Ozone and its precursors in the Treasure Valley, Idaho

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Executive Summary

Photochemical reactions of nitrogen oxides ($NO + NO_2 = NO_x$) and volatile organic compounds (VOCs) trigger the formation of ozone (O_3), a secondary air pollutant that contributes to the deterioration of air quality in urban areas and affects human health. Formation of O_3 is most intense in summer because of increased incoming solar radiation that intensifies photochemistry and in urban communities with comparatively dense emissions of NO_x and VOCs. A study was conducted in the Treasure Valley, Idaho by the Idaho Department of Environmental Quality (DEQ) to determine the prevailing atmospheric conditions, characteristics of O_3 chemistry, and the spatial and temporal variability of O_3 and its precursors. The Desert Research Institute (DRI) was contracted by DEQ to analyze ambient concentrations of O_3 and its precursors to obtain a better understanding of conditions that lead to the occurrence of elevated O_3 concentrations in the Treasure Valley. This report summarizes the results of the study which relied on a measurement campaign that was carried out from July 1, 2007 to September 30, 2007.

Ozone and nitrogen oxides mixing ratios were continuously measured using federal reference method (FRM) samplers at two locations, the Idaho Transportation Department offices on N. Clithero Drive (ITD) and St. Lukes Hospital near the intersection of Interstate 84 and S. Eagle Rd. An additional FRM monitor for O_3 was operated at the Whitney Elementary School (WHT). Speciated, time-resolved VOC concentrations were measured by VOCTEC Inc. using Pneumatic-Focused Gas Chromatograph methodology at ITD and St. Lukes. In addition to the FRM monitors, portable 2B O_3 monitors were installed at four sites, Parma (PAR), Nampa (NAM), Mountain View (MVW) and White Pine (WHP). A tethered-balloon system equipped with an ozonesonde monitor was deployed to determine the characteristics of the boundary layer, and the vertical profiles of wind conditions and O_3. Measurements with the balloon systems were conducted on August 9-15, 2007.

Instrument calibration problems resulted in loss of O_3 data at both the ITD and St Lukes sites for most of July. Fairly complete datasets of O_3 and its precursors were collected in August and September 2007. Two attempts to collocate the 2B O_3 monitors with FRM monitors were undertaken. However, due to calibration and other instrument difficulties, a side-by-side comparison was not completed. However, inter-instrument comparison among the 2B monitors showed precision and bias specifications that were within the criteria set for the study in the Quality Assurance Protocol Plan (QAPP).

Supplemental data were obtained to assist in the analysis effort. Those datasets included meteorological and air quality data from the DEQ monitoring network, air mass backward trajectories using the NOAA HYSPLIT model at several different elevations, the locations, durations, and associated burned areas of wildland events, satellite images for viewing the areal coverage of smoke plumes from wildfires, surface weather maps, model results for regional smoke aerosol concentrations, and road maintenance activities as documented by the Ada County Highway District (ACHD).

Hourly O_3 levels at all sites ranged from minimum nighttime values of a few parts per billion by volume (ppbv) to 83 ppbv at St. Lukes, 91 ppbv at ITD, 104 ppbv at Whitney, 80 ppbv at Parma, 91 ppbv at Nampa, 87 ppbv at Mountain View and 99 ppbv at White Pine. At ITD, NO hourly

levels varied from a few ppbv to 92 ppbv with an average of 10 ppbv, while NO_2 concentrations ranged from 0 to 30 ppbv with a mean value of 4 ppbv. At St. Lukes, the maximum 1-hour NO concentration was 192 ppbv and the mean was 18 ppbv; no NO_2 was measured at St Lukes. Forty-eight organic compounds were identified including twenty-two aliphatic saturated hydrocarbons, three cyclic saturated hydrocarbons, seven *n*-alkenes, two alkynes, thirteen aromatic hydrocarbons and one oxygenate. VOC levels at ITD were up to one order of magnitude higher than those measured at St. Lukes. The highest hourly concentrations were measured for propane (15 parts per million by volume, ppmv) and acetylene (3.9 ppmv) at ITD. Alkanes and alkenes were the predominant compound classes at ITD representing about 95% of VOCs (based on median values). Aromatic hydrocarbons accounted for about 13.0 ppbv at ITD and about 4 ppbv at St. Lukes. By excluding high propane and acetylene episodes.

Over the diurnal cycle, O_3 mixing ratios increased rapidly from a few ppbv during the nighttime hours starting in the morning (~8:00) through the early afternoon. The O_3 concentrations peaked late in the afternoon (~16:00) and then gradually declined in evening (starting at ~18:00). The precursors (NO, NO_2, and VOCs) generally followed an opposite diurnal pattern with the lowest concentrations measured during the daytime, while ozone levels were at their highest. NO and some VOC mixing ratios exhibited an early morning peak and an early evening gradual climb. This is consistent with the expectation that elevated concentrations of nitrogen oxides and VOCs are associated with traffic emissions during early morning and evening commute hours. For NO_2, elevated nighttime concentrations were likely due to the NO_x titration reaction. Alkanes and aromatic hydrocarbon mixing ratios remained relatively constant throughout the nighttime because removal of alkanes and aromatic hydrocarbons by $NO_3^{\cdot}$ radicals is quite slow. The progression of the mixing ratios of nitrogen compounds, VOCs, and ozone over the diurnal cycle was consistent with that observed in other urban areas.

There are two distinct regimes over the diurnal cycle that influences O_3 and its precursors, well mixed daytime conditions and stagnant, stable nighttime conditions. At sunrise, the heating of the surface by incoming solar radiation warms the air near the surface resulting in enhanced vertical mixing, increase in the height of the boundary layer, and increase in surface and aloft wind speeds. Although tethered balloon measurements were not conducted on high ozone days, measurements on four different days in August clearly show that the effective mixing height for surface pollutants grows fairly dramatically between sunrise and around 10:00. This results in rather comparable mixing ratios for O_3 throughout the Treasure Valley. Changes in surface wind direction that occur during the same morning period cause air to move from the northwest towards the southeast, accumulating pollutants in the southeast end of the valley. In the evening and nighttime, the cooling of earth surface results in lower wind speeds, a reduced mixing height, a change in the wind direction. These conditions favor the accumulation of ozone precursors emitted in the evening and early morning within a shallow layer near their respective sources.

