# Development of Ozone Thresholds for Vegetation Air Quality Related Value (AQRV)

Submitted to

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## EXECUTIVE SUMMARY

A.S.L. & Associates has provided the FCPC Air Resources Program with basic information to establish threshold levels for Vegetation Impacts (i.e., AQRV 2: Vegetation-ozone). The current ozone exposures in the area have been characterized and threshold effects levels for specific vegetation using biologically based exposure indices have been identified using results from published research investigations. The US EPA has summarized its basic conclusions concerning the research used to develop various ozone exposure indices to help quantify effects on growth and yield in crops, perennials, and trees (primarily seedlings). The EPA's key conclusions are (1) ozone effects in plants are cumulative; (2) higher ozone concentrations appear to be more important than lower concentrations in eliciting a response; (3) plant sensitivity to ozone varies with time of day and plant development stage; and (4) exposure indices that accumulate hourly ozone concentrations and preferentially weight the higher concentrations have better statistical fit to growth/yield response data than do the mean and peak indices.

As a result of the US EPA's 2008 ozone rulemaking and its 2010 re-evaluation of the ozone standard, the Agency concluded that the W126 form was the most biologically relevant cumulative, seasonal form appropriate for consideration as a secondary ozone standard to protect sensitive natural vegetation and ecosystems in specially designated areas. The W126 metric is a sigmoidally weighted index that preferentially weights the higher concentrations more than the mid- and lower-levels. In its 2010 re-evaluation of the ozone standard, the US EPA noted that the proposed secondary standard was not intended to provide additional protection to commercial crops; rather the Agency concluded that the highest priority should be given to those effects that occur on sensitive species that are known to or are likely to occur in federally protected areas, such as Class I areas or on lands set aside by States, Tribes, and public interest groups. The EPA indicated in its re-evaluation that the recommended W126 exposure level would reduce the incidence of injury that was likely to occur on some sensitive species. In protecting areas from ozone effects, the Agency noted the importance of cottonwood, black cherry, quaking aspen, red maple, yellow poplar, and white pine in eastern forests; white ash, black cherry, birch, and quaking aspen in midwestern forests; and ponderosa pine in western forests.

As a result of our review of the available scientific literature, we recommend use of the W126 exposure index accumulated over a 24-h period for a 3-month period as one of two indices to protect vegetation. In addition, because of the importance of peak concentrations affecting the results in the experiments used to develop exposure-response relationships for assessing vegetation, we recommend that the N100 metric (i.e., number of hourly average concentrations ≥ 0.10 ppm) be combined with the W126 exposure index for assessing vegetation impact. The two most sensitive and FCPC culturally significant species we identified for biomass loss are black cherry and aspen. Research data indicate from experimentally controlled studies that the 10% biomass reduction levels for black

cherry are associated with 24-h W126 ozone exposures of 6.51 ppm-h (N100=1) and 7.68 ppm-h (N100=10) of ozone exposure. The 10% biomass reduction levels for aspen are 6.37 and 6.72 ppm-h. In the experiments, the N100 values were 4, and 15, respectively. We recommend that the 3-month, 24-h W126 threshold be established at the 6.37 ppm-h level with an N100 value of 4. Based on the research results, this approach requires that both the 6.37 ppm-h and the N100 value of 4 be measured before the vegetation threshold effect is considered exceeded. Thus, an exceedance of the 3-month, 24-h W126 level of 6.37 ppm-h with an N100 value less than 4 would not be an exceedance of the threshold. Furthermore, we recommend that the determination of the 3-month, 24-h W126 and N100 exposures be restricted in the FCPC area to the summer months of June through August because this is the period when anthropogenic emissions have the greatest impact and vegetation is most susceptible to ozone exposure. We believe that some of the higher ozone concentrations experienced during March-May and April-June in the FCPC area appear to be associated with natural sources that are not controllable (i.e., stratospheric in origin).

The maximum 3-month, 24-h W126 ozone exposures experienced at the Potawatomi ozone monitoring site for 2004 through 2011 ranged from 4.816 to 13.218 ppm-h with no N100 values. These exposures were experienced during the springtime. Approximately 65% of the exposures for the maximum 3-month, 24-h W126 index are associated with the hours between 0800 to 1959 h. Over a 24-h period, approximately 35% of the W126 exposures are occurring during the nighttime period. These nighttime exposures have the potential for eliciting vegetation effects. The summertime (i.e., June-August) 24-h, W126 exposures experienced at the Potawatomi site were lower than the 6.37 ppm-h threshold level except in 2005. By restricting the determination to the summer months, the elevated 24-h, W126 exposures associated with stratospheric-tropospheric exchange events at the Potawatomi ozone monitoring site would not be considered when assessing possible vegetation impacts associated with anthropogenic emissions. The literature has discussed the potential importance of stratospheric ozone enhancing surface ozone concentrations with the result that vegetation may be affected with acute injuries. It may not be possible to prevent vegetation injury resulting from exposure to stratospheric ozone in the FCPC Class I area or other areas in the region. However, by minimizing increases in ozone exposures from anthropogenic sources, vegetation injury can be kept at a minimum.

For implementation purposes, we recommend that a 3-year average of the maximum 3-month, 24-h W126 level of 6.37 ppm-h and an N100 of 4 during the summertime be applied as an indication that possible vegetation effects are occurring in the FCPC area. We recognize that exposure levels in this range can still be influenced by stratospheric contributions. We suggest that if for any year that the cumulative 3-month, 24-h W126 and N100 values are experienced in the

range identified above, that vegetation survey activities be initiated in order to confirm that vegetation effects are occurring in the FCPC area.

## 1.0 INTRODUCTION

The Forest County Potawatomi Community (FCPC) wishes to establish threshold effects for FCPC Class I Air Quality Related Values. The FCPC is a federally recognized Indian Tribe with governmental headquarters located near Crandon, WI. In December of 1993 the FCPC submitted a letter of intent to the U.S. Environmental Protection Agency (USEPA) to request re-designation from a Class II area to a Class I area. By late 1994, FCPC had completed all of the requirements and submitted its application to the USEPA for approval. The FCPC Reservation received redesignation as Class I in April of 2008.

While federal/mandatory Class I areas located in some National Parks, National Forests, and National Wildlife Refuge units are required to list Air Quality Related Values (AQRVs), such as visibility, aquatic systems, and vegetation, non-federal/mandatory Class I areas are not required to name AQRVs. However, in the 1999 Class I Agreement with the state of Wisconsin, the FCPC agreed to list AQRVs, and was provided the opportunity to make changes to AQRVs and the threshold effects levels for AQRVs once every 10 years. The window to make changes to FCPC AQRVs and threshold effects levels is currently open until July 31, 2012. As of the 1999 Class I Agreement, the FCPC listed water quality and aquatic systems as AQRVs. In 2011, the Tribe adopted Visibility and Vegetation Impacts as AQRVs. Coupled with the designation of AQRVs, FCPC has the opportunity to provide threshold effects levels associated with each AQRV before July 31, 2012. The FCPC Air Resources Program is using the 2010 Federal Land Managers Air Quality Related Values Work Group (FLAG) document as a guide in developing AQRVs and related threshold effects levels.

An AQRV is a resource, as identified by the FLM, for one or more Federal areas that may be adversely affected by a change in air quality. "These values include visibility and those scenic, cultural, biological, and recreation resources of an area that are affected by air quality" (National Park Service, 1978). FLMs have determined that given the high ecological, aesthetic, and intrinsic value of federal lands, all native species are significant and warrant protection. In addition, for the FCPC Class I Area, there are specific plants that are of particular cultural importance to the FCPC. While ideally, protection efforts would focus on the identification and protection of the most sensitive species in an area, unfortunately, AQRV identification is limited by incomplete species inventories and/or lack of exposure-response data for most species of native vegetation.

In this report, A.S.L. & Associates provides the information to assist the FCPC Air Resources Program to establish threshold levels for Vegetation Impacts (i.e., AQRV 2: Vegetation-ozone). For the Vegetation-ozone AQRV, A.S.L. & Associates characterizes current ozone exposures in the area and establishes threshold effects levels for specific vegetation using data collected at the FCPC air monitoring station and/or through the adoption of current ozone exposures and threshold effects levels established for nearby federal/mandatory Class I areas – based on the FLAG document and other resources made available by Federal Land Managers (FLMs) for nearby Class I areas. In this report,

the units ppm and ppb (1000 times ppm) are used interchangeably to be consistent with the terminology used in the literature concerning various exposure metrics and their units.

Dr. Robert C. Musselman is a co-author with Dr. Allen S. Lefohn, A.S.L. & Associates, Helena, Montana for this report. Dr. Musselman is a US Forest Service employee who has participated in preparation of this report without financial remuneration. Mr. Bill Jackson, who is a US Forest Service employee, has participated as a private citizen as a reviewer of this report without financial remuneration.

## 2.0 ECOSYSTEMS IN THE FOREST COUNTY POTAWATOMI COMMUNITY AREA

The reservation lies within the Northern Highland geographical province, which includes roughly the northern one-third of Wisconsin. The maximum elevation is 1.700 feet above sea level. The local topographic relief in the reservation area is about 200 feet. The soil in the area is mostly of the Kennon and Vilas series and is poor to fair quality for agriculture; stone is common. The most common mineral soil series are the Iron River Stony Loam and the Monico Stony Loam soil with smaller areas of Worchester Loam, Cable Stony Silt Loam, and Padus Loam. These soils are commonly covered by tree species, such as sugar maple (*Acer saccharum*), aspen (*Populus tremuloides*), yellow birch (*Betula alleghaniensis*), red maple (*Acer rubrum*), white ash (*Fraxinus americana*), and American basswood (*Tilia americana*). The dominant organic soil series is the Greenwood Peat, Lupton Muck, and Cathro Muck. These soils are formed from decayed marsh and bog vegetation in depressions, low lying areas or along stream courses and are generally flat or gently sloping. The soils support a limited variety of plant species and are often covered by black spruce (*Picea mariana*) and tamarack (*Larix laricina*).

The forest of the Forest County Potawatomi is rich and varied with a wide variety of tree species. Of the total acreage of the reservation, 10,400 acres are wooded. The forest cover consists of 70 percent hardwoods, 27 percent mixed aspen, and 3 percent cedar and other species. The species and age composition is a direct result of timber harvesting practices and forest fires at the turn of the century. The forest is predominately even-aged although active forest management is converting many stands to an “all aged” forest. Seventeen commercial forest cover types have been identified on the forest. These cover types range from early successional tree species, such as aspen and white birch to climax tree species, such as sugar maple, white ash, and hemlock.

The close historical link between the Potawatomi people and the natural environment and the continuity of this tradition into modern times is well documented. Today, plants and animals obtained from the environment are a vital part of the religious rituals, ceremonials, and medicines which define unique aspects of the Potawatomi life and which form the vital link between their cultural past and future. In order to sustain the harvest of the basic plant and animal products important to their people, the Potawatomi

must have access to at least these communities that, in turn, must be capable of producing clean and abundant foods and medicines.

The Potawatomi forest includes 31 tree species which are found naturally inhabiting the various ecological habitat types across the forest. Twenty-seven species are considered to have commercial value (Table 2-1).

**Table 2-1. Summary of trees that have commercial value.**

| Softwoods | Hardwoods | |
|---|---|---|
| Eastern hemlock | Sugar maple | Bigtooth aspen |
| Balsam fir | Red maple | Black cherry |
| White pine | Northern red oak | Bitternut hickory |
| Red pine | White birch | Butternut |
| Jack pine | Yellow birch | American beech |
| White spruce | Basswood | American elm |
| Black spruce | White ash | Rock elm |
| Northern white cedar | Black ash | Slippery elm |
| Tamarack | Quaking aspen | White oak |

The four tree species that are not considered to be of commercial value are Black Willow, Silver Maple, Balsam Poplar, and Ironwood. Hard Maple or Sugar Maple is the most abundant species found on the forest.

Sensitive plants found in the National Parks, National Wildlife areas, and Forest Service units in the FCPC region, as well as those found on the Reservation are identified in Table 2-2.

**Table 2-2. Sensitive plant species in National Park, National Wildlife Areas, and Forest Service units in the FCPC region.**

| Scientific Name | Family | Common Name |
|---|---|---|
| *Alnus rugosa* | *Betulaceae* | Speckled alder, Tag alder, gray alder, Hoary alder |
| *Apocynum androsaemifolium* | *Apocynaceae* | Spreading dogbane, Common dogbane |
| *Apocynum cannabinum* | *Apocynaceae* | |
| *Artemisia ludoviciana* | *Asteraceae* | White sagebrush, Western wormwood, White sage, Silver King Artemisia, Silver queen |
| *Asclepias incarnata* | *Asclepiadaceae* | Swamp milkweed |
| *Asclepias syriaca* | *Asclepiadaceae* | Common milkweed, Tall milkweed |
| *Aster macrophyllus* | *Asteraceae* | Big-leaf aster, Large leaf aster |
| *Clematis virginiana* | *Ranunculaceae* | Virgin's bower |
| *Corylus americana* | *Betulaceae* | American hazelnut |
| *Eupatorium rugosum* | *Asteraceae* | White snakeroot, White sanicle |
| *Fraxinus americana* | *Oleaceae* | White ash |
| *Fraxinus pennsylvanica* | *Oleaceae* | Green ash |
| *Gaylussacia baccata* | *Ericaceae* | Black huckleberry |
| *Parthenocissus quinquefolia* | *Vitaceae* | Virginia creeper |
| *Pinus banksiana* | *Pinaceae* | Jack pine |
| *Populus tremuloides* | *Salicaceae* | Quaking aspen, Trembling aspen |
| *Prunus pensylvanica* | *Rosaceae* | Pin cherry |
| *Prunus serotina* | *Rosaceae* | Black cherry |
| *Prunus virginiana* | *Rosaceae* | Choke cherry |
| *Robinia pseudoacacia* | *Fabaceae* | Black locust |
| *Rubus allegheniensis* | *Rosaceae* | Allegheny blackberry, Common blackberry |
| *Rubus canadensis* | *Rosaceae* | Thornless blackberry |
| *Rubus parviflorus* | *Rosaceae* | Thimbleberry |
| *Rudbeckia laciniata* | *Asteraceae* | Cutleaf coneflower, Coneflower, Golden glow |
| *Sambucus canadensis* | *Caprifoliaceae* | American elder, White elder, Elderberry |
| *Sambucus racemosa* | *Caprifoliaceae* | Red elderberry, Scarlet elderberry |
| *S. canadensis* | *Asteraceae* | Goldenrod |
| *Symphoricarpos albus* | *Caprifoliaceae* | Common snowberry, Waxberry |

## 3.0 EXPOSURE AND DOSE CONSIDERATIONS

### 3.1 Introduction and Definitions

In assessing the thresholds for impact to vegetation, it is important to carefully define the various terminologies used in the scientific community for assessing potential injury and damage to vegetation, as well as terms such as “exposure” and “dose.” The following provides a brief explanation of these terms and the meaning ascribed to them in this report.

**Exposure**. The term exposure is the product of the concentration measured near the vegetation of interest and the length of time the vegetation is presumably exposed to the pollutant (Musselman et al., 2006). Musselman et al. (2006) noted

that exposure is the integral (i.e., accumulation) of the instantaneous concentration over the time period of interest. Seasonal average concentrations (e.g., 7- and 12-h daily average concentrations averaged over a growing season), although not considered exposure, have also been referred to as exposure indices (US EPA, 2006).

**Dose**. In contrast to exposure, dose is the total amount of pollutant that actually is absorbed into the plant through the stomata over a period of time. Dose is the integral over time of the instantaneous stomatal flux (Musselman et al., 2006). For the interested reader, Musselman et al. (2006) discuss additional terminology used in assessing vegetation effects.

**Exposure Metrics**. Exposure indices are metrics that quantify exposure as it relates to measured plant damage or injury. Exposure metrics are summary measures of monitored hourly ambient ozone concentrations over time, intended to provide a consistent metric for reviewing and comparing exposure-response effects obtained from various studies. Such indices may also provide a basis for developing a biologically relevant air quality standard for protecting vegetation and ecosystems.

**Dose Metrics**. Similarly, dose metrics include a measure of stomatal flux, which is a temporally dynamic measure of the rate of entry of the pollutant into the leaf (Musselman et al., 2006). Not all of the stomatal flux is associated with vegetation injury or damage (Musselman et al., 2006; Heath et al., 2009). These authors have discussed the need to take into consideration detoxification processes. These processes are important when discussing "Effective dose" rather than just "dose." "Effective dose" is the integral over time of the "Effective flux," which is the balance between stomatal flux and internal-leaf detoxification.

**Injury and Damage**. In evaluating the potential plant or vegetation response to a pollutant, it is important to distinguish between "injury" and "damage." Musselman et al. (2006) discussed the distinction and noted that injury is associated with leaf necrosis, premature leaf senescence, reduced photosynthesis, reduced carbohydrate production and allocation, reduced growth, and/or reduced plant vigor. Injury can be visible or invisible. Visible injury is observable as oxidant stipple, chlorotic mottle, bronzing, or any other visual leaf necrotic symptom. It can also be premature leaf senescence. Invisible injury, sometimes referred to as hidden injury, is that which is not visible to an observer, such as changes in photosynthesis, carbohydrate production and allocation, or plant vigor. Damage is a reduction in the intended value or use of a plant. Included in this definition are reductions in economic, ecologic, or aesthetic value. The distinction between injury and damage as discussed by Musselman et al. (2006), has been used in air pollution effects research since the 1970s (Guderian, 1977).

An important aspect associated with the use of exposure and flux-based indices for assessing vegetation effects is that the metrics associated with exposure- and

dose-response relationships take into consideration concentration, time of day, respite time (i.e., time between enhanced ozone concentration exposures), frequency of peak occurrence, plant phenology, predisposition, detoxification, and other important aspects influencing vegetation effects. However, such is not necessarily the case (US EPA, 2006; Musselman et al., 2006; Heath et al., 2009) for either exposure or flux-based indices. The effects of ozone on individual plants and the factors that modify plant response to ozone are complex and vary with biological and physical factors, such as plant species, environmental conditions, and soil moisture and nutrient conditions.

