For example, TBAC may find use in consumer products such as brake cleaners where the ARB has regulatory authority as well as other source categories such as architectural coatings where the Districts have authority. The source categories studied as part of the evaluation in this document include consumer products, architectural coatings, and other smaller categories such as automobile refinishing products.

In California, the Districts have the primary legal responsibility to adopt control measures for non-vehicular sources of air pollution, including architectural coatings and other smaller categories. However, the ARB is required by the California Legislature to provide technical assistance to the Districts when appropriate. Thus, the ARB often provides guidance and assistance to the Districts, including the development of model rules such as the Suggested Control Measure for Architectural Coatings, approved by the Board in June 2000. Therefore, architectural coatings and other smaller categories were also included in this analysis.

6. What VOCs would likely be replaced if TBAC were exempted?

After performing a review of the literature and consulting with industry representatives and the SCAQMD, a number of VOCs were identified as potential candidates for TBAC substitution. In the event that TBAC is granted an exemption, TBAC may be substituted for non-exempt VOCs of higher reactivity to allow reformulated products to meet VOC limits. In addition, TBAC may be substituted for other product ingredients to enhance overall product performance.

The compounds analyzed in this report as being candidates for replacement by TBAC in the event that it is exempted include (in alphabetical order) acetone, *n*-butyl acetate; 4-chlorobenzotrifluoride (PCBTF); 2-ethoxyethyl acetate; ethyl acetate; ethyl benzene; isobutyl acetate; methyl acetate; methyl *n*-amyl ketone; methyl ethyl ketone (MEK); methyl isoamyl ketone; methyl isobutyl ketone; methyl propyl ketone; methylene chloride; perchloroethylene; propyl acetate; propylene glycol methyl ether acetate; Texanol™ (2,2,4-trimethyl-1,3-pentanediol isobutyrate), toluene; 1,1,1-trichloroethane; 1,2,4-trimethyl benzene; xylenes (*m*-, *o*-, and *p*-xylene); and several others. Although several other compounds were also proposed as candidates for replacement, they are not widely used in consumer products and other categories, according to the recent ARB industry surveys. Therefore, these compounds were not included in the analysis.

Water was also suggested as a possible candidate for TBAC substitution. After careful evaluation, it was determined that TBAC replacement for water in the categories analyzed in this report is very unlikely. Therefore, water substitution scenarios are not included in the analysis presented in this report.

7. How much TBAC would be emitted if an exemption is granted?

To assess the potential impact that an exemption would have on the use and emissions of TBAC, a TBAC substitution analysis was conducted. The analysis considered several source categories including consumer products, architectural coatings, and other smaller categories. These categories are believed to represent most of the products that could be potentially reformulated with TBAC. Both compliant and non-compliant solvent-borne products were analyzed to determine the maximum potential usage of TBAC. As part of our analysis, different percentages of substitution with TBAC are presented. The substitution analysis reflects the volume of coating that might be suitable for reformulation.

If an exemption is granted, the total potential increased usage of TBAC ranges from 33 to 54 tons per day (TPD) Statewide with the majority of the use associated with consumer products (e.g., automotive specialty products), followed by architectural coatings, and degreasing.

Our substitution analysis also indicates that the top five compounds that could be replaced by TBAC for the source categories studied are toluene, xylenes (*m*-, *o*-, and *p*-xylene), and methyl ethyl ketone. The Statewide maximum potential replacement of TBAC for these five compounds is approximately 29 TPD for solvent-borne products, representing more than half of the TBAC potentially substituted for all of the substances considered in our analysis (i.e., 29 TPD out of a total of 54 TPD).

8. What is the estimated air quality impact from an exemption?

A reduction in ground-level ozone concentrations is expected since TBAC is less reactive than most of the VOCs, on a per-gram basis, that it is likely to replace. However, TBAC may replace several less reactive VOCs such as perchloroethylene, which would result in an ozone disbenefit. The overall impact, on a per-gram basis, indicates that TBAC substitution could result in a statewide ozone reduction of as much as 80 to 140 TPD if TBAC is substituted for VOCs in solvent-borne products. This is approximately one percent of the estimated average statewide total ozone formation of 10,300 TPD in 2001. Note that the ozone benefit would be less if the potential use of TBAC is less than predicted. For example, Lyondell has indicated that the potential use of TBAC (should a VOC exemption be granted) is approximately 10 TPD in California, which would result in significantly lower statewide ozone reductions. The increased use of TBAC may raise potential health concerns resulting from elevated near-source exposures. These concerns are addressed in the sections that follow.

9. What are the toxicological concerns regarding exposure to TBAC?

TBAC has low acute inhalation, oral, dermal, and ocular toxicity, and no impacts in several short-term genotoxicity assays. No chronic, developmental, or reproductive

toxicity data are available for TBAC. Additionally, no carcinogenicity data are available for TBAC. However, based on the absence of information regarding long-term exposure, birth defects, and cancer, it is not possible to assess the potential for non-cancer adverse health effects from long-term exposure to TBAC.

TBAC has been demonstrated to be substantially metabolized to *tertiary*-butyl alcohol (TBA) in rats. Genetic toxicity data for TBA are mixed, but information from a positive genotoxicity study for TBA suggests that TBA may cause oxidative DNA damage. Further, the assays employed in the negative studies are generally insensitive to oxidative DNA damage. TBA has been shown to induce tumors in both rats and mice. This raises a concern that exposure to TBAC may result in a cancer risk to humans because of its metabolic conversion to TBA. Therefore, an inhalation unit risk factor for TBAC of $4 \times 10^{-7} (\mu\text{g}/\text{m}^3)^{-1}$ was derived by the OEHHA from the cancer potency factor for TBAC. The unit risk factor for TBAC assumes 100 percent metabolic conversion to TBA. The calculation assumed a human breathing rate of 20 m³/day, 70 percent fractional absorption, and an average human body weight of 70 kg.

It has been proposed that the TBA carcinogenicity data may not be relevant to human cancer risk assessment. However, the data are insufficient to allow the determination that the TBA carcinogenicity data are not relevant to human cancer risk assessment. Therefore, TBAC should be considered to pose a potential cancer risk to humans.

10. What are the potential environmental impacts to ecosystems such as water and soil?

The potential environmental effects of increased use of TBAC with regard to adverse impacts on water were evaluated based on its intended use, data provided by Lyondell, and a literature search. Based on this information and assuming the material is stored, used, and disposed in accordance with hazardous materials regulations, the potential risk to surface waters 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 environment. For instance, the toxicity of TBAC to a wide range of aquatic species is not known and information on exposure of aquatic species to TBAC in California through monitoring data is not available. Both types of data are needed to make a definitive conclusion with respect to aquatic organisms.

The adverse environmental fate and transport in soil have been investigated through the use of two models. The CalToxTM simulation indicates that, assuming a relatively slow default environmental breakdown rate, TBAC tends to accumulate in vadose-zone soil (upper portion of the unsaturated zone, where both air and water are present in the pore spaces), moving slowly into air and water after the initial spill. However, the Equilibrium Criterion (EQC) model analysis concludes that if discharged to soil, about 78 percent of the TBAC will evaporate. If discharged to the

atmosphere, only a fraction of one percent will partition to soil and water. The model indicates that, if TBAC is discharged to water, approximately 60 percent will evaporate with negligible accumulation in the sediment. TBAC has little tendency to partition from air to soil, water, or sediment.

However, both model analyses are associated with high uncertainty since the breakdown rates for TBAC in various environmental compartments are not known and no comparative analysis was considered for those solvents that TBAC would replace. In addition, no validation data using measured transport data are available for the relative reliability analysis of a model dependent upon assumptions and physiological parameters to predict actual environmental fates.

11. What are the potential economic impacts from an exemption for TBAC?

Positive impacts could be expected on California businesses that use VOCs in the production of their products if an exemption for TBAC is granted. An exemption would provide these businesses with an alternative compound to reformulate their products to meet the low VOC requirements. The greater choices afforded for reformulation by this exemption would likely result in innovation and cost savings. Overall, businesses are not expected to substitute TBAC for other compounds unless they find that its use would be economically advantageous. Thus, it is expected that the exemption would bring about an overall reduction in costs of compliance to businesses affected by low VOC regulations for source categories such as consumer products and architectural coatings.

12. What are the possible impacts on human health in California if TBAC is exempted?

An analysis of three possible types of exposure scenarios was conducted: 1) an estimate of a population-weighted exposure to ambient TBAC; 2) an estimate of the maximum near-source concentrations near facilities which could potentially use large amounts of products which contain TBAC; and 3) personal exposure in the "worst-case" workplace.

As previously discussed, data concerning the adverse health effects from exposure to TBAC are limited. Therefore, it is not possible to characterize the potential for non-cancer health effects resulting from the potential exposures presented in this document. However, because TBAC is metabolized to TBA and because TBA has been shown to induce tumors in both rats and mice, exposure to TBAC may result in a cancer risk to humans. Therefore, the potential cancer risk is presented for the estimated exposures.

To estimate potential cancer risk, the inhalation unit risk factor is multiplied by the assumed 70-year exposure concentration. Using the population-weighted annual average concentration of TBAC calculated for the South Coast Air Basin (SoCAB) in 1999 of $2.8 \mu\text{g}/\text{m}^3$, the excess cancer risk to people exposed for 70 years to that

concentration would be 1.12×10^{-6} or one excess cancer case per one million exposed. This translates into a lifetime population cancer burden of 11 people in the SoCAB.

People in communities near facilities with high TBAC emissions could potentially have a much higher excess lifetime cancer risk. Based on the analysis presented in this document, the estimated risks range from 4.0×10^{-8} , or less than one excess lifetime cancer case per ten million, for the lowest Automotive Refinishing Paint Booths concentration of $0.10 \mu\text{g}/\text{m}^3$ to 7.9×10^{-6} , or eight excess lifetime cancer cases per one million for the highest Automotive Refinishing Paint Booths concentration of $19.7 \mu\text{g}/\text{m}^3$. The risks associated with "Brake Shops" ranged from less than one to four excess lifetime cancer cases per one million. By incorporating the cancer risk (i.e., one excess cancer case per one million) derived from the population-weighted exposure, the estimated cancer risks range from 1 to 9 excess cancer cases for the Automotive Refinishing Paint Booths and from 1 to 5 excess cancer cases for the "Brake Shops", respectively.

The concentrations associated with indoor exposure in the workplace are much higher than the near source concentrations, ranging from 14,000 to 532,000 $\mu\text{g}/\text{m}^3$. Further, increased exposures to TBAC in the workplace are likely to occur due to replacement of other compounds such as toluene and xylenes potentially leading to substantially reduced exposures to these compounds. This information will be provided to the organizations in California that address occupational exposure-related matters.

13. What is the possible ozone benefit if TBAC is exempted?

The health benefits associated with the potential reduction of ground-level ozone concentrations due to the replacement of more reactive VOCs with TBAC was quantified. Based on a methodology similar to the ARB's staff report for the ozone standard review, approximately 11 premature deaths annually or 770 premature deaths for the 70-year duration would be avoided statewide if a one percent reduction of total ozone occurs as a result of TBAC replacing more reactive solvents. Note that the ozone benefit would be less if the potential use of TBAC is less than predicted.

14. What is the public consultative process?

The U.S. EPA, South Coast Air Quality Management and other air districts, the ARB's Reactivity Research Advisory Committee (which is comprised of over 60 representatives from industry associations, consumer product manufacturers, regulatory agencies, academia, and other interested parties), and other stakeholders have participated in the impact assessment process. The draft TBAC impact assessment report was released in June 2005. Several comments were received and are provided in Appendix A, along with staff's responses.

15. What do we recommend?

Staff recommends exempting TBAC from the definition of VOC from the California Consumer Products Regulations based on its low reactivity. However, staff will further evaluate appropriate consumer products categories that are most likely to use TBAC, to determine whether or not use in these products could pose unacceptable exposures. If staff determines that the use of TBAC in certain products could cause unacceptable exposures, we will propose appropriate mitigation measures in the Consumer Products Regulations at the time the exemption is proposed as an amendment. We further encourage the air pollution control districts in California, as they update their applicable rules, to also determine whether or not use of TBAC in certain products would pose unacceptable exposures.

1. Introduction

This document is an assessment of the potential environmental impacts of increased usage of *tertiary*-butyl acetate (TBAC) associated with the exemption of the compound from the definitions of volatile organic compound (VOC) in both the 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 a request that the ARB remove TBAC from its definition of VOC for certain source categories. Before amending an existing regulation, the ARB is required by the California Environmental Quality Act (CEQA) to conduct an assessment of the environmental impacts. 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), the ARB, and the South Coast Air Quality Management District (SCAQMD) have been requested by Lyondell Chemical Company (Lyondell) to exempt TBAC from their respective VOC definitions. 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, TBAC is expected to find use in consumer products such as brake cleaners and adhesives where the ARB has authority. It may also find use in other source categories such as architectural coatings and automotive refinishing that are under District jurisdiction.

In September 1999, the U.S. EPA proposed to revise 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 B1). The U.S. EPA has indicated that it is considering adding TBAC to the list of compounds excluded from its definition of VOCs on the basis of negligible contribution to tropospheric ozone formation. This revision is based on a comparison of the reactivity of TBAC to that of ethane, the "benchmark" species chosen by the U.S. EPA. Data presented by Lyondell in support of the petition included both rate constants for TBAC's reaction with hydroxyl radicals (K_{OH} values) and estimates of TBAC's potential to form ozone or hydrocarbon reactivity (reactivity). The U.S. EPA indicates that its TBAC exemption revision is on a per-gram basis rather than a per-mole basis and recommends that the latter approach be used for future exemptions. On November 29, 2004, the U.S. EPA granted the exemption by excluding TBAC from its definition of volatile organic compounds and the final rule became effective on December 29, 2004 (Appendix B2).

On February 28, 2000, Lyondell submitted a letter to the ARB requesting that TBAC be exempted from the ARB's VOC definition. Upon receipt of Lyondell's petition, the ARB requested that the California Office of Environmental Health Hazard Assessment (OEHHA) evaluate the possible health effects associated with exposure to TBAC. 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.