These meteorological effects are corroborated by the fact that the end of the inhibition period (destruction of O_3 by NO) in the morning and the accumulation of O_3 for about 5-6 hours coincide at the St. Lukes and ITD sites. In addition, the high correlation coefficients among O_3 mixing ratios at all seven sites where ozone was monitored indicate that O_3 levels increase or decreases simultaneously, suggesting that the daytime O_3 mixing ratios are controlled by the same meteorological regimes at all the sites. Geographical characteristics and O_3 and precursor

temporal patterns suggested common characteristics for ITD and Mountain View (sites located close to each other and near downtown Boise), Whitney and White Pine (sites located on the southeast end of the valley) and Nampa and St. Lukes (sites located upwind of Boise, but with significant mobile sources). While these groupings might be useful for distinguishing these sites in a conceptual sense, as mentioned, in practice, site-to-site variations in O_3 concentrations were relatively low (about 3%).

The day-of-week trends of O_3, NO_x and VOCs mixing ratios in the Treasure Valley showed the presence of a "weekend O_3 effect", in which O_3 concentrations remain high on weekends despite decreases in emissions of precursors due to reduced motor vehicle activities. The weekend effect is caused by the shorter inhibition period on weekends because of the decrease in early morning emissions of NO_x, allowing for a longer accumulation time of O_3 (albeit at lower rates) compared to weekdays. In the Treasure Valley, the weekend effect is reflected in comparable O_3 levels throughout the week. This provides some initial guidance for the direction of O_3 control strategies in the Treasure Valley. The VOC/NO_x ratio indicates that the O_3 limiting factor at ITD is the NO_x, but that the limiting factor at St. Lukes is the VOC concentration except on Sundays when St Lukes exhibits NO_x-limited conditions. This suggests that reduction of NO_x emissions without controls of VOCs would likely decrease O_3 levels at ITD but increase them at St. Lukes. If VOC emissions were reduced without controlling NO_x, St.Lukes would likely exhibit lower O_3 levels, but no changes in O_3 would be observed at ITD, unless VOC are reduced quite substantially.

Smoke plumes from wildfires in the northwestern US during the summer may have impacted O_3 in the Treasure Valley. Wildfires during the study resulted in the burning of about 2,000,000 acres in Idaho and surrounding states. Three large fires in Twin Falls, and Payette and Boise National Forests occurred in July and August. About 500,000 acres were also burned in fires in northern Nevada. Wildfires in the surrounding states of Oregon, Washington and western Montana consumed about 1,000,000 acres. The back-trajectory calculations for air masses arriving in Boise at two different elevations (500 and 2500 m) showed clear differences in the paths of air masses near the ground and those at higher elevations. For air masses arriving at 500 m above ground level, a common route included passage through northeast Oregon and travel through the Columbia River Gorge along the I-84 corridor prior to arrival in the Treasure Valley. Once in the Treasure Valley, air masses often lingered for a couple of days at these low elevations. Air masses at higher elevations followed the prevailing weather patterns for summer, which are characterized by a fairly constant flow from southwest to northeast. These higher air masses were not limited by topography and covered a larger geographical area. Using a combination of satellite images, backward trajectory analysis, measurements of supplementary air quality parameters (e.g. $PM_{2.5}$), and results of regional aerosol models, it was possible to determine with a reasonable level of confidence whether or not wildfire smoke was impacting the Treasure Valley on a given day during the measurement campaign.

Partly to assess the impact of wildfires, days with high O_3 mixing ratios were further analyzed in comparison with days with moderate (typical) O_3 levels. The 80^{th} percentile of the maximum 8-hr average concentration was used as the threshold for "high" O_3 events for each site, while "typical" O_3 days were defined as those with maximum 8-hr ozone concentrations in the 40^{th} to 60^{th} percentiles. While the classification was done using the distributions on a site-by-site basis,

many of the high and typical O_3 days were coincident at several sites and often on consecutive days (O_3 "events"). The weather conditions, regional transport as well as local activities were examined for days on which more than three sites were identified as high or typical O_3 days. Nine high and five typical O_3 events were identified spanning in length from one to five days. High O_3 days were regularly associated with low surface wind speeds and stagnant conditions. For four the of the "high O_3" events (mostly in July and early August), there was substantial evidence that smoke plumes from wildland fires in Payette and Boise National Forest as well as from southern Idaho, northern Nevada and California were impacting air quality in the Treasure Valley. These events lasted for at least a couple of days and exhibited high 1-hr maximum O_3 mixing ratios and high VOC concentrations but low NO_x levels. During these events, $PM_{2.5}$ levels in Treasure Valley were consistently higher than 15 $\mu g\ m^{-3}$. Four "high O_3" events (in late August and September) showed moderate or little impact from wildfire smoke. These events were associated with higher NO_x and lower VOC levels and $PM_{2.5}$ levels lower than 15 $\mu g\ m^{-3}$. Hourly O_3 levels were slightly lower than those measured for "high O_3" days when smoke was present. A "high O_3" event in early July (July 5-6, 2007) may have been associated with the use of fireworks on July 4th, 2007. Two of the "typical" O_3 events followed "high O_3" events and showed some evidence of impact from wildfire smoke. The passage of a weather front and associated venting of the Valley may have been responsible for transitioning from "high" to "typical" ozone conditions. A clear relationship was not found between road paving activities and the occurrence of "high O_3" events.

Overall, factors that affect O_3 mixing ratios in the Treasure Valley include local emissions, regional fires, and local air circulation. Regional fires occur on an episodic basis and are associated with high PM and VOC levels. The contribution of local emissions (mobile, point and area sources) is more constant and associated with regular activities such as motor vehicle traffic. While emissions of O_3 precursors are variable, both spatially and temporally, O_3 mixing ratios across the valley are fairly uniform with slightly higher levels observed at sites in the more southeastern. Analysis of the observed "weekend O_3 effect" showed that efforts to reduce O_3 levels should focus on the reduction of VOC emissions while continuing to monitor NO_x emissions. Fortunately, this is in-line with findings from an earlier modeling effort (Stockwell et al., 2003) that examined the formation of secondary aerosols in the Treasure Valley. That work indicated that reduction of VOC emissions would decrease the formation of secondary aerosols while reduction of NO_x emissions would increase the amount of secondary aerosol in the Treasure Valley.