**Flux-Based Indices**. Because plant response is thought to be more closely related to ozone absorbed into leaf tissue, recent research has been focused on flux-based ozone parameters. Even though flux-based indices may appear to be more biologically relevant than concentration-based (i.e., exposure) indices, there are limitations associated with their use. While some flux-based indices attempt to compensate for defense mechanisms to detoxify ozone, they have serious limitations (Musselman et al., 2006). Heath et al. (2009) noted that ozone interacts with plant tissue through distinct temporal processes. Sequentially, plants are exposed to ambient ozone that (1) moves through the leaf boundary layer, (2) is taken up into plant tissue primarily through stomata, and (3) undergoes chemical interaction within plant tissue, first by initiating alterations and then as part of plant detoxification and repair. The authors note that temporal variability in concentration and uptake and conclude that the time incidence for maximum defense (i.e., detoxification) does not necessarily match diurnal patterns for maximum ozone concentration or maximum uptake. The fact that these out-of-phase processes affect the relationship between ozone exposure/dose and vegetation effects ultimately impacts the ability of flux-based indices to predict vegetation effects accurately for purposes of standard setting and critical levels. Some researchers have indicated that flux models can be used to better predict vegetation responses to ozone than exposure-based approaches (Panek et al., 2002). However, other research has suggested that flux models do not predict vegetation responses to ozone better than exposure-based models, such as AOT40 (Gonzalez-Fernandez et al., 2010).

## 3.2 Identifying the Important Components of Exposure for Assessing Biological Effects

Although there are shortcomings associated with the application of metrics that estimate vegetation injury and damage, it is important that these metrics adhere to the state-of-knowledge concerning what is known about the relationship between concentration exposure over time, uptake, and detoxification potential. In reviewing the state-of-knowledge, the US EPA (2006) summarized the Agency's basic conclusions concerning the research used to develop various exposure indices to help quantify effects on growth and yield in crops, perennials, and trees (primarily seedlings). The EPA's key conclusions from the 1996 and 2006 ozone

Air Quality Criteria Documents (US EPA, 1996a; US EPA, 2006, US EPA, 2011a) regarding an exposure index based on ambient exposures were stated as follows:

- Ozone effects in plants are cumulative;
- Higher ozone concentrations appear to be more important than lower concentrations in eliciting a response;
- Plant sensitivity to ozone varies with time of day and plant development stage; and
- Exposure indices that cumulate hourly ozone concentrations and preferentially weight the higher concentrations have a better statistical fit to growth/yield response data than do the mean and peak indices.

The US EPA conclusions listed above are based on research experiments that evaluated the importance of the higher ozone concentrations in plant response based on results from (1) controlled conditions in the laboratory and in the field, and (2) uncontrolled conditions in the San Bernardino National Forest. These studies provided a framework from which the US EPA developed biologically relevant exposure-response models that provide a consistent relationship between ozone conditions and vegetation biological endpoints.

For both injury and damage, moisture stressed plants exposed under ambient conditions to high ozone exposures may not respond as much as plants exposed to lower ozone levels with greater soil moisture. Most of the recent literature describing vegetation injury associated with ozone exposure has been performed by researchers under field survey conditions. Davis (2007), investigating ozone injury to plants within the Seney National Wildlife Refuge in Northern Michigan, reported that the incidence of ozone injury was not related to ambient ozone levels in his study. Eckert et al. (1999) have also reported the lack of a relationship between ambient ozone levels in Acadia National Park (Maine) and ozone injury, and attributed the lack of correlation to the confounding effects of moisture stress on stomatal functioning and resultant gas uptake. Kohut (2007) noted in his study that the levels of ozone exposure and soil moisture contents revealed an inverse relationship at many sites (i.e., years that exhibited elevated ozone levels experienced low soil moisture and drought-level conditions).

Over the years, vegetation researchers focused on identifying which parts of the distribution of the hourly average ozone concentrations were most important for eliciting vegetation effects. In the 1960s, there was evidence reported in the literature that peak ozone concentrations were more important than the lower values for affecting vegetation injury (Heck et al., 1966; Stan and Schicker, 1982). However, until the early 1980s, there was no evidence for peak exposures affecting growth loss to vegetation. In the late 1970s and early 1980s, the US EPA

discussed the possibility of proposing a vegetation standard that consisted of the seasonal average of the daily 7-h (0900-1600h) average concentration. During its consideration of the seasonal 7-h average concentration as a vegetation standard, the US EPA realized that if peak hourly average ozone concentrations were more important than the mid- and lower-level concentrations, then the use of a seasonal 7-h average concentration or any other long-term average concentration could mathematically "hide" the occurrence of the peak concentrations and the long-term average exposure metric would not correlate well with biological effects. In the 1980s, the US EPA abandoned consideration of the seasonal 7-h average concentration as a vegetation standard. In the early 1980s, there was considerable discussion about the possible importance of the higher hourly average ozone concentrations in affecting vegetation. Lefohn and Benedict (1982) proposed that the higher hourly average concentrations should be given greater weight than the mid- and low-level values when assessing crop growth reduction. In 1983, Musselman et al. (1983) provided experimental evidence of the importance of peak hourly average ozone concentrations in affecting vegetation growth and provided important support for the hypothesis associated with the peak values. In 1985, Hogsett et al. (1985), applying the exposure regimes designed specifically for their US EPA experiment by Dr. Lefohn, provided additional support for the importance of the higher hourly average ozone concentrations in affecting vegetation.

Controlled fumigation experimental results (Musselman et al., 1983, 1986, 1994; Hogsett et al., 1985) were cited by the EPA (US EPA, 1986, 1992, 1996a, 2006) as the experimental basis for emphasizing the importance of episodic peak exposures. Research by Nussbaum et al. (1995), Yun and Laurence (1999), Lee and Hogsett (1999), Oksanen and Holopaninen (2001), and Köllner and Krause (2003) provides additional support for the importance of the higher hourly average ozone concentrations. Using data from controlled experimental studies, Lee et al. (1987, 1988), Lefohn et al. (1988), Musselman et al. (1988), Tingey et al. (1989), and US EPA (1996a) concluded that the cumulative effects of peak hourly ozone concentrations were of greater importance than seasonal (i.e., long term) mean exposures in predicting vegetation damage.

Support for the importance of the higher concentrations in affecting vegetation comes also from retrospective studies reported in the literature. Studies in the US have used data from National Crop Loss Assessment Network (NCLAN) experiments using open-top fumigation chambers to compare different types of indices (Lefohn et al., 1988; Lee et al., 1988). These studies demonstrated that cumulative exposure indices, which emphasized higher concentrations, were best related to plant response. Similarly, Finnan et al. (1997) compared the performance of different ozone indices in exposure-response functions using crop yield and ozone monitoring data from spring wheat studies carried out within the framework of the European open-top chamber program. Cumulative indices, which employed continuous weighting functions or which censored

concentrations above threshold values, performed best as they attributed increasing weight to higher concentrations. The authors found that the best performing index employed a sigmoid function. Indices which simply summed concentrations greater than or equal to a threshold value did not perform as well. Indices which performed well were those which emphasized the very highest concentrations and gave little weight to the lower concentrations. Those indices which started to give increasing weight to concentrations above low or medium range values were not among the best performing indices. Ozone exposure indices accounted for a large proportion of the variability in data (91%) and the authors suggested that a strong link existed between exposure and dose.

Additional support for the importance of elevated hourly average ozone concentrations in affecting vegetation comes from biological field assessments, such as the observations from the conifer forest ecosystem of the San Bernardino National Forest in California. For the period 1973 to 1992, a population sample of 219 ponderosa pines in the conifer forest ecosystem of the San Bernardino National Forest showed that 84% had no change or an improvement in needle whorl retention (where abscission was due to ozone) (Miller and Rechel, 1999), while peak ozone concentrations decreased during this time period. A wider area of the San Bernardino National Forest examined between 1974 and 1988, using a broader index of injury (Forest Pest Management (FPM) method), also indicated an improvement of crown condition coincident with an improvement of ozone air quality (Miller and Rechel, 1999). Tingey et al. (2004) reported that reductions of ozone in the San Bernardino Mountains during the time period 1963-1999 benefited growth of Ponderosa pine.

During the period 1950-1980, extremely high ozone concentrations impacted the San Bernardino National Forest (US EPA, 1996a, 2006). However, over the past 30 years, significant reductions in the ozone concentrations have occurred in this area (Lloyd et al., 1989; Davidson, 1993; Lefohn and Shadwick, 2000; Lee et al., 2003, Tingey et al., 2004). Upon examination of the reduction in the hourly average concentrations over the period 1980 – 2003, several interesting patterns emerge. Musselman et al. (2006) point out that from 1989-2003, the 24-h cumulative W126 and SUM06 exposure indices decreased. Please see Table 5-1 and Sections 5.2-5.6 for definitions of the exposure indices. Over a 24-hour April-October period, a decreasing trend in the number of hourly average concentrations greater than or equal to 0.08, 0.12, and 0.15 ppm occurred. For the same period of time, the number of hourly average concentrations between 0.050 and 0.089 ppm increased or remained stable in the most recent years compared to the early 1980s. Thus, for the period 1980 – 2003, Musselman et al. (2006) showed that the reductions of ozone in the San Bernardino, California area appear to be associated with reductions in the higher hourly average concentrations because the peak concentrations decreased, while the concentrations in the range of 0.050-0.089 ppm appeared to be either stable or increasing. Other researchers have reported similar observations for other locations in the United States (Lefohn et al., 1998).

Thus, based on research experiments conducted under (1) controlled conditions in the laboratory and in the field, and (2) uncontrolled conditions in the San Bernardino National Forest, the higher ozone concentrations appear to be more important than lower concentrations in eliciting a response and show a better statistical fit in response functions used for ozone exposure response modeling. For use in developing response functions and comparing studies, as well as for defining future indices for vegetation protection, the US EPA (2006) concludes that given the current state of knowledge and the best available data, exposure indices that cumulate and differentially weight the higher hourly average concentrations and also include the mid-level values continue to offer the most reliable estimates for vegetation effects. In its most recent review of the peer-reviewed literature (September 2011), the US EPA has indicated that the conclusions associated with vegetation response reached in its 2006 Air Quality Criteria Document on ozone are still accurate. The latest draft of the US EPA's Integrated Assessment report (ISA), which summarizes its most current conclusions in regard to assessing vegetation effects, can be viewed at:

http://www.epa.gov/ttn/naaqs/standards/ozone/s_o3_2008_isa.html

### 3.3 Exposure-Response and Comparability of Open-Top Fumigation Chambers and Free Air Carbon-Dioxide Enrichment Systems

Most data on exposure-response of vegetation to ozone has relied on experiments conducted during the 1980s and 1990s in open-top fumigation chambers (OTCs) as a part of the National Crop Loss Assessment Network (NCLAN) and EPA National Health and Environmental Effects Research Laboratory, Western Ecology Division (NHEERL-WED) forest program in the US, where plants were fumigated with various levels of ozone to obtain exposure-response functions for injury and/or damage assessment. More recently, Free Air Carbon-dioxide Enrichment (FACE) systems have been utilized to fumigate vegetation with ozone. The FACE experimental setup requires no enclosure around the plants. Thus, plant growth occurs under more natural conditions. Some researchers have suggested that data derived from the OTCs were not as realistic or useful in exposure-response modeling as data from the less disturbing FACE systems. The US EPA (2006) indicates that evidence obtained using free-air exposure systems (e.g., FACE) and OTCs supports results observed previously in OTC studies. Specifically, a series of studies undertaken using free-air ozone enrichment in Rhinelander, WI (Isebrands et al., 2000, 2001) showed that ozone-symptom expression was generally similar in OTCs, FACE, and ambient-ozone gradient sites supporting the previously observed variation among trembling aspen clones (Populus tremuloides L.) using OTCs (Karnosky et al., 1999). The work by Isebrands et al. (2000, 2001) using FACE methodology confirms responses reported previously with the same clones grown in pots or soil in OTCs without

the alterations of microclimate induced by chambers. Similarly, the US EPA (2011a), using data from NCLAN and the EPA NHEERL-WED collected using OTCs, compared biomass predictions with the data derived from the SoyFACE and AspenFACE observations and reported notably close agreement in single-year comparisons. Overall, the studies at the Aspen FACE experiment were consistent with many of the open-top chamber (OTC) studies. These results strengthen our understanding of ozone effects on forests and demonstrate the relevance of the knowledge gained from trees grown in either open-top chamber or FACE studies. The good agreement between (1) median composite models (derived from data collected from NCLAN and NHEERL/WED experiments) and (2) FACE experiments provide very strong confirmation of the two projects' results with respect to the response of Aspen biomass to ozone exposure. The results from EPA suggest that the extensive database from the earlier OTCs experiments remains valid for current ozone exposure-response modeling.

# 4.0 REGULATORY HISTORY IN THE UNITED STATES

## 4.1 Introduction

National Ambient Air Quality Standards (NAAQS) are promulgated by the US EPA to meet requirements set forth in the US Clean Air Act (CAA).The EPA Administrator is required (1) to list widespread air pollutants that reasonably may be expected to endanger public health or welfare; (2) to issue air quality criteria that assess the latest available scientific information on nature and effects of ambient exposure; (3) to set "primary" NAAQS to protect human health with adequate margin of safety and to set "secondary" NAAQS to protect against welfare effects (e.g., effects on vegetation, ecosystems, visibility, climate, manmade materials, etc); and (4) to periodically review and revise, as appropriate, the criteria and NAAQS for a given listed pollutant or class of pollutants.

## 4.2 The 1996 and 2006 US EPA Reviews of the Ozone Standard

In its 1996 review of the ozone standard, the US EPA evaluated the statistical performance of cumulative exposure indices (i.e., metrics that accumulate over a specific time period) and reported that all of the metrics performed similarly and the Agency was unable to distinguish between them (US EPA, 1996a). In selecting between two of these cumulative forms, the SUM06 and the W126, in the absence of biological evidence to distinguish between them, EPA based its decision on both science and policy considerations. Specifically, the reasons were: (1) All cumulative, peak-weighted exposure indices considered, including W126 and SUM06, were about equally good as exposure measures to predict exposure-response relationships reported in the NCLAN crop studies; and (2) the SUM06 form would not be influenced by policy-relevant background ozone concentrations (this term is discussed in Section 5.3). On the basis of these

considerations, the US EPA selected the SUM06 in 1996 as the most appropriate cumulative, seasonal form to consider when proposing an alternative secondary standard to protect vegetation (US EPA, 1996b). The US EPA at that time decided the more stringent new primary standard was sufficient to protect vegetation and a different secondary standard was not necessary.

The US EPA (2007) later reassessed the NAAQS for ozone and recommended strengthening the primary standard for human health to 0.075 ppm for the 3-year average of the annual 4$^{th}$ highest daily maximum 8-hour average concentration. The issue of the secondary standard was revisited based on a National Research Council assessment of air quality management in the US. The assessment concluded that the Clean Air Act specifically required protection of ecosystems from air pollutants but the US EPA's allowing the primary standard and secondary standard to be the same does not provide sufficient protection to vegetation (NRC, 2004). The US EPA assessed whether the SUM06 was still the most appropriate choice of a cumulative, seasonal form for a secondary standard to protect the public welfare from known and anticipated adverse vegetation effects in light of the new information available in the Agency's review. Specifically, the US EPA considered: (1) the continued lack of evidence within the vegetation effects literature of a biological threshold for vegetation exposures of concern; and (2) new estimates of policy-relevant background ozone concentrations that were lower than in the Agency's 1996 review. The W126 form, also evaluated in the 1997 review, was again selected for comparison with the SUM06 form. Regarding the first consideration, the US EPA noted that the W126 form, by its incorporation of a continuous sigmoidal weighting scheme, does not create an artificially imposed concentration threshold, and provides proportionally more weight to the higher and typically more biologically important concentrations. Second, the W126 index value is not significantly influenced by ozone concentrations within the range of estimated policy-relevant background, as the weights assigned by the sigmoidal weighting scheme to concentrations in this range are near zero. Thus, the W126 metric would provide a more appropriate target for air quality management programs designed to reduce emissions from anthropogenic sources contributing to ozone formation. On the basis of these considerations, the US EPA concluded that the W126 form was the most biologically relevant cumulative, seasonal form appropriate to consider in the context of the Agency's 2008 ozone rulemaking (U.S. EPA, 2008; US EPA, 2010). In March 2008, the US EPA concluded that the new strengthened primary standard would provide additional protection to vegetation; thus a separate secondary standard for vegetation was not implemented.

### 4.3 The 2010 US EPA Re-evaluation of the Ozone Standard

On January 7, 2010, the US EPA, based on its latest scientific assessment (US EPA, 2007), announced its intent to further strengthen the national ambient air quality standards for ground-level ozone. The US EPA's proposal was to decrease

the 8-hour primary ozone standard level, designed to protect public health, to a level within the range of 0.060-0.070 ppm for the 3-year average of the annual 4th highest daily maximum 8-hour average concentration. The Agency proposed establishing a distinct cumulative, seasonal secondary standard, the W126 index, to protect sensitive vegetation and ecosystems, including forests, parks, wildlife refuges, and wilderness areas. The US EPA (2011b) noted that the proposed secondary standard was not intended to provide additional protection to commercial crops; rather the US EPA (2011b) concluded that the highest priority should be given to those effects that occur on sensitive species that are known to or are likely to occur in federally protected areas, such as Class I areas or on lands set aside by States, Tribes, and public interest groups. The US EPA proposed to set the level of the W126 secondary standard somewhere between the range of 7-15 ppm-h. The hourly W126 weighted concentrations accumulated over 12 hours per day (8 am to 8 pm) during 3 consecutive months are used to calculate the index. The Agency's final decision on its reconsideration of the March 2008 standards was scheduled for August 2010. However, in August, the Agency announced that it was going to delay its announcement to on or around the end of October. In early November, the US EPA announced that it would reach a final decision on the ozone standards by December 31, 2010. On December 8, 2010, the Agency announced that it would delay its final decision on the ozone standards until July 2011. EPA announced on July 26 that it would not make a decision on the ozone standards by its previously announced deadline of July 29. On August 12, EPA announced that it was "fully committed" to the ozone standards and it would move forward once the White House had reviewed its proposed changes to the ozone standards. Based on several considerations, on September 2, 2011, the President requested that the EPA withdraw its proposal for amending the March 2008 ozone standards. Thus, the current ozone standards to protect human health and vegetation in the US remain the 3-year average of the annual 4$^{th}$ highest daily maximum 8-hour average concentration at a level of 0.075 ppm. The US EPA announced on September 22, 2011 that it was moving forward on identifying nonattainment areas using the 2008 ozone standard.

