

Appendix E
Public Comments and ARB Responses

December 31, 2000

E.1 Introduction

Public comments were received from Jon M. Heuss (Air Improvement Resource, Inc.) and Jaroslav J. Vostal (Environmental Health Assessment Consultants, International), both in writing and verbally at the AQAC meeting. The written comments are included in Appendix E. The verbal comments made before AQAC were based on the written comments, and transcripts can be accessed at <http://www.OEHHA.ca/gpv/air/toxic-contaminants/AQAC1.html>.

E.2 Summary

The points raised by Messers Heuss and Vostal can be summarized into two categories. These points, along with ARB responses, are presented below.

Point 1. The Staff Report is an incomplete assessment and analysis of all publicly available information on the various pollutants. **ARB Response:** The purpose of the reviews presented in the staff report was to consider whether there was evidence suggesting that any of the California Ambient Air Quality Standards should be reviewed with reference to adequacy of protection of infants, children and other susceptible populations. It was not the intent of Staff to provide complete reviews on each pollutant.

Point 2. Insufficient information is presented on background concentrations of various pollutants, and on the extent to which the existing State standards are exceeded. **ARB Response:** Information on background pollutant concentrations has been added. Table 3.3.1. gives information on exceedances and maximal concentrations of the various criteria pollutants in the major air basins of the State. Also, see response to Point 1.

**Comments for the California ARB Public Meeting
of the Air Quality Advisory Committee.
on the Adequacy of California Ambient Air Quality Standards:
Senate Bill 25-Children's Environmental Health Protection
Berkeley, CA, October 12-13, 2000**

**Jon M. Heuss
Air Improvement Resource, Inc.**

**Jaroslav J. Vostal
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Senate Bill 25 requires that all existing California health-based ambient air quality standards be reviewed by the Air Resources Board (ARB) by December 31, 2000. The review should determine "whether, based on public health, scientific literature, and exposure pattern data, the standards adequately protect the health of the public, including infants and children, with an adequate margin of safety." In preparation for that review, a Draft Staff Report was made available in mid-September along with a request for written comments by October 4, 2000. This is insufficient time to adequately review, evaluate, and comment on the wide range of exposure and public health issues and studies included in the Draft. Nevertheless, we want to bring several important issues to the attention of the Staff and Advisory Committee. We will be providing further discussion during the public comment period at the Advisory Committee meeting.

The September 12, 2000 Draft Staff Report is an incomplete assessment and analysis of all publicly available information on several key issues in the review. Because the Draft raises concerns about the potential health effects that may occur- in infants, children, and other potentially susceptible groups - exposed to pollutants at levels corresponding to existing California ambient air quality standards for particulate matter (PM10), ozone, and nitrogen dioxide, we focus our comments on those pollutants.

One of the factors considered in assessing the standards' health protectiveness is the "degree of exposure relative to the level of the standard." Unfortunately, Chapter 3 and Appendix B of the Draft are inadequate. They fail to mention the existence of a significant background of ozone in the troposphere that arises from sources other than California or even U. S. precursor emissions. They fail to inform the reader of the extent to which the existing state standards are exceeded throughout the state. They fail to reference a significant body of probabilistic ozone exposure analyses that include studies of children conducted by the U.S. EPA. These failures result in the omission of important facts that will have a profound influence on the health protectiveness of the existing state ozone and PM10 standards.

For example, the substantial background of ozone in the troposphere (that averages about 0.04 ppm but reaches 0.08 ppm on the order of once per year) provides a practical limit as to how low any ozone air quality standard can be set. The state ozone standard of 0.09 ppm for 1-hour is defined as an extreme value standard; it is met when the Expected Peak Daily Concentration (EPDC, that concentration expected to occur once per year) is below the level of the standard. In fact, the EPDC in the cleanest,

lowest emission density counties and air basins of California are typically between 0.075 and 0.085 ppm. This means that the amount of man-made ozone allowed by the existing state standard is on the order of 0.01 ppm. The presence of a substantial background of ozone needs to be taken into account in any decisions regarding revision of the California ozone standard.

For PM₁₀, ARB data summaries indicate that the state 24-hour standard is exceeded throughout the state except for compliance in a few high elevation counties. The maximum EPDC in Lake County is substantially below the state 24-hour standard, but in all the other rural and remote basins, the maximum EPDC is substantially above the existing state 24-hour PM₁₀ standard. In the Great Basin Valleys, the maximum EPDC has been on the order of 400 $\mu\text{g}/\text{m}^3$ in recent years, or 8 times the state 24-hour standard. In contrast, the state annual geometric mean standard is met in the rural and remote areas of California but not in the more urbanized air basins. However, the maximum annual geometric mean PM₁₀ in the rural and remote basins of California (except for Lake County) varies between 20 and 30 $\mu\text{g}/\text{m}^3$. It is known that wind-blown crustal material is the major contributor to high PM₁₀ concentrations in rural and remote areas of California. While some wind-blown dust is controllable, much is not. Therefore, the level of PM₁₀ that is achievable with complete elimination of man-made pollution varies substantially across California. This needs to be taken into account in any decisions regarding revision of the California PM standards.

Section 3.6 on indoor and personal exposure needs to acknowledge that indoor ozone concentrations are dramatically reduced compared to outdoor concentrations (see Table B10-1) while PM exposures indoors are often elevated above outdoor concentrations. This also has important implications for the magnitude (and sources of) human personal exposure to ozone and PM₁₀. An informed discussion of the interpretation of the existing health studies must be predicated on what is known about human exposure patterns. Therefore, the discussion of individual pollutants in Chapter 4 and Appendix C needs to include a review of the body of information on human exposure. For ozone, this includes consideration of the probabilistic analyses carried out by EPA over the past decade. For PM, this includes an expanded discussion of the body of information concerning the relation of fixed monitors to indoor and personal exposures as well as factors such as the personal cloud, indoor combustion sources, and re-suspension of coarse particles.

When EPA last reviewed the national ambient air quality standards for ozone, the probabilistic risk assessment played a key role. The U. S. EPA's Clean Air Science Advisory Committee (CASAC) concluded that because it appears that ozone may elicit a continuum of biological responses down to background concentrations, risk assessments must play a central role in identifying an appropriate level for the standard. However, when CASAC viewed the results of the probabilistic modeling, the risks for all segments of the population including outdoor children were small and the committee concluded that there was no "bright line" that distinguished any of the proposed standards as being significantly more protective of public health. The standards considered ranged from the existing 1-hour federal standard of 0.12 ppm down to levels roughly equivalent to the current California standard.

In terms of children's health, it is important to note that clinical studies show that children tolerate ozone exposures with less symptoms than do adults. Concerns that this may

result in airway injury have not been validated because they have been based on an outdated concept of ozone-induced decreases of "lung function." Studies now demonstrate that declines in the forced expiratory volume (FEV1.0) are transient and are not caused by cellular injury in the respiratory airways. Since EPA's last review, published U.S. EPA studies show that the observed "lung function" decreases are only a physiological protective mechanism that involuntarily restricts the inhaled air volume determining the outcome of the test. Declines in forced expiratory volume only represent decreases in FEV test performance and do not signal any damage to actual pulmonary function. There should be a re-interpretation, therefore, of all field studies and clinical studies using forced expiratory volumes as an index of pulmonary function changes

Many conclusions of the review are based on epidemiological studies that correlate observed health effects with monitored ambient ozone or PM10 concentrations without validating the actual personal exposures, or the delivered pollutant doses and without establishing the causal role of pollutants in these changes. The review should acknowledge that the epidemiologic studies cannot exclude other possible confounding factors and, therefore, cannot establish the causal role of ambient air pollutants in the observed effects unless plausible mechanisms are offered to explain the reported changes. These restrictions apply to all observed statistical associations of pollutants with increases in morbidity, medication consumption, or mortality. Concerns about statistical conclusions in the reported time-series studies are supported by dosimetry studies that show that the amounts of pollutants inhaled during 24 hr-exposures to current pollutant levels are too low to be responsible for complex effects such as morbidity and mortality.

As the Draft indicates, ambient PM is a mixture of many different elements and compounds, including organic, inorganic, and biologic materials. Therefore it is not surprising that EPA acknowledged in its recent PM review that there are unusually large uncertainties associated with establishing standards for PM relative to other single component pollutants. In response to the many concerns over the scientific basis for PM2.5 or PM10 standards, Congress authorized a dramatic increase in federal PM research and a National Academy of Sciences Panel was used to focus the effort on key issues. Some of that new research is now becoming available. Much more will be published over the next several years. The U. S. EPA is scheduled to release a public review draft of a new PM Criteria Document shortly. However, new studies of relevance to PM standard-setting are published monthly. As California reviews its PM standards, we urge the Staff to fully evaluate all of the available information.