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1. Introduction

Tropospheric ozone (O_3), formed through the photo-oxidation of volatile organic compounds (VOCs) and nitrogen oxides ($NO_x = NO + NO_2$), is an air pollutant of concern in the Treasure Valley, Idaho, especially in summer. The Idaho Department of Environmental Quality (DEQ) sought to "*gather data depicting levels of precursor chemicals that contribute to the development of ozone pollution in the Treasure Valley for assessing what will be the most effective control strategies in Treasure Valley and improve DEQ's airshed modeling capabilities"*. As part of this effort, DEQ contracted VOCTEC Inc. to monitor VOC levels at two locations in the Treasure Valley and DRI to analyze air quality and meteorological data and investigate the patterns of ozone and its precursors.

This report summarizes the results of a field study to measure the levels of O_3, VOCs and NO_x conjointly with other pollutants, meteorological conditions and vertical profiles of ozone in the Treasure Valley. The monitoring campaign started on July 1, 2007 and continued through September 30, 2007. This study utilized: (*i*) Federal Reference Methods (FRM) monitors for measurements of O_3, NO_x and, other air pollutants and meteorological parameters; (*ii*) Pneumatic-Controlled Gas Chromatographers for continuous measurements of VOCs at two locations; (*iii*) portable O_3 monitors at four locations and; (*iv*) a tethered balloon system equipped with ozonesondes. The monitors were installed at sites that are part of the Air Quality Monitoring Network and the Air Toxics Study.

The remainder of Chapter 1 of this report provides a brief background on air quality in the Treasure Valley and ozone-related chemistry. In Chapter 2, we provide detailed information on the methods and technologies used in this study including the development of the Central Database (CD), data validation and quality control checks. Results of the field study are presented in Chapter 3 and Chapter 4 analyses the patterns and relationships of O_3 and its precursor. Chapter 5 summarizes the conclusions from this work. The Final Report and the CD are included in the attached CD-ROM.

1.1 Treasure Valley and Air Quality

The Treasure Valley is a region in southwestern Idaho which encompasses the five-county Boise Metropolitan Area (Ada, Boise, Canyon, Gem and Elmore), as well as Payette County and portions of Malheur County in eastern Oregon. It is located within the northwest-trending topographic depression of the western Snake River Plain and includes the lower Boise River basin. The metropolitan area is composed of Boise, Nampa and Meridian and smaller towns such as Middleton, Eagle, Star, Parma, Caldwell and Kuna (Figure 1-1). The population of the Boise Metropolitan Area (Boise City-Nampa Metropolitan Statistical Area (MSA)) for 2007 was about 600,000 inhabitants which accounted for approximately one-third of Idaho's population. Boise MSA is an important commercial hub for agricultural communities located in Idaho. The State Government and its associated organizations are hosted in Boise. Major corporations also have their headquarters and/or their facilities in Boise

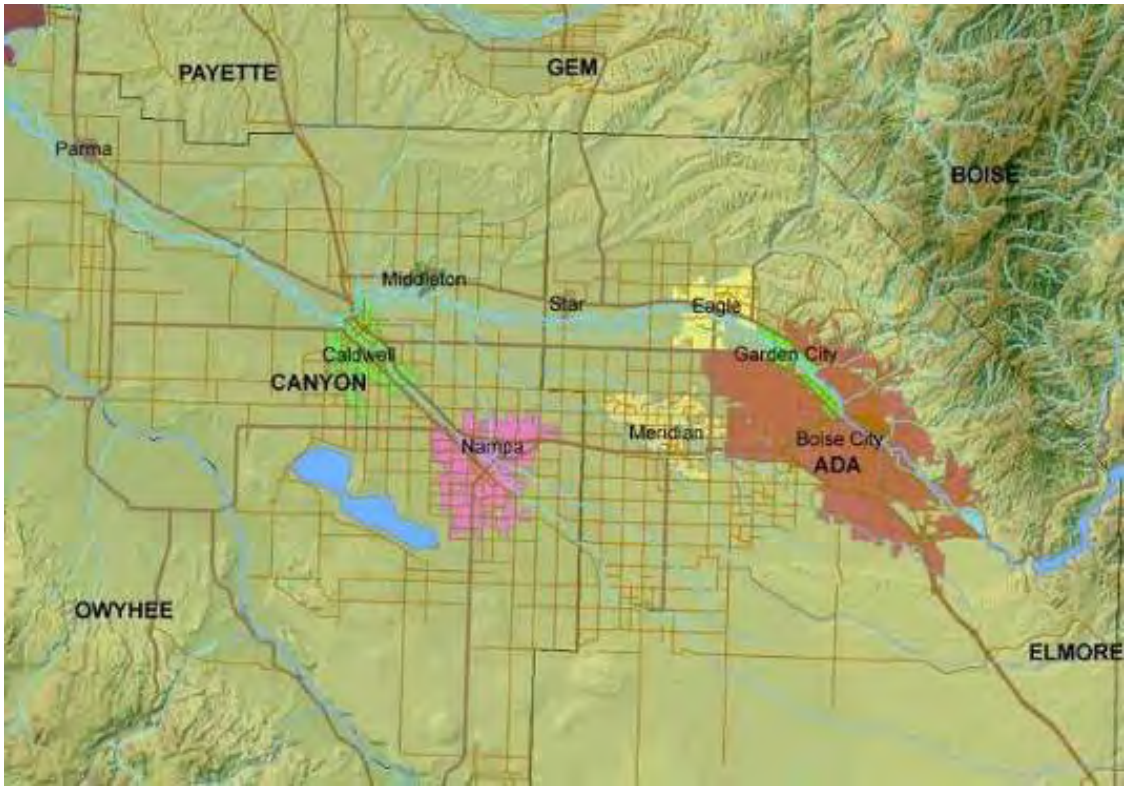

Figure 1-1 Map of cities and towns, highways and major roads, and rivers and lakes in Treasure Valley, Idaho

The Department of Environmental Quality (DEQ) monitors the levels of criteria pollutants in Idaho. Figure 1-2 shows the locations of air quality network sites operated by the Idaho DEQ in the Treasure Valley (Ada and Canyon Counties). DEQ has also carried out several air quality characterization studies to address potential air pollution episodes (Koracin et al., 1998; Kuhns et al., 2000). In the past, Treasure Valley has experienced air quality problems with PM_{10} (particles with aerodynamic diameter less than 10 μm) and carbon monoxide (CO) especially in the winter, because of wood smoke, emissions from unregulated older vehicles, and road dust. Due to local topography and wintertime weather patterns, the formation of temperature-inversion layers is frequent in Treasure Valley. During an inversion, colder air masses settle into the valley while warm air masses stay on top, trapping the cold air and pollutants in the valley and causing stagnation. Under these conditions, concentrations of pollutants build up until a weather system moves through and mixes the air (Koracin et al., 1998; Kuhns et al., 2000). During these events, recorded levels for $PM_{2.5}$, PM_{10} and CO were higher than the National Ambient Air Quality Standards (NAAQS). To address these issues, state and local governments adopted and implemented several comprehensive air quality management plans. To date, Treasure Valley remains a maintenance area for PM_{10} and CO.