The preliminary evaluation by the OEHHA indicated that the data regarding the potential human health effects associated with TBAC are limited (Appendix C). However, TBAC has been demonstrated to be metabolized to *tertiary*-butyl alcohol (TBA). Studies have shown that TBA is a carcinogen in rats and mice. This raises a concern that exposure to TBAC may result in an increased cancer risk to humans. The SWRCB and the DTSC stated that it is not possible to perform a complete evaluation of the potential impacts of TBAC on water and soil due to the lack of data (Appendices D and E). As a result of the preliminary evaluations, the ARB, the OEHHA, and the SWRCB expressed concerns in a letter to the U.S. EPA, dated August 28, 2000, about exempting TBAC based only on a consideration of TBAC's ozone-forming potential without a comprehensive assessment of possible health and multimedia impacts (Appendix F).

The CEQA requires the ARB to evaluate the potential adverse environmental impacts of proposed regulations. In addition to atmospheric impacts, the ARB believes that the health, multimedia and economic impacts should be considered in the case of TBAC, as well as for all future VOC exemption requests. Due to the toxicity of the metabolite and unknown multimedia effects, the ARB, OEHHA, SWRCB, and the DTSC concluded that a comprehensive evaluation was required. For this purpose, an integrated team of staff from several California Environmental Protection Agency (Cal/EPA) organizations (i.e., the ARB, OEHHA, SWRCB, and the DTSC) with expertise on air quality, health, water quality, and hazardous waste issues was formed. Other stakeholders, including the U.S. EPA, air districts, and the ARB's Reactivity Research Advisory Committee have also participated in the assessment process.

The focus of this assessment is on the use of TBAC in consumer products, the source category where ARB has regulatory authority, as well as architectural coatings and other smaller categories under District jurisdiction. In California, the Districts have the primary legal responsibility to adopt control measures for non-vehicular sources of air pollution, including architectural coatings and other smaller categories. However, the ARB is required by the California Legislature to provide technical assistance to the Districts when appropriate. Thus, the ARB often provides guidance and assistance to the Districts, including the development of model rules such as the Suggested Control Measure for Architectural coatings, approved by the Board in June 2000 (ARB, 2000a). Therefore, architectural coatings and other smaller categories were also included in this analysis.

The purpose of this assessment is to provide the ARB with a thorough technical evaluation of the potential impact of increased TBAC usage in consumer products, architectural coatings, and other smaller categories to serve as the basis for a recommendation concerning a VOC exemption for TBAC. This assessment is also intended to inform the Districts and interested parties of environmental impacts associated with the increased use of TBAC. This report includes an assessment of possible environmental impacts (air, water, soil, and health) of TBAC, an analysis of

possible substitutions, development of exposure scenarios, an analysis of the population-weighted exposure, modeling analyses of near-source and indoor impacts, and the associated potential health benefits and risks. Based on the overall assessment of possible benefits and risks to the environment and people of California, staff recommends exempting TBAC from the definition of VOC in the California Consumer Products Regulations.

2. Environmental and Economic Impacts of TBAC

This chapter presents an analysis of the expected impacts of increased usage of TBAC on the atmosphere, water and soil. In addition, the potential economic impacts associated with a VOC exemption is discussed.

The analysis is based on available literature on the environmental behavior of TBAC, information supplied by Lyondell and the results of two environmental fate models. While the reactions of TBAC in the atmosphere have been studied, there are very little data on the compound's behavior in water and soil. Thus, there is significant uncertainty associated with the conclusions for those media.

2.1 Physical Properties

tertiary-Butyl acetate ($\text{CH}_3\text{COOC}(\text{CH}_3)_3$) is the common name for acetic acid, 1,1-dimethylethyl ester. Other names include *t*-butyl acetate, *tert*-butyl acetate, and, informally, TBAC or TBACTM. It is a colorless, flammable liquid and an effective viscosity reducer with an intermediate flash point and vapor pressure. It is often used in organic chemistry laboratories as a solvent. Industrially, it can be used in a variety of coatings, and cleaners because of its excellent solvency for a variety of substances including nitrocellulose, acrylic, alkyd, polyester and urethane resins. TBAC has an odor threshold of less than one part per million (ppm) and smells similar to camphor or fruit.

2.2 Atmospheric Impacts

When released to the atmosphere, TBAC will 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

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, TBAC is expected to react primarily with hydroxyl radicals and is not expected to react with ozone and nitrate radicals (Atkinson, 1994) or to photolyze to a significant extent (Calvert and Pitts, 1977).

Several measurements of the rate constant (K_{OH}) for the reaction of TBAC with hydroxyl radicals have been conducted. Smith *et al.* (1992) and Atkinson (1994) derived rate constants of 4.4×10^{-13} and $4.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively, using a relative technique at ambient temperature. In addition, Le Calve *et al.* (1997) obtained a rate constant of $5.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ using an absolute technique. Because of the higher uncertainty associated with the absolute technique, an average value of the two rate constants derived using the relative technique, i.e., $4.25 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, was recommended (Carter *et al.*, 1997). Based on the reaction rate and ambient concentration of hydroxyl radicals (12-hour daytime average concentration of 5.0×10^6

molecule/cm³), the atmospheric lifetime of TBAC was estimated to be approximately 11 days.

The products of the gas-phase reactions of TBAC with hydroxyl radicals in the presence of oxides of nitrogen (NO_x) were investigated using *in situ* Fourier transform infrared spectroscopy and gas chromatography (Tuazon *et al.*, 1998). The major products identified were acetic anhydride and acetone, with yields of ~50 and ~20 percent, respectively. Minor products included acetic acid, acetaldehyde, and unidentified organic nitrate. The potential reaction pathway was investigated and it was determined that a novel α -ester rearrangement reaction occurs through a five-member transition state. This mechanistic information, together with available chamber data, was incorporated in the development of TBAC's atmospheric reaction mechanisms (Carter *et al.*, 1997).

2.2.2 Impacts on Ground-Level Ozone Formation

Tropospheric or ground-level ozone is formed from the gas-phase reactions of VOCs and NO_x in sunlight. Because the reaction rate and chemical mechanism rely primarily on the type of VOC, a chemical's ability to form ozone, defined as "reactivity", can vary by several orders of magnitude. While most VOCs react in the atmosphere and contribute, in varying degrees, to ground-level ozone formation, some VOCs such as chlorofluorocarbons (CFCs) and methane either do not react or react very slowly, thus making a negligible contribution to ozone formation. In recognition of their negligible effects on ozone formation, the U.S. EPA, as well as the ARB, have exempted certain VOCs from selected VOC control regulations.

Several methods have been proposed to assess the ozone-forming potential of a VOC. The reaction rate (K_{OH}) of a VOC with hydroxyl radicals on a per-mole basis is relatively straightforward since the reactions with hydroxyl radicals predominate for most atmospherically important VOCs. As discussed earlier, the recommended reaction rate for TBAC is $4.25 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ on a per-mole basis, which is approximately 1.6 times greater than that of ethane ($2.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$), the reference compound used by the U.S. EPA in its VOC exemption process. However, the reaction rate for TBAC on a per-gram basis is approximately half of ethane since the molecular weight of TBAC is almost four times greater than that of ethane.

Another method to characterize atmospheric reactivity was developed by Carter (1994). Carter's approach uses incremental reactivity scales to estimate a VOC's effect on ozone formation under conditions more representative of polluted urban atmospheres. Incremental reactivity is defined as the change in ozone caused by adding small amounts of a test VOC to the base case emissions. The scenarios employed in calculating incremental reactivity are those derived by the U.S. EPA for a series of single-day EKMA (Empirical Kinetic Modeling Approach) box models representing 39 different ozone exceedence areas around the United States. As discussed and recommended by Carter (1994), among the eighteen reactivity scales that have been developed, the Maximum Incremental Reactivity (MIR) scale is the most appropriate for

VOC control regulations for ozone reduction. The ARB uses MIR values as the measure of reactivity in the California Low Emission Vehicles/Clean Fuels (ARB, 1990) and Aerosol Coatings (ARB, 2000b) regulations. The MIR estimates are derived by adjusting NO_x input so that the final ozone is most sensitive to changes in VOC emissions.

To calculate a VOC's MIR, it is necessary to have a chemical mechanism that describes its reactions in the atmosphere. A series of environmental chamber experiments and computer model calculations were carried out to assess the atmospheric ozone formation potential of TBAC (Carter *et al.*, 1997). Despite its simple structure, the atmospheric reaction mechanism for TBAC is relatively complex. Several alternative chemical mechanisms were proposed and tested against the experimental chamber data. The mechanisms most consistent with the chamber data were used to calculate the atmospheric ozone impact of TBAC. The estimated MIR value for TBAC is 0.24 grams of ozone per gram of VOC (g O₃/g VOC) while ethane's MIR is 0.35 (g O₃/g VOC), indicating that the atmospheric ozone impact of TBAC is less than that of ethane on a per-gram basis. However, on a per-mole basis, the MIR of TBAC is 2.7 times greater than that of ethane due to the difference of molecular weights. It was also noted that the differences of reactivity estimates for TBAC derived under different atmospheric conditions and quantification methods are small.

In response to the concern that the single box model used in reactivity estimates lacks physical details such as pollutant transport and meteorology, a multiday, 3-dimensional airshed model was used to estimate the incremental reactivity (IR) of the ozone-forming potential for TBAC under various scenarios (Khan *et al.*, 1999). The averaged relative reactivity ratio of TBAC to ethane was 0.64, slightly lower than the ratio of MIRs (0.69). Derwent *et al.* (1995) calculated the photochemical ozone creation potential (POCP) of TBAC using a United Kingdom photochemical trajectory model with a Master Chemical Mechanism. The estimated POCP ratio of TBAC to ethane was approximately 0.53. Note that both of the studies compared the reactivity of TBAC to that of ethane on a per-gram basis.

The reaction rates of TBAC and ethane with hydroxyl radicals and their reactivity estimates are summarized in Table 1. It can be seen that TBAC is more reactive than ethane on a per-mole basis and less reactive on a per-gram basis under different atmospheric conditions. The ratio of reactivity of TBAC to ethane ranges from 0.42 to 0.69 on the per-gram basis while the ratio ranges from 1.57 to 2.65 on the per-mole basis.

The actual impact on ground-level ozone concentrations of increased usage of TBAC as a result of a VOC exemption will depend on the amounts and identities of the chemicals that are replaced with TBAC. If TBAC is substituted for more reactive compounds such as toluene, xylenes, and methyl ethyl ketone, less ground-level ozone will be formed. If TBAC were substituted for less reactive compounds, such as perchloroethylene, more ozone will be formed. To allow a qualitative estimation of the effects of increased TBAC usage, Chapter 4 presents a summary of possible substitution scenarios for various

categories. Based on that analysis, increased use of TBAC due to an exemption could result in an ozone reduction of as much as 140 tons/day on a Statewide basis.

Table 1. Reactivity Estimates of TBAC and Ethane

Reactivity Scale	TBAC	Ethane	Ratio (TBAC/Ethane)
K_{OH} (Atkinson, 1994) cm ³ gram ⁻¹ ·s ⁻¹ cm ³ molecule ⁻¹ s ⁻¹	2.28 x 10 ⁹ 4.25 x 10 ^{-12*}	5.37 x 10 ⁹ 2.7 x 10 ⁻¹³	0.42 1.57
MIR (Carter <i>et al.</i>, 1997) gram O ₃ /gram VOC mole O ₃ /mole VOC	0.24 27.88	0.35 10.52	0.69 2.65
IR (Khan <i>et al.</i>, 1999) gram O ₃ /gram VOC	0.70	1.10	0.64
POCP (Derwent <i>et al.</i>, 1995) gram O ₃ /gram VOC	6.5	12.3	0.53

* Average value is used.

2.2.3 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. TBAC has six carbon atoms and its primary photochemical products are acetic anhydride and acetone, which represent 70 percent of the products. Both acetic anhydride and acetone are highly volatile and are not expected to contribute to the formation of SOA. Thus, TBAC is not expected to generate SOA although no direct measurements of SOA resulting from TBAC exist in the literature.

2.2.4 Impacts on Stratospheric Ozone Depletion

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 halogen atoms (e.g., chlorine), which are highly reactive with ozone and establish a rapid cycle of ozone depletion (Seinfeld and Pandis, 1997). In spite of its low reactivity, TBAC does react in the troposphere with an atmospheric lifetime of approximately 11 days. Thus, TBAC is not expected to diffuse into the stratosphere. Further, since TBAC does not have any halogen atoms, it is not expected to contribute to stratospheric ozone depletion.

2.2.5 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). The primary greenhouse gases

include carbon dioxide, methane, nitrogen oxides, halogenated VOCs, and tropospheric ozone. Other VOCs are minor contributors to global warming. Thus, TBAC is not expected to contribute to global warming to a significant extent. Further, the products of TBAC's reactions in the atmosphere are also not expected to significantly contribute to global warming.

2.3 Multimedia Impacts

Multimedia impacts (e.g., ground water, surface water, and soil) associated with the potential use of TBAC have been investigated and are summarized in the following subsections.

2.3.1 Water Impacts

The potential environmental effects associated with the increased use of TBAC were evaluated with respect to water impacts. Specifically, the potential adverse impacts on water were evaluated based on TBAC's intended use, data provided by Lyondell, and via literature search. Lyondell has indicated that TBAC will likely be used as a formulation solvent in architectural coatings, printing inks, and adhesives but is not expected to be used in water-based paints or stored in underground storage tanks. 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 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 environment (Appendices D and G). For instance, the toxicity of TBAC to a wide range of aquatic species is not known and information on exposure of aquatic species to TBAC in California through monitoring data is not available. Both types of data are needed to make a definitive conclusion with respect to aquatic organisms.

2.3.2 Soil Impacts

The environmental fate and transport of TBAC in soil has been investigated using the CalTox™ model (Appendix E) and the EQC (Equilibrium Criterion) evaluative model (Lyondell, 2000). Both the CalTox™ and the EQC models use the physical and chemical properties of a chemical to predict its environmental fate and transport and its average exposure to humans over a specified exposure duration.