In summary, we acknowledge that the California PM10 standards need to be reviewed. However, the review should be focused on identifying which, if any, of the components of ambient PM are causally related to health effects. In the case of ozone, the existing California standard is very close to peak once-per-year background levels. Since tightening the standard would not result in significant reduction in risk to children or others and any tightening of the standard would render it unachievable, we recommend against making ozone a priority for review under SB 25. The case for putting nitrogen dioxide in the first tier is weak. The controlled exposure studies cited suggest possible concern at concentrations above the existing standard. On the other hand, the existing state standard has been met everywhere in California, and ambient concentrations are expected to continue to decline for at least the next decade.

Comments for the California OEHHA/ARB Public Meeting of the Air Quality Advisory Committee on the Adequacy of California Ambient Air Quality standards: Senate Bill 25 – Children’s Environmental Health Protection Berkeley, CA, October 12-13, 2000

**Jon M. Heuss
Air Improvement Resource, Inc.**

As noted in the comments submitted on October 4, 2000, we are focusing our comments on the first tier of pollutants recommended by OEHHA staff for review and possible revision. In particular I will focus on ozone and particulate matter (PM).

One of the five factors considered in assessing the standards’ health protectiveness is the “degree of exposure relative to the level of the standard.” Unfortunately, Chapter 3 and Appendix B of the Draft do not adequately discuss this factor. They fail to mention the existence of a significant background of ozone in the troposphere that arises from sources other than California or even U.S. precursor emissions. They also fail to inform the reader, except in very general terms, of the extent to which the existing state standards are exceeded throughout the state. These failures result in the omission of important facts that influence the determination of the health protectiveness of the existing state ozone and PM10 standards.

For example, there is a substantial background of ozone in the troposphere (that averages about 0.04 ppm but reaches 0.08 ppm on the order of once per year). It arises from several sources. One source is stratospheric ozone that mixes into the troposphere and is destroyed at the ground. Another source is photochemical reactions in the troposphere of natural geogenic and biogenic emissions: methane, isoprene, terpenes, and natural Nox from lightning and biological action in the soil. This background provides a practical limit as to how low any ozone air quality standard can be set. The transport of plumes of man-made ozone downwind of cities into rural areas is another phenomenon that occurs and can cause elevated ozone in rural and remote locations. However, there is also a well-documented phenomenon known as tropopause folding that inserts plumes with high concentrations of stratospheric ozone into the troposphere. These plumes are generally inserted well above ground level where they slowly mix into the general troposphere. But on rare occasions, they have been measured at ground-level with ozone concentrations up to 0.20 ppm or higher.

The state ozone standard of 0.09 ppm for 1-hour is defined as an extreme value standard; it is met when the Expected Peak daily Concentration (EPDC, that concentration expected to occur once per year) is below the level of the standard. In fact, the EPDC in the cleanest, lowest emission density counties and air basins of California are typically between .075 and .085 ppm. Similar

peak 1-hour ozone concentrations are also measured in other remote locations in the western U.S. This means that the amount of man-made ozone allowed by the existing state standard is on the order of 0.01 to 0.02 ppm. The presence of a substantial background of ozone needs to be taken into account in any decisions regarding revision of the California ozone standard. If the ARB decides to proceed with review of the state ozone standard, ARB staff should initiate detailed field studies of ozone levels and sources in remote California locations. When the current state standard was set in 1987, staff erroneously assumed that the ozone background did not exceed 0.04 ppm.

For PM₁₀, ARB data summaries indicate that the state 24-hour standard is exceeded throughout the state except for compliance in a few high elevation counties. The maximum EPDC in Lake County is substantially below the state 24-hour standard, but in all the other rural and remote basins, the maximum EPDC is substantially above the existing state 24-hour PM₁₀ standard. In the Great Basin Valleys, the maximum EPDC has been on the order of 400 $\mu\text{g}/\text{m}^3$ in recent years, or 8 times the state 24-hour standard. In contrast, the state annual geometric mean standard is met in the rural and remote areas of California but not in the more urbanized air basins. However, the maximum annual geometric mean PM₁₀ in the rural and remote basins of California (except for Lake County) varies between 20 and 30 $\mu\text{g}/\text{m}^3$. It is known that wind-blown crustal material is the major contributor to high PM₁₀ concentrations in rural and remote areas of California. While some wind-blown dust is controllable, much is not. Therefore, the level of PM₁₀ that is achievable with complete elimination of man-made pollution varies substantially across California. There is also significant variation in the composition of PM₁₀ across the state that would be expected to alter the toxicity per unit mass of PM. These variations need to be documented and taken into account in any decisions regarding revision of the California PM standards.

Section 3.6 on indoor and personal exposure needs to acknowledge that indoor ozone concentrations are dramatically reduced compared to outdoor concentrations (see Table B10-1) while PM exposures indoors are often elevated above outdoor concentrations. This also has important implications for the magnitude (and sources of) human personal exposure to ozone and PM₁₀. An informed discussion of the interpretation of the existing health studies must be predicated on what is known about human patterns. For ozone, this includes consideration of the probabilistic analyses carried out by EPA over the past decade. For PM, this includes consideration of the body of information concerning the relation of fixed monitors to indoor and personal exposures as well as factors such as the personal cloud, indoor combustion sources, and re-suspension of particles. Recent studies involving real-time measurements indicate that indoor activities such as cooking, cleaning, and even brisk walking generate high short-term exposures to ultrafine, coarse and fine PM. If outdoor PM is as dangerous as suggested by some epidemiologic studies, then these everyday human activities involve similar risks.

Another of the five factors that was considered in assessing the existing standards' health protectiveness is "the level of risk of effects anticipated at or near the level of the existing standard." When EPA last reviewed the national ambient air quality standards for ozone, the probabilistic risk assessment that will be discussed by Dr. Vostal played a key role. The U.S. EPA's Clean Air Science Advisory Committee (CASAC) concluded that because it appears that ozone may elicit a continuum of biological responses down to background concentrations, risk assessments must play a central role in identifying an appropriate level for the standard. However, when CASAC viewed the results of the probabilistic modeling, the risks for all segments of the population including outdoor children were small and the committee concluded that there was no "bright line" that distinguished any of the proposed standards as being significantly more protective of public health. The standards considered ranged from the existing 1-hour federal standard of 0.12 ppm down to levels roughly equivalent to the current California standard.

Although EPA promulgated an 8-hour ozone standard of 0.08 ppm, which is intermediate in stringency between the 1-hour federal standard and the existing California standard, EPA could not defend its choice adequately to the Court of Appeals when challenged by a group of small and large businesses as well as several states. The Court of Appeals noted that EPA regards ozone definitely and PM, likely, as non-threshold pollutants, that is ones that have some possibility of some adverse health impact (however slight) at any exposure level above zero. The court indicated that, therefore, the only concentration for ozone and PM that is utterly risk-free, in the sense of direct health impacts, is zero, and for EOA to pick any non-zero level, it must explain the degree of non-perfection permitted. However, the court found that EPA articulated no "intelligent principle" in applying the factors used to determine the public health concern associated with different levels of ozone and PM and remanded the new ozone and PM standards back to EPA. This issue is now in the U.S. Supreme Court.

No matter what the Supreme Court decides, California will have to address the same issues under SB 25 of what standards protect the public health, with an adequate margin of safety. Before any of the existing standards are revised, a much more extensive and critical review of the literature must be carried out, and some formal decision analytic framework or risk assessment procedure will be required.

For ozone, there is another factor that EPA is required to consider. The Court of Appeals ruled that the beneficial effects of ground-level ozone (in shielding the public from the harmful effects of the sun's ultraviolet rays, including cataracts and skin cancers) must be weighed in the same manner that ground-level ozone's ill effects are weighed. Although stratospheric ozone provides the main protection against UV, it is actually the total column of ozone that provides protection.

Turning to PM, as the Draft indicates, ambient PM is a mixture of many different elements and compounds, including organic, inorganic, and biologic materials. Therefore it is not surprising that EPA acknowledged in its recent PM review that there are unusually large uncertainties associated with establishing standards for PM relative to other single component pollutants. In response to the many concerns over the scientific basis for PM_{2.5} or PM₁₀ standards, Congress authorized a dramatic increase in federal PM research and a National Academy of Sciences Panel was used to focus the effort on key issues. Some of that new research is now becoming available. Much more will be published over the next several years. The U.S. EPA is scheduled to release a public review draft of a new PM Criteria document shortly. However, new studies of relevance to PM standard-setting are published monthly. As California reviews its PM standards, we urge the Staff to fully evaluate all of the available information.