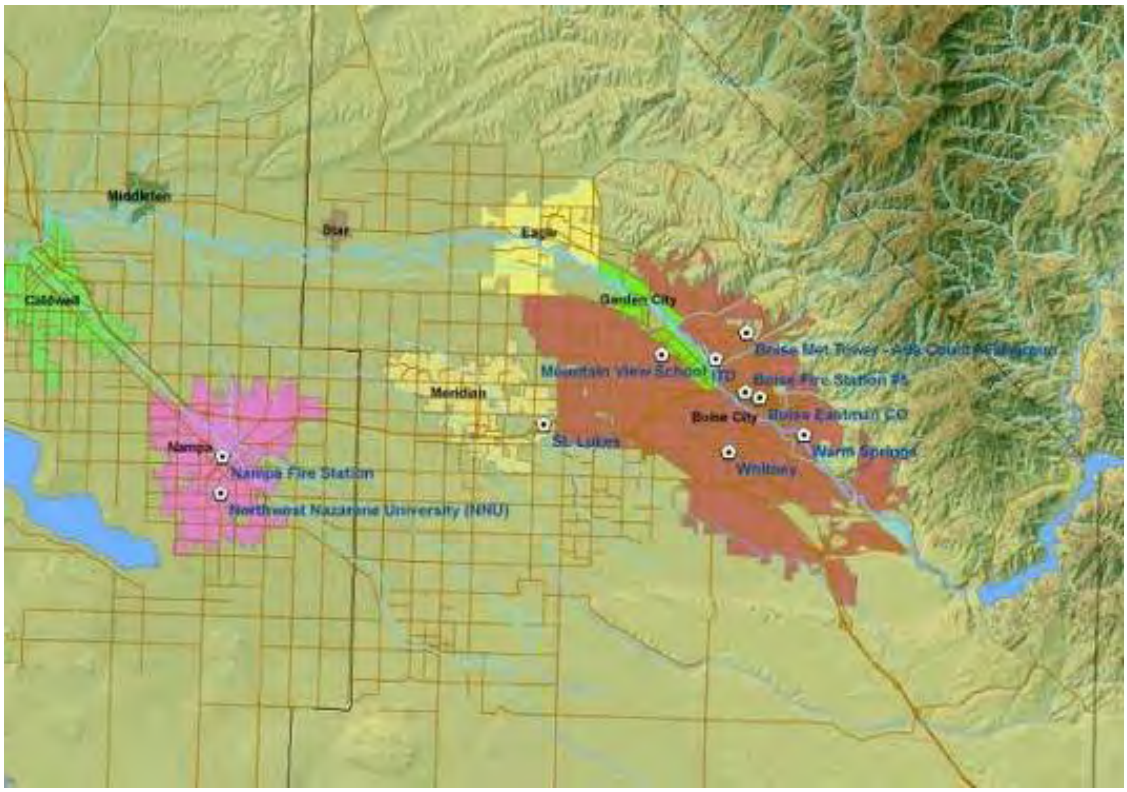

Figure 1-2 Locations of the Idaho DEQ Air Quality Network in Treasure Valley

In recent years, O_3 mixing ratios have shown an upward trend especially during the summers. In the summer of 2002, O_3 in the Treasure Valley occasionally exceeded daily NAAQS for a number of days (DEQ, 2003; EPA 2004). For 2005, measurements of criteria pollutants in Treasure Valley confirmed that the concentration of most of the pollutants are declining below the EPA NAAQS, but O_3 and, to a lesser extent, $PM_{2.5}$, remain of concern. More specifically, O_3 levels in the Treasure Valley have increased during recent years, with a mean 3-year average of 78 ppbv that is above the newly revised 8-hr NAAQS of 75 ppbv. DEQ conducted a study to determine the spatial variation of O_3 mixing ratios in the Treasure Valley using Ogawa passive samplers (DEQ, 2005). As shown in Figure 1-3, stagnant air conditions created by heat, intense sunlight and the topography blocked the movement of air masses, and triggered the accumulation of O_3 at sites located downwind of the Boise MSA (southeast Treasure Valley, along I-84) and on the mountain edge of Boise (Eagle, Foothills, SE Boise) on August 3, 2004. In contrast, low O_3 mixing ratios were measured at sites located upwind of Boise (Emmett) and in downtown Boise. This was likely due to the destruction of O_3 by traffic emissions of NO_x.