Following President Obama's announcement on October 3, 2011, the US EPA published on its website its rationale for setting new human health and vegetation ozone standards that it had recommended for President Obama's review (US EPA, 2011b) (see: http://www.epa.gov/airquality/ozonepollution/pdfs/201107_OMBdraft-OzoneNAAQSpreamble.pdf). Although the document was in draft form, it represented the final recommendation by the US EPA and was awaiting the President's approval. The US EPA determined that different standards than those set in 2008 were necessary to provide requisite protection of public health and welfare, respectively. With regard to the primary standard for ozone, the Agency desired to set the level of the 8-hour standard at 0.070 ppm. With regard to the secondary standard for ozone, the US EPA desired to establish a new cumulative, seasonal standard to replace the standard set in 2008. This secondary standard was

defined in terms of a concentration-weighted index (W126), which is used to sum weighted hourly ozone concentrations over 12 hours per day (8:00 am to 8:00 pm) and over 3-month periods within each calendar year. The proposed standard was based on the 3-year average of the maximum 3-month 12-h W126 index values for each year. The EPA proposed that the new secondary standard be set at a W126 value of 13 ppm-h.

The basis for the decision by the US EPA to recommend the 13 ppm-h level was associated with the Administrator's desire to provide protection primarily for sensitive tree species growing in specially designated areas (US EPA, 2011b). In particular, the Administrator noted that for a standard level of 13 ppm-h, important benefits were estimated by the Agency in its analysis in terms of a reduction in ozone-related growth losses in sensitive tree seedlings (including black cherry, Ponderosa pine, and quaking aspen) and mature trees and less wide-spread visible foliar injury (US EPA, 2011b). The Administrator noted that the evidence related to ozone-induced effect of visible foliar injury, which included the database from the ambient field-based bio-monitoring network managed by the USFS Forest Inventory and Analysis (FIA) Program. An analysis by the US EPA of the incidence of visible foliar injury at different levels of air quality in monitored counties showed that the percent of counties with some degree of documented foliar injury was appreciably reduced at a level approximately equivalent to an annual 12-hW126 index value of 13 ppm-h, ranging from an annual incidence of 12 to 35%, relative to higher levels analyzed above the proposed range. The Administrator concluded that it was likely that some sensitive species occurring in specially protected areas would also exhibit visible foliar injury symptoms to a similar degree at these exposure levels. She further noted that while direct links between ozone-induced visible foliar injury symptoms and other effects (e.g., biomass loss) are not always found, visible foliar injury in itself is considered by the National Park Service (NPS) to adversely affect air quality related values (AQRV) in Class I areas.

Thus, the Administrator found that the type of information most useful in informing the selection of an appropriate level for the secondary ozone standard was information that focused on exposures and responses of sensitive trees and other native species known or anticipated to occur in protected areas, such as Class I areas or on lands set aside by States, Tribes, and public interest groups to provide similar benefits to the public welfare. In considering such information, she noted that a large number of ozone-sensitive tree species were prevalent in state and national parks and forested ecosystems across the U.S. These species included many ecologically and commercially important species, such as cottonwood (*Populus deltoids*), black cherry (*Prunus serotina*), quaking aspen (*Populus tremuloides*), red maple (*Acer rubrum*), yellow poplar (*Lirodendron tulipifera*), and white pine (*Pinus strobus*) in eastern forests; white ash (*Fraxinus americana*), black cherry (*Prunus serotina*), birch (*Betula spp.*), quaking aspen

(*Populus tremuloides*) in midwestern forests; and ponderosa pine (*Pinus ponderosa*) in western forests.

## 5.0 STRENGTHS AND WEAKNESSES OF EXPOSURE/DOSE INDICES

### 5.1 Exposure and Dose Considerations

The 1-hour average ozone concentration is the basis for the derivation of exposure indices. The importance of peak hourly average concentrations versus the mid- and low-level values described previously provides guidance for the development of biologically relevant exposure indices. In a recent review of the US EPA's decision to recommend an ozone standard to protect vegetation, the Agency discussed in detail the biologically relevant exposure indices it evaluated (US EPA, 2011b). The Agency concluded that exposure indices that accumulate and differentially weight higher hourly average ozone concentrations and include the mid-level values provide the most defensible approach for use in developing response functions for protecting vegetation effects.

As mentioned previously, researchers recognize that ozone exposure and flux-based indices, as well as dose-based metrics, do not fully characterize the potential for plant uptake, detoxification, and resulting vegetation effects (US EPA, 2006). The exposure indices are measures of ambient condition independent of the vegetation present in the environment. They do not take into consideration the physical, biological, and meteorological processes controlling the transfer of ozone from the atmosphere through the leaf and into the leaf interior, and subsequent biochemical reactions within the leaf. It is well documented in the literature that exposure indices, as well as flux-based indices, can under- or over-estimate vegetation injury and damage (US EPA, 2006). It should be recognized that exposure- and dose-based indices provide only estimates of vegetation injury and damage and that many times these estimates may not be as accurate as desired.

Single season, year-long, or multiyear experimental results indicate that greater yield losses occur when plants are exposed for the longer duration and that a cumulative-type index is better able to describe the exposure-yield relationship (US EPA, 1996a, 2006). Indices that do not consider duration, such as 7-hour seasonal mean concentration metric, 8-hour average concentrations, single peak event index, or the index that cumulated all concentrations (i.e., SUM00), are unable to adequately describe the relationship between exposure and damage (US EPA, 2006). These single event or mean-type indices do not consider factors most important in plant response to ozone as described previously in this report and summarized by EPA (EPA 2006), particularly those indices that are cumulative and preferentially weight the higher concentrations (Musselman et al., 2006).

In its review of exposure indices, the US EPA (2006) concluded that indices based on long-term averages were inadequate to differentiate among the different types of exposure regimes. One such index is the SUM00, the sum of all hourly average concentrations over a specified time period. It is also referred to as the total exposure index. The SUM00, when it is divided by the hours during the period of accumulation, is a long-term average concentration. The SUM00 index weights all concentrations equally, thus focusing on the more numerous lower concentrations that have been found to be of less biological importance for assessing vegetation response (US EPA, 1996a, 2006). Given the importance of the higher hourly average ozone concentrations, the SUM00 (or average) concentration metric is inadequate for characterizing plant exposure to ozone, except in those areas where numerous occurrences of high hourly average concentrations result in a high correlation between the peaks and the SUM00 index.

Although the SUM00 exposure metric is not anticipated to work well in most locations where episodic events do not occur on a routine basis, Arbaugh et al. (1998) reported that the SUM00 exposure index performed better for describing visible injury than the SUM06, W126, number of hours ≥0.08 ppm, and the number of days between measurement periods. Because in California at some locations, a large number of high hourly average ozone concentrations occur, the SUM00 is likely highly correlated with the frequency of elevated hourly average concentrations and therefore would be anticipated to be a good predictor of vegetation effects. However, outside of California, the SUM00 or average concentrations over an extended period would be not be anticipated to be a good metric to use in exposure-response relationships for vegetation.

An important concern with using cumulative exposure indices in predicting yield loss for agricultural crops or trees is that the same value of an exposure index may relate to different vegetation responses (Musselman et al., 2006). Results reported by Yun and Laurence (1999) showed that the same SUM06 value resulted in very different foliar injury when exposure regimes with different numbers of high concentrations were applied. Similarly, Hogsett et al. (1985) showed that the same SUM07 value resulted in different yield when exposure regimes, some containing peaks and some without peaks, were used. Nussbaum et al. (1995), using identical AOT40 exposure regimes with some that contained peaks and some without peaks, suggested that peak concentrations > 0.11 ppm were important for describing the effect of ozone on total forage yield. To eliminate the concern that the same exposure value of an exposure index might provide different vegetation responses, Lefohn and Foley (1992) recommended that an additional exposure parameter, the number of hourly averaged ozone concentrations ≥ 100 ppb (N100), be combined with either the W126 or the SUM06 exposure indices. The N100 was selected by Lefohn and Foley (1992) because the fumigation methodology used in the experimental chambers resulted in numerous occurrences of hourly average ozone concentrations ≥ 100 ppb; Lefohn and Foley

(1992) believed that it was necessary to take into consideration the numerous peak exposures experienced in the chambers prior to developing exposure-response functions based on these treatments. Because the fumigation methodologies resulted in treatments that were higher than experienced under ambient ozone conditions, Lefohn and Foley (1992) believed that the applicability of the exposure-response functions may be relevant only to locations that were naturally subjected to the higher ambient ozone levels (US EPA, 2006).

Results from Davis and Orendovici (2006) indicate that the numbers of hours ≥ 100 ppb during the growing season may be an important indicator for assessing vegetation effects. Using 7 years of data from a field site in New Jersey, Davis and Orendovici (2006) developed a model that illustrated that peak ozone concentrations (N100) were a significant factor in determining vegetation injury symptom incidence. Recently, Smith (2011) reported that it is not always obvious whether the amount and severity of foliar injury was primarily a function of cumulative ozone exposure (SUM06) over the course of the growing season or if the number and frequency of peak ozone concentrations (N100) were the determining factor. Smith (2011) concluded that both the SUM06 and N100 data were required to gain a full appreciation of the ozone exposure conditions and their possible impact on vegetation for a given growing season.

In December 2000, the Federal Land Manager's Air Quality Related Values Workgroup (FLAG) Phase I Report was published. The authors of the report were the US Forest Service, National Park Service, and the US Fish and Wildlife Service. FLAG was formed to develop a more consistent approach for the Federal Land Managers to evaluate air pollution effects on their resources. Of particular importance was the New Source Review program, especially in the review of Prevention of Significant Deterioration of air quality permit applications. The goals of FLAG were to provide consistent policies and processes both for identifying air quality related values (AQRVs) and for evaluating the effects of air pollution on AQRVs, primarily those in Federal Class I air quality areas, but in some instances, in Class II areas.

For protecting vegetation from ozone exposure, FLAG (2000) selected the 24-h seasonal (April-October) W126 exposure index. Based on years of research published in the peer-reviewed literature, FLAG recognized the importance of the potential for the higher hourly average ozone concentrations (i.e., greater than or equal to 100 ppb) to affect vegetation more than the mid-level (i.e., 0.06 – 0.09 ppm) and lower values (below 0.06 ppm). FLAG recommended that both the 24-h W126 cumulative exposure index and the number of hours greater than or equal to 100 ppb (N100) be coupled together.

The FLAG document was revised in 2010 (http://www.nature.nps.gov/air/pubs/pdf/flag/FLAG_2010.pdf), and refers the reader to the agency websites for site-specific ozone information and to the A.S.L.

& Associates website (http://www.asl-associates.com/) for a review of appropriate ozone exposure metrics for the agencies to use for vegetation assessment. The US Forest Service has an ozone calculator (http://webcam.srs.fs.fed.us/tools/calculator/how_to.shtml) available for downloading and use in calculating the W126 and N100 values for all US states and territories.

The implications of utilizing both a cumulative exposure index (e.g., SUM06 or W126), as well as an index that describes the peak exposures (N100), implies that when one characterizes hourly average ozone concentrations at a specific monitoring site, special care is required. The simple characterization of hourly average concentrations in the form of a SUM06, W126, or AOT40 is not necessarily adequate in capturing the importance of the peak and cumulative nature of the total exposure.

Another important consideration is the time of day of accumulation. A large number of species have varying degrees of nocturnal stomatal conductance (Musselman and Minnick, 2000). Although nocturnal stomatal conductance is much lower compared to daytime conductance, stomatal conductance coupled with enhanced ozone exposures can possibly affect vegetation injury and growth if these two are matched with low nighttime detoxification potential (Heath et al., 2009). The implication is that the additional evidence of ozone uptake at night may interfere with recovery and this evidence should be considered in establishing an appropriate time period for accumulation. Vegetation growing in remote, high-elevation, and rural areas is more likely to experience some conductance, enhanced ozone concentrations, and low defense capability during the nighttime and early morning hours. Thus, accumulating exposure over daylight hours (i.e., 12-hour periods) may not be as accurate as accumulating over a 24-h period for assessing vegetation effects.

In the subsections that follow, we comment on the exposure- and dose-based indices that are listed in Table 5-1. We place into perspective the advantages as well as the limitations associated with the application of each index.

**Table 5-1. Summary of exposure- and dose-based indices.**

| Index | Description |
|---|---|
| SUM06 | The summation of all hourly ozone concentrations at or above 0.06 ppm. |
| W126 | A sigmoidally weighted index that preferentially weights the higher concentrations more than the mid- and lower-levels. |
| AOT40 | The accumulation over a threshold by subtracting 40 ppb (0.040 ppm) from the value of each hourly concentration above that threshold and accumulating each hourly difference over a specified time window. |
| Avg. Conc. | 7-h seasonal mean concentrations, 8-h average concentrations, or a seasonal average concentration. |
| Flux-Based | Accumulation of a temporally dynamic measure of the rate of entry of the pollutant into the leaf. |

## 5.2 SUM06

The SUM06 exposure metric is calculated as the summation of all hourly ozone concentrations at or above 0.06 ppm and its units are ppm-h. In applying a threshold, the use of the SUM06 exposure metric assumes that hourly average concentrations less than 0.06 ppm are not biologically important for assessing vegetation effects. Such is not necessarily the case. Concentrations below 0.06 ppm have been observed to result in vegetation injury (US EPA, 1996a; 2006). Extensive exposure-response information on a wide variety of plant species has been produced by two long-term projects that were designed with the explicit goal of obtaining quantitative characterizations of the response of such an assortment of crop plants (National Crop Loss Assessment Network) and tree seedlings (EPA National Health and Environmental Effects Research Laboratory, Western Ecology Division tree seedling project-NHEERL/WED) to ozone under North American conditions. The exposure-response information generated from both programs includes both the SUM06 (SUM06) and W126 exposure metrics for predictive purposes (US EPA, 2006). Since the completion of the NCLAN and NHEERL/WED projects, few studies have been published that provide a basis for estimates of exposure-response that can be compared to those described by US EPA (1996a, 2006).

## 5.3 W126

The W126 index is a cumulative exposure index that is biologically based (US EPA, 2011b). The W126 ozone index focuses on the higher hourly average concentrations, while retaining the mid- and lower-level values. The W126

applies a sigmoidally weighted function (i.e., "S" shaped curve) that preferentially weights the higher concentrations (Lefohn and Runeckles, 1987; Lefohn et al., 1988). By applying a continuous weighting, the W126 index has the advantage of not utilizing an artificial threshold and therefore, includes the lower hourly average ozone concentrations. The W126 is the sum of the hourly average ozone concentration ($C_i$ in ppm units) times a weighting function, W, where W is $W = 1/[1+4403 \cdot e^{-(126 \cdot Ci)}]$. The W126 integrated exposure index weights the lower concentrations less, but does not ignore them. The W126 index is accumulated over a specified time period. The name for the W126 exposure index was derived from the following: "W" was associated with the word "weighted" and the number "126" was associated with the 126 value of one of the constants in the above W126 equation (see http://www.asl-associates.com/w126.htm for more information). The metric has been found to be fairly robust for different ecosystems (US EPA, 2007).

The EPA (2007) noted that the W126 form, by its incorporation of a continuous sigmoidal weighting scheme, does not create an artificially imposed concentration threshold, yet also gives proportionally more weight to the higher and typically more biologically potent concentrations, as supported by the scientific evidence. Second, the index value is not significantly influenced by ozone concentrations within the range of estimated Policy-Relevant Background (PRB), as the weights assigned to concentrations in this range are very small. PRB ozone concentrations, as defined by the US EPA (2006), are those concentrations that would result in the United States in the absence of anthropogenic emissions in continental North America (i.e., the United States, Canada and Mexico). PRB concentrations include contributions from natural sources everywhere in the world and from anthropogenic sources outside of North America. The US EPA recommended in 2007 and 2010 that the W126 cumulative exposure index be designated as the secondary ozone standard to protect vegetation (US EPA, 2008, 2011b).

## 5.4 AOT40

The AOT40 is calculated as the accumulation over the threshold (AOT) by subtracting 40 ppb from the value of each hourly concentration above that threshold and then cumulating each hourly difference over a specified window. The AOT40 is used to predict effects on most crops and forest trees (Harmens et al., 2004; Harmens et al., 2010). The AOT40 is accumulated over a 3-month (crops) or 6-month (forest trees) period of time. The European level for protecting crops (based on the AOT40 index) was derived from Open Top Chamber (OTC) studies of ozone-induced yield loss in wheat observed in experiments conducted mostly in non-Mediterranean locations. As noted earlier, the AOT40 index provides an inaccurate assessment of the regional distribution of the risk of damage to vegetation by ozone across Europe (ICP-Vegetation/EMEP, 2002). For example, the impact of ambient ozone on wheat yields in the Po Valley of

northern Italy was much less than the devastatingly high loss (>60%) suggested by the seasonal exceedances of the observed AOT40 level (US EPA, 2006).

In its evaluation of exposure indices, the US EPA (2011b) discussed the AOT40. Similar to the SUM06 index, the AOT40 index incorporates a threshold. Although the AOT40 threshold is lower than the threshold value in the SUM06, the US EPA (2011b) concluded that the vegetation effects information did not provide evidence of an effects threshold that applies to all species. Thus, the US EPA concluded that neither the AOT40 nor the SUM06 was as biologically relevant as the W126 form (US EPA, 2011b).

## 5.5 Average Concentrations

Single season, year-long, or multiyear experimental results indicate that exposure indices that do not consider cumulative duration (e.g., 7-hour seasonal mean concentration metric, 8-hour average concentrations, or a seasonal average concentration) are unable to adequately describe the relationship between exposure and damage (Lefohn et al., 1988; US EPA, 2006). In addition, the season mean-type indices focus on the lower hourly average concentrations that are less likely to cause vegetation injury or damage (Musselman et al., 2006).