In summary, we acknowledge that the California PM₁₀ standards need to be reviewed. However, the review should be focused on identifying which, if any, of the components of ambient PM are casually related to health effects. Among the hypotheses offered that may explain the PM-health associations are PM₁₀ mass itself, fine particle mass, ultra fine PM, particle number count, particle surface area, reactive transition metals, acids, organic compounds, biogenic particles, sulfates, peroxides, elemental carbon, and gaseous co-pollutants. As noted above, there is substantial work underway to evaluate and discriminate among all these hypotheses. It is critically important to do this so that PM controls are focused on actions that improve public health.

In the case of ozone, the existing California standard is very close to peak once-per-year background levels. Since tightening the standard would not result in significant reduction in risk to children or others and any tightening of the standard would render it unachievable, we recommend against making ozone a priority for review under SB 25. The case for putting nitrogen dioxide in the first tier is weak. The controlled exposure studies cited suggest possible concern at concentrations above the existing standard. On the other hand, the existing state standard has been met everywhere in California, and ambient concentrations are expected to continue to decline for at least the next decade.

E.3 Comments to the Board

The Board received written comments from Mr. Jon Heuss prior to the December 7, 2000 Board Hearing. Copies of these comments follow, along with the ARB Staff response.

E.4 Response to Comments to the Board

As discussed in several reference books (Finlayson-Pitts and Pitts, 1999; Seinfeld and Pandis, 1998), levels of ozone worldwide before the industrial revolution appear to have been about 10-15 ppb. However, at the present time, levels of 30-40 ppb are found in even the most remote regions. This increase has been attributed to increased anthropogenic emissions of oxides of nitrogen (NO_x) and volatile organic compounds (VOCs). Much of the evidence for increased baseline levels of tropospheric ozone comes from European studies. An analysis (Volz and Kley, 1988) showed that surface ozone near Paris 100 years ago averaged about 10 ppb; current mixing ratios in the most unpolluted parts of Europe average between 20 to 45 ppb. An analysis of ozone measurements made in relatively remote European sites indicates a 1 to 2 % annual increase in average concentrations over the past 30 years.

The database of ground-level ozone observations for urban and suburban areas in California is fairly extensive. At most urban surface sites, ozone concentrations have been found to vary over a diurnal cycle with a low value recorded in the early morning hours and a maximum in the late afternoon. In addition to variation over a diurnal cycle, ozone concentrations at a given location also can vary significantly from one day to the next. It is not uncommon for the daily maximum ozone concentrations at an urban site, for instance, to vary by a factor of 2 or 3 from day to day as local meteorological conditions change. In and downwind of large urban areas, under certain meteorological conditions, emissions of NO_x and VOCs can result in ozone concentrations as high as 200 to 400 ppb. Apart from remote regions, where the *in situ* tropospheric chemical generation of ozone is driven essentially by methane, a large number of VOCs participate in ozone generation. Measurements of nonmethane organic compounds in southern California revealed over 280 hydrocarbon and oxygenated organic species, many of which contribute in some degree to ozone generation.

Background concentrations for ozone are defined as concentrations that would be observed in the absence of the ozone formed from anthropogenic precursor emissions of VOC and NO_x. Mr. Heuss's letter states that "the peak once-per-year 1-hour ozone concentrations at the most remote California monitoring sites are between 0.078 and 0.087 ppm". Due to pervasive anthropogenic influences, these do not represent a "natural background". The real challenge is to estimate what the natural background concentrations (which exclude all anthropogenic sources) are for ozone at the remote monitoring sites in California. Transported ozone, VOCs, and NO_x all affect ozone concentrations in downwind areas. It has been demonstrated that photochemically generated ozone starts accumulating during the daylight hours in urban areas, and then is transported downwind, and that precursors can continue to form ozone over distances greater than hundreds of kilometers for one or more days. Thus, the reported peak 1-hour ozone concentrations of 0.078 and 0.087 ppm at the remote California monitoring sites are likely indicative of both anthropogenic and natural impacts at those sites.

The U.S. EPA has accepted the approach of using remote monitoring sites in the world as a reasonable way to establish limits on natural ozone exposures, and believes that natural background levels of ozone range from 0.03 to 0.05 ppm. In its human health risk assessment, U.S. EPA assigned a health risk to every hourly average concentration above 0.04 ppm.

Global background ozone concentrations (typically around 40 ppb annual average) are used to estimate the anthropogenic reductions needed to attain Ambient Air Quality Standards. Due to stratospheric intrusion, this value could be higher on design value days, as Mr. Huess stated in his letter. However, stratospheric intrusion is relatively infrequent, and data are almost never available to document and quantify its influence on the design days. Also, the processes associated with stratospheric intrusion are often not associated with days with design value ozone concentrations.

Figure 1 below presents vertical profiles of temperature, relative humidity, and ozone concentration at Trinidad Head in November 2000. Data from this remote coastal site indicates a background tropospheric ozone concentration of about 40 ppb. Once the tropopause is reached (where the temperature ceases to decline adiabatically (about 12.5 km in this case), the ozone concentration in the lower stratosphere begins to increase rapidly.

The high ozone concentrations in the stratosphere can advect into the troposphere under a variety of relatively rare processes. Figure 2 illustrates some days during 1999 when ozone concentrations on Mauna Loa increased substantially (max/mean ratio ≥ 1.5). This ratio occurred about 5% of the time during 1999. These events are not necessarily due to stratospheric ozone intrusion, and much more research would be needed to determine the cause(s).

One potential technique for differentiating between natural and anthropogenic ozone episodes is to look at the O₃/CO ratio. Theoretically, this ratio would be higher than ~0.35 (assuming background ozone about 0.035 ppm and background CO about 0.1 ppm). Unfortunately, most remote monitoring sites do not collect CO data, and often the level of detection of the instruments is too high. Figure 3 is a sample of some data collected during SCOS97 (Southern California Ozone Study, 1997) at Mt. Baldy. This is a mountain site downwind of the Southern California Air Basin, and had two observations that could possibly have some non-anthropogenic contribution.

Figure 4 provides some information on the variations in global background ozone concentrations at some "clean" sites around the world, indicating that most of these remote areas averaged between 20 and 40 ppb ozone.

A logistically sound procedure to establish an environmental quality standard must involve several steps. First, one should establish the risk to human health or welfare as a function of the dosage of a pollutant. This step involves study of the onset of adverse health effects due to a pollutant or a group of pollutants. Second, one should determine the maximum acceptable risk based on risk-benefit and other considerations. This risk level constitutes the basis for an environmental quality standard, and corresponds to a specific level of exposure. In this connection, the California air quality standards are designed to protect public health.

Thus, as the California Clean Air Act requires, we must review and consider possible revision of the health-based ambient air quality standards to assure that standards are based on the latest scientific information, and that the standards protect public health with an adequate margin of safety. The California Clean Air Act mandates that ambient air quality standards be health based. Possible impacts of stratospheric ozone or background pollutant concentrations on ambient air quality are considered in the planning process for standard implementation. Whether standards are currently achievable is also an issue for implementation of the standards, not for selection of the level of the standards.

References

Finlayson-Pitts, B.J., and J.N. Pitts, Jr. Chemistry of the Upper and Lower Atmosphere. Theory, Experiments and Applications. Academic Press, San Diego, CA. 1999.

Seinfeld, J.H., and S.N. Pandis. Atmospheric Chemistry and Physics. From Air Pollution to Climate Change. John Wiley & Sons, Inc. New York. 1998.

Volz, A., and D. Kley. Evaluation of the Montsouris series of ozone measurements made in the Nineteenth Century. *Nature.* 332: 240-242. 1988.