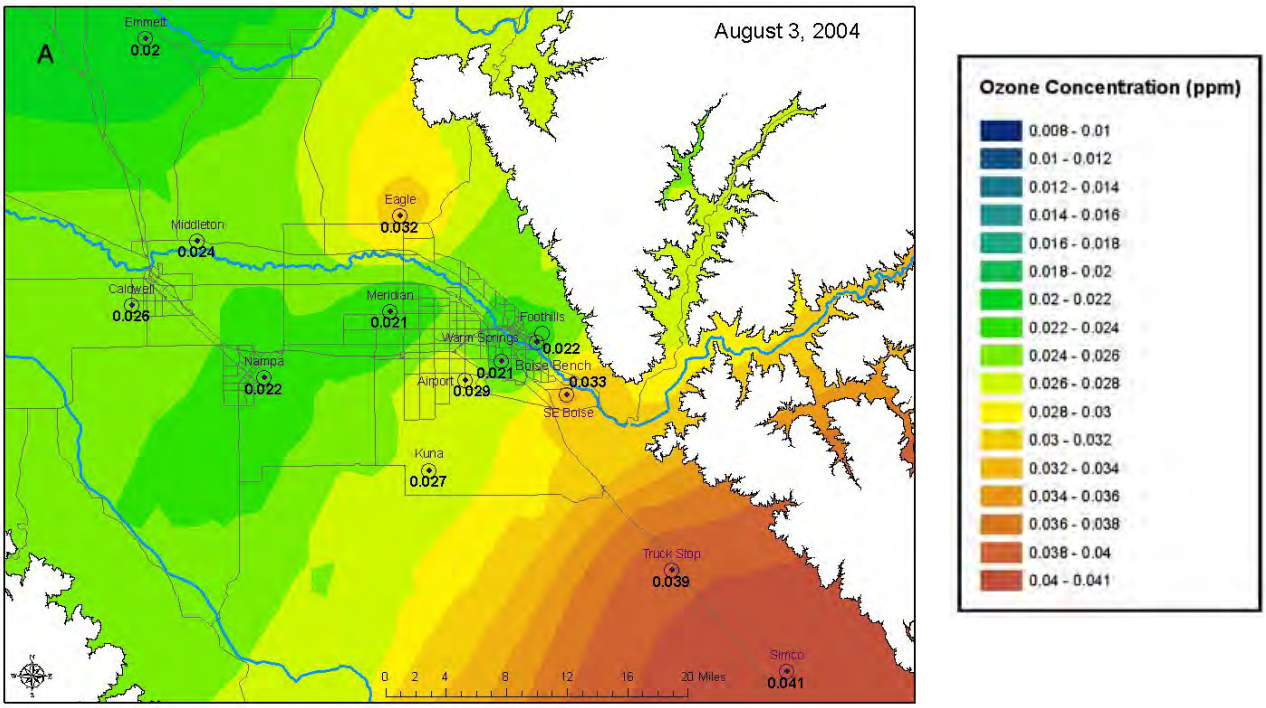

Figure 1-3 Interpolated ozone concentrations for August 3, 2004 using passive O_3 monitors and Kriging interpolation method (DEQ 2005)

1.2 Ozone formation

Ozone (O_3), a secondary air pollutant, is formed through the photo-oxidation of volatile organic compounds (VOCs) and nitrogen oxides ($NO + NO_2 = NO_x$). Exposure to O_3 damages cells and the linings of the human lungs causing adverse health effects, such as aggravation of asthma and decreased lung function. The formation of O_3 in the troposphere is a complex process involving the reactions of hundreds of precursors. The key elements, as summarized in Finlayson-Pitts and Pitts (2000), and in Seinfeld and Pandis (1998), are discussed below. The general reaction scheme is:

$$VOC + NO_x + Sunlight \rightarrow O_3 + PAN + HNO_3 + Particles + Others \qquad (1)$$

The formation of ozone in the troposphere results from the addition of atomic oxygen (O) to molecular oxygen (O_2). Blacet (1952) proposed the “nitrogen cycle” (Reaction scheme (2)).

$$\begin{aligned} O_2 + O^{\cdot} &\xrightarrow{M} O_3 \\ NO_2 &\xrightarrow{hv} NO + O^{\cdot} \qquad (2) \\ O_3 + NO &\longrightarrow NO_2 + O_2 \end{aligned}$$

The oxygen atoms ($O^{\cdot}$) are produced from photolysis of NO_2. O_3 is converted back to O_2 and NO back to NO_2, completing the "nitrogen cycle." Considering the kinetics of the nitrogen cycle

(lifetime of a few minutes), under typical atmospheric conditions in urban areas and downwind locations and in the absence of other chemicals, the “nitrogen cycle” neither generates nor consumes O_3. However, photochemical oxidation of VOCs is an alternative reaction pathway in which NO can be converted to NO_2 and thus, alter the balance of the “nitrogen cycle.”

$$\begin{aligned} &\mathrm{VOC} + \mathrm{OH}^{\cdot} \xrightarrow{[O_2]} \mathrm{RO}_2^{\cdot} + \mathrm{H_2O} \\ &\mathrm{RO}_2^{\cdot} + \mathrm{NO} \xrightarrow{[O_2]} \mathrm{Carbonyl} + \mathrm{HO}_2^{\cdot} + \mathrm{NO_2} \qquad (3) \\ &\mathrm{HO}_2^{\cdot} + \mathrm{NO} \longrightarrow \mathrm{NO_2} + \mathrm{OH}^{\cdot} \end{aligned}$$

The oxidation of VOCs is initiated by hydroxy radicals ($OH^{\cdot}$) (formed from the photolysis of ozone/water, nitrous acid, hydrogen peroxide) and results in the formation of alkylperoxy radicals ($RO_2^{\cdot}$). RO_2 radicals, in turn, react with NO to produce NO_2. Oxidation of carbonyls may result in the formation of hydroperoxy radicals ($HO_2^{\cdot}$) that also effectively convert NO to NO_2.

The relative balance of VOCs and NO_x at a specific location helps to determine whether NO_x tends to contribute to the formation or the destruction of O_3. When the VOC/ NO_x ratio in the ambient air is low (NO_x is in excess relative to VOC), NO_x tends to inhibit ozone formation. In such cases, the amount of VOC tends to limit the amount of ozone formed, and the ozone formation cycle is referred to as "*VOC-limited*". When the VOC/NO_x ratio is high (VOC is in excess relative to NO_x), NO_x tends to generate ozone. In such cases, the amount of NO_x tends to limit the amount of ozone formed, and ozone formation is called "*NO_x -limited*". The VOC/NO_x ratio can differ substantially by location and time-of-day within a geographic area. Note that the VOC/NO_x ratio is an indicator of the instantaneous production rate of O_3, not of the ambient O_3 mixing ratio, which is the net outcome of photochemistry and transport. Values of the VOC/NO_x ratio lower than 5.5 result in suppression of the ozone production reactions because OH radicals predominantly react with NO_x. On the other hand, $OH^{\cdot}$ radicals preferentially react with VOCs, promoting ozone production, at VOC/NO_x ratio values higher than 5.5. The threshold value of 5.5 is related to the rate constants of the reactions of VOCs and NO_x with $OH^{\cdot}$ radicals. The O_3/VOC/NO_x scheme is usually represented by ozone isopleth diagrams (Figure 1-4). Overall, O_3 production is favored as VOC levels increase, while higher NO_x concentrations may either enhance or reduce ozone levels, depending on the presence of VOCs (Chameides, 1992; National Research Council, 1991).