A recent analysis has suggested that the growing season 4$^{th}$ highest daily maximum 8-hour average ozone concentration index is a more relevant exposure index than the SUM06, AOT40, or W126 cumulative-type exposure metrics (Percy et al., 2007, 2009). The 4$^{th}$ highest daily maximum 8-hour average concentration metric focuses on the highest concentrations in an exposure distribution. As part of its review for using the 8-hour average to predict vegetation effects, the US EPA (2011b) identified analytical problems with this work described in Percy et al. (2007, 2009). The Agency noted that the authors in attempting to relate growth of aspen trees that occurred during the five-year period (1999-2003) to ozone exposure treated each plot and each year as an independent exposure experiment to create an exposure-response relationship over multiple years. The US EPA (2011b) believed that the major problem with this approach was that the authors did not take into account that the size of the trees changed over time independent of the ozone exposures and thus, neglected to take the age of the trees into consideration. For example, the authors attributed the small size of the trees in the first year of the experiment to ozone being especially elevated that year, not to the fact that the trees had just been planted two years prior. In subsequent years, ambient and elevated exposures were lower, due to local meteorology, and the trees grew larger with age. The EPA (2011b) concluded that the authors incorrectly attributed the greater size of the trees to less ozone exposure rather than to normal growth. Additional concerns expressed by the US EPA (2011b) included the observation that (1) appropriate comparisons between the predictive capabilities of the 8-hour and cumulative metrics were never made in either Percy et al. (2007) or Percy et al. (2009) and (2) the conclusion by Percy et al. (2009) that the W126 metric overestimated the effects

of exposure to ozone was not substantiated. Following its extensive review comparing the 8-hour average with cumulative exposure metrics, the US EPA (2011b) concluded that the 4$^{th}$ highest daily maximum 8-hour average and the long-term average concentration indices were not appropriate metrics to use in predicting vegetation response.

## 5.6 Flux-Based Indices

It is possible to estimate the ozone concentration from the atmosphere that enters the leaf (i.e., flux or deposition). Interest has been increasing in recent years, particularly in Europe, in using flux models for ozone assessments at the regional, national, and European scale (US EPA, 2006). While some efforts have been made in the US to calculate ozone flux into leaves and canopies (see US EPA, 2011a), little information has been published relating these fluxes to effects on vegetation. There is also concern that not all ozone stomatal uptake directly results in a yield reduction because response depends on the amount of internal detoxification occurring with each particular species. Those species having high amounts of detoxification potential may, in fact, show little relationship between ozone stomatal uptake and plant response (Musselman and Massman, 1999). The lack of data in the US and the lack of understanding of detoxification processes have made this technique less viable for assessing vegetation effects.

Models that ignore the combination of uptake and detoxification processes might not provide sufficient predictive power when applied under ambient ecosystem conditions (Musselman et al., 2006; US EPA, 2006). Europeans have attempted to address detoxification by use of a threshold for plant response in their flux models, but detoxification processes are dynamic and cannot be represented in response modeling by a constant threshold value.

Harmens et al. (2010) and Grünhage et al. (2012) have described the use of a threshold to represent the detoxification capacity of several species. The critical level uses a parameter, the $POD_x$ (Phytotoxic Ozone Dose above a threshold Y), where Y is the flux threshold above which the flux is accumulated. However, Musselman et al. (2006) have discussed the limitations of using a flux-threshold approach. In their example, Musselman et al. (2006) showed that most of the flux was associated with concentrations below 0.06 ppm; the conductance was highest when the concentrations were below 0.06 ppm. The flux-based approach showed that the measured effects appeared to be mostly associated with concentrations at the lower end of the concentration distribution. However, this did not agree with the results associated with controlled and uncontrolled experiments showing the importance of the higher ozone concentrations in plant response (US EPA, 1996a, 2006, 2011a).

Defense and repair mechanisms vary diurnally as well as seasonally and that may make it difficult to use simple flux thresholds in instantaneous flux measurements

to compensate for detoxification processes. Musselman et al. (2006) provided results showing that a flux threshold preferentially weighted the daylight hours between 10 am and 3 pm and did not address the additional accumulation occurring during the late afternoon, nighttime, and early morning hours. Musselman et al. (2006) found that the application of a flux threshold underemphasized or eliminated the fluxes occurring at these biologically important times. Flux-based models that use a fixed threshold do not allow for the temporal (i.e., daily and seasonal) variability of defense mechanisms and the predicted results associated with these models may not provide consistent results.

### 5.7 Most Suitable Exposure Indices for the FCPC Class I Area

The US EPA concluded that the most relevant exposure indices to protect vegetation for use in the standard-setting process are those that accumulate $O_3$ exposures, focus on the higher concentrations but include the mid- and low-level values, and do not use a threshold concentration, but rather a weighting scheme. The US EPA noted that the W126 exposure index uses a continuous sigmoidal weighting scheme and provides proportionally more weight to the higher and typically more biologically important concentrations. In addition, the W126 index, according to the US EPA, provides a more appropriate target for air quality management programs designed to reduce emissions from anthropogenic sources contributing to ozone formation. Currently, the US EPA considers the W126 the most biologically relevant cumulative, seasonal form appropriate to consider in the context of the Agency's 2008 ozone rulemaking (U.S. EPA, 2008; US EPA, 2010). The US EPA has not changed its opinion since the 2008 ozone rulemaking and it currently appears to be considering the W126 as a possible secondary standard in its current evaluation of the literature (US EPA, 2011a). Because the W126 has been found to be biological relevant for assessing vegetation effects, we believe that the index is most suitable to the FCPC Class I area.

## 6. CHARACTERIZING OZONE EXPOSURES

### 6.1 Determining Ozone Exposure Levels at Sites Representative of North American Background

It is important to place in proper perspective the 24-h W126 exposures that affect vegetation with those exposures that are experienced at ozone monitoring sites that are representative of North American background. North American background (NAB) concentrations have been defined by the US EPA (2011a) as those levels that would occur in the United States in the absence of anthropogenic emissions in continental North America (i.e., the United States, Canada, and Mexico). Therefore, NAB consists of the sum of those concentrations from natural sources everywhere in the world and from anthropogenic sources outside of continental North America. If one were able to subtract anthropogenic sources

from predicted NAB estimates, the natural background could be predicted. Natural background sources of $O_3$ are associated with (1) transport from the stratosphere and (2) chemical production associated with lightning, the biosphere, and open fires (Zhang et al., 2011).

The estimate of background ozone concentrations at locations that are representative of NAB, such as Trinidad Head, California, have provided important insights regarding the relative importance of processes that contribute to background ozone concentrations (McDonald-Buller et al., 2011). Meteorological evidence exists to support the observation that conditions representative of background ozone are routinely encountered at the low-elevation monitoring site at Trinidad Head, California (Oltmans et al., 2008). Trinidad Head is situated on a large domed prominence to the west of the town of Trinidad, which is a small town of about 400 people on California's north coast. The site is located at 124.1° W and 41.1° N at an elevation of 107m. The site is connected to the mainland only on its northern end. Long-range transport outside of North America and natural processes, such as stratospheric enhancement, contribute to ozone concentrations measured at this site (Cooper et al., 2011; Lefohn et al., 2011). The site at Trinidad Head, CA, experiences its airflow pattern overwhelmingly from the North Pacific Ocean during all seasons, with stronger flow during the winter and spring months that regularly indicate background conditions. The frequency of hourly average concentrations ≥ 0.05 ppm in the springtime, when almost all of the high concentrations occur at the site, varies from year to year.

Because of EPA's recommendation for the W126 exposure index as the recommended secondary ozone standard to protect vegetation and the FLAG (2000) recommendation for the 24-h W126, we have characterized ozone exposures in the form of the W126. For the period 2003-2011, the maximum 3-month, 24-h W126 values range from 3.312 to 5.571 ppm-h (Table 6-1). The highest 3-month period at Trinidad Head occurs during the late winter to spring period.

**Table 6-1. Summary of the maximum 3-month, 24-h W126 (ppm-h), 3-month and number of hourly average concentrations ≥ 100 ppb (N100) measured at Trinidad Head, California (LST) for the 9-year period, 2003 through 2011. Source: Modified from Lefohn and Musselman (2012).**

| Year | W126 | N100 | 3-Month Maximum Period |
|---|---|---|---|
| 2003 | 5.571 | 0 | March-May |
| 2004 | 3.312 | 0 | February-April |
| 2005 | 3.392 | 0 | March-May |
| 2006 | 4.461 | 0 | March-May |
| 2007 | 3.396 | 0 | March-May |
| 2008 | 4.373 | 0 | March-May |
| 2009 | 3.616 | 0 | February-April |
| 2010 | 3.620 | 0 | March-May |
| 2011 | 3.376 | 0 | March-May |

Oltmans et al. (2010) reported that Eurasian emissions associated with biomass burning in the spring of 2008 contributed to ozone concentrations at west coast ozone monitoring sites in the US and Canada, as well as inland ozone monitoring sites in Montana, Wyoming, and North Dakota. At Denali National Park in central Alaska, an hourly average of 0.079 ppm was recorded during an 8-hour period in which the 8-hour average was over 0.075 ppm. Surface ozone observations on Vancouver Island showed enhanced ozone concentrations on several days in April. Back trajectories from Vancouver Island on these days suggest that Eurasian biomass burning could be the source of the enhanced ozone concentrations. At Trinidad Head, hourly ozone readings were > 0.05 ppm almost continuously for a 35-hour period. A 3-month, 24-hW126 value of 4.373 ppm-h was experienced during the March-May period, which included the April 2008 period. As the biomass burning-enhanced ozone plume moved further into the interior of the US between 18-20 April through a northern tier of states (Montana, Wyoming, North Dakota), surface ozone measurements at several monitoring sites appeared to have intercepted the plume (Oltmans et al., 2010). The 8-h average ozone enhancements were above the normal background concentrations observed at these monitoring sites (i.e., 45-0.055 ppm for Montana and North Dakota and 0.05-0.06 ppm for Wyoming). The 8-h daily maximum at Yellowstone on 19 April (0.069 ppm) suggests an enhancement during the period of suspected plume influence of 0.05-0.010 ppm above the other relatively high values observed at this site. This is also about the amount of the perturbation seen at the other interior monitoring sites (Oltmans et al., 2010). At Trinidad Head in April 2008, the occurrences of hourly averaged ozone concentrations ≥ 0.05 ppm were similar in magnitude to the number of events in April 2003, which over the 2002-2010 period experienced the highest occurrences of hourly average concentrations ≥ 0.05 ppm. Although a thorough study of 2003 was not undertaken by Oltmans et al. (2010), modeling of 2003 data found that biomass burning impacted the west coast of North

America (Pfister et al., 2010) and may have been the cause of the elevated surface ozone amounts at Trinidad Head in April 2003 (see Table 6-1) as well (Oltmans et al., 2010).

It is important to characterize background so that these ozone exposures can be compared with those that are occurring at the Potawatomi monitoring site. We have found that at background site at Trinidad Head for the period 2003-2011, (1) the maximum 3-month, 24-h W126 values range from 3.312 to 5.571 ppm-h, (2) no hourly average ozone concentrations ≥ 0.10 ppm occur, and (3) the highest 3-month W126 exposures occur during the late winter to spring period. These background ozone exposures provide a basis for assessing whether the exposures occurring at the Potawatomi monitoring site are comparable to these levels or whether the exposures experienced have the potential for FCPC AQRV vegetation violations.

## 6.2 Characterizing Ozone Exposure Levels at the Potawatomi Ozone Monitoring Site

Table 6-2 summarizes the exposures for the maximum 3-month, 24-h W126, N100 values, and the 3-month, 24-h W126 over the June-August period at the Potawatomi ozone monitoring site (550410007) located in Forest County. The information described in Table 6-2 is derived from the summarized characterization of the hourly average ozone concentrations that can be reviewed in Appendix A (Table A-1). We have found that for the period 2004-2011, (1) the maximum 3-month, 24-h W126 values range from 4.816 to 13.218 ppm-h, (2) no hourly average ozone concentrations ≥ 0.10 ppm occur, and (3) the highest 3-month W126 exposures occur during the March-May and April-June periods. Approximately 65% of the exposures for the maximum 3-month, 24-h W126 index are associated with the hours between 0800 to 1959 h (Table 6-3). Over a 24-h period, approximately 35% of the W126 exposures are occurring during the nighttime period. These nighttime exposures have the potential for eliciting vegetation effects as summarized by Musselman and Minnick (1999), Musselman et al. (2006), and Heath et al. (2009). Table A-2 in the Appendix summarizes the top 10 8-h daily maximum values.

**Table 6-2. Summary of the maximum 3-month, 24-h W126 (ppm-h), number of hourly average concentrations ≥ 100 ppb (N100), and W126 (ppm-h) for June-August measured at the Potawatomi ozone monitoring site (550410007).**

| Year | W126 3-Month Maximum | N100 | 3-Month Max. Period | W126 June-August |
|---|---|---|---|---|
| 2004 | 4.816 | 0 | March-May | 2.591 |
| 2005 | 13.218 | 0 | April-June | 9.937 |
| 2006 | 6.979 | 0 | April-June | 5.060 |
| 2007 | 12.628 | 0 | April-June | 5.195 |
| 2008 | 10.603 | 0 | April-June | 3.466 |
| 2009 | 5.814 | 0 | March-May | 1.982 |
| 2010 | 10.604 | 0 | March-May | 2.228 |
| 2011 | 7.247 | 0 | March-May | 3.277 |

**Table 6-3. Comparison of the maximum 3-month, 24-h W126 (ppm-h) with the maximum 3-month, 12-hour W126 (ppm-h) measured at the Potawatomi ozone monitoring site (550410007).**

| Year | W126 (12-h) | W126 (24-h) | Percent 12-h/24-h |
|---|---|---|---|
| 2004 | 3.174 | 4.816 | 65.9% |
| 2005 | 8.621 | 13.218 | 65.2% |
| 2006 | 4.753 | 6.979 | 68.1% |
| 2007 | 8.694 | 12.628 | 68.8% |
| 2008 | 7.185 | 10.603 | 67.8% |
| 2009 | 3.598 | 5.814 | 61.9% |
| 2010 | 6.472 | 10.604 | 61.0% |
| 2011 | 4.366 | 7.247 | 60.2% |

## 6.3 The Importance of Stratospheric-Tropospheric Exchange Processes in Affecting Surface Ozone Exposures at the Potawatomi Site

Skelly (2000) noted that subsidence inversions from aloft may bring high ozone concentrations of stratospheric origin to the surface, with vegetation on higher mountains sometimes showing acute injuries. Research from the 1970s to the present has shown that hourly average ozone concentrations within the troposphere are affected by both stratospheric and photochemical sources. The results of the analysis by Singh et al. (1978) of long-term ozone data collected at

remote sites between latitudes 19°N and 48°N, complemented by aircraft data, support the conclusion that a significant reservoir of ozone is present in the troposphere. The authors reported that evidence suggested that this ozone reservoir was predominantly of stratospheric origin and that photochemical oxidation processes resulting in ozone production from hydrocarbons (HC's), carbon monoxide (CO), and nitrogen oxides ($NO_x$) of natural origin do not contribute significantly to the net ozone balance in this reservoir. The authors concluded that the predominant source of tropospheric ozone at these remote sites was due to injections from the stratosphere. The tropospheric ozone showed a distinct seasonal variation, with a maximum in the spring when 1-hour ozone concentrations approached or exceeded 0.080 ppm. The authors concluded that cyclic behavior of ozone at widely separated sites with an early spring maximum strongly suggested a stratospheric source.

Lefohn et al. (2001) investigated the hourly average ozone concentrations ≥ 0.05 and ≥ 0.06 ppm that were experienced during the photochemically quiescent months in the winter and spring at several rural sites across southern Canada, the northern United States, and northern Europe. Their results indicated that hourly average ozone concentrations ≥ 0.05 and ≥ 0.06 ppm occur frequently during the winter and spring months. Most occurrences were during April and May but sometimes as late as June. In some, but not all, of the cases that were studied, a plausible explanation for the higher hourly ozone values was the presence of upper tropospheric and stratospheric air that was transported down to the surface. Even in cases where the enhanced ozone concentrations could not be traced directly to the presence of a stratospheric source, the conditions were such that air parcels reaching the designated site would be unlikely to experience significant photochemical ozone production. Thus, anthropogenic emissions of $NO_2$ were unlikely to have contributed to the ozone concentrations.

Lefohn et al. (2011) recently described the importance of stratospheric-tropospheric exchange (STE) processes enhancing hourly average ozone concentrations at both high- and low-elevation monitoring sites across the Western and Northern Tier of the US (Lefohn et al., 2011). The authors discussed the importance of stratospheric intrusions contributing to enhanced hourly average surface ozone concentrations ≥ 0.05 ppm for the years 2006, 2007, and 2008. The authors used the Lagrangian Analysis Tool (LAGRANTO) trajectory model to identify specific days when stratosphere-to-troposphere transport was optimal to elevate surface ozone levels. The coincidences between the number of days with a daily maximum hourly average ozone concentration ≥ 0.05 ppm and stratosphere-to-troposphere transport to surface (STT-S) were quantified. At many of the lower-elevation sites, Lefohn et al. (2011) indicated that there was a preference for ozone enhancements to be coincident with STT-S events during the springtime, although summertime occurrences were sometimes observed. Lefohn et al. (2011) noted that for the Potawatomi site (identified as the Crandon, WI site in the publication), the spring months of April 2006, April 2007, May 2007, April 2008, and May 2008 exhibited enhanced $O_3$ concentrations that were statistically related to STT-S

events that reached the surface. Although not reported in Lefohn et al. (2011), the actual data indicated that although not statistically significant, March and June 2008 were also months in which STT-S appeared to be related to enhanced ozone hourly average concentrations (i.e., ≥ 0.05 ppm). In the springtime, for the 3-year period when coincidences occurred, there appeared to be no preference for the enhanced $O_3$ concentrations to occur during daylight or nighttime hours. Fig. 6.1 illustrates the number of STT-S counts (i.e., occurrences) for April through August reaching the Potawatomi site in 2006, 2007, and 2008. Note that the greatest frequency of STT-S occurred during the springtime and sometimes in June, while less frequent occurrences were evident during the summertime. It is important to note that the there are times when low ozone concentrations are associated with STT-S events. Thus, there is no correlation between the number of STT-S events and the level of enhancement associated with ozone concentrations. However, it would be anticipated that the greater the frequency of STT-S events, the greater the probability of ozone concentration enhancements. The ozone content in the stratosphere over the northern hemisphere is greatest during the late winter, springtime, and fall and is at a minimum during the summertime. At times, STT-S events occurring during the summertime can be associated with ozone concentration enhancements (Ambrose et al., 2011; Lefohn et al., 2011).