Figure 1:

Ozonesonde, Trinidad Head, Nov. 2, 2000

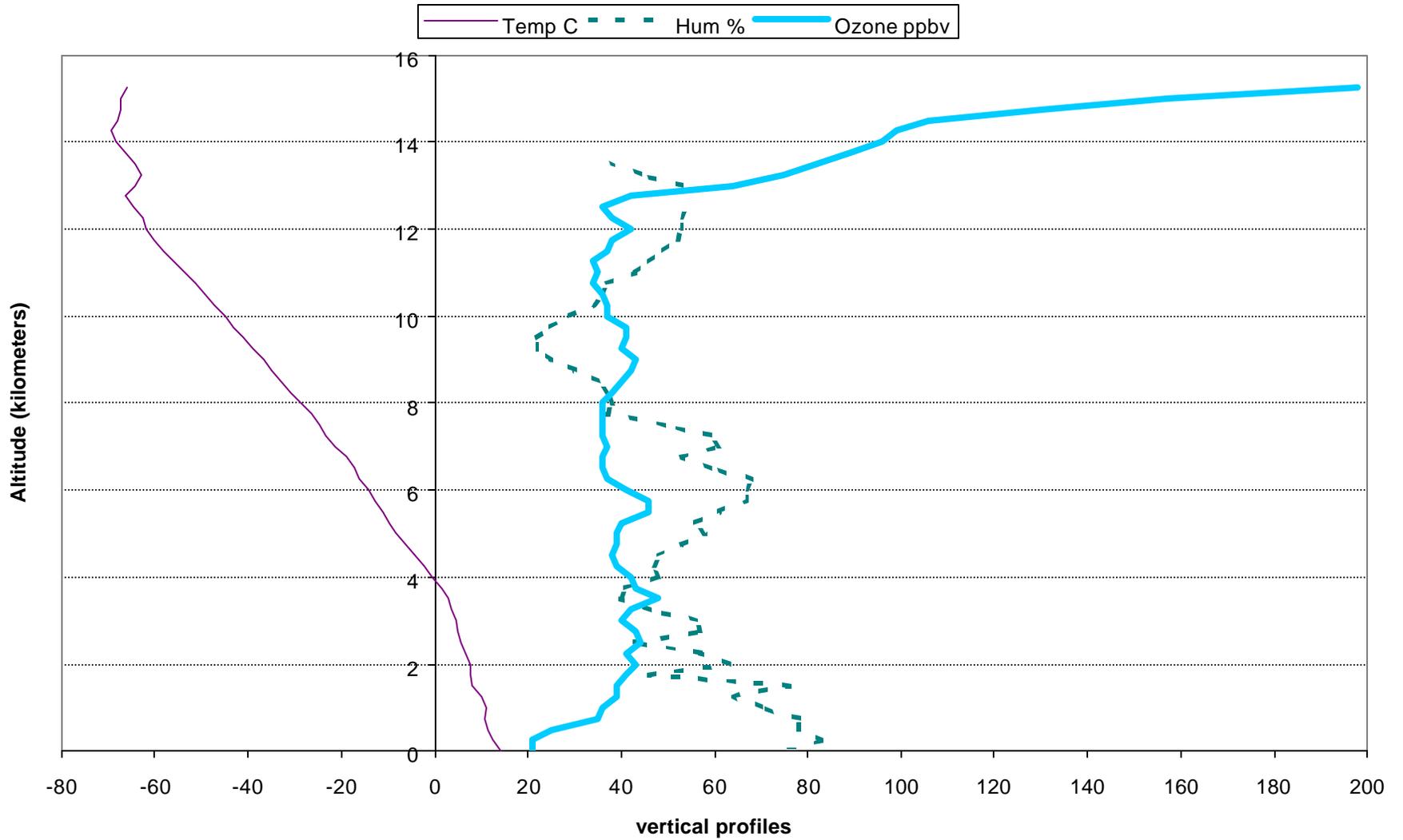


Figure 2:

Diurnal Ozone Concentrations (ppb) at Mauna Loa, HI during 1999 on days when max/mean ≥ 1.50

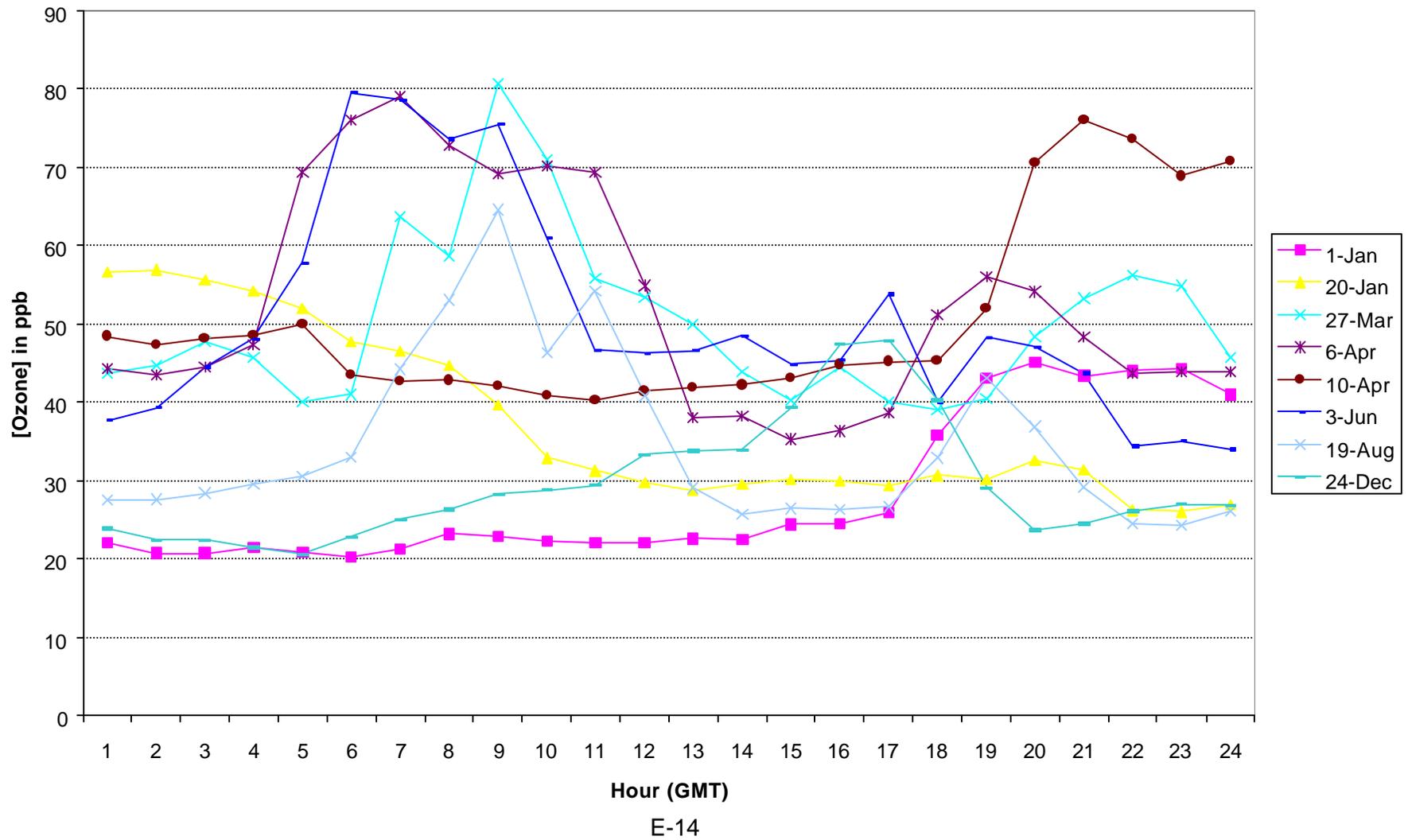


Figure 3: CO, O3 and Their Ratio on Mt. Baldy.