Ambient O_3 concentrations can vary from non-detectable levels near combustion sources, where nitric oxide (NO) is emitted into the air, to several hundred parts per billion (ppbv) in areas downwind of VOC and NO_x emissions. In remote continental areas, O_3 concentrations are generally 20 - 40 ppbv. In rural areas downwind of urban centers, O_3 concentrations are higher, typically 50 - 80 ppbv, and occasionally 100 - 200 ppbv. In urban and suburban areas, O_3 concentrations can be high (well over 100 ppbv), with peaks in late afternoon before reaction with NO emissions cause O_3 levels to decline (Finlayson- Pitts and Pitts 2000, Seinfeld and Pandis 1998, Chameides et al. 1992, Smith et al. 1997). For a typical traffic-impacted urban area, the VOC/NO_x ratios are lower than 5.5, thus O_3 production is suppressed because of the NO_x titration reaction (last reaction in (2)). The same reaction is responsible for the destruction of O_3

at night since there is no photolysis of NO_2, which is required for O_3 formation (2). As the air parcel moves downwind (and in the absence of additional NO_x input), NO_x react with $OH^{\cdot}$ radicals to form nitrous (HNO_2) and nitric (HNO_3) acids. Consequently, the VOC/NO_x threshold value is reached and exceeded, facilitating ozone production. Although, O_3 formation should virtually stop once the VOC/NO_x ratio is lower than 5.5, in reality, more O_3 is produced as peroxy ($HO_2^{\cdot}$) and alkylperoxy ($RO_2^{\cdot}$) radicals –intermediate products of O_3 production scheme (2)- are photolyzed. Therefore, this dependence of O_3 formation on VOC/NO_x emissions and sunlight can result in significant spatial and temporal gradients in O_3 concentrations.

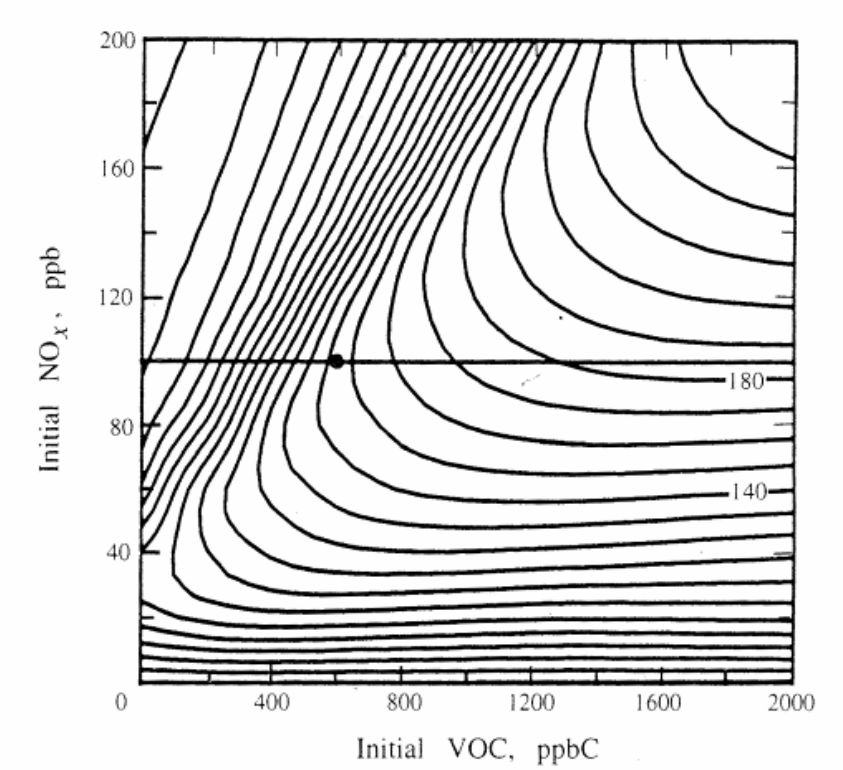

Figure 1-4 O_3 isopleth diagram showing the estimated ozone concentration for different VOC and NO_x concentrations (Seinfeld, J.H. and Pandis, S. 1999)

NO_x and VOCs are emitted from anthropogenic activities as well as from natural sources. Natural sources of NO_x account for very little as compared to anthropogenic emissions, with NO_x production from lightning being the most important natural source. Anthropogenic sources include emissions from on-road vehicles, non-road vehicles and combustion engines, fuel combustion from power plants and other industrial activities, solvent utilization, and storage and transport of fuels and chemicals. Biogenic sources of VOCs include emissions of isoprene and terpenes (e.g. pinene, limonene) from terrestrial plants and vegetation and they depend on ambient temperature and incoming solar radiation. Large amounts of VOCs also are released during biomass burning (wildfires, prescribed burning, woodsmoke). On a global basis, biogenic VOCs are up to one order of magnitude higher than the man-made emission; however, in urban environments, the contribution of natural VOCs is usually minimal. Biomass burning (wildfires and to a lesser extent prescribed/domestic burning) has been found to be associated with air pollution episodes in downwind areas (Pfister et al., 2006; Morris et al., 2006). In a wildland fire

episode in Houston/Galveston area, Junquera et al., (2005) estimated that 3700 tons of CO, 250 tons of VOCs, 340 tons of $PM_{2.5}$, and 50 tons of NO_x were released from the burning of 96,100 acres. Estimated CO and VOC emissions from the fires exceeded light duty gasoline vehicle emissions in the Houston area on those days. Using a photochemical model, the greatest enhancements of CO and O_3 concentrations due to the fire emissions were generally confined to regions within 10-100 km of the fire. Within 10 km of these fires, O_3 concentrations were likely enhanced by up to 60 ppb.

2. Methods

2.1 Monitoring Network

The monitoring sites of the Air Quality Monitoring Network and the Air Toxics Network that were included in this study are shown in Table 2-1. A detailed description of the sites is presented in the Workplan for this study (Kavouras et al., 2007).

Table 2-1. Summary of main and supplemental monitoring sites.