CalTox™ is a time-dependent multi-compartment model. The CalTox™ simulation indicates that assuming a relatively slow default environmental breakdown rate, TBAC tends to accumulate in vadose-zone soil (the upper portion of the unsaturated zone, where both air and water are present in the pore spaces), moving slowly into air and water after the initial spill. After 1,000 days, the TBAC concentration is halved with over 99 percent of the remaining compound in the vadose zone. Of the predicted average daily dosage to humans, about two-thirds is from ingestion of products grown in contaminated soil with one-third from the inhalation of vapors from the soil. The ground water pathway contributes insignificantly to the total daily dose.

The EQC model analysis conducted by Webster and Mackay (Lyondell, 2000) concludes that if discharged to soil, about 78 percent of the TBAC will evaporate. If discharged to the atmosphere, only a fraction of one percent will partition to soil and water. If discharged to surface water, approximately 60 percent will evaporate with negligible accumulation in the sediment. In summary, TBAC has little tendency to partition from air to soil, water, or sediment.

Both analyses are associated with high uncertainty since the breakdown rates for TBAC in various environmental compartments are not known. No comparative analysis was considered between current products that could be reformulated with TBAC and future TBAC-based products. In addition, no validation data using measured transport data are available for the relative reliability analysis of a model dependent upon assumptions and physiological parameters to predict actual environmental fates.

2.4 Economic Impacts

A regulation that exempts TBAC 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. An exemption would provide these businesses with an alternative compound to reformulate their products to meet the low VOC requirements. The greater choices afforded for reformulation with an exemption would likely result in innovation and cost savings. In addition, businesses are likely to develop complying formulations sooner than would be the case in the absence of a VOC exemption for TBAC. This is because, under exemption TBAC would not be considered a VOC, thus allowing products reformulated to contain TBAC to meet lower VOC limits. Overall, businesses are not expected to substitute TBAC for other compounds unless they find that its use would be economically advantageous. The cost of TBAC is expected to be comparable with major substituted compounds. Thus, it is expected that the exemption would bring about an overall reduction in costs of compliance to businesses affected by low VOC regulations for source categories such as architectural coatings, consumer products, degreasing, etc.

A VOC exemption for TBAC, however, may have adverse economic impacts on some suppliers that currently supply raw materials for existing solvent- and waterborne products. These suppliers may experience a reduction in demand for their compounds if demand for TBAC increases significantly. This adverse impact is likely to be insignificant because most suppliers of TBAC also supply the substituted compounds.

In addition, a VOC exemption for TBAC would have an overall positive impact on California employment, business competitiveness, and business status. Since the exemption would allow greater flexibility in reformulation of VOC content products, manufacturers that choose to use TBAC are expected to experience lower compliance costs. The cost savings, whether they are kept by affected businesses or passed on to consumers in the form of lower prices, would result in an improvement in California business competitiveness and an expansion of output and employment in the affected industries or other related industries.

If the exemption is granted, it is not expected to cause a noticeable change in the cost or savings to any State, local agency, or school district. Neither is it 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 TBAC on the atmosphere, water, soil and economy of the State. Increased use of the compound is not expected to increase the formation of secondary organic aerosol, depletion of stratospheric ozone or contribute to global warming. Substitution of TBAC for more reactive compounds would result in the reduction of ground-level ozone, a seasonal problem in many areas of California. The potential risk to surface waters and soil of the State is expected to be low. However, due to the lack of data on TBAC's aquatic toxicity, breakdown rate in various environmental compartments and measured transport data, this conclusion has a large uncertainty associated with it. An exemption of TBAC from the ARB's and the Districts' respective VOC definitions could be expected to have positive economic impacts on California businesses.

3 Health Effects

This section summarizes the OEHHA's evaluation of the potential human health effects associated with exposure to TBAC. The evaluation includes an update to a previous review of TBAC prepared by the OEHHA as well as a partial review of *tertiary*-butanol (TBA) toxicity data gathered from the open literature. This evaluation also considers the potential adverse health effects resulting from the metabolism of TBAC to TBA. The following subsections summarize the available information on the acute, subchronic /chronic toxicity data on TBAC. In addition, health effects data concerning TBA including results from studies where TBA was demonstrated to cause tumors in rats and mice are discussed. Finally, this section provides an estimated inhalation unit risk value for TBAC (based on its metabolism to TBA). The complete text of the OEHHA's TBAC health effects evaluation is included as Appendix H. A peer-reviewed article on the evaluation has recently been published by Budroe et al. (2004).

3.1 Acute Toxicity

Acute inhalation TBAC toxicity studies were performed in rats at relatively high concentrations (5,000 - 5,066 mg/m³). Clinical effects included pulmonary edema and central nervous system (CNS) effects. The median lethal concentrations (LC₅₀) ranged from 1,330 mg/m³ (281 ppm) to 20,000 mg/m³ (4,211 ppm) (Industrial Biotest Laboratories Inc., 1958; Stillmeadow, Inc., 1997; Huntingdon Life Sciences Ltd., 1999). The Lowest Observable Adverse Effect Levels (LOAELs) for CNS effects ranged from 5,000 mg/m³ (1,050 ppm) to 8,878 mg/m³ (1,873 ppm).

Single dose acute oral TBAC toxicity studies in rats generated LD₅₀ values ranging from approximately 3,265 mg/kg body weight to 4,750 mg/kg body weight (Industrial Biotest Laboratories Inc., 1958; MB Research Laboratories, 1997a). A No Observable Adverse Effect Levels (NOAEL) of approximately 859 mg/kg body weight was noted for CNS effects (Industrial Biotest Laboratories Inc., 1958).

TBAC has been observed to cause mild dermal irritation in rabbits (Industrial Biotest Laboratories Inc., 1958; MB Research Laboratories, 1997b, 1997c). The dermal LD₅₀ in rabbits was cited as being greater than 2,000 mg/kg body weight (MB Research Laboratories, 1997b). TBAC did not cause delayed dermal sensitization in guinea pigs (MB Research Laboratories, 1997d). TBAC was observed to cause ocular irritation in rabbits (Industrial Biotest Laboratories Inc., 1958; MB Research Laboratories, 1997e), but was not corrosive.

3.2 Subchronic and Chronic Toxicity

No chronic TBAC exposure studies are available. However, a single subchronic (six hours/day, five days/week for two weeks) TBAC inhalation study was performed using rats (Huntingdon Life Sciences Ltd., 2000a). Animals exposed to 1,643 ppm (7,788 mg/m³) developed increased absolute and relative liver weights. An increased degree of renal cortical tubules with hyaline droplets was reported in all male treated groups; however, no statistical analysis of these data was reported.

3.2.1 Metabolism and Pharmacokinetics

TBAC has been demonstrated to be metabolized to *tert*-butanol (TBA) in rats (Groth and Freundt, 1994). Blood concentrations of TBA were slightly higher than those of TBAC at the end of a 5-hour exposure period. Forty-five minutes post-exposure, the TBAC blood concentration decreased by approximately 50 percent, but the TBA blood concentration remained unchanged.

A metabolism and pharmacokinetics study by Huntingdon Life Sciences Ltd. (2000b) exposed rats to either 100 or 1,000 ppm ¹⁴C-*tert*-butyl acetate (¹⁴C-TBAC) by inhalation for six hours. Low-dose animals excreted most of the radioactivity from the inhaled TBAC in urine. The remaining TBAC-derived radioactivity was found in feces, expired air and tissues. The primary excretion route of TBAC-derived radioactivity for high-dose animals was also urine, but a larger proportion was found in expired air compared to low-dose animals. The remaining TBAC-derived radioactivity was found in feces and tissues. A lower proportion of available radioactivity was absorbed by animals at the high dose level. The authors stated that the reduction in the proportion of radioactivity absorbed at the high dose level and the increased proportion in expired air may indicate some saturation of absorption and metabolism.

The authors concluded that TBAC metabolism appears to follow two major routes. One involved hydroxylation of the TBA portion of TBAC to produce 2-hydroxymethylisopropyl acetate, which then formed a glucuronide conjugate, or was oxidized to 2-hydroxyisobutyric acid (the major urinary metabolite). The second route was by cleavage of the ester linkage to produce TBA, which formed a glucuronide, or was oxidized to 2-hydroxyisobutyric acid.

3.2.2 Biochemical Effects and Cell Proliferation (*tert*-Butanol)

Male rats exposed to 250, 450 or 1,750 ppm TBA (six hours/day for ten days) by inhalation demonstrated a dose-dependent accumulation of protein droplets in the renal proximal tubules, an increase in renal α_2 -microglobulin ($\alpha_2\mu$) concentration in the 1,750 ppm exposure group, and a dose-dependent increase in cell proliferation in the renal proximal tubule epithelial cells (Borghoff *et al.*, 2001). These effects were not noted in female rats. Further, $\alpha_2\mu$ immunohistochemical staining in the renal proximal tubule protein droplets was slightly greater in male rats exposed to TBA as compared to control male rats, but this slight increase was not dose-dependent. The renal $\alpha_2\mu$ concentration in the 1,750 ppm group compared to controls also appears to be substantially less than that observed for the strong $\alpha_2\mu$ inducer TMP (Prescott-Matthews *et al.*, 1997), and cell proliferation was strongly induced at TBA concentrations which did not cause $\alpha_2\mu$ concentrations to increase.

Relative kidney weights (percent body weight) were significantly increased in male rats exposed to 1,750 ppm and in female rats exposed to 450 and 1,750 ppm TBA compared to controls. Male rat TBA kidney/blood ratios tended to increase from two to six hours post-exposure, while female rat TBA kidney/blood ratios tended to remain the same or decrease from two to six hours post-exposure.

Kidney TBA levels were marginally increased in male rats compared to female rats dosed once by gavage with 500 mg/kg TBA, and liver, blood and urine TBA levels were significantly increased in male animals compared to female animals (Williams and Borghoff, 2001). However, the kidney: blood ratios were not substantially different between male and female animals. Gel filtration and anion-exchange chromatography analysis of male rat kidney cytosol indicated that an a2 μ protein standard coeluted with the low-molecular-weight protein fraction (LMWPF), and ¹⁴C-TBA-derived radioactivity coeluted with a2 μ from male rat kidney cytosol. Protein dialysis studies demonstrated reversible binding between ¹⁴C-TBA-derived radioactivity and a2 μ . Incubation of *d*-limonene oxide (a known high affinity a2 μ ligand) with LMWPF isolated from ¹⁴C-TBA-treated male rat kidneys displaced ¹⁴C-TBA-derived radioactivity. Gas chromatography- mass spectrometry (GC-MS) analysis confirmed that TBA was present in this LMWPF fraction.

3.2.3 Developmental/Reproductive Toxicity

No developmental or reproductive toxicity studies are available for TBAC.

3.2.4 Genotoxicity

Negative mutagenicity results were reported by Huntingdon Life Sciences Ltd. (2000b) for TBAC when evaluated in *Salmonella typhimurium* strains TA1535, TA1537, TA98, TA100 and TA 102, and a tryptophan dependent mutant of *Escherichia coli*, strain WP2uvrA/pKM 101 (CM891) in the presence and absence of Aroclor 1254-induced rat liver with S9. TBA was also negative in *Salmonella* strain TA102 only, employing the same methodology. However, both TBAC and TBA were dissolved in DMSO, which penetrates bacterial and mammalian cell membranes readily, and is a free radical scavenger. A similar study by Williams-Hill *et al.* (1999) in which TBA induced mutations in strain TA102 used water as a carrier solvent for TBA. The use of DMSO as a carrier solvent in the study by Huntingdon Life Sciences Ltd. (2000c) is sufficiently confounding that the results of this study should be considered inconclusive.

TBAC did not induce micronuclei (indicative of chromosomal damage) in the bone marrow cells of rats exposed by inhalation (Huntingdon Life Sciences Ltd., 2000d), or induce chromosomal aberrations in human lymphocytes exposed to TBAC *in vitro* in both the absence and presence of S9 (Huntingdon Life Sciences Ltd., 2000e).

National Toxicology Program (NTP, 1995) tested TBA using several short-term genetic toxicology assays. TBA was negative in the *Salmonella*/mammalian microsomal mutation assay in the presence and absence of rat or hamster liver S9 in test strains TA98, TA100, TA1537 and TA1538. TBA also did not induce mutations in the presence and absence of rat liver S9 in the L5178Y mouse lymphoma mutation assay, and induced neither sister chromatid exchanges (SCEs) nor chromosomal aberrations *in vitro* in Chinese hamster ovary (CHO) cells in the presence and absence of rat liver S9. Additionally, TBA did not induce micronuclei (indicative of cytogenetic damage) in normochromatic erythrocytes (NCEs) obtained from male and female B6C3F₁ mice exposed to TBA in drinking water for 13 weeks.

The genotoxicity of TBA was assayed using the standard *Salmonella*/mammalian microsomal mutation assay with TA102, a strain that detects oxidative DNA damage and contains a functional *uvrB* gene, rendering it excision repair proficient (Williams-Hill *et al.*, 1999). The assay was performed in the presence of Aroclor-induced rat liver S-9, using concentrations ranging from approximately 750 to 3,750 µg/plate. TBA caused a dose-dependent increase in mutations (approximately 2-fold greater than control). The authors concluded that TBA induces a mutagenic pathway involving oxidation of DNA bases and an intact repair system.

3.2.5 Carcinogenicity

No carcinogenicity studies are available for TBAC. However, exposure to TBA, the primary metabolite of TBAC, has been demonstrated to cause tumors in rats and mice. A NTP 2-year cancer bioassay was conducted in Fischer 344 rats and B6C3F₁ mice exposed to TBA in drinking water (NTP, 1995; Cirvello *et al.*, 1995).

F-344 rats were exposed to TBA in drinking water at doses of approximately 0, 85, 195, and 420 mg/kg-day in males and 0, 175, 330, and 650 mg/kg-day in females. All treated groups of females showed a dose-related increase in kidney weight at the 15-month evaluation. Males exhibited increased kidney weight at the mid and high doses. Nephropathy was seen in all groups of treated females and caused early mortality in high exposure groups. In addition, B6C3F₁ mice of each sex were administered TBA in drinking water at doses of approximately 0, 535, 1,035, and 2,065 mg/kg-day in males and 0, 510, 1,015, and 2,105 mg/kg-day in females. Reduced survival was observed in the high dose groups.