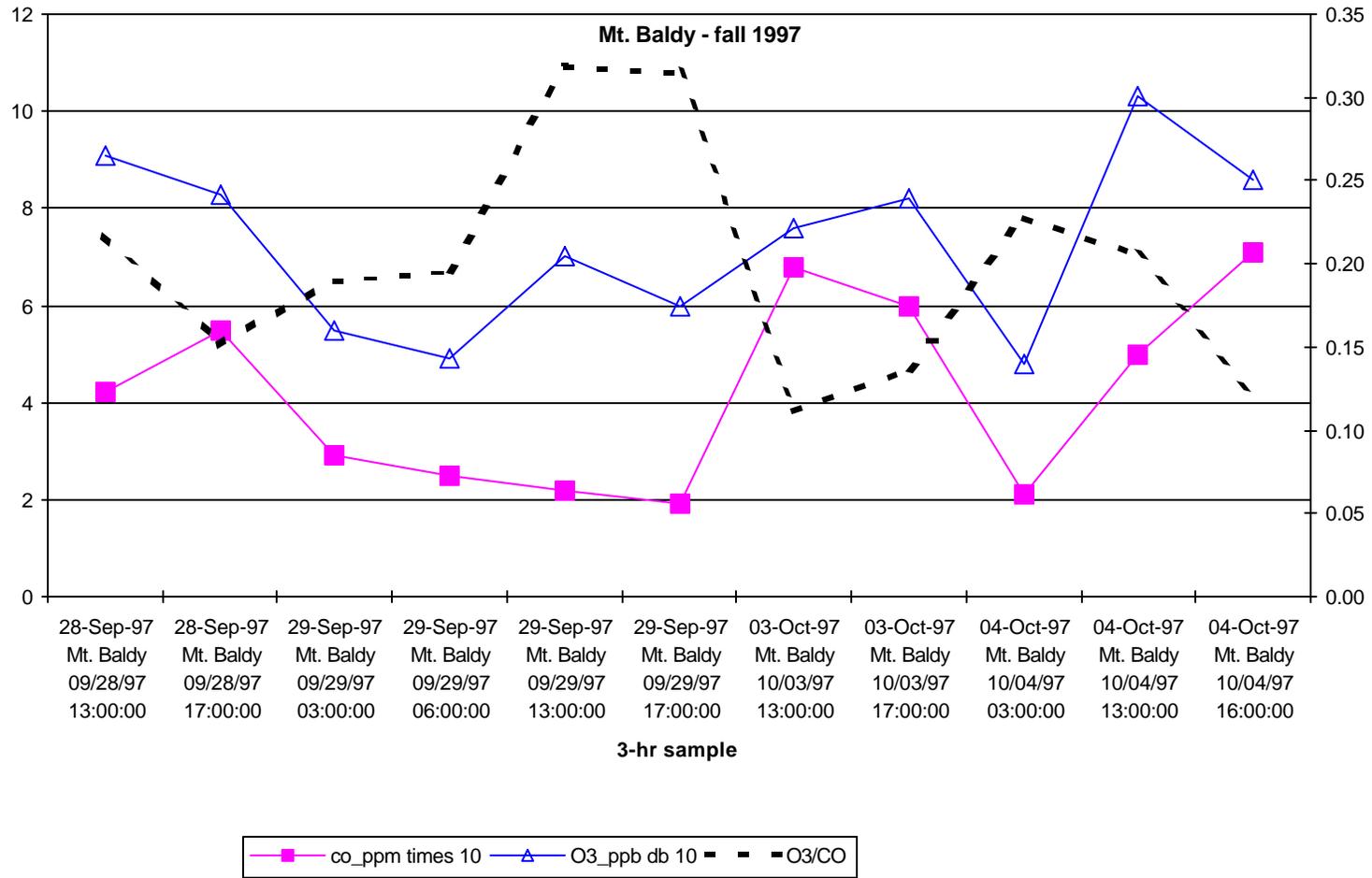
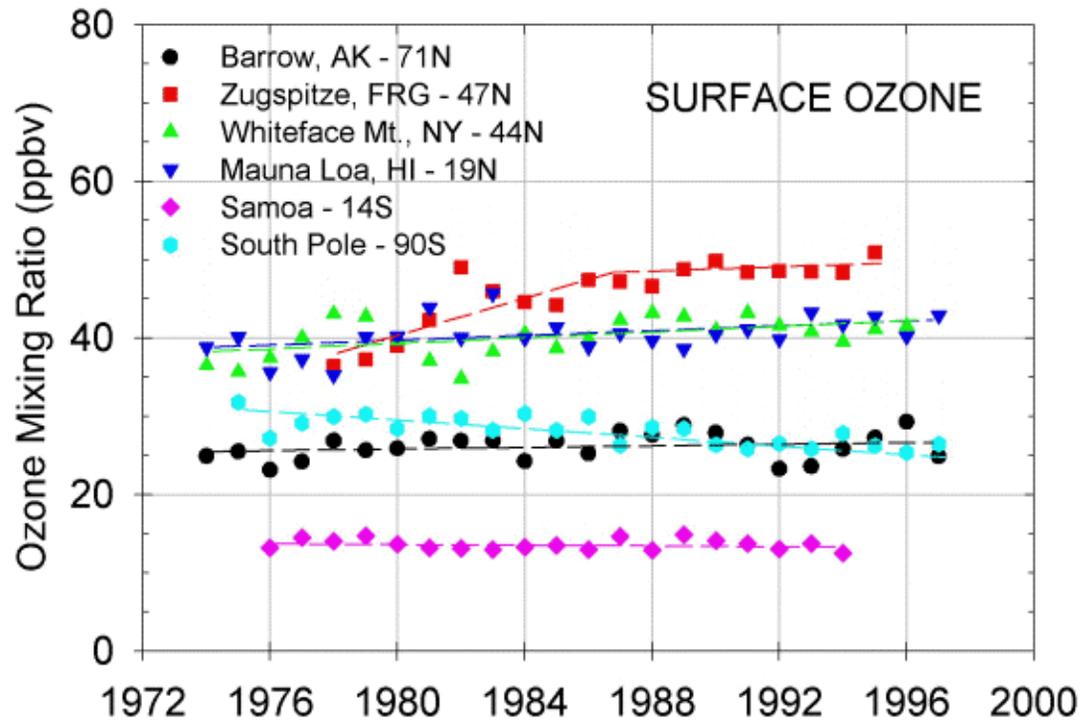


Figure 4: Surface ozone at remote sites





December 4, 2000

Clerk of the Board
Air Resources Board
P. O. Box 2815
Sacramento, CA 95812

**Re: November 2, 2000 Staff Report
Adequacy of California Ambient Air Quality
Standards:
Children's Environmental Health Protection Act**

At the request of General Motors Corporation, Dr. J. J. Vostal of Environmental Health Consultants International and I provided written and oral comments on the September 12, 2000 Draft Staff Report. We were pleased that the written comments provided prior to or at the October 12-13 meeting of the Air Quality Advisory Committee were included in Attachment E of the November 2, 2000 Staff Report. However, we were disappointed in the ARB summary of and response to our comments. The summary on page E-2 lumps our comments into two general points and responds to each point in a general fashion. We believe the specific comments we made are relevant to the strength of the evidence concerning the adequacy of the current California air quality standards to protect children's health and the priority for review under SB 25.

Three points concerning the current ozone standard are particularly relevant to the recommendation that ozone should be a priority one pollutant.

First, background ozone provides a practical limit as to how low any ozone air quality standard can be set, and the current California standard is already very close to the background of ozone. The statement on page C-2 that "the background concentration of ozone is currently about ½ of the state standard, or 0.04 ppm" is misleading because it is an "apples-to-oranges" comparison. The ozone background does average about 0.04 ppm over a year, but the state standard is not an annual average concentration. The state standard is a once-per-year peak 1-hour concentration of 0.09 ppm. The peak once-per-year 1-hour ozone concentrations at the most remote California monitoring sites are between 0.078 and 0.087 ppm. The peak once-per-year 1-hour background ozone concentration has been estimated by the U. S EPA at between 0.060 and 0.075 ppm. Substantially higher concentrations of ozone due to stratospheric intrusions have been measured at ground level, albeit rarely. Although stratospheric intrusions rarely bring high ozone concentrations

directly to the ground, they routinely insert layers of elevated ozone in the free troposphere which contribute to a substantially varying background.

A more complete analysis of the sources and levels of background ozone is attached. If the peak 1-hour background ozone at a site is 0.078 ppm, for example, that represents 87 % of the current 1-hour standard at the site and would allow only 0.012 ppm ozone from man-made emissions on the day in question.

Second, the risk assessment carried out by the U. S. EPA during its latest review of the federal ozone air quality standard documents that exposures of concern for outdoor children will be rare upon attainment of the current California standard. As noted in the Staff Report, the effects most consistently reported at low ambient concentrations in epidemiological studies are decrements in several measures of lung function. When the U. S. EPA and its Clean Air Science Advisory Committee (CASAC) evaluated the significance of small functional changes, it concluded that small functional responses in either healthy or asthmatic individuals would not be considered medically significant and would not be expected to interfere with normal activity. Even isolated events with moderate functional changes were not considered to be of public health significance. Only when moderate responses were repeated did CASAC members indicate that it was a matter of public health concern.

Third, since the 1996/1997 EPA review, new information on the mechanism of reported lung function changes has been published which substantially reduces the concern over measured changes or decrements in lung function. A 1998 U. S. EPA study has documented that the changes in performance of respiratory function tests are primarily the result of irritated nerve receptors not cellular injury in the respiratory airways. In essence, the measured declines in lung function are only declines in test performance due to the body's nervous system sensing the presence of an irritating gas and limiting maximal inspiration and not any damage or change to pulmonary function. Based on this new information, which is not discussed in the Staff Report, the public health significance of field and clinical studies using forced expiratory volume as an index of pulmonary function changes needs to be re-evaluated.

In summary, these three points taken together document the very conservative, health-protective nature of the current California ozone standard. They need to be considered by the Staff and the Air Resources Board before the decision is made to make ozone a high priority for review.