Site	Coordinates (NAD83 datum)	Location	Purpose
St. Lukes Hospital-Meridian	Lat: 43.6007 Lon: -116.3483 Elev.: 814 m	Interstate-84 and S. Eagle Rd.	Upwind background concentrations, nighttime elevated plume concentrations, defining extent of ozone plume west of Boise
Idaho Transportation Department	Lat: 43.6347 Lon: -116.2341 Elev.: 808 m	N. Clithero Dr.	Urban site, area of high ozone concentrations.
Whitney Elem. School	Lat: 43.5892 Lon: -116.2244 Elev.: 840 m	W. Overland Rd and S. Owyhee St	Urban site, area of high ozone concentrations, located 2 miles from the airport
Northwestern Nazarene Univ. Nampa	Lat: 43.5626 Lon: -116.5631 Elev.: 766 m	16th Ave. and E. Clark Ave.	Between Purple Sage and St.Lukes and located above influence of I-84; Define extent of ozone plume in southwest Treasure Valley; Measure possible upslope or inter/intra-basin ozone transport at the southwest edge of the Treasure Valley.
Parma	Lat: 43.7871 Lon: -116.9595 Elev.: 679 m	Off W. Roswell Ave.	Study boundary site northwest of Boise MSA; upwind background concentrations.
Mountain View Elem. School	Lat: 43.6368 Lon: -116.2702 Elev.: 831 m	W. Kingston Dr.	Measure possible upslope or inter/intra-basin ozone transport near the east edge of the Treasure Valley; potential area of peak concentrations.
White Pine Elem. School	Lat: 43.5776 Lon: -116.1777 Elev.: 847 m	E. Linden St and E. Boise Ave.	Study boundary site southeast of Boise; Potential area of peak concentrations.
Boise Fairgrounds Met Tower	Lat: 43.6477 Lon: -116.2136	Off Lancaster Drive	Meteorological tower
Boise Eastman CO	Lat: 43.6163 Lon: -116.2038	N. 9th Str. and W. Main Str.	Traffic site
Boise PM10	Lat: 43.6188 Lon: -116.2136	S. 16th Str and W. Front Str.	Downtown PM_{10} site
Warm Springs	Lat: 43.5988 Lon: -116.1734	Off Warm Springs Ave.	Meteorological tower

Figure 2-1 Locations of the Main (Green balloon), the Supplementary (Yellow balloon) ozone sites. Other sites include Boise CO (blue balloon), Fairgrounds and Warm Springs Met towers (red balloon) and Downtown Boise PM_{10} monitoring site (white balloon). Map source: Google Earth.

Figure 2-1 and Figure 2-2 show the locations and photographs (only the seven main and supplementary ozone sites) of the sites. The remaining four sites (two meteorological towers and two sites in downtown Boise that measure CO and PM_{10}) were included in the study after the completion of the monitoring campaign as data were available. The Idaho Transportation Department (ITD) is off the Boise River approximately 2.2 miles northwest of the center of Boise. The site is about 0.2 miles south of W. State Street, a heavily trafficked corridor that connects the City of Boise with Garden City, Eagle and Caldwell. St. Lukes Hospital at Meridian (STL) is located approximately 8.0 miles west/southwest of Boise and on the east side of Meridian. The site is in an open area ~1000 ft east of the St. Lukes Hospital main building. The hospital is surrounded by open parking lots. The I-84 highway that connects the city of Boise with Meridian and Nampa is located 995 ft south of the site with the intersection of I-84 and S Eagle St. at ~0.42 miles. Whitney Elementary School site is located in southwest Boise in a mixed commercial and residential area at the intersection of Overland Rd and Owyhee St. The site is less than 1.5 miles north/northeast of Boise Airport and the I-84. The site is surrounded by residences and a few commercial buildings mostly to the northwest.

The Parma monitoring site is located about 45 miles west of Boise, off the town of Parma, by the water treatment facilities (~0.53 from Highway 20/26). The site is surrounded by open fields and served to gauge background transport to the airshed. The monitoring site in Nampa is located on the roof of a building at the Northwestern Nazarene University campus, at the intersection of 16th Avenue and E. Clark Avenue. The building is surrounded by open parking lots to the east and open land (covered with grass) to the west. The site is located within a predominantly residential area. The White Pine Elementary site is located in southeast Boise (approximately 2.7 miles) in a residential area on the intersection of E. Boise Avenue and E. Linden Street. There are three open parking lots located west, northwest and northeast of the site. Larger parking lots for the needs of a few commercial businesses are located northeast of the site between E. Boise Avenue and E. Parkcenter Blvd. The Mountain View Elementary School site is located in northwest Boise in a residential area adjoining busy Chinden Blvd. (US 20/26) and numerous light industrial areas. It is in a suburban neighborhood ~ 3 miles northwest of the center of Boise. The site is located on top of a geologic bench ~ 30 m above the Boise River. The Boise River (~ 1 mile) and the City of Boise's waste treatment facility are also in close proximity.

(a)

(b)