At the 24-month termination of the NTP rat bioassay, the incidence of combined adenoma and carcinoma of the renal tubules was found to be significantly increased in the male mid dose group. The increased mortality in the male high dose group may have reduced the observed incidence of renal tumors. Renal tubule hyperplasia was elevated in all treatment groups. Although no renal tumors were observed in female rats, the incidence of renal hyperplasia was significantly elevated in the high dose group. No renal tubule adenoma or carcinoma was observed in 227 control male rats in the four studies comprising the recent NTP historical control database for drinking water studies indicating the rarity of these neoplasms in male rats. The pathogenesis of proliferative lesions of renal tubule epithelium is thought to proceed from hyperplasia to adenoma to carcinoma (Cirvello *et al.*, 1995).

In the mouse NTP bioassay, the incidence of thyroid follicular cell hyperplasia was significantly elevated in all treatment groups of males and in the mid and high dose groups of females. Follicular cell adenomas were significantly higher in high dose females. The increased incidence of renal tubule adenoma or carcinoma, combined, in male rats and of thyroid gland follicular cell adenoma in female mice is evidence of a carcinogenic response to TBA.

3.2.6 Cancer Hazard Evaluation

It has been established that TBAC is metabolized in rats to TBA (Groth and Freundt, 1994; Huntingdon Life Sciences Ltd., 2000b). Oral TBA exposure has been demonstrated to induce renal tumors in male rats (NTP, 1995). The possibility that the male rat kidney tumors observed after oral TBA exposure may be related to a TBA-a₂μ interaction resulting in a₂μ nephropathy has been raised by Borghoff *et al.* (2001) and McGregor and Hard (2001). a₂μ nephropathy is believed to only occur in male rats, and not in female rats or other species. This implies that male rat kidney tumors resulting from induced a₂μ nephropathy may not be relevant to human cancer risk assessment.

A criteria list for determining whether chemicals that induce male rat kidney tumors and may cause increased renal a₂μ production should be considered to be potential human carcinogens has been defined in an International Agency for Research on Cancer (IARC) publication (Swenberg and Lehman-McKeeman, 1999). TBA fits some of these criteria. Specifically, renal tumors, exacerbated renal tubule hyaline droplet formation, and chronic histopathological changes have only been observed in male rats. These effects have not been demonstrated in either female rats or mice.

The data indicate that it would not be appropriate to determine that the increased renal tumors observed in TBA-exposed male rats are solely due to a₂μ-induced nephropathy. That is because: 1) the dose response relationship between hyaline droplet severity and renal tumor incidence is weak; 2) increased cell proliferation is observed at TBA doses where renal proximal tubule necrosis should not be occurring because hyaline droplet concentrations are not increased; 3) positive TBA genotoxicity data exists; 4) TBA exposure has been demonstrated to cause adverse renal effects (nephropathy, inflammation, transitional epithelial hyperplasia) in female rats. Therefore, the increased renal tumor incidences observed by NTP (1995) in TBA-exposed male rats should be considered to be suitable for use in human cancer risk assessment.

McClain (2001) prepared an expert opinion for Lyondell Chemical Company regarding the increased thyroid follicular cell tumor incidence observed by NTP (1995) in female TBA-exposed mice which stated that the thyroid gland hyperplasia and neoplasia observed in the TBA-exposed animals are the consequence of microsomal enzyme induction of thyroid hormone metabolism. This opinion did not state that the female mouse thyroid tumor data was not applicable to human cancer risk assessment; however, Lyondell Chemical Company (2001) has taken the position that the above opinion indicates that the thyroid tumors observed in the high dose female mice are due to a threshold mechanism, one to which humans are much less susceptible than rodents.

However, the available mouse data does not support a threshold mechanism for TBA carcinogenicity in that species. There is no TBA cytochrome P450 induction data available for mice. The indirectly supporting evidence for cytochrome P450 induction in rats is weak. No data exists indicating that TBA results in increased thyroid stimulating hormone (TSH) or decreased thyroxine (T4) levels in either rats or mice. Additionally,

NTP (1995) noted that no evidence of thyroid follicular cell hyperplasia was observed in mice exposed orally to TBA for 13 weeks. Such hyperplasia would be a likely outcome of altered TSH or T4 levels. This information, plus the fact that positive genotoxicity data for TBA has been published, indicates that TBA should not be considered a hormonally-mediated threshold carcinogen. As such, mouse thyroid follicular cell tumor data is relevant for use in determining the potential human cancer risk from TBA exposure.

3.2.7 Quantitative Cancer Risk Assessment

The OEHHA has previously calculated an oral cancer slope factor (CSF) for TBA of $0.003 \text{ (mg/kg-day)}^{-1}$ (OEHHA, 1999). The oral TBA CSF value was calculated using data from the most sensitive species and sex; in this case, the CSF was derived from the NTP (1995) male F344 rat kidney tumor data.

A CSF of $0.002 \text{ (mg/kg-day)}^{-1}$ can be derived for TBAC, assuming 100 percent metabolism of TBAC to TBA and a molar conversion factor of 0.64 (TBA molecular weight 74.12 / TBAC molecular weight 116.16). Relatively high-dose (100 ppm) exposures to TBAC by inhalation in rats (Huntingdon Life Sciences Ltd., 2000b) indicated that greater than 95 percent of the inhaled TBAC dose was excreted in urine or feces or retained in tissues as metabolites. This calculation conservatively assumed that at the lower environmental exposure levels expected to result from TBAC commercial use, 100 percent of inhaled TBAC would be metabolized to TBA.

An inhalation unit risk value for TBAC of $4 \times 10^{-7} \text{ (}\mu\text{g/m}^3\text{)}^{-1}$ was derived from the CSF value for TBAC by assuming a human breathing rate of $20 \text{ m}^3\text{/day}$, 70 percent fractional absorption, and an average human body weight of 70 kg.

3.3 Summary

TBAC has low acute inhalation, oral, dermal and ocular toxicity, and has produced negative results in several short-term genotoxicity assays. No chronic, developmental or reproductive toxicity data are available for TBAC. Additionally, no carcinogenicity data are available for TBAC. However, based on the absence of information regarding long-term exposure, birth defects and cancer, it is not possible to assess the potential for adverse effects from long-term exposure to TBAC.

TBAC has been demonstrated to be substantially metabolized to TBA in rats (Groth and Freundt, 1994). The genetic toxicity data for TBA are mixed, but information from the positive genotoxicity study of TBA (Williams-Hill *et al.*, 1999) suggests that TBA may cause oxidative DNA damage, and the assays employed in the negative studies are generally insensitive to oxidative DNA damage.

TBA has been shown to induce tumors in both rats and mice (NTP, 1995; Cirvello *et al.*, 1995), and OEHHA (1999) has calculated a cancer potency factor for TBA of $3 \times 10^{-3} \text{ (mg/kg-day)}^{-1}$, corresponding to an air unit risk of $9 \times 10^{-7} \text{ (}\mu\text{g/m}^3\text{)}^{-1}$. (This was part of an expedited evaluation supporting a drinking water Action Level for TBA developed by OEHHA (OEHHA, 1999) and adopted by the Department of Health Services.) This

raises a concern that exposure to TBAC may result in a cancer risk because of its metabolic conversion to TBA. . As part of the analysis presented in this document, the OEHHA has developed an inhalation unit risk factor for TBAC that considers its metabolism to TBA. Specifically, an inhalation unit risk value for TBAC of 4×10^{-7} ($\mu\text{g}/\text{m}^3$)⁻¹ was derived from the CSF value for TBAC by assuming a human breathing rate of 20 m³/day, 70 percent fractional absorption, and an average human body weight of 70 kg.

It has been proposed that the NTP (1995) TBA carcinogenicity data may not be relevant to human cancer risk assessment because 1) the male rat kidney tumors are the result of TBA-induced a2 μ nephropathy, a pathological effect specific for male rats, and 2) the female mouse thyroid follicular cell tumors may be due to an effect on thyroid hormone levels, which would have a threshold above the level of expected human exposures. However, the data pertaining to both these possibilities are insufficient to allow the determination that the NTP (1995) TBA carcinogenicity data are not relevant to human cancer risk assessment. Therefore, the OEHHA has concluded that TBAC should be considered to pose a potential cancer risk to humans.

4 Substitution Analyses

Increased emissions of TBAC are expected if a VOC exemption is granted. It is necessary to estimate the mass of TBAC that potentially could be used in California to quantify both the air quality impacts and possible exposures. This chapter presents an analysis of the potential uses of TBAC, an estimate of the resulting mass of TBAC emissions and the resultant effect on ground-level ozone formation. The ARB's emissions inventory was analyzed on a category-by-category basis to identify VOCs for which TBAC could be substituted. The product categories considered include consumer products, architectural coatings, and other smaller categories.

4.1 Categories/Chemicals

After consultation with industry representatives, the SCAQMD, and reviewing the literature, a number of VOCs were identified as potential candidates for TBAC substitution. Some of the VOCs identified as potential candidates for substitution were selected due to their greater reactivity than TBAC. Other components would potentially be replaced with TBAC to improve overall product performance. The compounds analyzed in this report as potential candidates for replacement by TBAC, together with their associated MIR value, are listed in Table 2. Because of the different solvent properties of TBAC and water, replacement of water with TBAC does not appear to be likely. Although several other compounds were also proposed as candidates for replacement, according to a recent ARB industry survey (ARB, 1996), they are not widely used in the categories considered in this analysis. Therefore, these compounds are not included in this analysis.

The categories examined in this analysis include consumer products, architectural coatings, and other smaller categories such as automobile refinishing and degreasing. Consumer products are chemically formulated products used by household and institutional consumers including, but not limited to, personal care products, aerosol coatings, automotive specialty products, detergents, cleaning compounds, and home, lawn, and garden products. Not included in the consumer product category are other paint products, furniture coatings, automotive refinishing products, and architectural coatings. These categories were analyzed separately. Architectural coatings are defined as coatings to be applied to stationary structures, portable buildings, and pavements or curbs.

Emission data used in this analysis were obtained from a variety of sources including manufacturer surveys for consumer products (ARB, 1996) and architectural coatings (ARB, 1999), and the California Emission Inventory Development and Reporting System (CEIDARS) database (ARB, 2001a). Note that the survey emissions are reported data only and are not adjusted for market coverage or to reflect growth to the current year.

Table 2. Compounds Selected as Having Potential for Replacement with TBAC and their Associated MIR Values

Compounds	MIR Value ¹ (g O ₃ /g VOC)
Acetone	0.40
<i>n</i> -Butyl Acetate	0.89
<i>tertiary</i> -Butyl Acetate ² (TBAC)	0.20
4-Chlorobenzotrifluoride (PCBTF)	0.11
2-Ethoxyethyl Acetate	1.50
Ethyl Acetate	0.64
Ethyl Benzene	2.79
Isobutyl Acetate	0.67
Methyl Acetate	0.07
Methyl <i>n</i> -Amyl Ketone	2.80
Methyl Ethyl Ketone (MEK)	1.49
Methyl Isoamyl Ketone	2.10
Methyl Isobutyl Ketone	4.31
Methyl Propyl Acetate	3.07
Methylene Chloride	0.07
Perchloroethylene	0.04
Propyl Acetate	0.87
Propylene Glycol Methyl Ether Acetate	1.71
Texanol™	0.89
Toluene	3.97
1,1,1-Trichloroethane	0.00
1,2,4-Trimethylbenzene	7.18
Xylenes	7.37
<i>meta</i> -Xylene	10.61
<i>ortho</i> -Xylene	7.49
<i>para</i> -Xylene	4.25

1. Reference: Title 17, California Code of Regulations, Article 1, section 94700-94701.
2. TBAC is included to provide a comparison of its MIR with the other compounds. TBAC's MIR of 0.20 is based on work performed by Carter in 2000 that was used in the ARB's aerosol coatings regulation. The value of 0.24 used in Chapter 2 was based on an earlier work by Carter *et al.* (1997)

4.2 Methods

Several assumptions were made in the substitution analysis presented in this section. The assumptions, which are discussed, differ for the categories evaluated as they reflect a consideration of the current information for each category (e.g., type of solvents used and how the solvents are used).

For consumer products, a drop-in replacement (one-for-one replacement) of TBAC was assumed for the substituted chlorinated VOCs such as perchloroethylene. Since the use of chlorinated solvents is currently prohibited in several automotive products such as automotive brake cleaners and engine degreasers, the use of TBAC to replace

chlorinated compounds is expected. As evidence, it has been noted that xylenes and toluene, listed as potential candidates for TBAC replacement, are already used in these automotive products in lieu of chlorinated VOCs. To obtain a plausible range of the potential use of TBAC, a range of 50 to 100 percent of TBAC replacement was considered to be reasonable based on the volume of coating that might be suitable for reformulation.

For architectural coatings, it was assumed that TBAC would be primarily used as a drop-in replacement for selected categories of compliant and non-compliant (i.e., architectural coatings that do not currently meet the limits identified in the ARB's Suggested Control Measure) solvent-borne coatings. The replacements in both compliant and non-compliant solvent-borne coatings were analyzed to determine the maximum potential use of TBAC while the minimum use of TBAC replacement was derived from the use of TBAC in non-compliant solvent-borne coatings.

For other smaller categories included in this assessment, a range of TBAC substitution from 25 to 100 percent for selected compounds was used based on the volume of coating that might be suitable for reformulation. A range of 25 to 50 percent substitutions was used for several coatings (e.g., wood furniture coatings, metal furniture coatings, metal parts and products coatings) while 100 percent substitution was used for the degreasing category.