The Notice for the December 7, 2000 ARB hearing indicates that the ARB under SB 25 requires the Board to review, and if necessary revise, air quality standards "determined to be inadequate to protect infants and children with an adequate margin of safety." However, the Staff Report does not make or recommend a determination that certain standards are inadequate to protect public health. Rather it identifies pollutants "representing greater potential risks to public health at the concentrations of the current air quality standards." Further, it is indicated that "recent scientific publications suggest that health effects may occur when ambient levels of these pollutants are at or near the current State ambient air quality standards." In the response to comments (page E-2), staff indicates:

"The purpose of the reviews presented in the staff report was to consider whether there was evidence suggesting that any of the California Ambient Air Quality

Standards should be reviewed with reference to adequacy of protection of infants, children and other susceptible populations. It was not the intent of staff to provide complete reviews on each pollutant.”

Given the stated purpose and limited nature of the Staff/OEHHA review and the many caveats in the way the results are presented, it would miss-characterize the recommendations for review as a determination that the current standards for these pollutants are inadequate. Rather the recommendations indicate that some of the current standards may or may not be adequate and thus should be reviewed, and revised if necessary, based on a full analysis of all the relevant information.

Finally, we were also disappointed that Dr. Vostal’s written comments provided to OEHHA after the Advisory Committee meeting but prior to the issuance of the November 2, 2000 Staff Report were not included in Appendix E. Please include those comments in the record.

I appreciate the opportunity to provide these comments. Thank you for your consideration.

Yours truly,

Jon Heuss
Principal Scientist
Air Improvement Resource, Inc.

cc: Members of the Air Resources Board
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Att:

Summary of the scientific evidence for the sources And levels of background ozone in California

Ozone is present in the atmosphere due to both natural processes and the photochemical reactions of man-made emissions. During the Air Quality Advisory Committee meeting on October 12 Dr. Kleinman indicated:

“ozone is one of those rare environmental pollutants that we do have a natural background of which strangely enough is right around the 30 ppb level” AQAC Transcript at page 62.

One of the main points raised by Mr. Heuss during public comments at the meeting was that there is a variable background of ozone that averages 0.04 ppm (40 ppb) but that reaches as high as 0.08 ppm (80 ppb) about once-per-year in remote locations. In response to a request from Dr. Lipsett of OEHHA to address the issue of background ozone and stratospheric intrusions into the troposphere “because we rely on you for those assessments as to what background levels are in California,” ARB staff indicated:

“We’re certainly aware of the research done on tropopause folding in the eastern U. S. We have not done a comprehensive study here in California, but the data that we have looked at from our field studies and from background ozone monitors off shore indicate that the global background that we see is 0.04 ppm with no – and every excursion about the 0.04 level appears to be associated with transport from urban areas.” AQAC Transcript at page 115-116.

There is particular interest in what we will call “background ozone” because it defines a lower boundary for the amount of ozone that will exist in the absence of man-made emissions. This attachment discusses the various sources of ozone in the atmosphere as well as the levels of ozone that arise from the various sources. In addition, the definition of background ozone is discussed.

Sources of ozone in the troposphere

It is well established that there is a background of ozone in that atmosphere. The U. S. EPA’s 1996 Criteria Document (CD) summarizes the sources of background ozone as follows:

“The background of O₃ can be attributed to the following sources: downward transport of stratospheric O₃ through the free troposphere to near ground level, in situ O₃ production from methane emitted from swamps and wetlands reacting with natural NO_x emitted from soils and lightning strikes and from downward transport of NO from the stratosphere into the troposphere, and in situ production of O₃ from the reactions of biogenic VOCs with natural NO_x. Another source to be considered is the long-range transport of O₃ from distant pollutant sources.” 1996 Ozone CD at page 3-6

For the purposes of the State of California, the important question is what level of ozone would exist with total elimination of anthropogenic or man-made emissions in California. Although other definitions are possible, the practical question in California is how low ozone would be if all California man-made emissions were eliminated. There is some evidence that the background of ozone may have risen over the past hundred years, as global methane and NO_x emissions have risen. There is also evidence for long range transport of man-made ozone influencing distant sites. However, the issue for California is not what natural ozone may have been in some pre-industrial past but rather what the concentrations of ozone are now due to sources outside the state and non-anthropogenic sources within the state.

The photochemical production of ozone was discovered in Los Angeles in the late 1940's when Prof. Haagen-Smit demonstrated that photochemical reactions between oxides of nitrogen and hydrocarbons in the presence of sunlight produce ozone. In the intervening years, it has been shown that natural biogenic and geogenic emissions as well as man-made emissions participate in these photochemical reactions. It has also been shown that ozone itself photolyzes in the atmosphere and reacts with various other constituents. Thus, there is both photochemical production and destruction of ozone occurring in the atmosphere.

It is also well known that ozone is formed in high concentrations in the stratosphere due to oxygen molecules absorbing short wavelength radiation from the sun (175 to 240 nm). In fact, the presence of stratospheric ozone (which absorbs the sun's radiation below 290 nm) protects humans and ecosystems by filtering out dangerous ultraviolet radiation. A major sink process for the ozone in the stratosphere is transfer into the troposphere and eventual destruction at the ground. Several mechanisms for stratospheric-tropospheric exchange have been postulated and studied. Shapiroⁱ summarizes these mechanisms as follows: "The various meteorological processes by which air and its chemical constituents are exchanged between the stratosphere and troposphere may be summarized as 1) the mean meridional Hadley cell circulation; 2) the seasonal variation in the height and potential temperature of the tropical tropopause; 3) changes in the potential temperature and vertical displacement of the tropopause through radiative cooling above the jet stream and cumulonimbus cirrus clouds at the tropopause; 4) transverse mass circulations about subtropical jet stream systems; 5) vertical mass exchange during tropopause "folding" events associated with extratropical cyclonic systems; 6) cumulonimbus towers which penetrate the tropical and extratropical tropopause; 7) clear air turbulence (CAT) in the vicinity of jet streams (resulting from vertical wind shear instabilities within tropopause folds) and in the region of decreasing winds in the stratosphere above the jet core; and 8) weak eddy diffusion across the vast quiescent expanses of the tropopause."

The fifth mechanism noted above, tropopause folding events, is of particular interest because it has been amply documented that it inserts layers of high ozone concentrations into the troposphere.

Evidence concerning tropopause folding events

Published observations of stratospheric ozone in the troposphere during intrusion events began appearing in the literature in the 1960's. In 1981, Johnson and Viezeeⁱⁱ reported

on the results of 10 aircraft flights during the spring and fall of 1978 mapping the structure of stratospheric ozone intrusions over the central U. S. They concluded:

“The intrusions typically are characterized by peak ozone concentrations at higher altitudes (6-8 km) in the range of 240-400 ppb, diminishing to 100-200 ppb at lower altitudes as mixing with surrounding air occurs. The data show that stratospheric ozone intrusions are typically 100-300 km wide in the cross-wind direction, are several hundreds of kilometers long, and can be tracked down at least as far as the top of the atmospheric boundary layer (about 2 km). Possible mechanisms for downward transport within the boundary layer include normal convective mixing, organized convection associated with cloud and precipitation processes, and organized downward motion within frontal zones.”

In a follow-up paper by Viezee, Johnson and Singh,ⁱⁱⁱ the authors assessed the downward flux of ozone and its probable impact on ground-level ozone. They summarized and evaluated 17 aloft observations of stratospheric ozone made by aircraft or balloons and 10 published studies that in which elevated ground-level ozone measurements have been ascribed to stratospheric ozone. They estimated that direct ground-level impacts are infrequent (less than 1 percent of the time) and most likely are associated with ozone concentrations of 100 ppb or less.

One of the reasons that that direct ground-level impact seems rare is that, as documented by Johnson and Viezee, the ozone intrusion tends to become more nearly horizontal as it progresses toward lower altitudes. Viezee et al note:

“Several investigators maintain that the stratospheric air reaches ground-level in about two days by way of surface high-pressure systems that follows travelling upper tropospheric low-pressure troughs. If this concept is correct, it will be difficult to quantify (on the basis of measurements) the stratospheric component of the near-surface ozone budget, since high-pressure areas also are favorable for air stagnation and surface transport of anthropogenic ozone.”

Indeed, Wolff et al.^{iv} have reported on field studies in rural locations in Kentucky and North Carolina and a remote location in South Dakota. They found that ⁷Be, a tracer of stratospheric air, is higher on the backside of high-pressure system than on the front side. Although there are limitations to using ⁷Be as a tracer for stratospheric air, this finding suggests that a substantial amount of stratospheric ozone does mix to the ground under conditions where anthropogenic ozone formation is also expected.

Shapiro¹ has also reported evidence for the seventh mechanism noted above - clear air turbulence (CAT) in the vicinity of jet streams (resulting from vertical wind shear instabilities within tropopause folds). He reports ozone concentrations of over 200 ppb over Southern California in March 1978.