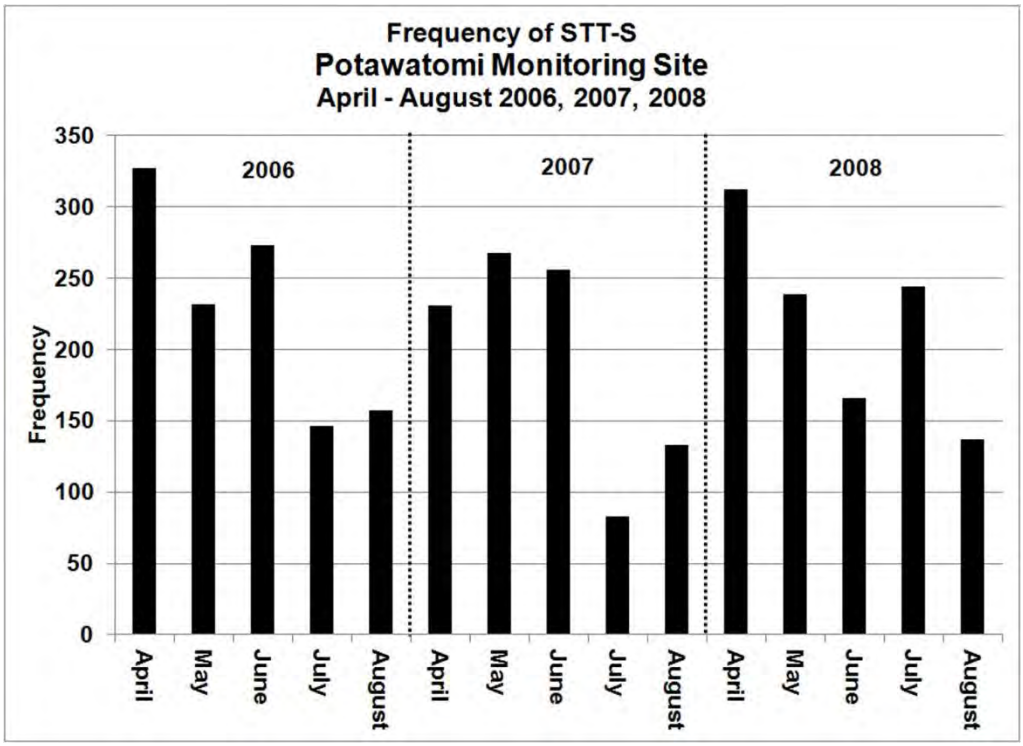


**Fig. 6.1. Frequency of STT-S events occurring during April-August 2006, 2007, and 2008 at the Potawatomi ozone monitoring site. Source: Lefohn, personal communication.**

In reviewing the ozone data for the Potawatomi site that is summarized in Table A-1, the most frequent occurrences of hourly average concentrations ≥ 0.05 ppm were experienced during the springtime versus the summertime. Several times during April 2008, hourly average concentrations ≥ 0.05 ppm were experienced during both daytime and nighttime hours. Because the information in Table 6-2 indicates that the annual highest 3-month W126 cumulative exposure occurred during either the March-May or April-June periods, coupled with the results reported by Lefohn et al. (2011), it appears that STE processes may be contributing to the enhanced ozone concentrations at the Potawatomi site. During the springtime when STT-S enhancements were observed by Lefohn et al. (2011), coniferous trees and some early emerging groundcover species may be sensitive to the ozone concentrations associated with STT-S-caused enhancements during these time periods.

It is important to realize that during the springtime the ozone exposures occurring at the Potawatomi monitoring site appear to be influenced by stratospheric ozone. For assessing whether controllable emissions can be modified to reduce vegetation injury in the FCPC region, it will be important to identify whether AQRV threshold ozone concentrations are exceeded during the springtime or during the summertime. If the exceedances occur during the springtime, then vegetation injury occurring during this period may not be ameliorated by reduction in emissions because of the contribution of ozone concentrations associated with stratospheric transport to the surface.

# 7.0 RECOMMENDING AN EXPOSURE INDEX AND OZONE THRESHOLDS FOR VEGETATION AIR QUALITY RELATED VALUE

## 7.1 Selecting an Exposure Index

Researchers recognize that ozone exposure and flux-based indices, as well as dose-based metrics, do not fully characterize the potential for plant uptake, detoxification, and resulting vegetation effects (US EPA, 2006). Exposure indices do not take into consideration the physical, biological, and meteorological processes controlling the transfer of ozone from the atmosphere through the leaf and into the leaf interior, and subsequent biochemical reactions within the leaf. Exposure indices, as well as flux-based indices, can under- or over-estimate vegetation injury and damage (US EPA, 2006, 2011b). It should be recognized that currently, exposure- and dose-based indices provide only estimates of vegetation injury and damage and that many times these estimates may not be as accurate as desired (US EPA, 2006; Musselman et al., 2006).

Given the limitations associated with each of the exposure/dose metrics, the US EPA (2011b) concluded that exposure metrics offered the most relevant opportunity to develop vegetation response relationships. When assessing the various exposure indices, the US EPA (2011b) concluded that the W126 form, by

its incorporation of a continuous sigmoidal weighting scheme did not create an artificially imposed concentration threshold and also provided more weight to the higher and typically more biologically important concentrations. Using the W126 exposure index, the US EPA (2011a) compared results from the EPA NHEERL-WED OTC experiments with the Aspen FACE experiments and concluded that the extensive database from the earlier OTC experiments are still relevant for developing ozone exposure-response models. As discussed earlier, based on exposure-response models, the US EPA recommended that a 3-month, 12-hour W126 exposure index at the 13 ppm-h level be established as the secondary vegetation standard (US EPA, 2011b).

As indicated in the literature, both the SUM06 and the W126 perform well in predicting vegetation damage effects (US EPA, 2006). At this time, the US has not adopted the W126 exposure index as a secondary ozone standard. However, indications are that the US EPA is continuing to support utilization of the W126 exposure index as an ozone standard (US EPA, 2011a, 2011b). Currently, the US Forest Service is utilizing the 24-h W126 exposure index for assessing vegetation effects (http://webcam.srs.fs.fed.us/pollutants/ozone/index.shtml). Although it is not possible to separate out the performance of the W126 and the SUM06 exposure indices (US EPA, 2006, 2011b), we agree with the US EPA (2011b) that the W126 is preferred over the SUM06 because the exposure metric does not incorporate an arbitrary threshold concentration and seems to be more biologically based. It may be possible when assessing exposure-response relationships in future years that hourly average concentrations below 0.06 ppm are important. The SUM06 index ignores all hourly average concentrations below 0.06 ppm.

In addition to recommending the W126 exposure index, we believe it is important to note that there is concern in utilizing either the SUM06 or W126 exposure indices in predicting yield loss for agricultural crops or trees without considering the numerous peak concentrations that were used in the NCLAN and NHEERL-WED OTC experiments. Researchers have noted that the same value of an exposure index may relate to different vegetation responses. Musselman et al. (2006) discussed the use of the N100 exposure index (number of hourly average concentrations ≥ 100 ppb) in combination with either the SUM06 or W126 in order to address this concern. The implication of the use of the N100 in combination with either the SUM06 or W126 is that the numerous high hourly average concentrations that were experienced in the NLCAN and EPA NHEERL-WED OTC experiments are taken into consideration when the exposure-response relationships are applied for predicting vegetation effects. Musselman et al. (2006) believed that not quantifying the frequency of occurrences of hourly average concentrations ≥ 100 ppb (high concentrations that were used in the fumigation experiments that derived the exposure response functions) would result in the SUM06 or W126 exposure indices overestimating vegetation effects. Even though the W126 is preferentially weighted for the higher concentrations,

the accumulation of a large number of mid-level concentrations causing less impact on vegetation can lead to a large W126 value with the result that ignoring N100 values may provide inadequate predictions.

Another important concern in the use of the exposure indices is the time of day of accumulation. As mentioned previously, a large number of species have varying degrees of nocturnal stomatal conductance. Although nocturnal stomatal conductance is much lower compared to daytime conductance, stomatal conductance coupled with enhanced ozone exposures can possibly affect vegetation injury and growth if these two are matched with low nighttime detoxification potential. The implication is that the additional evidence of ozone uptake at night may interfere with recovery and this evidence should be considered in establishing an appropriate time period for accumulation. Thus, an important consideration is the use of a 12-h or a 24-h accumulation period. Vegetation growing in remote, rural areas is more likely to experience some conductance, enhanced ozone concentrations, and low defense capability during the nighttime and early morning hours. Therefore, the assumption of accumulating exposure indices over daylight hours (i.e., 12-hour periods) versus 24-hours may not provide adequate predictions of non-crop vegetation effects.

To account for these limitations of the W126 index when used for response of natural vegetation to ozone, we recommend a 3-month W126 exposure index that is accumulated over a 24-h period and is coupled with the N100 index.

## 7.2 Identifying Vegetation Injury and Damage Levels in the FCPC Class I Area

### 7.2.1 Identifying the Sensitivity of Ozone Injury to Plants Important to the FCPC

The following three conditions must exist for a plant to become injured by ozone:

- The plant must be susceptible to injury from ambient ozone.
- The amount of ozone in ambient air must be enough to cause injury to plant tissue.
- The individual health of the plant is important in how it will respond to ozone.

Based on surveys identifying ozone injury symptoms in the field or in laboratory or field fumigations at ambient ozone levels, the sensitivity of the plant must result in injury from ambient ozone levels. There is a large amount of genetic variability in susceptibility of plants to ozone. In addition to the species and genera differences, there are differences within species. One plant of a species may be more tolerant or susceptible to ozone than others.

For those plants that are injured, the amount of ozone in ambient air must be sufficient to cause injury to plant tissue. The amount of ambient ozone sufficient to cause injury is determined from field surveys identifying ozone injury on plant foliage coordinated with summarization of ambient ozone occurring during the exposure period. Similar results can be obtained from fumigation experiments.

The individual health of the plant determines how it will respond to ozone. The primary factors affecting plant heath are environmental conditions and other biotic stresses such as insects and diseases. Ozone must be taken up into leaf tissue through stomata for injury to occur. Plants must be healthy and non-stressed for optimal uptake of ozone. Environmental conditions, such as drought, amount of sunlight or cloudiness, temperature, and humidity all influence plant condition and subsequent ozone susceptibility. Additional biotic stresses such as those from insects, diseases, or competing vegetation can influence susceptibility to injury from ozone.

Although ozone can stress plants before visible symptoms are evident, injury to vegetation from ozone is typically expressed by leaf necrosis. The necrotic or dead tissue occurs only on the upper surface of the leaf and is most prevalent and more severe on the older leaves that have had longer exposure to ozone. The injury initially occurs between the veins because ozone first attacks the mesophyll cells that are located under the epidermis between the veins. Brown or black interveinal necrosis is called oxidant stipple. Other symptoms less specific to ozone-induced injury include chlorosis or yellowing of the leaf, and sometimes a bronzing appearance on the leaf surface. Leaf injury leads to leaf death and early leaf drop, called premature senescence. There are several on-line sources that show typical ozone injury to leaf tissue that can be used as a guide for field identification. For example see [**http://www.fs.fed.us/r8/foresthealth/pubs/ozone/r8-pr25/ozoneh2.htm**] or [**http://science.nature.nps.gov/im/monitor/protocols/OzoneInjuryAssessment.pdf**] for the US Forest Service and National Park Service guides. Nevertheless, a trained expert is best consulted to determine or verify ozone-caused symptoms on foliage. Environmental and biotic factors that stress plants can cause symptoms that are similar to ozone injury.

Because these species are prominent on tribal lands and have specific cultural importance to the FCPC, the FCPC requested that A.S.L. & Associates focus on the following ten plant species that were identified in Table 2-2:

- Black cherry (*Prunus serotina*)
- Quaking aspen (*Populus tremuloides*)
- Common milkweed, tall milkweed (*Asclepias syriaca*);
- American Hazelnut (*Corylus americana*);
- Pin cherry (*Prunus pensylvanica*);

- Choke cherry *(Prunus virginiana*);
- Allegheny blackberry, common blackberry (*Rubus allegheniensis*);
- Cutleaf coneflower, coneflower, golden glow (*Rudbeckia laciniata*);
- American elder, white elder, elderberry (*Sambucus canadensis*);
- Goldenrod (*S. canadensis*)

In addition to the above 10 plant species, we have identified the ozone sensitivity of additional plant species important to FCPC, as well as the ambient ozone data in the FCPC area (i.e., Potawatomi monitoring site). Four separate species lists were provided to A.S.L. & Associates of plants and other species that are important to the FCPC:

1. Ozone Sensitive and Bioindicator Species: a list of 29 plant species of which 10 were listed as used by FCPC members and 17 of which in addition to be ozone sensitive, are considered bioindicators. (Table 2-2).
2. Other Important FCPC Plants: a listing of 63 additional plant species. Twenty-one of these species were indicated as bioindicators for ozone or in a family or genus that had other ozone bioindicator species.
3. Critical Natural Resources: including plant and animal species.
4. Commercial Tree Species: Four of these were also on the list of Ozone Bioindicator Species but were not listed as being used by FCPC members.

The plant species from these four lists were combined, except for the plant species on the bioindicator list that were not listed as being used by FCPC or were not present in Forest County and were not on any of the other lists. A few additional genera were later identified so species level and their sensitivity to ozone was determined. A review of literature for sensitivity to ozone was conducted for all 101 species on this combined list. When foliar injury was reported in the field under ambient concentrations or in fumigations at ambient concentrations, the species were listed as sensitive. Tolerant species showed no foliar symptoms of ozone injury in the field or under ambient ozone fumigations. Moderately sensitive species were those showing less ozone injury than the most sensitive species or showing injury only under limited conditions. Thirty-five species were found to be sensitive to ozone, seven likely sensitive given most other species in the same genera are sensitive, two were moderately sensitive, 12 tolerant, and one was likely tolerant given other species in the same genera are known to be tolerant. Because no data were found in the literature on ozone sensitivity for 44 of the species, their status is unknown. The complete listing with reference sources is included in the Appendix in Table A-3. The most extensive sources of information on sensitivity of native plants to ozone for this review were from the US Forest Service (Smith et al., 2007) and the National Park Service and Fish and Wildlife Service (NPS/FWS, 2003).

Our findings demonstrate and confirm that large variability in susceptibility to ozone exists for plant species. A large number (i.e., approximately 44%) of the plant species were of unknown sensitivity and many of these might be expected to be tolerant, because they have not been specifically identified as susceptible in field surveys, or they truly may have not been observed for susceptibility to ozone. Alternatively, they may be sensitive to ozone without showing typical symptoms of ozone injury. It is important to note that for plant species important to the FCPC, of those that were not listed as unknown, nearly ¾ were sensitive or likely sensitive to ozone, while less than ¼ were tolerant or likely tolerant.

### 7.2.2 Identifying Ozone Exposures for Assessing Vegetation Injury

A paucity of exposure-response data for assessing vegetation injury and damage in the FCFC area are available. Most AQRV analyses provide a list of bioindicator plants and possible sensitivity (e.g., Boundary Waters: http://www.fs.fed.us/air/technical/class_1/wilds.php?recordID=6, Rainbow Lakes: http://www.fs.fed.us/air/technical/class_1/wilds.php?recordID=61, Seney NWR: http://www.fws.gov/refuges/AirQuality/ARIS/SENE/AQRV.html, Isle Royal National Park: http://www.nature.nps.gov/air/Permits/aris/isro/index.cfm and http://www.nature.nps.gov/air/Pubs/pdf/SwackHorn20040901.pdf and http://www.nature.nps.gov/air/Permits/aris/isro/aqrv.cfm).

Information is available from some vegetation surveys that provide estimates of ozone exposure that may indicate possible injury thresholds for vegetation in the FCPC area. Davis (2007) performed annual field surveys from 1999–2004 within the Seney National Wildlife Refuge in northern Michigan, which is approximately 210 km NE of FCPC lands, to determine if ambient ozone levels were sufficient enough to injure refuge vegetation. Ozone injury was observed on bioindicator plants during each survey year. The incidence (percentage) of plants exhibiting symptoms was low and varied among species and years. Ozone-induced symptoms occurred on *Sambucus canadensis* (American elder*), Prunus serotina* (black cherry), *Asclepias syriaca* (common milkweed), and *Apocynum androsaemifolium* (spreading dogbane). The most sensitive species was spreading dogbane. Davis (2007), using ambient hourly averaged ozone concentrations monitored at the EPA AQS monitoring site (261530001) within the refuge, calculated 24-h cumulative SUM06 exposure levels between the beginning of the ozone season (early April) until the beginning of his survey (typically during the second to third week in August). The author reported that for each survey year, the 24-h SUM06 was greatest in 2003, followed by 2002, and least in 2004 (15.373, 12.747, and 5.229 ppm-h, respectively). Davis (2007) reported that the annual incidence of ozone injury for the 3 years was not directly related to level of ambient ozone and appeared to be confounded by environmental factors, such as drought. Based on the 2004 survey, Davis (2007) estimated that the threshold level of SUM06 ozone exposure required to induce visible symptoms on sensitive

vegetation in the Seney National Wildlife Refuge was approximately 5.0 ppm-h. This estimate was based on the ozone exposure that occurred between early April and mid-August 2004. Using hourly averaged ozone data for 2004, the comparable threshold for the 24-h W126 ozone exposure was 7.563 ppm-h. During 2004, there were no N100 values experienced at the site, while in 2003 and 2002 there were nine and one N100 values, respectively.

Kohut (2007) discussed assessing the risk of foliar injury from ozone on vegetation in parks in the U.S. National Park Service's Vital Signs Network. The assessment examined bioindicator species, evaluated levels of ozone exposure, and investigated soil moisture conditions during periods of exposure for a 5-year period in each park. The assessment assigned each park a risk rating of high, moderate, or low. Kohut (2007) did not calculate exposure-response relationships for injury, but rather utilized data from other sources (Heck and Cowling, 1997; Lefohn et al., 1997). For the 244 parks for which assessments were conducted, the risk of foliar injury was high in 65 parks, moderate in 46 parks, and low in 131 parks. Among the well-known parks with a high risk of ozone injury were Gettysburg, Valley Forge, Delaware Water Gap, Cape Cod, Fire Island, Antietam, Harpers Ferry, Manassas, Wolf Trap Farm Park, Mammoth Cave, Shiloh, Sleeping Bear Dunes, Great Smoky Mountains, Joshua Tree, Sequoia and Kings Canyon, and Yosemite. Kohut (2007) noted that the process of risk assignment was not quantitative, but based upon three primary evaluations: the extent and consistency by which the 12-h SUM06 and 24-h W126 ozone exposure injury thresholds were exceeded, the nature of the relationship between exposure and soil moisture, and the extent to which soil moisture conditions constrained the uptake of ozone in high exposure years. The evaluation of these factors and the assessment of their interactions with ozone-sensitive plant species comprised the framework for determining whether the risk of foliar ozone injury was high, moderate or low. Kohut (2007) applied a 12-h, running 3-month SUM06 index, as well as the 24-h, W126 exposure index that was coupled with the N100 values as described by Lefohn et al. (1997). Lefohn et al. (1997) summarized the range of ozone exposures and effects from various open-top research results. Exposure-response vegetation damage information was provided for black cherry, slash pine, yellow-poplar, Eastern white pine, sugar maple, red oak, Virginia pine, loblolly pine, and red maple. The authors described three tree response categories based on the 24-h, W126 exposures and associated N100 values (Table 7-1).