4.3 Substitution Results

The percent of substitution and resultant use expressed in tons per days (TPD) for the different categories are presented in Table 3. Because the substitution of TBAC into waterborne products appears at this time to be less likely, only solvent-borne categories are presented. The range of potential TBAC use for each category was derived by considering both the percentage of substitution and the inclusion of compliant and non-compliant products. As previously discussed, the percent of TBAC replacement was determined based on estimates for the volume of coating that might be suitable for reformulation from a variety of sources for the categories identified in Table 3. Based on this substitution analysis, the majority of TBAC replacement in solvent-borne categories would likely be in consumer products, followed by architectural coatings and degreasing. Smaller amounts of TBAC are expected to be used in other categories since they are small categories in terms of the current use of the substances likely to be replaced with TBAC.

While 24 compounds were considered as candidates for substitution with TBAC, five compounds, i.e., the three isomers of xylenes, toluene, and MEK, account for over half of the mass of all of the substitutions in the selected categories.

Table 3. Summary of TBAC Substitution Analysis for Selected Categories Based on Pre-2002 Surveys and 2001 CEIDARS Database

Categories	Percent of Substitution	Potential Use of TBAC (TPD)	Ozone Benefit (TPD)
Consumer products	50% - 100%	13.3 - 26.6	23.5 – 47.0
Architectural coatings	100%	6.1 - 6.9	23.8 – 27.9
Degreasing	100%	6.4	8.5
Automotive refinishing*	25% - 50%	2.8 - 5.6	12.3 – 24.6
Metal furniture & parts/products	25% - 50%	2.1 - 4.2	7.4 – 14.8
Wood furniture	25% - 50%	2.1 - 4.2	7.6 – 15.1
Total		33 - 54	80 - 140

* The new 2002 survey in automotive refinishing indicates that the total emissions of xylenes, toluene, and MEK are approximately half of the emissions obtained from the previous survey (ARB, 2005b)

As presented in Table 3, the total potential increased use of TBAC was estimated to range from 33 to 54 TPD. The potential use of TBAC presented in Table 3 considers the total use of the 24 compounds listed in Table 2 for each category and the estimated percentage (i.e., percent of substitution) of those compounds potentially replaced with TBAC. The maximum potential use of TBAC (54 TPD) was obtained by considering TBAC use in both compliant and non-compliant solvent-borne products. The minimum potential usage of TBAC (33 TPD) was obtained by only considering minimum expected levels of substitution in solvent-borne products. It should be noted that the actual minimum use could be below that presented in Table 3 if substitution with TBAC does not occur for some of the analyzed categories or, for a given category, to a lesser degree than that assumed. Lyondell has indicated that the potential use of TBAC is approximately 10 TPD in California.

Table 4 shows the potential use of TBAC based on the maximum percent substitutions by source category for formulations. The right hand column gives the percent of total substitution in the category represented by these compounds. For example, in the consumer products category, xylenes, toluene, and MEK make up 40 percent of the total VOC considered to be candidates for TBAC substitution. The highest percent use of these VOCs can be found in automotive refinishing, where they represent 80 percent of the possible TBAC use. The total amount of TBAC substitution for these five compounds for solvent-borne products is approximately 29 TPD, which is more than half of the TBAC use (54 TPD) for all the substituted compounds combined for solvent-borne products.

4.4 Ozone Formation

The possible air quality impact with respect to tropospheric ozone formation was estimated based on the substitutions described in the previous sections. The scale used for this analysis, the Maximum Incremental Reactivity (MIR) scale, is briefly

discussed in Section 2.1 and the MIR values are listed in Table 2 for the compounds as being potentially replaced with TBAC. To calculate the mass of ozone produced under MIR conditions, the mass of a VOC is multiplied by the VOC's MIR. The MIR value for TBAC on a per-gram basis is lower than most of the substituted VOCs such as xylenes, toluene, and MEK, indicating that TBAC substitution could benefit air quality since it is not photochemically reactive. However, on a per-mole basis, the air quality benefit is less significant since the molar MIR value for TBAC is much higher. In addition, several VOCs including chlorinated compounds such as perchloroethylene and methylene chloride are less reactive than TBAC. Therefore, replacement of TBAC for such low reactive VOCs would result in an increase in ozone formation. The overall impact indicates that TBAC substitution could result in a statewide ozone reduction of between 80 and 140 TPD if TBAC is substituted for VOCs in solvent-borne products. This is approximately one percent of an estimated average Statewide ozone formation of 10,300 TPD in 2001 (Allen, 2002). Note that the ozone benefit would be less if the potential use of TBAC is less than the estimate presented in this document. For example, Lyondell has indicated that the potential use of TBAC is approximately 10 TPD in California, which would result in significantly lower statewide ozone reductions.

Table 4. TBAC Substitution Results for Xylenes, Toluene, and MEK in Selected Products Based on Pre-2002 Surveys and 2001 CEIDARS Database

Category	Chemical	Potential TBAC Use for Substitution of Top Five Chemicals (TPD)	Percent of Total Potential Candidates Substituted
Consumer products	Xylenes	3.4	40%
	Toluene	5.6	
	MEK	1.7	
	Total	10.7	
Architectural coatings	Xylenes	2.3	61%
	Toluene	1.2	
	MEK	0.7	
	Total	4.2	
Degreasing	Xylenes	0.4	45%
	Toluene	0.8	
	MEK	1.7	
	Total	2.9	
Automotive refinishing *	Xylenes	2.4	80%
	Toluene	1.1	
	MEK	1.0	
	Total	4.5	
Metal furniture & parts/products	Xylenes	0.6	76%
	Toluene	2.6	
	MEK	0.0	
	Total	3.2	
Wood furniture	Xylenes	0.6	79%
	Toluene	2.7	
	MEK	0.0	
	Total	3.3	
TOTAL		28.8	

* The new 2002 survey in automotive refinishing (ARB, 2005b) indicates that the total emissions of xylenes, toluene, and MEK are approximately 69% of the emissions obtained from the previous 1999 survey used in this table. Therefore, the estimates for automotive refinishing presented in Table 4 should be considered an upper bound.

5 Health Impacts

As presented in Chapter 3, the currently available data indicate that TBAC should be considered to pose a potential cancer risk to humans. Therefore, as part of the ARB's mission of protecting the health of all Californians, an analysis of three possible types of exposure was performed. The first analysis was an estimate of the population-weighted exposure to ambient TBAC. In addition, it is possible that people living near facilities that use large amounts of TBAC may be exposed to significantly higher concentrations. For that reason, near-source exposures for "high TBAC use" facilities were modeled. Lastly, while industry representatives believe that a majority of TBAC will be used in industrial settings where occupational hygiene equipment should limit workers' exposure to TBAC, there may be situations where workers are exposed to elevated levels of TBAC. Therefore, personal exposure in a "worst case" workplace was also modeled. These three exposure scenarios, which represent increasing levels of exposure, are presented in the following sections.

On the other hand, the health benefits could be expected due to the potential reduction of ground-level ozone concentrations resulting from the replacement of more reactive VOCs with TBAC. The estimated decrease in mortality due to possible reductions in ozone is presented in Section 5.6.

5.1 *Population-Weighted Exposure*

In this section, the emission inventory and air quality data were used to estimate the potential ambient concentration of TBAC. There are few or no measurements of the ambient concentration of many of the VOCs listed in Table 2 as being possible candidates for replacement with TBAC. However, ambient air quality data for toluene, xylenes (*m*-, *o*-, and *p*-xylene), and MEK are available from the ARB's air toxics monitoring network. As discussed in Chapter 4, these five compounds represent over half of the mass of the VOCs potentially replaced with TBAC. Therefore, these substances are used in this analysis as surrogates for estimating potential ambient concentrations of TBAC.

The ARB's emissions inventory and the previously described substitution scenarios were used to estimate the fraction of ambient toluene, xylenes, and MEK measured at six monitoring sites which could be replaced by TBAC. The estimated ambient concentration of TBAC and census data were then used to estimate the potential population-weighted exposure. This analysis does not take into account differences in TBAC's atmospheric chemistry or lifetime as compared to those of toluene, xylenes, and MEK. Further, this analysis was only done for the South Coast Air Basin (SoCAB) since, as the most populated and most polluted air basin in California, it has the greatest wealth of emission and air quality data.

5.1.1 Emission Inventory Data

Because the ambient measured concentrations of toluene, xylenes, and MEK reflect the emissions of these compounds from the entire emissions inventory, the first step in this analysis is to estimate the fraction of the total emissions inventory for these compounds

which might be replaced by TBAC. In order to estimate the potential ambient concentration of TBAC, 1997 emission grid-cell inventory data (Allen, 2002) were used to calculate the fraction of the total emissions of toluene, xylenes, and MEK emitted by the categories considered in our assessment. This was done by comparing the sum of the emissions data (i.e., of toluene, xylenes, and MEK) attributed to the categories considered in our assessment (i.e., consumer products, architectural coatings, and other smaller categories) to the total emissions (i.e., of toluene, xylenes, and MEK) from all source categories in the SoCAB. The resulting ratio was used to estimate the annual average concentration ($\mu\text{g}/\text{m}^3$) at each monitoring station associated with emissions of toluene, xylenes, and MEK from the categories considered in our analysis.

Assuming an average of 50 percent of these compounds (i.e., toluene, xylenes, and MEK) is replaced with TBAC (this assumption is consistent with the percent of substitution information presented in Table 3), the estimates of potential TBAC emissions for these compounds can be obtained. Accordingly, the ratios of the potential TBAC emissions to the total emissions for toluene, xylenes, and MEK were calculated to be 14, 11, and 44 percent by weight (11, 10, and 27 percent in units of ppb), respectively. These data are presented in Table 5. The ratios presented in Table 5 were used to estimate the potential concentration of TBAC that would be associated with substitutions of TBAC for toluene, xylenes, and MEK as described in this section.

As can be seen from Table 5, a substantial fraction of MEK (i.e., 44 percent) is estimated to be replaced with TBAC because MEK is primarily used as a solvent ingredient while toluene and xylenes are primarily emitted from motor vehicle-related sources. Thus, a much smaller percentage of toluene (14 percent by weight) and xylenes (11 percent by weight) are expected to be replaced by TBAC as the majority of the emissions of these chemicals are from categories that are not expected to use TBAC (e.g., motor vehicles) or are emitted from categories outside the scope of this analysis. Though the 1997 emission inventory was used for this analysis, the results are not expected to be substantially different for more recent years. Specifically, the ratios presented in Table 5 (i.e., selected categories/total inventory) are not expected to significantly change for subsequent years (i.e., 1998-2001).

Table 5. Estimates of Ratio of the Amount of Chemical Potentially Replaced with TBAC for Selected Categories to the Total Amount from All Source Categories (1997 Emission Inventory Data for the SoCAB)

Chemicals	Ratio (Selected Categories/Total SoCAB Inventory)*	
	(tons/tons)	(ppb/ppb)
Toluene	14%	11%
Xylenes	11%	10%
MEK	44%	27%

* One-half of the emissions of toluene, xylenes, and MEK used by the selected categories (i.e., consumer products, architectural coatings, and other smaller categories) in the SoCAB are assumed to be replaced with TBAC.

5.1.2 Potential Ambient Concentration of TBAC

The ARB operates an air toxics monitoring network, which consists of 21 monitoring sites throughout California. This network measures 64 pollutants including toluene, xylenes, and MEK. 24-hour toxics samples are collected on every 12th day. The sampling sites in the SoCAB are Burbank-West Palm Avenue, Los Angeles-North Main St., North Long Beach, Azusa, Riverside-Rubidoux, and Fontana-Arrow Highway.

The annual average concentration for each selected compound (i.e., toluene, *m*-xylene, *o*-xylene, *p*-xylene, and MEK) at each monitoring site in the SoCAB was extracted from the California Ambient Air Quality Data: 1980-2000 Data CD (ARB, 2002). The annual average concentration is calculated by the mean-of-monthly-means (MMM) technique. The averages of MMM of three years, i.e., 1998 to 2000, at each monitoring site were employed to account for natural year-to-year meteorological fluctuations.

Subsequently, the three-year average for each compound at each monitoring site was used to estimate the potential concentration of TBAC by multiplying the average concentration of a compound (e.g., toluene) by the applicable ratio presented in Table 5. The total potential concentration of TBAC at each site, given in Table 6, is the sum of potential concentration derived for each selected compound (i.e., toluene, *m*-xylene, *o*-xylene, *p*-xylene, and MEK) at the same site. The estimated concentration is 2.6 $\mu\text{g}/\text{m}^3$ at Azusa, 3.8 $\mu\text{g}/\text{m}^3$ at Burbank, 2.8 $\mu\text{g}/\text{m}^3$ at Los Angeles–North Main Street, 2.6 $\mu\text{g}/\text{m}^3$ at North Long Beach, 2.1 $\mu\text{g}/\text{m}^3$ at Riverside, and 2.0 $\mu\text{g}/\text{m}^3$ at Fontana. As expected, the potential concentration of TBAC is the highest at Burbank, followed by the Los Angeles-North Main St.

Table 6. Potential Annual Average Concentrations of TBAC at the Monitoring Sites in the South Coast Air Basin

Monitoring Sites	Potential Concentration of TBAC	
	(ppb)	($\mu\text{g}/\text{m}^3$)
Azusa	0.54	2.6
Burbank – West Plum Ave.	0.81	3.8
Los Angeles – North Main St.	0.59	2.8
North Long Beach	0.54	2.6
Riverside – Rubidoux	0.45	2.1
Fontana – Arrow Highway	0.43	2.0

5.1.3 Population-Weighted Annual Exposure

The potential annual average concentrations of TBAC presented in Table 6 were used with census data to calculate the population-weighted annual average concentration by interpolating between the six monitoring sites using a previously developed modeling technique (ARB, 1993). The interpolation process uses population data by census tract

and an associated centroid of population for the tract. Data for any monitoring site within 25 kilometers of the centroid is used in determining a representative concentration to which people in the census tract are exposed. In determining this representative concentration, the contribution from each monitoring site is weighted in proportion to the inverse of the square of the distance from the population centroid to the monitoring site. To determine the population-weighted exposure, the population of individual census tracts is multiplied by their representative concentration, summed over all census tracts and then divided by the total population across all census tracts. The resulting population-weighted annual average concentration calculated to represent the SoCAB in 1999 was $2.8 \mu\text{g}/\text{m}^3$ for TBAC. At 10.5 million people, this represents approximately 82 percent of the total population (12.8 million) in the SoCAB. In other words, approximately 82 percent of the total population in the SoCAB could be potentially exposed to an ambient TBAC concentration of 0.59 ppb. Note that 1990 population data were used since the 2000 census data were not readily available at the time of this analysis.