With multiple mechanisms of stratospheric-tropospheric exchange and with multiple ways that stratospheric ozone may mix with tropospheric ozone, it is not surprising that there is a great deal of variation in free tropospheric ozone concentrations. For example, Gregory et al.^v report ozone measurements in the free troposphere at altitudes from 5 to 7.5 km measured by aircraft traversing from 44 N latitude to 46 S latitude in the fall of 1982. They reported higher ozone concentrations in the Southern Hemisphere (with a 2 degree zonal average as high as 80 ppb). During one flight, a region of elevated ozone

was determined to be of stratospheric origin with a maximum ozone concentration of 110 ppb. In contrast, similar flights in 1978 had shown higher ozone in the Northern Hemisphere. The combined data sets demonstrate that ozone levels in the free troposphere can be highly variable, so that one cannot assume that the free troposphere is a well-mixed reservoir of ozone.

Aircraft measurement over the eastern U. S. and western Atlantic during the spring of 1996 reported by Parrish et al.^{vi} confirm the significant variability in tropospheric ozone concentrations. In 72 hours of measurement during nine flights, ozone concentrations varied between 30 ppb and 285 ppb. The authors used the CO-ozone relationship to discriminate between stratospheric and anthropogenic influences. The authors indicate that strong stratospheric influences were observed on more than half the flights with ozone levels as high as 285 ppb. There was evidence of anthropogenic influence that resulted in net production of ozone at some times and net destruction of ozone at other times. Most data points reflected both stratospheric and anthropogenic influences

Parrish et al. also evaluated the transport of NO_x species out of the boundary layer and reported that, in this springtime period, only a few percent of the emitted NO_x is transported out of the boundary layer either as NO_x or its oxidation products. Therefore, the authors concluded that the potential for photochemical ozone production from exported anthropogenic pollution is limited. Finally, they concluded that these measurements suggest that the direct effect of anthropogenic surface emissions on tropospheric ozone is approximately neutral in the spring.

A recent study by Beekmann, et al.^{vii} used several techniques to evaluate the presence of tropopause folds. They report that:

“on the average, folds occur twice as much in the Northern than in the Southern Hemisphere. In the Northern Hemisphere they are concentrated in the latitude band 40-70 degrees. On the average, 18.4 folds are simultaneously present in the Northern Hemisphere.”

The number of simultaneous folds (estimated through analysis of a 10-year meteorological data set) is roughly four times the number estimated by Viezee, et al. in 1983. Beekmann et al. also refer to a 1996 study that shows tropopause folds are often detected in the front side of troughs, but also in their rear and in regions of zonal flow of the polar jet stream. With the meteorological analysis, Beekmann et al. found that significant tropopause folding activity was present over the ten-year period over the Northern Pacific as well as over California. (See Figure 2 of Beekmann et al.)

Emmons et al.^{viii} have recently compiled data for ozone and other chemical species from a number of aircraft studies into global maps. The maps provide information on ozone averaged onto 5 degree latitude by 5 degree longitude horizontal grids with 1 km vertical resolution. The available data show elevated ozone concentrations of between 40 and 100 ppb in the grids 6-8 km over the west coast of the U. S. in the March-April-May quarter (see Plate 1 of Emmons et al.). The data for other locations, heights and time periods demonstrate significant variability in tropospheric ozone levels. This large data set clearly demonstrates that ozone levels in the troposphere are highly variable, so that one cannot assume that the free troposphere is a well-mixed reservoir of ozone.

Contributions of various sources to ground-level ozone

The evidence for tropopause folding events as a large source of stratospheric ozone that is inserted into the troposphere is overwhelming. However, the contribution of this large ozone source to ground-level ozone is still somewhat uncertain. For example, Beekmann et al. indicate:

“Although the formation mechanisms of tropopause folds are now well-understood, detailed knowledge to which extent intruded air masses succeed in entering the lower troposphere, the planetary boundary layer, or even the ground level, is still lacking”

There is also substantial uncertainty regarding other source and sink processes that determine the tropospheric ozone budget. In 1985 Vukovich, et al.^{ix} indicated:

“Thus it is now recognized that the tropospheric ozone budget consists of four components: transport from the stratosphere; photochemical production; deposition at the ground; and photochemical destruction. Although each term contributes significantly to the tropospheric ozone budget and the estimates of each one yield a comparable order of magnitude, the quantification of each of these terms is difficult. Thus, a global estimate of any of them at the present time probably cannot be achieved to better than a factor of 2 or 3.”

Even today, there is still significant uncertainty in the strengths of the various photochemical sources and sinks. For example, Parrish et al. note that many photochemical model results indicate that the net anthropogenic effect on tropospheric ozone levels is positive in all seasons, a finding which disagrees with the observations they report in the spring. There is also disagreement over how many ozone molecules are produced, on average, from each NO molecule emitted. The recent NARSTO Synthesis Report^x indicates that more recent studies have reduced the estimated ozone production efficiency from 7 to 10 molecules ozone per molecule NO_x emitted down to 1 to 3. In addition, the NARSTO report acknowledges there is substantial disagreement over key factors such as the magnitude of U. S. biogenic VOC emissions (uncertain by a factor of 2 or 3) and natural NO_x emissions from soil and lightning.

Although there are various estimates in the literature for the strength of the various sources and sinks for tropospheric ozone, they all contain significant uncertainty due to the extremely complex chemistry and meteorology that is involved. Emmons et al. include several comparisons of predictions from global chemical transport models with observations. They indicate that the comparison with available observations has been able to identify incorrect emission sources, incorrect strength of convection and missing chemistry in the models. Although the problem cannot be successfully modeled yet, there is another approach that has been used to bound the problem. As discussed in the next section, actual measurements of ground-level ozone and other atmospheric constituents in upwind and remote locations have historically been used to estimate background ozone.

Background deduced from measurements

The level of background ozone became a policy issue in 1971 when EPA set the first National Ambient Air Quality Standard for Photochemical Oxidants at a concentration of

0.08 ppm for 1-hour, not to be exceeded more than once per year. In 1978, Singh et al.^{xi} reported an analysis of long-term ozone data from remote sites that indicated summertime average 1-hour maxima in the 40 to 50 ppb range but maximum 1-hour concentrations that can approach or exceed 80 ppb in the spring. Singh et al. concluded that achievement of a yearly 1-hour ozone standard of 80 ppb may be impossible.

In the U. S. EPA's 1978 Criteria Document for Ozone and other Photochemical Oxidants, the Agency concluded:

Based on the evidence of stratospheric-tropospheric interchange, the annual average stratospheric contribution to ozone concentrations at ground level is estimated to be 0.022 to 0.05 ppm. The highest concentrations, at or above 0.08 ppm, from that source are expected to occur mostly during April and May."

When EPA revised the federal 1-hour ozone standard in 1979, the Agency acknowledged that:

"Field measurements at some remote sites, where man-caused ozone is likely to be negligible, have shown low-but not insignificant- rates of exceedances of the 0.08 ppm level originally proposed for the secondary standard." 44 Fed. Reg. 8212, February 8, 1979.

In 1989, Logan^{xii} reported the results of an analysis of ozone data from rural locations in the U. S. She reported that ozone concentrations above 80 ppb were common in rural areas of the eastern U. S. in spring and summer (occurring between about 2 and 8 % of the time) but were unusual at remote western sites, occurring less than 0.5 % of the time. She also pointed out that concentrations of NO_x in rural areas of the east are frequently high enough to permit significant photochemical formation of ozone during favorable weather conditions, but that NO_x is much lower in remote regions of the west. Importantly, Logan reported that the median ozone concentrations of 30 to 40 ppb were similar at rural sites across the country even though there is a much greater population and emission density in the eastern U. S. than in the western U. S.

Lefohn and Foley^{xiii} reported in 1991 on an analysis of ozone data from 26 Class I national parks and wilderness areas. For the seven cleanest sites, the yearly maximum 1-hour average concentrations were in the range of 0.06 to 0.075 ppm.

In 1996, Altshuller and Lefohn^{xiv} published an analysis of background ozone in the planetary boundary layer of the U. S. They used the following definition of background ozone:

"The background of ozone may be considered as that portion of total surface ozone that results from photochemical reactions of biogenic or geogenic precursors and from downwind transport of stratospheric air into a specified area. The concentration of background ozone varies as a function of geographic area, elevation, season, and averaging time."