**Table 7-1. Summary of sensitivity levels and their associated 24-h W126 and N100 values. The 24-h W126 exposure index is in units of ppm-h. The N100 index is in units of hours. Source: Lefohn et al. (1997).**

| Sensitivity Level | W126 | N100 |
|---|---|---|
| Level 1 only high sensitive species affected (e.g., black cherry) | 5.9 | ≥ 6 |
| Level 2 moderately sensitive species affected (e.g., yellow-poplar) | 23.8 | ≥ 23.8 |
| Level 3 resistant species affected (e.g., red oak) | 66.6 | ≥135 |

The sensitivity levels and exposures used by Kohut (2007) that were described by Lefohn et al. (1997) were associated with experiments that were run in open-top chambers over various periods of time. Therefore, the W126 and N100 values were not accumulated over a specific time period. The ozone exposures reflected the values associated with the range of experiments. Black cherry (*Prunus serotina*) and slash pine (*Pinus elliottii*) were rated with the greatest sensitivity. Yellow-poplar (*Liriodendron tulipifera*), white pine (*Pinus strobus*), and sugar maple (*Acer saccharum*) were rated moderately sensitive. Red oak (*Quercus rubra*), Virginia pine (*Pinus Virginian*), loblolly pine (*Pinus taeda*), and red maple (*Acer rubrum*) were rated resistant. Kohut (2007) utilized the levels listed in Table 7-1 to assign rankings of vegetation ozone injury. For the period 1995-1999, areas closest to the FCPC area, such as Saint Croix/Lower St. Croix NSR (WI), Apostle Islands NL (WI), and Voyageurs National Park (MN), were rated by Kohut (2007) as low risk for vegetation injury resulting from ozone exposure. Kohut (2007) noted that the threshold for injury for the SUM06 index was routinely exceeded in many parks for each year of the 5-year period of evaluation. The two threshold criteria for the W126 index and N100 were satisfied less frequently. In some parks the W126 index was surpassed, but the threshold for hours ≥ 100 ppb was not. Consequently, in many parks the SUM06 index was satisfied, while the W126 was not. The high frequency with which the SUM06 was satisfied, in contrast to the apparently more demanding nature of meeting the two criteria associated with the W126 index, led to the W126 index serving as an important factor according to Kohut (2007) in determining whether a park was a candidate for a risk rating of high. In general, both the SUM06 and W126 indices of exposure were consistently satisfied at parks rated at high risk.

Bennett et al. (2006) utilized higher ozone concentrations east of southern Lake Michigan, compared to west of the lake, to test hypotheses about injury and growth effects on two plant species. They measured approximately 1000 black cherry trees and over 3000 milkweed stems from 1999 to 2001 for this purpose. Black cherry branch elongation and milkweed growth and pod formation were significantly higher west of Lake Michigan, while ozone injury was greater east of Lake Michigan. Using classification and regression tree (CART) analyses, they determined that departures from normal precipitation, soil nitrogen, and ozone

exposure/peak hourly concentrations were the most important variables affecting cherry branch elongation, and milkweed stem height and pod formation. The effects of ozone were not consistently comparable with the effects of soil nutrients, weather, insect, or disease injury, and depended upon species. Ozone 12-h SUM06 exposures greater than 13 ppm-h decreased cherry branch elongation 18%; peak 1-h exposures greater than 0.093 ppm reduced milkweed stem height 13%; and peak 1-h concentrations greater than 0.098 ppm reduced pod formation 11% in milkweed.

Schaub et al. (2005) noted the presence of ozone injury at 24-h SUM06 values between 17-19 ppm-h for mature trees. The crowns of five canopy dominant black cherry (*Prunus serotina*), five white ash (*Fraxinus americana*), and six red maple (*Acer rubrum*) trees on naturally differing environmental conditions were accessed within a mixed hardwood forest stand in central Pennsylvania. Ambient ozone concentrations, meteorological parameters, leaf gas exchange, and leaf water potential were measured at the sites during the growing seasons of 1998 and 1999. Ambient ozone exposures were sufficient to induce typical symptoms on black cherry (0–5% total affected leaf area, LAA), whereas foliar injury was not observed on ash or maple. The W126 exposure value tends to be greater than the SUM06 values because the W126 includes hourly average concentrations below 0.06 ppm. While it not possible to determine the 24-h W126 exposures from Schaub et al. (2005), the W126 values were more than likely greater than the 24-h SUM06 exposure values of 17-19 ppm-h reported by Schaub et al. (2005).

Lefohn (1998) summarized ozone exposures for vegetation injury and damage. As part of the study, the author obtained open-top chamber (OTC) experiment data from Dr. Howard Neufeld, Department of Biology, Appalachian State University (Boone, NC), who provided exposure information that was related to observed visible injury. Table 7-2 is a summary of the exposures that resulted in no visible injury in Dr. Neufeld's experiments. The exposures that were calculated were determined by noting at what treatment level in the OTC no visible injury was observed. Note that some species experienced no visible injury, even at the highest ozone exposures (i.e., ginseng, Eastern hemlock, and Northern red oak). Alternatively, other species were sensitive and suffered visible injuries just above the charcoal-filtered treatment. Additional information on the experiments is provided in Neufeld et al. (1995) and Neufeld et al. (2000).

**Table 7-2. Summary of exposures that resulted in no visible injury using chamber data from Dr. Howard Neufeld. Source: Lefohn (1998).**

| Species | Year | Treatment | 24-h SUM06 | 24-h W126 | N100 |
|---|---|---|---|---|---|
| Black Cherry | 1989 | No Injury at 1.0x | 2.7 | 2.7 | 0 |
| Tall Milkweed | 1989 | No Injury at CF | NA | NA | 0 |
| Black-eyed Susan | 1989 | No Injury at 1.5x | 6.2 | 5.2 | 8 |
| Cutleaf Coneflower | 1990 | No injury at 1.0x | 1.0 | 1.3 | 0 |
| Ginseng | 1991 | No injury | 52.7 | 44.3 | 104 |
| Eastern Hemlock | 1989 | No injury observed | 46.1 | 39.8 | 111 |
| Northern Red Oak | 1991 | No injury | 54.5 | 45.8 | 106 |

### 7.2.3 Identifying Ozone Exposures for Assessing Vegetation Damage

Table 7-3 summarizes the 3-month, 24-h W126 and N100 values that were experienced in the OTC experiments that are relevant in the FCPC area. Recently, Lefohn and Musselman (2012) reviewed the results from aspen data for ozone damage from the EPA NHEERL-WED OTC experiments and the exposure-response equations provided by Dr. Henry Lee from the EPA laboratory (see Lefohn, 1998). Lefohn and Musselman (2012) focused their analysis on statistically significant results for Aspen 216, 259, and 271. Because black cherry was not grown in the area, the authors selected aspen clones as the most relevant for establishing threshold levels for the Athabasca Oil Sands Region. However, both black cherry and aspen are grown in the FCPC Class I area and are similar in sensitivity. The range of lowest 3-month, 24-h W126 values for black cherry and aspen at the 10% biomass loss level is 6.51 to 7.68 ppm-h (black cherry) and 6.37 to 6.72 ppm-h (aspen). The number of hourly average concentrations ≥ 100 ppb in the experiments is estimated to be 1 to 10 (black cherry) and 4 to 5 (aspen).

**Table 7-3. 24-h, W126 (ppm-h) and number of hours greater than or equal to 0.10 ppm (peaks) exposure level estimates that predict the 10% growth loss for several vegetation species. The N100 index is in units of hours. Source: Lefohn (1998).**

| Common Name/Trial | Year | W126 | N100 | Response |
|---|---|---|---|---|
| Aspen Wild Oregon | 1990 | 71.39 | 243 | Total Dry Weight |
| Aspen Wild Oregon | 1991 | 57.96 | 204 | Total Dry Weight |
| Aspen 216 | 1990 | 20.64 | 34 | Total Dry Weight |
| Aspen 216 | 1991 | 12.38 | 28 | Total Dry Weight |
| Aspen 259 | 1990 | 6.37 | 4 | Total Dry Weight |
| Aspen 259 | 1991 | 6.72 | 15 | Total Dry Weight |
| Aspen 271 | 1990 | 21.07 | 35 | Total Dry Weight |
| Aspen 253* | 1990 | 10.41 | 10 | Total Dry Weight |
| Aspen 271* | 1991 | 38.23 | 84 | Total Dry Weight |
| Aspen Wild Michigan* | 1991 | 18.15 | 41 | Total Dry Weight |
| Black Cherry | 1989 | 7.68 | 10 | Total Dry Weight |
| Black Cherry | 1992 | 6.51 | 1 | Total Dry Weight |
| Red Maple | 1988 | 85.35 | 245 | Total Dry Weight |
| Eastern white pine* | 1990 | 30.22 | 66 | Total Dry Weight |
| Sugar Maple* | 1990 | 44.66 | 131 | Total Dry Weight |

* Not statistically significant.

## 7.3 Recommending Levels to Protect Vegetation from Injury and Damage

As noted in Section 4, the US EPA in its recommendation for the 3-month, 12-h W126 13 ppm-h secondary standard focused on the desire to provide protection for sensitive tree species growing in specially designated areas. The Agency noted that the 13 ppm-h level would reduce ozone-related growth losses in sensitive tree seedlings (including black cherry, Ponderosa pine, and quaking aspen) and mature trees and less wide-spread visible foliar injury. The EPA indicated that the 13 ppm-h level would not prevent all vegetation injury, but rather reduce the incidence that was likely to occur on some sensitive species in specially protected areas. In protecting areas from ozone effects, such as Class I areas or on lands set aside by States, Tribes, and public interest groups, the Agency noted the importance of cottonwood, black cherry, quaking aspen, red maple, yellow poplar, and white pine in eastern forests; white ash, black cherry, birch, and quaking aspen in midwestern forests; and ponderosa pine in western forests.

The two most sensitive species in Table 7-3 for biomass loss are black cherry and aspen. As indicated in the table, the OTC data indicate that the 10% biomass

reduction levels for black cherry were associated with 24-h W126 ozone exposures of 6.51 ppm-h (N100=1) over 140 days of ozone exposure and 7.68 ppm-h (N100=10) over 76 days of ozone exposure. Neufeld et al. (1995) describe details of the black cherry OTC experiment. The 10% biomass reduction levels for aspen were 6.37 and 6.72 ppm-h. The 10% biomass reduction level is used as an accepted threshold level because researchers believe that biomass reduction levels below this threshold can be associated with other causes such as pests and edaphic conditions. The N100 values were 4, and 15, respectively. The 24-h W126 exposures described in Lefohn (1998) for the aspen clones approximated a 90-day exposure period for each year. The length of ozone exposure for each experiment was 88 days (1990) and 97 days (1991) Karnowsky et al. (1996).

The Davis (2007) threshold for vegetation injury was 7.563 ppm-h over an approximate 120-day period, while the 10% biomass loss levels for the most sensitive aspen clone were less than this value (6.37 and 6.72 ppm-h) over approximately 90-day exposure period. Given that the US EPA has recommended a 3-month W126 exposure metric as the form of the ozone standard to protect vegetation, we have used experimental data reported over this 3-month (i.e., 90-day) period.

Based on the above, we recommend using the 90-day aspen clone results, which experienced a 6.37 ppm-h exposure accumulated over a 24-h period. Because there were 4 hourly average concentration values ≥ 100 ppb experienced in the OTC chambers at the 10% biomass loss level for Aspen 259 at the 6.37 ppm-h exposure level, we recommend that the N100 index be coupled with the 3-month, 24-h W126 exposure to avoid the possibility of overestimating effects. The 6.37 ppm-h level is above the exposure levels experienced at the Trinidad Head background ozone monitoring site, which experienced maximum 3-month, 24-h W126 values of 3.312 to 5.571 ppm-h over the 2003-2011 period and experienced no N100 values (Table 6-1). Thus, vegetation injury associated with the Aspen 259 clone would not be anticipated at the Trinidad Head site.

In addition, we recommend that the determination of the maximum 3-month, 24-h W126 and N100 exposures be restricted in the FCPC area to the summer months because this is the period when anthropogenic emissions have the greatest impact and vegetation is most susceptible to ozone exposure. Plants are injured by ozone uptake into leaf tissue through stomata. Certain criteria favor this uptake. Mature leaves that have fully expanded have the most functional stomata, so ozone is more likely to be taken up into mature leaves that have reached full size in later spring or early summer. Older leaves have had more time of exposure to ozone and generally have more uptake and more injury. Within a plant canopy, leaves that are most exposed to solar radiation generally have higher uptake and often show more injury to ozone than shaded leaves.

Other factors associated with later season injury from ozone are also important, particularly the direct influence of solar radiation on plants and the indirect influence of solar radiation induced temperature increase on plants. First, the longer solar day length extends the amount of hours per day that stomata are open for maximum uptake, although we cannot discount the lesser but often important night time uptake. Second, extended solar radiation is associated with higher air and soil temperatures that are important in plant response to ozone. Higher early summer temperatures favor stomatal opening and plant growth. Given these parameters, it is expected that young aspen leaves that are not fully expanded in April or May of the growing season are less susceptible to ozone injury than are fully expanded and more susceptible mature leaves that have had longer exposure to ozone by mid-summer or later.

Increased temperature also increases the rate of photochemical reactions that form ambient ozone. This can often be an important reason for higher mid-season ozone concentrations, but higher ozone concentrations in April-June in FCPC are likely of stratospheric origin. These stratospheric sources early in the season are often not occurring at a time when the leaves are most susceptible as described here. By restricting the determination to the summer months, the elevated 24-h, W126 exposures associated with STT events that occur during the springtime at the Potawatomi ozone monitoring site would not be considered when assessing possible vegetation impacts associated with anthropogenic emissions. Nevertheless, ozone injury may occur on plant foliage of early season species during springtime.

As indicated in Section 6, Lefohn et al. (2011) reported that springtime was identified as the most important time when ozone concentration enhancements (i.e., hourly average concentrations ≥ 0.05 ppm) were coincident with stratospheric events at the Potawatomi site. The highest 3-month cumulative 24-h W126 exposures occurred during the March-May and April-June period at the Potawatomi ozone monitoring site. As indicated earlier, Skelly (2000) discussed the potential importance of stratospheric ozone enhancing surface ozone concentrations with the result that vegetation may be affected with acute injuries. Thus, depending upon the level of ozone concentration enhancements associated with STT-S events, it may not be possible to prevent vegetation injury resulting from ozone exposures in the FCPC Class I area or other areas in the region. However, by minimizing increases in ozone exposures from anthropogenic sources, vegetation injury can be kept at a minimum.

The 3-month maximum ozone exposures occurred during the springtime and there were no hourly average ozone concentrations ≥ 100 ppb experienced at the site. The maximum 3-month, 24-h W126 ozone exposures experienced at the Potawatomi ozone monitoring site for 2004 through 2011 ranged from 4.816 to 13.218 ppm-h (see Table 6-2). No hourly average ozone concentrations were ≥ 100 ppb over the 8-year period. It would be anticipated that if the effect of

anthropogenic sources were to increase in the FCPC area, the 3-month, 24-h W126 ozone exposures would shift from the springtime towards the summertime period. For the period 2004-2011, the summertime (i.e., June-August) 24-h, W126 exposures experienced at the Potawatomi site were lower than the 6.37 ppm-h threshold level except in 2005. If anthropogenic emissions affecting the FCPC area were to increase, it would be anticipated that vegetation in the area would begin to exhibit more injury symptoms during the summertime than observed currently.

Exceeding a maximum 3-month, 24-h W126 6.37 ppm-h level during the summertime provides an indication that possible vegetation effects are occurring in the FCPC area. We recognize that exposure levels in this range can still be influenced by stratospheric contributions. We suggest that if cumulative 3-month, 24-h W126 exposure and N100 values are experienced in the range identified above, that vegetation survey activities be initiated in order to confirm that vegetation effects are occurring in the FCPC area.

## 8.0 SUMMARY AND FINDINGS

A.S.L. & Associates has provided the information to assist the FCPC Air Resources Program to establish threshold levels for Vegetation Impacts (i.e., AQRV 2: Vegetation-ozone). As a result of our review of the available scientific literature, we recommend that the biologically based W126 exposure index accumulated over a 24-h period for a 3-month period be used as the metric to protect vegetation. In addition, we recommend that the N100 metric also be combined with the W126 exposure index. The two most sensitive and FCPC culturally significant species we identified for biomass loss are black cherry and aspen. Research data indicate that the 10% biomass reduction levels for black cherry are associated with 24-h W126 ozone exposures of 6.51 ppm-h (N100=1) and 7.68 ppm-h (N100=10) of ozone exposure. The 10% biomass reduction levels for aspen are 6.37 and 6.72 ppm-h. The N100 values were 4, and 15, respectively. We recommend that the 3-month, 24-h W126 threshold be established at the 6.37 ppm-h level with an N100 value of 4. The N100 level of 4 is derived from the experimental results. Based on the research results, this approach requires that both the 6.37 ppm-h and the N100 value of 4 be measured before the threshold effect is exceeded. Thus, an exceedance of the 3-month, 24-h W126 level of 6.37 ppm-h with an N100 value less than 4 would not be an exceedance of the threshold for effects. Furthermore, we recommend that the determination of the 3-month, 24-h W126 and N100 exposures be restricted in the FCPC area to the summer months of June through August because this is the period when anthropogenic emissions have the greatest impact and vegetation is most susceptible to ozone exposure; some of the higher ozone concentrations

experienced during March-May and April-June in the FCPC area are likely associated with natural sources that are not controllable (i.e., stratospheric origin).