Sources of uncertainties in our analysis include uncertainties associated with the actual mass of TBAC emissions, infrequent data collection and limited sample sites (six sites) in the SoCAB and no consideration of errors introduced by the sampling system and analytical instruments. In addition, the exposure estimates assume 24 hours/day of outdoor exposure without considering indoor exposure to this compound. Caution should be exercised when applying these results for estimating the population exposure.

5.1.4 Exposure Estimate Using Perchloroethylene as a Surrogate

An alternative method to estimate ambient exposure was also evaluated. This approach uses perchloroethylene as a surrogate for estimating potential ambient TBAC concentrations since both perchloroethylene and TBAC are not photochemically reactive and would be expected to have similar emission characteristics (e.g., emitted from many sources throughout the basin). Based on recent emission inventory data (ARB, 2001b), the estimated perchloroethylene emission is 5,781 tons per year or 16 TPD in 2000 in the SoCAB, which is approximately 51 percent of Statewide perchloroethylene emissions (i.e., 11,431 tons per year). The annual average concentration of ambient perchloroethylene is 0.24 ppb or $1.62 \mu\text{g}/\text{m}^3$ from 1999 to 2000 in SoCAB (ARB, 2002). Thus, the ratio of the ambient concentration of perchloroethylene (i.e., $1.62 \mu\text{g}/\text{m}^3$) to the daily emission (i.e., 16 TPD) in the SoCAB can be calculated to be $0.10 (\mu\text{g}/\text{m}^3)/\text{TPD}$. Assuming the same ratio is applicable to TBAC, the potential ambient concentration of TBAC in the SoCAB can be estimated to range from 1.7 to $2.8 \mu\text{g}/\text{m}^3$ based on the potential usage (i.e., 17 to 28 TPD) of TBAC in the SoCAB. Note that these values (i.e., 17 to 28 TPD) are calculated by multiplying the Statewide potential TBAC of 33 to 54 TPD described in Section 4 by the same fraction (i.e., 51 percent) as used for perchloroethylene. This range is in close agreement with the population-weighted annual exposure of $2.8 \mu\text{g}/\text{m}^3$ presented in section 5.1.3.

5.2 Scenario Development for Near Source and Indoor Exposure

The ARB is committed to ensuring that environmental justice considerations are an integral part of its activities. In December 2001, the Board (2001c) adopted Environmental Justice Policies to establish a framework for incorporating environmental justice into the ARB's programs, consistent with the directives of State law. Although the Statewide exposure to TBAC is expected to be low, evaluating the potential health impacts associated with TBAC emitted from emission sources on the community level near potential emission sources is a critical part of an exemption. In the following sections, potential exposure scenarios are described based on facilities that have the potential to use large amounts of TBAC. Based on the scenarios, potential near-source and indoor exposures were estimated using modeling techniques. Finally, the estimated exposures were used to characterize possible health risks associated with the scenarios.

Exposure scenarios were developed for two source categories, automotive maintenance and repair facilities performing brake-related work ("Brake Shops") and automotive refinishing facilities performing body repair work (Automotive Refinishing Paint Booths). These facilities represent situations where relatively high exposures of TBAC could occur if, as described in Chapter 4, TBAC is substituted for perchloroethylene in brake cleaners and for toluene, xylenes, and MEK in automotive coatings. These source categories were selected for evaluation because they are believed to lead to the greatest exposures to TBAC should these substitutions occur. Therefore, these exposure scenarios were considered as plausible upper-bound estimates rather than typical exposures.

5.2.1 "Brake Shops"

The "Brake Shops" were chosen as a possible high exposure scenario because some automotive products at one time contained high concentrations of perchloroethylene, xylenes, and toluene; compounds identified as possible candidates for TBAC substitution. Thus, if an exemption for TBAC is granted, these facilities could have high use as well as high emissions of TBAC.

Table 7 provides data for several product categories and proposed substitution scenarios. The product categories include automotive brake cleaners, carburetor and choke cleaners, engine degreasers, and general-purpose degreasers. The "high use" scenarios are derived from the products where there is a potential for a high percentage of TBAC to be substituted. Specifically, this would occur if TBAC replaced all of the perchloroethylene in these products. The "moderate use" scenarios represent cases where TBAC would be substituted for xylenes and toluene.

Automotive brake cleaners were selected as a potential "high use" scenario because an Airborne Toxic Control Measure (ATCM) was recently adopted which eliminated the use of chlorinated solvents such as perchloroethylene in automotive maintenance and repair products by December 31, 2002 (ARB, 2000c). To comply with the ATCM, perchloroethylene may be replaced with TBAC. According to the California Consumer Products Survey (ARB, 1996), in some cases the perchloroethylene content in brake

cleaners and engine degreasers is as high as 98 percent of the product by weight. For the “high use” scenario, it was assumed that 100 percent of the perchloroethylene in the brake cleaners would be replaced with TBAC. Thus, the brake cleaners and engine degreasers represent the highest TBAC substitution scenarios and are therefore used in the subsequent exposure analysis.

Table 7. TBAC Use Scenarios for “Brake Shops”

Product Categories Analyzed: Automotive Brake Cleaners, Carburetor and Choke Cleaners, Engine Degreasers, and General Purpose Degreasers			
Assumptions: Average can size is 16 ounces Number of cans per cleaning is 2 100% of perchloroethylene or criteria solvent will be replaced with TBAC 2% to 20% of product is propellant			
High Use:	Automotive Brake Cleaners, Product A	High Use:	Engine Degreasers, Product A
98% perchloroethylene	98% TBAC	98% perchloroethylene	98% TBAC
2% propellant	2% propellant	2% propellant	2% propellant
Moderate Use:	Automotive Brake Cleaners, Product B	Moderate Use:	Engine Degreasers, Product B
33% xylene	33% TBAC	24.9% xylene	24.9% TBAC
5.6% propellant	5.6% propellant	19.67% propellant	19.67% propellant
61.4% other	61.4% other	4% toluene	4% TBAC
		51.43% other	51.43% other
High Use:	Carburetor and Choke Cleaners, Product A	High Use:	General Purpose Degreasers, Product A
67.5% perchloroethylene	67.5% TBAC	48.5% perchloroethylene	48.5% TBAC
3% propellant	3% propellant	3% propellant	3% propellant
29.5% other	29.5% other	48.5% other	48.5% other
Moderate Use:	Carburetor and Choke Cleaners, Product B	Moderate Use:	General Purpose Degreasers, Product B
67.8% xylene	67.8% TBAC	6.43% xylene	6.43% TBAC
3.1% propellant	3.1% propellant	19.68% propellant	19.68% propellant
29.1% acetone	29.1% acetone	73.89% other	73.89% other

5.2.2 Automotive Refinishing Paint Booths

Another scenario where there is a potential for relatively high exposure to TBAC involves receptors located near facilities with large numbers of automotive refinishing paint booths. According to the automotive refinish speciation profiles, toluene, xylenes, and MEK represent over half of the VOCs in automotive refinishing coatings.

Assuming that an average automotive refinishing coating has 4.5 pounds of VOC per gallon, the average amount of toluene, xylenes and MEK present in automotive coatings is estimated at 2.25 pounds per gallon (a VOC content of 4.5 pounds per gallon is a reasonable content for an automotive refinishing coatings since this is the VOC limit for multistage topcoats in many district rules and the multistage topcoats are the most

popular automotive refinishing coatings sold). Assuming that a large body shop uses 3,000 gallons of coatings products per year, the potential emissions of TBAC could be more than 6,500 pounds per year if TBAC is substituted for toluene, xylenes and MEK on a one-for-one basis.

Emissions data were extracted from the CEIDARS database (ARB, 2001a) for each facility and grouped into three categories based on total emissions. Review of permit files and industry databases indicates that approximately 6,000 automotive refinishing shops exist in California. However, emissions information is available for only 1,131 of those facilities. Table 8 shows the distribution of reported facilities with automotive refinishing paint booths in the State with: A) combined emissions of xylenes, toluene, and MEK of less than 1,000 pounds per year; B) emissions between 1,000 and 2,000 pounds per year; and C) emissions above 2,000 pounds per year. Note that approximately 90 percent of the facilities included in the CEIDARS database emit less than 1,000 pounds per year of these five VOCs. If other VOC candidates for TBAC substitution are considered in the analysis, the amount of potential TBAC use could be higher. For the subsequent modeling analysis, a total of ten facilities (2 type A, 3 type B, and 5 type C) were selected.

Note that the most recent 2002 survey in automobile refinishing (ARB, 2005b) indicates that the total emissions of toluene, xylenes, and MEK are approximately 69% of the emissions from the previous 1999 survey. This analysis was performed before the results of the 2002 survey were readily available. Thus, actual emissions of these compounds in this category is lower than estimated in this analysis

Table 8. Automotive Refinishing Paint Booth Emissions for Xylenes, Toluene, and MEK

Facility Type	Emission Range (lb/yr)	Number of Facilities
A	<1,000	999
B	1,000-2,000	83
C	>2,000	49
Total		1,131

5.3 Near Source Impacts

As discussed earlier, the ARB's Environmental Justice program focuses on reducing exposures and risk on a community level (ARB, 2001c). As part of the assessment of potential environment impacts associated with increased TBAC usage, the possible exposure of receptors located near brake shops and paint booth facilities using products reformulated to contain large amounts of TBAC was evaluated. Specifically, ambient downwind concentrations of TBAC emissions from "Brake Shops" and Automotive Refinishing Paint Booths were investigated through the use of air dispersion models.

The TBAC emissions from these facilities are based on the assumed substitution scenarios presented in Table 7 and Table 8, respectively. The modeling results were extrapolated from previous evaluations performed for the ATCM for perchloroethylene (ARB, 2000c) from automotive maintenance and repair activities and for toluene, xylenes, and MEK from automotive refinishing products (ARB, 2001d).

5.3.1 Methods

Air dispersion models are used extensively to estimate the downwind, ground level concentrations of a pollutant after it is released from a facility. Data needs for air dispersion models include emission estimates, physical descriptions of the source, and emission release parameters. The U.S. EPA regulatory approved model used in this analysis is the Industrial Source Complex-Short Term3 (ISCST3) model. A more complete description of the model, including the input assumptions, is presented elsewhere (ARB, 2000b). The ISCST3 model is recommended by the U.S. EPA for refined air dispersion modeling. It uses actual region-specific meteorological data and receptors that are generally placed beyond the facility fenceline. Currently, this model is widely used by the ARB, the Districts, and other states.

The near-source impact of TBAC was estimated based on emission substitution scenarios previously described (i.e., “Brake Shops” and Automotive Refinishing Paint Booths). This is an appropriate substitution since the emissions are treated as inert in the atmosphere, and the air dispersion modeling results are directly proportional to the emission rate.

5.3.2 “Brake Shops”

The ranges of ambient concentrations of TBAC near several facilities performing brake-related work were estimated using the refined ISCST3 model. The results are shown in Table 9. These results were extrapolated from a previous evaluation for automotive maintenance and repair activities (ARB, 2000b) and are calculated at the nearest off-site receptor which may be either at the property line or at a minimum of approximately 20 to 30 meters from the source. For more details on the model assumptions, refer to Appendix I.

The “Brake Shops” scenarios were modeled with the ISCST3 model. The facilities were modeled with the appropriate regional meteorological data for each facility location. In addition, the minimum receptor placement is at the facility fenceline or 20 meters. The results predicted by the ISCST3 model are provided in Table 9. Specifically, the potential maximum annual average ambient concentration of TBAC is estimated to range from 0.4 to 10.1 $\mu\text{g}/\text{m}^3$ for the categories evaluated. The ISCST3 model also predicts that the general automotive category will have the highest concentrations. The range of emissions and concentrations are due to evaluating multiple facilities and the variation of perchloroethylene used.

A screening modeling evaluation was also performed to characterize the potential maximum one-hour concentrations of TBAC for the highest use scenario for “Brake

Shops” (i.e., annual emissions of 2,092 pounds). The highest maximum one-hour concentration is estimated at 2,800 $\mu\text{g}/\text{m}^3$.

Table 9. ISCST3 Results: Predicted Ambient TBAC Concentrations from “Brake Shops”

Facility Category	Number of Facilities	Emissions (lbs/yr)	Max. Ann. Avg. Conc. (mg/m^3)*
Service stations	1	120 to 175	0.6 to 0.8
Fleets	2	404 to 1306	1.9 to 3.0
New and used car dealership	1	909 to 1501	1.4 to 2.2
Brake repair shops	1	106 to 151	0.4 to 0.6
General automotive	8	162 to 2092	0.8 to 10.1

* Contribution from modeled source only and does not include potential ambient background.

5.3.3 Automotive Refinishing Paint Booths

Emissions from Automotive Refinishing Paint Booths were modeled using the same refined ISCST3 model. As shown in Table 8, facilities were grouped into three categories, depending on the mass of potential TBAC emissions. The model results were extrapolated from a previous evaluation for hexavalent chromium emissions from Automotive Refinishing Paint Booths (ARB, 2001d). The ISCST3 model was used for four Automotive Refinishing Paint Booths in conjunction with actual region-specific meteorological data. The details of the model results are presented in Appendix J.