They selected 11 sites for analysis. The criteria they used included using sites receiving the cleanest air masses from the upwind flow off a continent or ocean, and sites isolated from the influence of urban plumes or regional ozone formation from anthropogenic emissions. They reported that the maximum 1-hour concentrations in the western

United States in the April through October period ranged from 50 to 98 ppb and the maximum 1-hour concentrations at coastal sites ranged from 44 to 80 ppb. Most of the exceedances of 80 ppb they reported were from Yellowstone National Park and were influenced, apparently, by forest fires.

The U. S. EPA estimated background ozone during review of the federal ozone standard in 1996/7. At that time, the agency's Staff Paper concluded:

“...a reasonable estimate of the background O₃ concentrations near sea level in the U. S. for a 1-hour daily maximum during the summer is usually in the range of 0.03 to 0.05 ppm. At clean sites in the western U. S., the maximum annual hourly values are in the range of 0.06 to 0.075 ppm.” OAQPS Staff Paper at page 20

In California, the Expected Peak Day Concentrations in the most remote California sites are also significantly above 0.04 ppm. As reported in attachment E of the September 29, 2000 ARB Staff Report on Area Designations, the yearly peak 1-hour ozone concentrations in the most remote sites are in the range of 0.07 to 0.087.

In addition to the evaluation of peak hourly concentrations in long-term monitoring at remote sites, there is also observational data and analyses in the literature that focus on specific episodes of elevated ground-level ozone that may be of stratospheric origin. As noted above, Viezee, Johnson and Singh compiled 10 episodes in which elevated ground-level ozone had been ascribed by various authors to a stratospheric source. For the purpose of this review, I will summarize four other episodes. This is not a complete list of the episodes that have been identified; rather they are meant to serve as examples.

Chung and Dann^{xv} report an observation of elevated ozone that lasted for about a day in December 1980 in Regina, Saskatchewan that they ascribe to downward transport from the stratosphere. There were several peaks during the episode including one with an ozone concentration of 228 ppb. Proyou, et al.^{xvi} report a three day episode of 60 ppb ozone with a peak of 85 ppb in February 1988 in Aubere France that they ascribe to stratospheric origin. Chan and Smith^{xvii} report an episode of elevated ozone accompanying a frontal passage in December 1974 at a remote site in eastern Utah that averaged about 60 ppb for a day and had a peak of 80 ppb. Finally, Logan¹² in her analysis of rural ozone in the U. S. reports on a large-scale regional episode of elevated ozone in March 1978 that lasted several days and had daily maximum concentrations exceeding 120 ppb on two days. A detailed meteorological analysis by Mukammal et al.^{xviii} has ascribed the high values of ozone in this episode to a stratospheric intrusion event. These examples together with the earlier examples in the literature demonstrate that ozone of stratospheric origin does reach ground-level in concentrations considerably higher than 0.04 ppm. They also demonstrate that the concentrations, duration, and meteorological conditions under which such episodes are found vary significantly. This suggests that there are several different mechanisms by which stratospheric ozone reaches ground-level at various times and places.

In many of these episodes, the elevated ozone was monitored at times when photochemical production from man-made precursors was not expected, so the data attracted attention and further analysis. However, the known patterns of tropospheric folds together with the ground-level ozone-⁷Be analyses by Wolff et al. suggest that

stratospheric ozone also contributes significantly to ground-level ozone during times when man-made ozone is present. In these situations, routine monitoring data will not be able to distinguish the anthropogenic contribution from the stratospheric contribution.

Logan indicated that the regional intrusion episode noted above was only one of 17 multi-day episodes she found over the eastern U. S. during a two-year period. However, it is likely that stratospheric ozone contributed to some of the other 16 episodes that occurred under conditions favorable for photochemical production. Although the ARB and the U. S. EPA have "exceptional event" policies, it is clear that only a small portion of the stratospheric intrusions that affect ground-level ozone concentrations will be uniquely identified and thereby qualify for the exceptional event policy.

In summary, the scientific literature on background ozone indicates that it may average about 40 ppb, but that it is highly variable and can reach levels close to the current California 1-hour standard on the order of once per year.

ⁱ M. A. Shapiro, "Turbulent Mixing within Tropopause Folds as a Mechanism for the Exchange of Chemical Constituents between the Stratosphere and Troposphere," *J. Atmospheric Sciences*, **37**, page 994, 1980.

ⁱⁱ W. B. Johnson and W. Viezee, "Stratospheric Ozone in the Lower Troposphere- I. Presentation and Interpretation of Aircraft Measurements," *Atmos. Environ.*, **15**, page 1309, 1981.

ⁱⁱⁱ W. Viezee, W. B. Johnson and H. B. Singh, "Stratospheric Ozone in the Lower Troposphere- II. Assessment of Downward Flux and Ground-level Impact," *Atmos. Environ.*, **17**, page 1979, 1983.

^{iv} G. T. Wolff, M. A. Ferman and P. R. Monson, "The distribution of beryllium-7 within high-pressure systems in the eastern United States," *Geophys. Res. Lett.*, **6**, page 637, 1979; N. A. Kelly, G. T. Wolff and M. A. Ferman, "Background pollutant measurements in air masses affecting the eastern half of the United States-I. Air masses arriving from the northwest," *Atmos. Environ.*, **16**, page 1077, 1982.

^v G. L. Gregory, S. M. Beck and J. A. Williams, "Measurements of Free Tropospheric Ozone: An aircraft Survey from 44 degrees North to 46 degrees South Latitude," *J. Geophys. Res.*, **89**, D6, page 9642, 1984.

^{vi} D. D. Parrish, T. B. Ryerson, J. S. Holloway, M. Trainer and F. C. Fehsenfeld, "New Directions: Does pollution increase or decrease tropospheric ozone in Winter-Spring?," *Atmos. Environ.*, **33**, page 5147, 1999.

^{vii} M. Beekmann, G. Ancellet, S. Blonsky, D. DeMuer, A. Ebal, H. Elbern, J. Hendricks, J. Kowol, C. Mancier, R. Sladkovic, H. G. J. Smit, P. Speth, T. Trickl and Ph. Van Haver, "Regional and Global Tropopause Fold Occurrence and Related Ozone Flux Across the Tropopause," *J. of Atmospheric Chemistry*, **28**, page 29, 1997.

^{viii} L. K. Emmons, D. A. Hauglustaine, J-F. Muller, M. A. Carroll, G. P. Brasseur, D. Brunner, J. Staehelin, V. Thouret and A. Marengo, "Data composite of airborne observations of tropospheric ozone and its precursors," *J. Geophys. Res.*, **105**, D16, page 20,497, 2000.

^{ix} F. M. Vukovich, J. Fishman and E. V. Browell, "The Reservoir of Ozone in the Boundary Layer of the Eastern United States and Its Potential Impact on the Global Tropospheric Ozone Budget," *J. Geophys. Res.*, **90**, D3, page 5687, 1985.

^x The NARSTO Synthesis Team, "An Assessment of Tropospheric Ozone Pollution: A North American Perspective," July 2000, pages 3-19 and 3-31.

^{xi} H. B. Singh, F. L. Ludwig and W. B. Johnson, "Tropospheric ozone concentrations and variabilities in clean remote atmospheres," *Atmos. Environ.*, **12**, page 2185, 1978.

^{xii} J. A. Logan, "Ozone in Rural Areas of the United States," *J. Geophys. Res.*, **94**, D6, page 8511, 1989.

^{xiii} A. S. Lefohn and J. K. Foley, "Estimated Surface-level Ozone Exposures in Selected Class I Areas of the United States," paper 91-144.2, presented at the 84th Annual Meeting of the Air and Waste Management Association, Vancouver, British Columbia, June 1991.

^{xiv} A. P. Altshuller and A. S. Lefohn, "Background Ozone in the Planetary Boundary Layer Over the United States," *J. Air & Waste Manage. Assoc.*, **46**, page 134, 1996.

^{xv} Y. S. Chung and T. Dann, "Observations of Stratospheric Ozone at the Ground Level in Regina, Canada," *Atmos. Environ.*, **19**, page 157, 1985.

^{xvi} A. G. Proyou, G. Toupance, and P. E. Perros, "A two-year study of ozone behavior at rural and forested sites in eastern France," *Atmos. Environ.*, **25A**, page 2145, 1991.

^{xvii} M. W. Chan and M. I. Smith, "Long-term Variations in Ozone Measurements in a Remote Area in Northeastern Utah," paper 81-6.3, presented at the 74th Annual Meeting of the Air Pollution Control Association, Philadelphia, Pennsylvania, June 1981.

^{xviii} E. I. Mukammal, H. H. Neumann and T. R. Nichols, "Some Features of the Ozone Climatology of Ontario, Canada and Possible Contributions of Stratospheric Ozone to Surface Concentrations," *Arch. Met. Geoph. Biocl., Ser. A* **34**, page 179, 1985.