The maximum 3-month, 24-h W126 ozone exposures experienced at the Potawatomi ozone monitoring site for 2004 through 2011 ranged from 4.816 to 13.218 ppm-h with no N100 values and those exposures were experienced during the springtime. Approximately 65% of the exposures for the maximum 3-month, 24-h W126 index are associated with the hours between 0800 to 1959 h. Over a 24-h period, approximately 35% of the W126 exposures are occurring during the nighttime period. These nighttime exposures have the potential for eliciting vegetation effects. The summertime (i.e., June-August) 24-h, W126 exposures experienced at the Potawatomi site were lower than the 6.37 ppm-h threshold level except in 2005. By restricting the determination to the summer months, the elevated 24-h, W126 exposures associated with stratospheric-tropospheric exchange events that occur during the springtime at the Potawatomi ozone monitoring site would not be considered when assessing possible vegetation impacts associated with anthropogenic emissions. The literature has discussed the potential importance of stratospheric ozone enhancing surface ozone concentrations with the result that vegetation may be affected with acute injuries. It may not be possible to prevent vegetation injury resulting from exposure to stratospheric ozone in the FCPC Class I area or other areas in the region. However, by minimizing increases in ozone exposures from anthropogenic sources, vegetation injury can be kept at a minimum.

For implementation purposes, we recommend that a 3-year average of the maximum 3-month, 24-h W126 level of 6.37 ppm-h and an N100 of 4 during the summertime be applied as an indication that possible vegetation effects are occurring in the FCPC area. We further recommend that the protocol for data capture requirements, as well as the correction for missing data, should be followed as per the instructions summarized by the US EPA (2011b) in its description of the proposal for the W126 secondary ozone standard. We recognize that exposure levels in this range can still be influenced by stratospheric contributions. We suggest that if for any year that the cumulative 3-month, 24-h W126 and N100 values are experienced in the range identified above, that vegetation survey activities be initiated in order to confirm that vegetation effects are occurring in the FCPC area.

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# APPENDIX A

**Table A-1. Summary of hourly average percentiles (ppm), number of hourly occurrences ≥ 0.05 ppm (N50), 24-h SUM60 (ppm-h), and 24-h W126 (ppm-h) cumulative exposure values for 2004-2011 for Potawatomi (550410007). LST time period.**

| Year | Month | N | Min | P10 | P30 | P50 | P70 | P90 | P95 | P99 | Max | N50 | SUM60 | W126 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2004 | 1 | 376 | 0.015 | 0.029 | 0.033 | 0.036 | 0.038 | 0.040 | 0.041 | 0.042 | 0.043 | 0 | 0.000 | 0.295 |
| 2004 | 2 | 664 | 0.024 | 0.034 | 0.038 | 0.041 | 0.043 | 0.046 | 0.049 | 0.056 | 0.064 | 28 | 0.249 | 1.276 |
| 2004 | 3 | 712 | 0.020 | 0.027 | 0.034 | 0.040 | 0.044 | 0.047 | 0.049 | 0.052 | 0.053 | 26 | 0.000 | 1.261 |
| 2004 | 4 | 615 | 0.018 | 0.031 | 0.037 | 0.042 | 0.047 | 0.052 | 0.056 | 0.064 | 0.067 | 114 | 0.890 | 2.067 |
| 2004 | 5 | 705 | 0.017 | 0.025 | 0.035 | 0.039 | 0.044 | 0.049 | 0.051 | 0.059 | 0.066 | 56 | 0.379 | 1.488 |
| 2004 | 6 | 684 | 0.011 | 0.022 | 0.029 | 0.034 | 0.039 | 0.050 | 0.053 | 0.058 | 0.060 | 72 | 0.060 | 1.166 |
| 2004 | 7 | 711 | 0.013 | 0.021 | 0.029 | 0.034 | 0.039 | 0.046 | 0.051 | 0.060 | 0.064 | 45 | 0.551 | 1.094 |
| 2004 | 8 | 705 | 0.008 | 0.018 | 0.024 | 0.028 | 0.032 | 0.039 | 0.042 | 0.047 | 0.050 | 3 | 0.000 | 0.331 |
| 2004 | 9 | 687 | 0.007 | 0.020 | 0.029 | 0.037 | 0.046 | 0.057 | 0.063 | 0.072 | 0.076 | 144 | 3.214 | 3.079 |
| 2004 | 10 | 343 | 0.015 | 0.021 | 0.029 | 0.033 | 0.037 | 0.045 | 0.054 | 0.059 | 0.060 | 23 | 0.060 | 0.493 |
| 2004 | 11 | 688 | 0.007 | 0.017 | 0.024 | 0.029 | 0.032 | 0.036 | 0.037 | 0.039 | 0.041 | 0 | 0.000 | 0.212 |
| 2004 | 12 | 706 | 0.006 | 0.016 | 0.023 | 0.029 | 0.033 | 0.037 | 0.038 | 0.040 | 0.041 | 0 | 0.000 | 0.259 |
| 2005 | 1 | 742 | 0.003 | 0.025 | 0.030 | 0.034 | 0.036 | 0.040 | 0.041 | 0.043 | 0.044 | 0 | 0.000 | 0.460 |
| 2005 | 2 | 642 | 0.014 | 0.030 | 0.034 | 0.040 | 0.043 | 0.046 | 0.047 | 0.050 | 0.054 | 6 | 0.000 | 0.953 |
| 2005 | 3 | 741 | 0.024 | 0.039 | 0.043 | 0.045 | 0.048 | 0.053 | 0.057 | 0.063 | 0.070 | 176 | 1.546 | 3.194 |
| 2005 | 4 | 639 | 0.003 | 0.036 | 0.043 | 0.048 | 0.052 | 0.059 | 0.065 | 0.081 | 0.084 | 249 | 3.815 | 4.839 |
| 2005 | 5 | 671 | 0.020 | 0.027 | 0.033 | 0.040 | 0.051 | 0.060 | 0.065 | 0.069 | 0.070 | 217 | 5.054 | 4.135 |
| 2005 | 6 | 715 | 0.003 | 0.027 | 0.034 | 0.041 | 0.048 | 0.061 | 0.065 | 0.077 | 0.080 | 189 | 5.289 | 4.283 |
| 2005 | 7 | 674 | 0.003 | 0.022 | 0.031 | 0.039 | 0.047 | 0.061 | 0.067 | 0.078 | 0.090 | 154 | 5.122 | 4.114 |
| 2005 | 8 | 739 | 0.009 | 0.020 | 0.026 | 0.031 | 0.038 | 0.050 | 0.057 | 0.063 | 0.065 | 75 | 1.315 | 1.540 |
| 2005 | 9 | 660 | 0.008 | 0.019 | 0.025 | 0.032 | 0.042 | 0.055 | 0.061 | 0.070 | 0.078 | 111 | 2.552 | 2.335 |
| 2005 | 10 | 739 | 0.007 | 0.016 | 0.022 | 0.027 | 0.030 | 0.038 | 0.049 | 0.057 | 0.059 | 35 | 0.000 | 0.567 |
| 2005 | 11 | 691 | 0.003 | 0.011 | 0.019 | 0.023 | 0.027 | 0.031 | 0.033 | 0.036 | 0.039 | 0 | 0.000 | 0.103 |
| 2005 | 12 | 742 | 0.004 | 0.014 | 0.020 | 0.024 | 0.027 | 0.031 | 0.034 | 0.038 | 0.038 | 0 | 0.000 | 0.120 |
| 2006 | 1 | 735 | 0.006 | 0.013 | 0.022 | 0.026 | 0.029 | 0.033 | 0.035 | 0.038 | 0.039 | 0 | 0.000 | 0.156 |
| 2006 | 2 | 669 | 0.003 | 0.028 | 0.033 | 0.037 | 0.039 | 0.041 | 0.042 | 0.043 | 0.046 | 0 | 0.000 | 0.598 |
| 2006 | 3 | 740 | 0.014 | 0.032 | 0.038 | 0.042 | 0.045 | 0.050 | 0.052 | 0.057 | 0.059 | 76 | 0.000 | 1.766 |
| 2006 | 4 | 712 | 0.014 | 0.035 | 0.041 | 0.044 | 0.048 | 0.052 | 0.055 | 0.064 | 0.067 | 154 | 0.763 | 2.607 |
| 2006 | 5 | 738 | 0.003 | 0.023 | 0.033 | 0.038 | 0.042 | 0.050 | 0.053 | 0.069 | 0.070 | 75 | 1.127 | 1.820 |
| 2006 | 6 | 675 | 0.014 | 0.026 | 0.032 | 0.037 | 0.042 | 0.056 | 0.062 | 0.070 | 0.073 | 108 | 2.676 | 2.552 |
| 2006 | 7 | 719 | 0.003 | 0.021 | 0.032 | 0.037 | 0.044 | 0.052 | 0.055 | 0.059 | 0.064 | 112 | 0.185 | 1.759 |
| 2006 | 8 | 742 | 0.006 | 0.019 | 0.026 | 0.031 | 0.037 | 0.046 | 0.048 | 0.052 | 0.055 | 24 | 0.000 | 0.749 |
| 2006 | 9 | 716 | 0.010 | 0.016 | 0.021 | 0.026 | 0.030 | 0.039 | 0.043 | 0.057 | 0.062 | 18 | 0.184 | 0.456 |
| 2006 | 10 | 722 | 0.003 | 0.018 | 0.024 | 0.027 | 0.030 | 0.036 | 0.040 | 0.047 | 0.050 | 2 | 0.000 | 0.253 |
| 2006 | 11 | 718 | 0.009 | 0.018 | 0.023 | 0.026 | 0.028 | 0.033 | 0.034 | 0.038 | 0.043 | 0 | 0.000 | 0.145 |
| 2006 | 12 | 739 | 0.003 | 0.014 | 0.019 | 0.023 | 0.026 | 0.031 | 0.033 | 0.037 | 0.038 | 0 | 0.000 | 0.109 |

**Table A-1. Summary of hourly average percentiles (ppm), number of hourly occurrences ≥ 0.05 ppm (N50), 24-h SUM60 (ppm-h), and 24-h W126 (ppm-h) cumulative exposure values for 2004-2011 for Potawatomi (550410007). LST time period.**

| Year | Month | N | Min | P10 | P30 | P50 | P70 | P90 | P95 | P99 | Max | N50 | SUM60 | W126 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2007 | 1 | 736 | 0.012 | 0.021 | 0.026 | 0.029 | 0.032 | 0.034 | 0.036 | 0.037 | 0.037 | 0 | 0.000 | 0.226 |
| 2007 | 2 | 669 | 0.022 | 0.028 | 0.030 | 0.032 | 0.034 | 0.037 | 0.038 | 0.039 | 0.040 | 0 | 0.000 | 0.319 |
| 2007 | 3 | 518 | 0.013 | 0.032 | 0.037 | 0.039 | 0.044 | 0.054 | 0.056 | 0.059 | 0.060 | 77 | 0.180 | 1.431 |
| 2007 | 4 | 711 | 0.013 | 0.033 | 0.040 | 0.046 | 0.050 | 0.056 | 0.062 | 0.074 | 0.078 | 226 | 2.836 | 4.054 |
| 2007 | 5 | 741 | 0.014 | 0.028 | 0.036 | 0.042 | 0.048 | 0.059 | 0.065 | 0.078 | 0.086 | 197 | 4.278 | 4.451 |
| 2007 | 6 | 711 | 0.014 | 0.026 | 0.034 | 0.041 | 0.049 | 0.059 | 0.065 | 0.075 | 0.082 | 190 | 4.414 | 4.123 |
| 2007 | 7 | 238 | 0.012 | 0.018 | 0.023 | 0.027 | 0.033 | 0.042 | 0.045 | 0.060 | 0.061 | 6 | 0.181 | 0.195 |
| 2007 | 8 | 741 | 0.008 | 0.021 | 0.027 | 0.032 | 0.038 | 0.045 | 0.049 | 0.056 | 0.061 | 36 | 0.061 | 0.877 |
| 2007 | 9 | 684 | 0.011 | 0.020 | 0.026 | 0.032 | 0.038 | 0.052 | 0.056 | 0.063 | 0.067 | 84 | 1.123 | 1.468 |
| 2007 | 10 | 724 | 0.014 | 0.022 | 0.027 | 0.031 | 0.035 | 0.041 | 0.048 | 0.057 | 0.060 | 28 | 0.060 | 0.654 |
| 2007 | 11 | 717 | 0.008 | 0.019 | 0.025 | 0.030 | 0.032 | 0.036 | 0.037 | 0.038 | 0.039 | 0 | 0.000 | 0.233 |
| 2007 | 12 | 739 | 0.002 | 0.020 | 0.027 | 0.031 | 0.035 | 0.038 | 0.040 | 0.041 | 0.045 | 0 | 0.000 | 0.352 |
| 2008 | 1 | 742 | 0.010 | 0.020 | 0.027 | 0.031 | 0.035 | 0.038 | 0.039 | 0.041 | 0.046 | 0 | 0.000 | 0.343 |
| 2008 | 2 | 692 | 0.025 | 0.032 | 0.036 | 0.038 | 0.040 | 0.045 | 0.047 | 0.052 | 0.054 | 15 | 0.000 | 0.902 |
| 2008 | 3 | 733 | 0.007 | 0.031 | 0.040 | 0.043 | 0.046 | 0.050 | 0.051 | 0.055 | 0.058 | 80 | 0.000 | 1.843 |
| 2008 | 4 | 717 | 0.024 | 0.038 | 0.045 | 0.049 | 0.054 | 0.062 | 0.064 | 0.072 | 0.074 | 331 | 6.579 | 5.926 |
| 2008 | 5 | 696 | 0.022 | 0.034 | 0.040 | 0.044 | 0.048 | 0.056 | 0.060 | 0.065 | 0.068 | 170 | 2.499 | 3.212 |
| 2008 | 6 | 716 | 0.013 | 0.025 | 0.033 | 0.038 | 0.043 | 0.049 | 0.052 | 0.060 | 0.062 | 61 | 0.425 | 1.465 |
| 2008 | 7 | 742 | 0.012 | 0.025 | 0.030 | 0.034 | 0.038 | 0.047 | 0.052 | 0.058 | 0.064 | 51 | 0.126 | 1.097 |
| 2008 | 8 | 739 | 0.014 | 0.020 | 0.027 | 0.031 | 0.035 | 0.044 | 0.052 | 0.058 | 0.061 | 43 | 0.061 | 0.904 |
| 2008 | 9 | 716 | 0.009 | 0.016 | 0.022 | 0.027 | 0.036 | 0.051 | 0.060 | 0.068 | 0.071 | 80 | 2.325 | 1.821 |
| 2008 | 10 | 742 | 0.011 | 0.022 | 0.026 | 0.029 | 0.033 | 0.040 | 0.046 | 0.053 | 0.062 | 17 | 0.184 | 0.553 |
| 2008 | 11 | 716 | 0.004 | 0.017 | 0.024 | 0.029 | 0.032 | 0.036 | 0.040 | 0.052 | 0.054 | 9 | 0.000 | 0.343 |
| 2008 | 12 | 740 | 0.011 | 0.023 | 0.028 | 0.031 | 0.033 | 0.037 | 0.038 | 0.040 | 0.041 | 0 | 0.000 | 0.302 |
| 2009 | 1 | 742 | 0.020 | 0.028 | 0.032 | 0.034 | 0.036 | 0.039 | 0.040 | 0.045 | 0.046 | 0 | 0.000 | 0.477 |
| 2009 | 2 | 668 | 0.015 | 0.028 | 0.033 | 0.036 | 0.038 | 0.041 | 0.042 | 0.044 | 0.045 | 0 | 0.000 | 0.570 |
| 2009 | 3 | 726 | 0.019 | 0.030 | 0.034 | 0.038 | 0.043 | 0.048 | 0.051 | 0.058 | 0.061 | 46 | 0.181 | 1.396 |
| 2009 | 4 | 704 | 0.000 | 0.031 | 0.038 | 0.043 | 0.047 | 0.053 | 0.056 | 0.065 | 0.070 | 122 | 1.403 | 2.509 |
| 2009 | 5 | 736 | 0.013 | 0.026 | 0.036 | 0.041 | 0.045 | 0.050 | 0.055 | 0.059 | 0.062 | 95 | 0.243 | 1.909 |
| 2009 | 6 | 717 | 0.010 | 0.018 | 0.028 | 0.034 | 0.042 | 0.051 | 0.053 | 0.059 | 0.063 | 87 | 0.304 | 1.385 |
| 2009 | 7 | 741 | 0.008 | 0.013 | 0.020 | 0.025 | 0.030 | 0.039 | 0.042 | 0.052 | 0.054 | 10 | 0.000 | 0.338 |
| 2009 | 8 | 713 | 0.001 | 0.014 | 0.022 | 0.025 | 0.029 | 0.037 | 0.040 | 0.047 | 0.049 | 0 | 0.000 | 0.259 |
| 2009 | 9 | 707 | 0.001 | 0.021 | 0.027 | 0.032 | 0.039 | 0.046 | 0.048 | 0.054 | 0.057 | 21 | 0.000 | 0.801 |
| 2009 | 10 | 743 | 0.007 | 0.014 | 0.019 | 0.022 | 0.025 | 0.029 | 0.031 | 0.034 | 0.036 | 0 | 0.000 | 0.087 |
| 2009 | 11 | 714 | 0.008 | 0.019 | 0.023 | 0.027 | 0.031 | 0.037 | 0.038 | 0.041 | 0.041 | 0 | 0.000 | 0.230 |
| 2009 | 12 | 742 | 0.013 | 0.023 | 0.029 | 0.031 | 0.034 | 0.037 | 0.038 | 0.039 | 0.040 | 0 | 0.000 | 0.307 |