Table 10 shows a summary of the predicted near-source TBAC concentrations associated with each of the three categories of paint booth facilities. Emissions of toluene, xylenes, and MEK were extracted from the current CEIDARS database for the ten different Automotive Refinishing Paint Booths (ARB, 2001d). The combined emissions of toluene, xylenes, and MEK were substituted on one-for-two (50 percent) basis for TBAC, which is consistent with the assumption made in Table 3. The modeling was based on a previous evaluation from the ATCM for Hexavalent Chromium and Cadmium Emissions from Motor Vehicle and Mobile Equipment Coatings (ARB, 2001d). For the ATCM, the parameters from four automotive paint booths were used to conduct air dispersion modeling. For the purpose of the TBAC assessment, it was assumed that each of these four modeled facilities had the potential to emit TBAC at the same rate as each of the ten different facilities from CEIDARS. Our previous results based on the 1999 survey data indicate that the largest facilities have emission rates of 1,060 to 2,692 pounds of TBAC per year, resulting in a maximum annual average ambient concentration of TBAC ranging from 0.85 to 28.54 $\mu\text{g}/\text{m}^3$ (ARB, 2005a). Since then, the new 2002 automotive refinishing survey data became available and the result suggests lower use (69%) of toluene, xylenes, and MEK than assumed in this analysis (ARB, 2005b). Thus, the maximum average ambient concentration of TBAC was revised here to reflect the new survey result. The maximum annual average

concentration predicted here represents a high emissions, nearby receptor scenario. Specifically, the maximum annual average concentration of $19.7 \mu\text{g}/\text{m}^3$ represents the highest exposure estimated. It is anticipated that the vast majority of facilities using TBAC would result in considerably lower annual average exposures. The variability in Table 10 is due to variable emissions of toluene, xylenes, and MEK from the facilities and from the varying emission release parameters, and different meteorological conditions.

Table 10. ISCST3 Results: Predicted Ambient TBAC Concentrations from Automotive Refinishing Paint Booths Using the 2002 Survey Data

Facility Type	Number of Facilities	Emissions (lbs/yr)	Max. Ann. Avg. Conc. (mg/m^3)*
A	2	124 to 257	0.1 to 2.7
B	3	479 to 579	0.4 to 5.8
C	5	731 to 1856	0.6 to 19.7

* Contribution from modeled source only and does not include potential ambient background.

A screening modeling evaluation was also performed to characterize the potential maximum one-hour concentrations of TBAC for the highest use scenario for Automotive Refinishing Paint Booths (i.e., annual emissions of 1,856 pounds). The highest maximum one-hour concentration is estimated at $1,280 \mu\text{g}/\text{m}^3$.

5.4 Indoor Exposure

As part of this analysis, the potential indoor exposure associated with the use of TBAC was also evaluated. Specifically, the ARB is charged with assessing human exposure to toxic air contaminants in indoor environments and identifying the relative contribution of indoor exposures to total human exposure, taking into account both ambient and indoor air environments. To fully account for exposure to TBAC and its toxic breakdown products, potential scenarios likely to result in the highest “realistic worst case” exposures indoors were examined.

The following provides a scenario-based estimate for indoor exposure in an automotive repair environment where brake cleaners are used. Other exposure scenarios such as that which would occur inside a paint booth and inside a neighboring house were considered, but estimates were not developed for those scenarios because the exposure in those circumstances would be much lower than that from the automotive repair scenarios.

Exposure in the paint booth is expected to be lower due to removal by the booth’s ventilation system and the workers’ use of protective equipment such as a respirator. However, if the booth’s ventilation system is not operating as designed or the worker does not use the required protective equipment, exposure could be much greater. Exposure inside a house is also expected to be lower than occupational exposures since the only source of TBAC exposure would likely be from the outdoor air since

TBAC is not expected to be used in household products due to its camphor-like odor. However, this can be changed in actual applications since various fragrances have been evaluated to alter the odor of TBAC. Some of the formulation additives can mask the odor while others will provide a fragrance to the TBAC.

5.4.1 Method of Evaluation

Indoor concentrations of TBAC were estimated for “personal workspace”, “typical” of small and large automotive maintenance facilities. Indoor facility concentrations of TBAC have been calculated in order to estimate the workers’ exposures under the assumption that workers will have the greatest exposure to this compound. These analyses utilize information found in existing ARB documents when appropriate.

Exposure in the workplace during a full workday was determined using the 8-hour time-weighted average (TWA) model used in the *Initial Statement of Reasons for Proposed Amendments to the California Regulations for Reducing Volatile Organic Compound Emissions From Consumer Products and Aerosol Coating Products* (ARB, 1996). That model was developed specifically to predict perchloroethylene air concentrations after the use of chemical brake cleaners in automotive repair facilities. Because perchloroethylene is one of the compounds expected to be substituted by TBAC on a pound-per-pound basis, the use of the model is appropriate. The model equation is:

$$C_s = \frac{(24.45 \times 10^{-3} \text{ m}^3/\text{mol}) (A)(B)(10^6)}{(M)(V)(1 + D)}$$

Where,

- C_s = predicted room concentration of TBAC (ppm)
 A = TBAC content per can (grams/can), In the 20 oz. can, assuming the 544 grams of perchloroethylene in a can of brake cleaner to be substituted by TBAC on a pound-per-pound basis (ARB, 1996).
 B = number of cans used per work period per worker, assumed to be about 0.5 can per day based on the range of 1.0 -1.5 cans used in a work period for the entire facility and an average of 3 workers using such products per facility (Norton, 1993 and ARB, 1996).
 M = molecular weight of TBAC = 116.2 grams/mole
 V = shop volume, m^3
 D = shop air changes/work period
 $\frac{(F)(60 \text{ min/hr})(8 \text{ hr/work period})}{H}$

Where F = air exchange rate, Assumed to be the recommended $1.5 \text{ ft}^3/\text{min-ft}^2$. This is also the ASHRAE 62-1989 standard for this type of facility. It should be noted that if the recommended air exchange rate were not maintained in a facility, TBAC levels

$$\begin{aligned}
 & \text{would be proportionately higher (ARB, 1996)} \\
 H &= \text{repair shop ceiling height, 15.6 ft. (ARB, 1996)} \\
 10^6 &= \text{constant for conversion to parts per million} \\
 24.45 \times 10^{-3} &= \text{volume of one mole of ideal gas at 25°C and one atmosphere (cubic meter)}
 \end{aligned}$$

5.4.2 Scenarios

Three different scenarios were developed and these are personal workspace (scenario A), small facility (scenario B), and large facility (scenario C). Several inputs/assumptions were used to estimate indoor concentrations in these three scenarios for the worker when the brake cleaner is used. The worker's workspace air volume, obtained from the previous evaluation, is 27 m³ for the personal workspace, 1,874 m³ for the small facility, and 4,733 m³ for the large facility (ARB, 1996). The air exchange rates per 8-hour work period were assumed to be low according to Norton's study (1993). Specifically, the assumed exchange rates are 18 air changes per work period for personal workspace, 11.5 for both the small facility and the large facility. These inputs/assumptions for each scenario are presented in Table 11.

5.4.3 Results and Conclusions

The results of the evaluation are summarized in Table 11. The use of aerosol brake cleaners with TBAC in automotive maintenance facilities would result in increased air concentrations in the facilities and notably higher personal exposures for the workers, even for facilities with effective exhaust ventilation. This is because the personal workspace scenario does not completely capture the actual "breathing zone" exposure levels of the worker, which could be somewhat higher than the 112 ppm estimated for the area around the worker. The worker's nose and mouth would typically be very close to the directly emitted TBAC, which would represent a higher concentration than the average level in the simulated 27 m³. However, assuming normal use rates of aerosol brake cleaners and maintenance of the required air exchange rates, the results indicate that the worker's TBAC exposure would not be expected to exceed the current workplace exposure standard. The current California Department of Industrial Relations (Cal-OSHA) Permissible Exposure Limit (PEL) is 200 ppm, or 955 mg/m³, for an 8-hour time-weighted-average (CCR, 2001). With regard to acute effects, TBAC can cause irritation of the eyes and nose at 200-300 ppm.

The ARB is also concerned regarding the overall (total) exposure of those in the population who would be most exposed to TBAC. To estimate such exposure, the 8-hour workplace exposure level estimated here was combined with the estimated near source exposure levels to estimate a 24-hour time-weighted exposure for those potentially most exposed. For this evaluation, those most exposed to TBAC would be the automotive workers using aerosol brake cleaning products containing TBAC in a small, personal workspace for 8 hours of their 24-hour day, and who live near a large paint booth facility for most of the 16 non-working hours each day. Using the upper estimate of workplace exposure concentration of 532,000 µg/m³ (from Table 11) and the

upper estimate of near source concentration of $19.7 \mu\text{g}/\text{m}^3$ (from Table 10), and assuming the worker works 8 hours a day for 5 days a week, the calculation would be:

Ave. Total Exposure Conc.

$$= 5/7 [(8/24) \times (\text{Work exposure}) + (16/24) \times (\text{Non-work exposure})] + 2/7 [19.7]$$

$$= 5/7 [(8/24) \times 532,000 + (16/24) \times 19.7] + 8.15$$

$$= 126684 \mu\text{g}/\text{m}^3, \text{ or about } 127,000 \mu\text{g}/\text{m}^3$$

Thus, members of the most exposed group, workers who also live near a TBAC source, would be exposed to an average daily exposure of about $127,000 \mu\text{g}/\text{m}^3$.

Table 11. Summary of Indoor Exposure Evaluation Results

		Scenario A Personal Workspace	Scenario B Small Facility	Scenario C Large Facility
Results – Predicted air Concentration of TBAC	ppm $\mu\text{g}/\text{m}^3$	112 532,000	7.3 35,000	2.9 14,000
Inputs				
ppm conversion factor		10^6	10^6	10^6
ppm factor for 25°C and 1 atm		24.45×10^{-3}	24.45×10^{-3}	24.45×10^{-3}
TBAC content/can (grams/can)	A	544	544	544
Number of cans used per work Period	B	0.5	1.5	1.5
Molecular weight of TBAC (gram/mol)	M	116.2	116.2	116.2
Shop volume (cubic meters)	V	27	1874	4733
Shop air changes/work period (25% of typical)	D	18	11.5	11.5
Air exchange rate (cubic feet per minute per square foot)	F	1.5	1.5	1.5
Repair shop ceiling height (feet)	H	10.0	15.6	15.6

5.5 Potential Health Impacts

As discussed In the Chapter 3, data concerning the adverse health effects from exposure to TBAC are limited. Therefore, it is not possible to characterize the potential for non-cancer health effects resulting from the potential exposures presented in this document. However, because TBAC is metabolized to TBA and because TBA has been shown to induce tumors in both rats and mice, exposure to TBAC may result in a cancer risk. An inhalation unit risk value for TBAC of $4 \times 10^{-7} (\mu\text{g}/\text{m}^3)^{-1}$ was derived by the OEHHA. This unit risk factor was used to estimate the population-weighted cancer burden in the SoCAB as well as to estimate the potential cancer risk near emission sources of TBAC.

To estimate potential cancer risk, the inhalation unit risk value is multiplied by the assumed 70-year exposure concentration. Using the population-weighted annual average concentration of TBAC calculated for the SoCAB in 1999 of $2.8 \mu\text{g}/\text{m}^3$, the excess cancer risk to people exposed for 70 years to that concentration would be 1.12×10^{-6} or one excess cancer case per one million. This translates into a lifetime population cancer burden of 11 people in the SoCAB or 24 people statewide.

People in communities near facilities with high TBAC emissions could potentially have a much higher excess lifetime cancer risk. Based on the analysis presented in this document, the estimated risks range from 4.0×10^{-8} , or less than one excess lifetime cancer case per ten million, for the lowest Automotive Refinishing Paint Booths concentration of $0.10 \mu\text{g}/\text{m}^3$ to 7.9×10^{-6} , or eight excess lifetime cancer cases per one million for the highest Automotive Refinishing Paint Booths concentration of $19.7 \mu\text{g}/\text{m}^3$. The risks associated with "Brake Shops" ranged from less than one to four excess lifetime cancer cases per one million. By incorporating the cancer risk (i.e., one excess cancer case per one million) derived from the population-weighted exposure, the estimated cancer risks range from 1 to 9 excess cancer cases for the Automotive Refinishing Paint Booths and from 1 to 5 excess cancer cases for the "Brake Shops", respectively.

Maximum one-hour concentrations were also estimated near the highest potential TBAC use scenarios for "Brake Shops" and Automotive Refinishing Paint Booths. However, the OEHHA has indicated that there is not an acute reference exposure level (REL) for TBAC to definitely place the predicted maximum hourly concentrations (i.e., $2,800 \mu\text{g}/\text{m}^3$ and $1,700 \mu\text{g}/\text{m}^3$) into context. However, the available information suggests that an acute REL would likely be about $10,000 \mu\text{g}/\text{m}^3$ (Budroe, 2005). If it is assumed that toluene, xylenes, or MEK is used (i.e., the substances that TBAC would be expected to replace), the resulting maximum hourly concentrations are well below the acute RELs for these chemicals. The concentrations associated with indoor exposure in the workplace are much higher than the near-source concentrations, ranging from 14,000 to $532,000 \mu\text{g}/\text{m}^3$.

5.6 Potential Health Benefits of Reducing Ozone Exposure

The objective of this section is to quantify the health benefits associated with the potential reduction of ground-level ozone concentrations due to the replacement of more reactive VOCs with TBAC. While current ozone levels in California are associated with a number of adverse health effects, this analysis focused on premature mortality due to short-term exposures. The methodology used here to estimate the change in mortality is similar to the ARB's ozone standard staff report (ARB, 2004). Full details of the methodology are discussed in the report (ARB, 2004), which can be found on the ARB's website at <http://www.arb.ca.gov/research/aaqs/ozone-rs/ozone-rs.htm>.

The estimated impact on the health outcome is calculated as follows:

$$?y = \text{PAR} \times y_0 \times \text{pop}$$

where:

Δy = changes in the incidence of a health endpoint, in this case premature mortality, corresponding to a particular change in ozone,

PAR is the population attributable risk

y_0 = baseline incidence rate/person within a defined at-risk subgroup, and

pop = population size of the group exposed.

The population attributable risk (PAR) represents the proportion of the health effects in the whole population that may be prevented if the cause (ozone pollution in our case) is reduced by a given amount. Specifically, $PAR = (RR-1) / RR$ where RR is the relative risk (RR) for a specified change in ozone concentrations, such as 10 ppb 1-hour maximum. The RR is defined as the ratio of the health effect predicted from the higher exposure relative to some baseline exposure. A 0.4% change in daily mortality (0.2% to 0.6% as a probable range) per 10 ppb change in 1-hour maximum ozone was assumed. For 24-hour ozone low, central and high estimates of 0.5% per 10 ppb, 1% per 10 ppb, and 1.5% per 10 ppb respectively were used. When these results with 24-hour ozone are converted to 1-hour maximum ozone, the central estimate becomes 0.4% (0.2% and 0.6% as a probably range) per 10 ppb change. Note that the probable range should not be interpreted as a 95% confidence interval. It is merely the OEHHA's best estimate of a range. Our range of estimates is applied to all age groups. This analysis has not undergone peer review.

The percent change in mortality per ppb ozone was applied to changes in ozone concentrations at each monitoring site. The change in ozone is the difference between the current observed ozone 1-hour maximum concentration and the assumed background of 0.04 ppm, calculated for each day of the 3 years 2001-2003. Health effects were then estimated for each day in a given year, summed across sites over the year, and then averaged over the three years of data.

The population assigned to each monitor equals the county population according to the 2000 census divided by the number of monitors in each county. To check the sensitivity of this assumption, an alternative method based on the actual population in each census tract was performed. For this method, the ozone concentration in each tract was estimated using an interpolation scheme that averages the monitored ozone values within 50 km of the centroid, with weights equal to the inverse square of the distance from each monitor to the centroid. Using this alternative method, the health effects were lower than those presented below.

The total change in annual mortality in California due to ozone levels above background is estimated to be 1100 (540 to 1600 deaths as a probable range). This was found from the sum of changes across monitors for each of the 3 years, then averaged over the 3 years. These results represent the annual effects of the current ozone levels on mortality due to short-term exposures in California.

The substitution analysis in Chapter 4 estimated that as much as 33 – 54 tons per day of TBAC could be substituted for more reactive solvents in consumer products,

architectural coatings and several other categories. This could result in a statewide reduction of approximately 80–140 tons per day of ozone, a reduction of one percent of the estimated statewide ozone formation. This factor of one percent was then applied to the calculated total mortality and the result indicates that about 11 (5 to 16 deaths as a probable range) fewer premature deaths would occur statewide on an annual basis due to the reduction in ambient ozone associated with maximum use of TBAC. For the 70-year duration, the potential premature deaths that can be avoided are about 770 (350 to 1120 as a probable range) assuming constant population (number and distribution) and no change in air quality for the purpose of the simplified comparison with the estimated cancer risk discussed in Section 5.5. This calculation also assumes that there will be no change in the effect of ozone due to a lifetime exposure of 70 years. Hence, the reduction in premature deaths due to ozone reduction relative to the increase in estimated cancer risk due to TBAC is approximately 30:1. Note that the ozone benefit would be less if the potential use of TBAC is less than predicted (i.e., 54 tons per day). For example, if Lyondell's estimate of 23 tons per day ozone reductions associated with TBAC usage in consumer products and coatings of TBAC is assumed, TBAC substitution for more reactive VOC would lead to a 0.2% the statewide reduction in ozone, leading to a decrease of about 2 deaths annually from reduced ozone exposure or 140 deaths for the 70-year duration.

A more detailed analysis of possible benefits was performed for the South Coast Air Basin. It is estimated that a reduction of one percent of the estimated ozone formation in the South Coast would avoid a significant number of adverse health effects each year. The central estimates for the reduction in adverse health effects are based on reductions in maximum 1-hour ozone exposures (at the 95% confidence interval) and are provided below:

- 5 premature deaths (2 to 7 as a probable range) avoided for all ages
- 34 hospitalizations (19 to 48 as probable range) avoided due to respiratory diseases for all ages
- 5 emergency room visits (3 to 7 as a probable range) avoided for children under 18 years of age
- 34,000 school absences (3,500 to 77,000 as a probable range) avoided among children 5 to 17 years of age
- 19,000 minor restricted activity days (10,100 to 41,000 as probable range) avoided for adults above 18 years of age

Details about the estimation methodology, including limitations and assumptions, are discussed in the ozone standard report (ARB, 2004),

5.7 Summary

This chapter has attempted to quantify the possible impacts on human health that might occur if large amounts of TBAC are used to replace other VOCs in consumer products and other categories. Exposure scenarios were constructed to estimate ambient concentration that might occur near large facilities. These concentrations were combined with an inhalation cancer unit risk to estimate cancer burden. Substitution of

TBAC for more reactive VOCs could lead to a reduction in ozone formation. The decrease in premature mortality due to a possible reduction in ambient ozone is also estimated.

An analysis of three possible types of exposure scenarios was conducted: 1) an estimate of a population-weighted exposure to ambient TBAC; 2) an estimate of near source concentrations near facilities which could potentially use large amounts of products which contain TBAC; and 3) personal exposure in the “worst-case” workplace.

Using ambient concentrations of several VOCs identified as candidates for substitution with TBAC and census data for the SoCAB, a population-weighted annual average TBAC concentration of $2.8 \mu\text{g}/\text{m}^3$ was estimated. Based on the inhalation unit risk value for TBAC of $4 \times 10^{-7} (\mu\text{g}/\text{m}^3)^{-1}$ derived by the OEHHA, the cancer risk associated with a 70-year exposure to this concentration translates into a lifetime cancer burden of 11 excess cancer cases for the exposed population in the SoCAB.

Evaluating the potential health impacts associated with TBAC emitted from emission sources on the community level is a critical part of an evaluation of the potential environmental impacts of exempting TBAC from the ARB’s and Districts’ VOC definitions. Exposure scenarios were developed for two source categories believed to represent plausible upper-bound situations if substitutions of TBAC occur as described in Chapter 4 in brake cleaners and automotive refinishing products (i.e., TBAC is substituted for perchloroethylene in brake cleaners and for toluene, xylenes, and MEK in automotive coatings). Near source air dispersion model results predict that annual average concentrations due to emissions from the modeled facilities could range from 0.1 to $19.7 \mu\text{g}/\text{m}^3$. The cancer risk associated with these concentrations ranges from less than one lifetime excess cancer case per ten million, to eight lifetime excess cancer cases per one million. By incorporating the cancer risk (i.e., one lifetime excess cancer case per one million) derived from the population-weighted exposure, the estimated cancer risks range from 1 to 9 lifetime excess cancer cases per one million for the Automotive Refinishing Paint Booths and from 1 to 5 lifetime excess cancer cases per one million for the “Brake Shops”, respectively.

In addition, while industry representatives believe that a majority of TBAC will be used in industrial settings where occupational hygiene equipment should limit workers’ exposure to TBAC, there may be situations where workers are exposed to significant levels of TBAC. For that reason, personal exposure in a “worst case” workplace was also modeled. The concentrations associated with indoor exposures in the workplace are ranged from 14,000 to $532,000 \mu\text{g}/\text{m}^3$. However, the ARB is concerned about the total exposure of those in the population who would be most exposed to TBAC. To estimate such exposure, the 8-hour workplace exposure level estimated here was combined with the estimated ambient or near source exposure levels to estimate a 24-hour time-weighted exposure for those potentially most exposed.

Lastly, the health benefits associated with the potential reduction of ground-level ozone concentrations were quantified. Based on a methodology similar to the ARB’s staff

report of the ozone standard review, approximately 11 premature deaths annually (5 to 16 deaths as a possible range) or 770 premature deaths (350 to 1120 as a probable range) for the 70-year duration would be avoided statewide (using several simplifying assumptions) for a one percent reduction of total ozone associated with TBAC uses. Note that the ozone benefit would be less if the potential use of TBAC is less than predicted.

6. Conclusions and Recommendations

This document presents the ARB's technical evaluation of the potential impacts associated with the increased use of TBAC in consumer products, architectural coatings, and other smaller categories if a VOC exemption is granted. This includes an assessment of possible environmental impacts (air, water, soil, and health) of TBAC, an analysis of possible substitution scenarios, and estimates of the potential associated health benefits and risks. The conclusions derived are summarized below.

- Increased use of TBAC is not expected to increase formation of secondary organic aerosol, depletion of stratospheric ozone or contribute to global warming. Substitution of TBAC for more reactive compounds would result in the reduction of ground-level ozone, a seasonal problem in many areas of California. The potential risk to surface waters and soil is expected to be low. However, due to the lack of data on TBAC's aquatic toxicity, breakdown rate in various environmental compartments and measured transport data, this conclusion has a large uncertainty. An exemption of TBAC from the ARB's and the Districts' VOC definition could be expected to have positive impacts on California businesses by providing additional reformulation options.
- TBAC has been demonstrated to be substantially metabolized to TBA, which has been shown to induce tumors in both rats and mice. Although neither TBAC nor TBA have been identified as a Toxic Air Contaminant, there is a concern that exposure to TBAC may result in a cancer risk to humans because of its metabolic conversion to TBA. Therefore, an inhalation unit risk factor for TBAC of 4×10^{-7} ($\mu\text{g}/\text{m}^3$)⁻¹ was derived by the OEHHA. It has been proposed that the TBA carcinogenicity data may not be relevant to human cancer risk assessment. However, the data are insufficient to allow such a determination. Therefore, TBAC has been evaluated as a substance that could pose a potential cancer risk to humans.
- A total of 24 VOCs were considered as candidates for potential substitution with TBAC in several categories such as consumer products, architectural coatings, and automotive refinishing if such an exemption is granted. The estimated increase in the statewide use of TBAC resulting from the substitutions that may follow a VOC exemption for TBAC ranges from 33 to 54 TPD. Correspondingly, use at this level could result in an ozone reduction of approximately one percent of an estimated daily average of statewide total ozone formation of 10,300 TPD in 2001. Note that the statewide potential cancer risk and ozone benefit would be less if the actual use of TBAC is less than the estimate presented in this document. For example, Lyondell has indicated that the potential use of TBAC is approximately 10 TPD in California, which would result in significantly lower statewide ozone benefits and Statewide potential cancer risk.
- Three possible types of exposure scenarios were analyzed to determine the potential concentrations of TBAC to which California may be exposed. The

calculated population-weighted health risk in SoCAB is one lifetime excess cancer case per one million resulting in a lifetime population cancer burden of 11 cases for the SoCAB or 24 cases statewide. The near-source impact analysis indicates that the upper-bounds of estimated health risk are eight lifetime excess cancer cases per million exposed for the automotive refinishing paint booths and four lifetime excess cancer cases per million exposed for the "Brake Shops", respectively. The concentrations associated with indoor exposure in the workplace are much higher than the near-source concentrations, ranging from 14,000 to 532,000 $\mu\text{g}/\text{m}^3$.

- The health benefits were quantified associated with the potential reduction of ground-level ozone concentrations due to the replacement of more reactive VOCs with TBAC. Based on methodology similar to the ARB's staff report of the ozone standard review, approximately 11 premature deaths annually (5 to 16 deaths as a possible range) or 770 premature deaths (350 to 1120 as a probable range) for the 70-year duration (using several simplifying assumptions) would be avoided with one percent reduction of total ozone associated with TBAC uses. Note that the ozone benefit would be less if the use of TBAC is less than predicted.

Staff recommends exempting TBAC from the definition of VOC from the California Consumer Products Regulations based on its low reactivity. However, staff will further evaluate appropriate consumer products categories that are most likely to use TBAC, to determine whether or not use in these products could pose unacceptable exposures. If staff determines that the use of TBAC in certain products could cause unacceptable exposures, we will propose appropriate mitigation measures in the Consumer Products Regulations at the time the exemption is proposed as an amendment. We further encourage the air pollution control districts in California, as they update their applicable rules, to also determine whether or not use of TBAC in certain products would pose unacceptable exposures.

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Acronyms and Abbreviation

$\alpha_2\mu$	α_2 -Microglobulin
ARB	California Air Resources Board
ATCM	Airborne Toxic Control Measure
Cal/EPA	California Environmental Protection Agency
Cal-OSHA	California Department of Industrial Relations
CalTox	California Department of Toxic Substances Control time-dependent multi-compartment model
CCR	California Code of Regulations
CEIDARS	California Emission Inventory Development and Reporting System
CEQA	California Environmental Quality Act
CFCs	Chlorofluorocarbons
CHO	Chinese hamster ovary
CNS	Central nervous system
CSP	Cancer slope factor
District	Air Pollution Control Districts/Air quality Management District
DTSC	Department of Toxic Substances Control
EKMA	Empirical Kinetic Modeling Approach
EQC	Equilibrium Criterion evaluative model
GC-MS	Gas Chromatograph-Mass Spectrometry
IARC	International Agency for Research on Cancer
IPCC	Intergovernmental Panel on Climate Change
IR	Incremental reactivity
ISCST3	Industrial Source Complex-Short Term 3
K_{OH}	Reaction rate with hydroxyl radicals
LC_{50}	Median lethal concentrations
LMWPF	Low-molecular-weight protein fraction
LOAELs	Lowest Observable Adverse Effect Levels
Lyondell	Lyondell Chemical Company
MEK	Methyl ethyl ketone
MIR	Maximum Incremental Reactivity
MMM	Mean of monthly mean
NCEs	Normochromatic erythrocytes
NOAEL	No Observable Adverse Effect Levels
NO _x	Oxides of nitrogen
NO ₃	Nitrate radicals
NTP	National Toxicology Program
O ₃	Ozone
OEHHA	Office of Environmental Health Hazard Assessment
OH	Hydroxyl radicals
PAR	Population Attributable risk
PEL	Permissible Exposure Limit
POCP	Photochemical ozone creation potential
PP	Relative risk
REL	Reference Exposure Level

SCAQMD	South Coast Air Quality Management District
SOA	Secondary Organic Aerosol
SoCAB	South Coast Air Basin
SWRCB	State Water Resources Control Board
TBA	<i>tertiary</i> -Butyl alcohol
TBAC	<i>tertiary</i> -Butyl acetate
TPD	Tons per day
TSH	Thyroid stimulating hormone
TWA	Time-weighted average
U.S.EPA	United State Environmental Protection Agency
VOC	Volatile Organic Compound
WHO	World Health Organization