**Table A-1. Summary of hourly average percentiles (ppm), number of hourly occurrences ≥ 0.05 ppm (N50), 24-h SUM60 (ppm-h), and 24-h W126 (ppm-h) cumulative exposure values for 2004-2011 for Potawatomi (550410007). LST time period.**

| Year | Month | N | Min | P10 | P30 | P50 | P70 | P90 | P95 | P99 | Max | N50 | SUM60 | W126 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2010 | 1 | 742 | 0.008 | 0.026 | 0.032 | 0.034 | 0.037 | 0.040 | 0.041 | 0.042 | 0.043 | 0 | 0.000 | 0.499 |
| 2010 | 2 | 664 | 0.032 | 0.037 | 0.040 | 0.042 | 0.044 | 0.046 | 0.047 | 0.049 | 0.050 | 3 | 0.000 | 1.285 |
| 2010 | 3 | 741 | 0.030 | 0.037 | 0.041 | 0.045 | 0.050 | 0.059 | 0.061 | 0.064 | 0.065 | 227 | 3.602 | 4.039 |
| 2010 | 4 | 716 | 0.026 | 0.038 | 0.042 | 0.047 | 0.051 | 0.055 | 0.058 | 0.065 | 0.074 | 260 | 1.530 | 3.719 |
| 2010 | 5 | 733 | 0.019 | 0.033 | 0.039 | 0.044 | 0.047 | 0.054 | 0.057 | 0.066 | 0.067 | 146 | 1.584 | 2.846 |
| 2010 | 6 | 712 | 0.010 | 0.019 | 0.025 | 0.029 | 0.033 | 0.040 | 0.044 | 0.056 | 0.060 | 15 | 0.060 | 0.510 |
| 2010 | 7 | 741 | 0.010 | 0.021 | 0.027 | 0.031 | 0.035 | 0.044 | 0.051 | 0.060 | 0.066 | 47 | 0.615 | 0.966 |
| 2010 | 8 | 742 | 0.014 | 0.023 | 0.027 | 0.030 | 0.035 | 0.043 | 0.049 | 0.056 | 0.059 | 34 | 0.000 | 0.752 |
| 2010 | 9 | 701 | 0.000 | 0.016 | 0.020 | 0.024 | 0.028 | 0.033 | 0.035 | 0.040 | 0.042 | 0 | 0.000 | 0.143 |
| 2010 | 10 | 713 | 0.000 | 0.021 | 0.028 | 0.032 | 0.037 | 0.042 | 0.046 | 0.056 | 0.059 | 15 | 0.000 | 0.657 |
| 2010 | 11 | 714 | 0.012 | 0.019 | 0.026 | 0.029 | 0.032 | 0.037 | 0.038 | 0.043 | 0.049 | 0 | 0.000 | 0.262 |
| 2010 | 12 | 739 | 0.015 | 0.027 | 0.031 | 0.034 | 0.037 | 0.039 | 0.041 | 0.043 | 0.045 | 0 | 0.000 | 0.480 |
| 2011 | 1 | 740 | 0.020 | 0.030 | 0.033 | 0.036 | 0.038 | 0.041 | 0.042 | 0.044 | 0.046 | 0 | 0.000 | 0.645 |
| 2011 | 2 | 668 | 0.023 | 0.036 | 0.039 | 0.041 | 0.042 | 0.045 | 0.046 | 0.049 | 0.050 | 2 | 0.000 | 1.080 |
| 2011 | 3 | 736 | 0.025 | 0.034 | 0.040 | 0.044 | 0.046 | 0.051 | 0.055 | 0.062 | 0.063 | 108 | 0.979 | 2.404 |
| 2011 | 4 | 712 | 0.022 | 0.038 | 0.043 | 0.047 | 0.049 | 0.054 | 0.056 | 0.063 | 0.066 | 204 | 0.694 | 3.166 |
| 2011 | 5 | 737 | 0.014 | 0.026 | 0.035 | 0.041 | 0.045 | 0.049 | 0.052 | 0.056 | 0.059 | 72 | 0.000 | 1.677 |
| 2011 | 6 | 705 | 0.012 | 0.020 | 0.028 | 0.035 | 0.042 | 0.052 | 0.058 | 0.074 | 0.078 | 91 | 2.104 | 2.315 |
| 2011 | 7 | 730 | 0.006 | 0.019 | 0.025 | 0.032 | 0.037 | 0.043 | 0.049 | 0.053 | 0.061 | 35 | 0.061 | 0.719 |
| 2011 | 8 | 729 | 0.008 | 0.016 | 0.021 | 0.025 | 0.029 | 0.037 | 0.040 | 0.045 | 0.052 | 1 | 0.000 | 0.243 |
| 2011 | 9 | 707 | 0.008 | 0.015 | 0.021 | 0.025 | 0.029 | 0.036 | 0.042 | 0.049 | 0.054 | 5 | 0.000 | 0.270 |
| 2011 | 10 | 737 | 0.012 | 0.021 | 0.026 | 0.030 | 0.036 | 0.056 | 0.059 | 0.066 | 0.073 | 131 | 2.082 | 2.191 |
| 2011 | 11 | 715 | 0.013 | 0.021 | 0.025 | 0.028 | 0.031 | 0.034 | 0.036 | 0.039 | 0.042 | 0 | 0.000 | 0.195 |
| 2011 | 12 | 736 | 0.002 | 0.014 | 0.024 | 0.028 | 0.031 | 0.034 | 0.035 | 0.038 | 0.040 | 0 | 0.000 | 0.187 |

**Table A-2. Top 10 8-h daily maximum values for Potawatomi (550410007). All concentrations are in ppm units.**

| Year | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| 2004 | 0.073 | 0.070 | 0.064 | 0.063 | 0.062 | 0.062 | 0.060 | 0.059 | 0.059 | 0.059 |
| 2005 | 0.082 | 0.077 | 0.077 | 0.075 | 0.073 | 0.070 | 0.069 | 0.067 | 0.067 | 0.067 |
| 2006 | 0.069 | 0.067 | 0.067 | 0.066 | 0.064 | 0.061 | 0.060 | 0.058 | 0.058 | 0.057 |
| 2007 | 0.080 | 0.073 | 0.073 | 0.073 | 0.072 | 0.070 | 0.069 | 0.068 | 0.065 | 0.064 |
| 2008 | 0.072 | 0.069 | 0.069 | 0.066 | 0.066 | 0.065 | 0.064 | 0.063 | 0.062 | 0.062 |
| 2009 | 0.067 | 0.058 | 0.058 | 0.058 | 0.058 | 0.057 | 0.057 | 0.057 | 0.056 | 0.056 |
| 2010 | 0.068 | 0.065 | 0.063 | 0.063 | 0.061 | 0.061 | 0.061 | 0.061 | 0.060 | 0.060 |
| 2011 | 0.075 | 0.070 | 0.068 | 0.063 | 0.062 | 0.061 | 0.060 | 0.059 | 0.059 | 0.058 |

**Table A-3. All species relevant to FCPC.**

| Species | Family | Common Name | Sensitivity to Ozone | Reference |
|---|---|---|---|---|
| *Abies balsamea* | *Pinaceae* | Balsam fir | tolerant | Smith et al. (2007). |
| *Acer rubrum* | *Aceraceae* | Red maple | tolerant | Findley et al.(1996). |
| *Acer saccharum* | *Aceraceae* | Sugar maple | tolerant | Laurence et al. (1996); Orendovici et al. (2002). |
| *Achillea spp.* | *Asteraceae* | Yarrow | sensitive | Scebba et al. (2006). *A. millefolium* sensitive occurs in WI |
| *Actaea pachypoda* | *Ranunculaceae* | White baneberry | unknown | |
| *Actaea rubra* | *Ranunculaceae* | Red baneberry | unknown | |
| *Allium ampelopra* | *Liliaceae* | Wild leek | likely sensitive | Engle and Gableman (1966). other *Allium* species sensitive. *A. tricoccum* is WI wild leek |
| *Allium cernuum* | *Liliaceae* | Wild onion | likely sensitive | Glasencnik et al. (2004). other *Allium* species sensitive |
| *Asclepias syriaca* | *Asclepiadaceae* | Common milkweed, Tall milkweed | sensitive | numerous citations |
| *Anaphalis margaritacea* | *Asteraceae* | Pearly everlasting, Wild sage | unknown | |
| *Aralia nudicaulis* | *Araliaceae* | Wild Sarsasparilla | sensitive | Smith. and Manning (1990). |
| *Arctostaphylos uva-ursi* | *Ericaceae* | Kinnickinnick, Red willow | unknown | |
| *Arisaema atrorubens* | *Araceae* | Jack-in-the-pulpit | unknown | also *A. triphyllum* |
| *Asarum canadense* | *Aristolochiaceae* | Wild ginger | unknown | |
| *Betula alleghaniensis* | *Betulaceae* | Yellow birch | sensitive | Smith et al. (2007). |
| *Betula papyrifera* | *Betulaceae* | Paper birch | sensitive | numerous papers - grown in the aspen FACE experiment |
| *Carya spp.* | *Juglandaceae* | Bitternut hickory | unknown | Smith et al. (2007). bitternut hickory is *C. cordiformis* |
| *Ceanothus americanus* | *Rhamnaceae* | New Jersey tea | unknown | |
| *Comptonia peregrina* | *Myricaceae* | Sweet fern | unknown | |
| *Coptis trifolia.* | *Ranunculaceae* | Gold thread, Canker root | unknown | |
| *Cornus amomum* | *Cornaceae* | Red willow | tolerant | Davis and Coppolino (1976). |
| *Corylus americana* | *Betulaceae* | American hazelnut | sensitive | Smith et al. (2007). |
| *Echinacea spp.* | *Asteraceae* | Purple coneflower, Echinacea | sensitive | NPS/FWS (2003). |
| *Epilobium angustifolium* | *Onagraceae* | Fireweed | sensitive | Orendovici et al. (2002). *Epilobium spp*. sensitive |
| *Erythronium americana* | *Liliaceae* | Trout lily | unknown | |
| *Eupatorium perfoliatum.* | *Asteraceae* | Boneset | likely sensitive | NPS/FWS (2003). *E. rugosum* sensitive |
| *Fagus grandifolia* | *Fagaceae* | American beech | tolerant | Rhoads and Brennan (1980). |
| *Fragaria americana* | *Rosaceae* | Strawberry | sensitive | Smith et al. (2007). |
| *Fraxinus americana* | *Oleaceae* | White ash | sensitive | NPS/FWS (2003). |
| *Fraxinus nigra* | *Oleaceae* | black ash | sensitive | Smith et al. (2007). |
| *Fraxinus pennsylvanica* | *Oleaceae* | Black ash | sensitive | NPS/FWS (2003). |
| *Gaultheria spp.* | *Ericaceae* | Wintergreen | likely sensitive | Krzyzanowski et al. (2006). *G. shallon* sensitive *G. procumbens* in WI |
| *Gnaphalium obtusifolium* | *Asteraceae* | Sweet everlasting, Rabbit tobacco, Wild sage | unknown | |
| *Hierochloe odorata* | *Poaceae* | Sweet grass | unknown | |

**Table A-3 (continued). All species relevant to FCPC.**

| Species | Family | Common Name | Sensitivity to Ozone | Reference |
|---|---|---|---|---|
| *Hypericum perforatum* | *Hypericaceae* | St. John's wort | unknown | |
| *Ipomoea pandurata* | *Convolvulaceae* | Wild potato vine | unknown | |
| *Juglans cinerea* | *Juglandaceae* | Butternut | likely tolerant | Rhoads et al. (1980). *J. nigra* tolerant |
| *Juncus spp.* | *Juncaceae* | Rushes | unknown | |
| *Larix laricina* | *Pinaceae* | Tamarack | unknown | |
| *Ledum groenlandicum* | *Ericaceae* | Labrador tea | unknown | |
| *Medeola virginiana* | *Liliaceae* | Indian cucumber | unknown | |
| *Mitchella repens* | *Rubiaceae* | Partridge berry | unknown | |
| *Monarda didyma* | *Lamiaceae* | Oswego | moderately sensitive | Kline et al. (2008). |
| *Monarda spp.* | *Lamiaceae* | Wild bergamont | unknown | |
| *Monotropa spp.* | *Monotropaceae* | Indian pipe | unknown | |
| *Nymphaea tuberosa* | *Nymphaeaceae* | water lily | unknown | also known as *N. odorata* |
| *Osmorhiza spp.* | *Apiales* | Sweet cicely | sensitive | Peterson et al. (1992). *O. brachypoda* sensitive *O. claytonii* in WI |
| *Panax quinquefolium* | *Araliaceae* | Ginseng | tolerant | Lefohn (1998). |
| *Picea glauca* | *Pinaceae* | White spruce | tolerant | Gilman and Watson (1994). |
| *Picea mariana* | *Pinaceae* | Black spruce | unknown | |
| *Pinus banksiana* | *Pinaceae* | Jack pine | sensitive | NPS/FWS (2003). |
| *Pinus resinosa* | *Pinaceae* | Red pine | unknown | |
| *Pinus strobus* | *Pinaceae* | White pine | sensitive | |
| *Plantago spp.* | *Plantaginaceae* | Common plantain | sensitive | Davison et al. (2003). |
| *Polenomium spp.* | *Polemoniaceae* | Greek valerian, Jacob's ladder | unknown | Treshow & Stewart (1973) Injury at 0.30 ppm ozone for 2h |
| *Polygala senaga* | *Polygalaceae* | Seneca snakeroot | unknown | |
| *Populus grangidentata* | *Salicaceae* | Bigtooth zspen | unknown | |
| *Populus tremuloides* | *Salicaceae* | Quaking aspen, Trembling aspen | sensitive | numerous papers - grown in the aspen FACE experiment |
| *Prunus americana* | *Rosaceae* | Wild plum | sensitive | Orendovici et al. (2002). sensitive to moderate ozone |
| *Prunus pensylvanica* | *Rosaceae* | Pin cherry | moderately sensitive | Smith et al. (2007). |
| *Prunus pumila* | *Rosaceae* | Sand cherry | unknown | |
| *Prunus serotina* | *Rosaceae* | Black cherry | sensitive | Smith et al. (2007). |
| *Prunus virginiana* | *Rosaceae* | Choke cherry | sensitive | Smith et al. (2007). ModSens<br>Mavity et al. (no date). sensitive |
| *Quercus alba* | *Fagaceae* | White oak | unknown | |
| *Quercus rubra* | *Fagaceae* | Northern red oak | tolerant | Rhoads et al. (1980). |
| *Rhus spp.* | *Anacardiaceae* | Sumacs | sensitive | Smith et al. (2007). *R. copallina* and *R. trolobata* sensitive |
| *Ribes spp,* | *Grossulariaceae* | Currants | unknown | |
| *Rubus allegheniensis* | *Rosaceae* | Allegheny blackberry, Common blackberry | sensitive | NPS/FWS (2003). |
| *Rubus spp.* | *Rosaceae* | Dewberries | sensitive | most *Rubus* are sensitive |

**Table A-3 (continued). All species relevant to FCPC.**

| Species | Family | Common Name | Sensitivity to Ozone | Reference |
|---|---|---|---|---|
| *Rubus spp.* | *Rosaceae* | blackberry | sensitive | NPS/FWS (2003); Smith et al. (2007); *R. allegheniensis* |
| *Rubus spp.* | *Rosaceae* | Raspberry | sensitive | symptoms suspected on raspberry in Central Europe (personal observations RCM) |
| *Rudbeckia laciniata* | *Asteraceae* | Cutleaf coneflower, Coneflower, Golden glow | sensitive | Davison et al. (2003). |
| *Rudbeckia serotina* | *Asteraceae* | Black eyed Susans | likely sensitive | NPS/FWS (2003). *R. laciniata* and *R. hirta* sensitive |
| *Sagittaria spp.* | *Alismataceae* | Arrowhead | unknown | |
| *Sambucus canadensis* | *Caprifoliaceae* | American elder, White elder, Elderberry | sensitive | Smith et al. (2007); NPS/FWS (2003). |
| *Sanguinaria canadensis* | *Papveraceae* | Bloodroot | unknown | |
| *Scirpus spp.* | *Cyperaceae* | Bullrushes | unknown | |
| *Silphium perfoliatum* | *Asteraceae* | Cup plant | likely sensitive | NPS/FWS (2003). *S. asteriscus* sensitive |
| *Sisyrinchium spp.* | *Iridaceae* | Blue-eyed grass; Yellow-eyed grass | unknown | |
| *Solidago canadensis* | *Asteraceae* | Goldenrod | sensitive | *S. altissima* in NPS FLAG http://www.nature.nps.gov/ air/pubs/pdf/flag/NPSozonesensppFLAG06.pdf |
| *Symplocarpus foetidus* | *Araceae* | Skunk cabbage | unknown | |
| *Taraxacum officinale* | *Asteraceae* | Dandelion | sensitive | symptoms shown in the field http://www.ozoneinjury.org/ index.php?option=com_content&view= article&id=48&Itemid=51 |
| *Thuja occidentalis* | *Cupressaceae* | cedar | tolerant | Gilman and Watson (1994); Smith et al. (2007). |
| *Tilia americana* | *Tiliaceae* | Basswood | sensitive | Gilman and Watson (1994). |
| *Trifolium pratense* | *Fabaceae* | Red clover | sensitive | Karlsson et al. (1995). but less sensitive than white clover |
| *Tsuga canadensis* | *Pinaceae* | Hemlock | tolerant | Smith et al. (2007). |
| *Typha spp.* | *Typhaceae* | Cattails | unknown | |
| *Ulmus americana* | *Ulmaceae* | American elm | tolerant | Rhoads et al. (1980). Gilman and Watson (1994). |
| *Ulmus thomasii* | *Ulmaceae* | Rock elm | tolerant | Gilman and Watson (1994). |
| *Ulmus rubra* | *Ulmaceae* | Slippery elm | unknown | Manning et al. (2002). *U. excelsior, U. laevis, U montana* reported with possible ozone symptoms in the field |
| *Urtica dioica* | *Urticaceae* | Stinging nettle | unknown | |
| *Uvularia spp.* | *Colchicaceae* | Wild oats, Bellwort | unknown | |
| *Vaccinium macrocarpon* | *Ericaceae* | Large cranberry | likely sensitive | NPS/FWS (2003), Smith et al. (2007). |
| *V. membranaceum* | | | sensitive | |
| *Vaccinium spp.* | *Ericaceae* | Blueberries | sensitive | Smith and Manning (1990). |
| *Valeriana spp.* | *Valerianaceae* | Valerian | sensitive | Gerosa and Ballarin-Denti (2003). *V. montana* injured |
| *Verbascum spp.* | *Scrophulariaceae* | Common mullein | unknown | *V.thaspus* in WI |
| *Veronicastrum virginicum* | *Plantaginaceae* | Culver's root | unknown | |
| *Vitis spp.* | *Vitaceae* | Wild grape | sensitive | NPS/FWS (2003); Smith et al. (2007). *V. labrusca* in WI |
| *Zizania aquatica* | *Poaceae* | Wild rice, Manoomin | unknown | |
| *Zizania palustris* | *Poaceae* | Wild rice | unknown | |