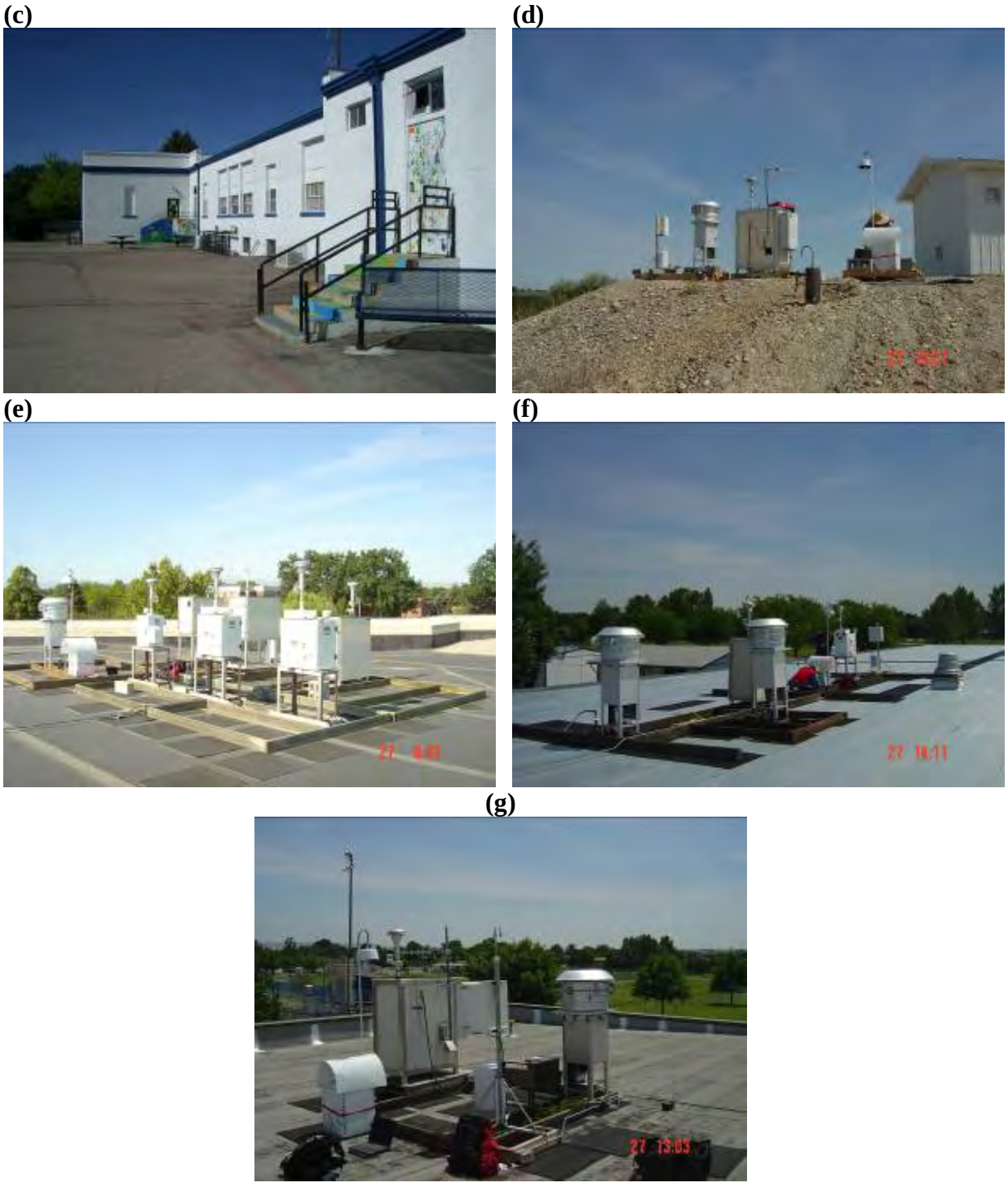

Figure 2-2 Photographs of the sites at Idaho Transportation Dept. (a), St. Lukes (b), Whitney (c), Parma (d), Nampa (e), Mountain View (g) and White Pine (g)

Table 2-2 shows the air quality parameters including O_3 and its precursors measured at each site including the two meteorological towers at Fairgrounds and Warm Springs. O_3, NO and NO_2 were continuously measured at the ITD and St. Lukes sites using FRM methods. VOCs were also continuously monitored at these two locations using online Pneumatic-Focused Gas

Chromatographers. Meteorological data were obtained from the Boise Met Tower at the Fairground and Warm Springs. O_3 mixing ratios were continuously measured at four sites (Parma, Nampa, White Pine and Mountain View) using portable 2B Technologies O_3 monitors. Continuous PM_{10} measurements were obtained from two sites in downtown Boise and Nampa, while $PM_{2.5}$ mass concentrations were retrieved from Parma, Nampa, St. Lukes, White Pine and Mountain View sites. Finally, CO concentrations were only obtained from the downtown Boise-Eastman site.

Table 2-2 Air quality and meteorological parameters measured at each site

	O_3	NO/NO_2	VOCs	PM_{10}	$PM_{2.5}$	CO	Meteorology
Idaho Transport. Dept.	✓	✓	✓				
St. Lukes	✓	✓	✓		✓		
Whitney	✓						
Parma	✓				✓		
Nampa	✓			✓	✓		
White Pine	✓				✓		
Mountain View	✓				✓		
Boise Eastman						✓	
Boise Downtown				✓			
Boise Faigrounds							✓
Warm Springs							✓

2.2 Measurement Methods

Table 2-3 shows the instrumentation used for the monitoring of O_3, NO/NO_2 and meteorological parameters at ITD, St. Lukes Hospital and Whitney sites. Description of the instruments, quality control requirements, calibration and maintenance procedures, and data management and validation are included in the Quality Assurance Project Plan for the State of Idaho Ambient Air Quality Monitoring Program (DEQ-QAPP, 2003).

Table 2-3 Instrumentation for regular monitoring of O_3, NO and NO_2 and meteorological parameters

Parameter	Instrument
O_3	Advanced Pollution Instrumentation, Inc. (API) Analyzer
NO_x ($NO+NO_2$)	Advanced Pollution Instrumentation, Inc. (API) Analyzer
Meteorological parameters (wind direction/speed, temperature, relative humidity, barometric pressure, solar radiation)	Multiple sensors

VOCs were measured by a Pneumatic Focusing Gas Chromatograph equipped with a flame ionization detector (PFGC/FID). Sample air was pulled continuously through the sample loop during chromatographic processing of the previous sample. Every hour, ambient air was drawn through a 50' coil of ¼" copper tubing which is pneumatically focused to 600 psi (Copper sampling lines also remove ozone, preventing reaction artifacts during sampling). For optimal sensitivity

(nominal 50 pptV LOD for benzene), a sample volume of 279 cc was required. Methane, constant at ~1.8 ppm in ambient air served as an internal standard on every chromatogram, including calibration chromatograms.

Table 2-4 Sampling and analytical specifications of the PFGC/FID

Parameter	Configuration		
Sampling Mode	150 ml/minute continuously flowing through the 279 mL sample loop.		
Sample Injection Pressure	600 psi of Helium.		
Column flow and pressure	105 cc/min at 600 psi.		
FID temperature	280^0C		
Hydrogen Flow Rate	27 mL/min	Nominal pressure to achieve: 40 psi	
Oxygen Flow Rate	180 mL/min	Nominal pressure to achieve: 60 psi	
Oven program	Rate	Final Temperature	Hold Time
Step1	10^0C	120^0C	0 minutes
Step2	7^0C	250^0C	to finish

Four portable continuous 2B Technologies Model 202 O_3 analyzers were installed and operated at Mountain View Elementary School, White Pine Elementary School, Northwestern Nazarene University and Parma from July 1, 2007 to September 30, 2007. Prior to deployment to the field, O_3 monitors were maintained and calibrated by 2B Technologies.

Figure 2-3 Environmental enclosure of the 202 O_3 Monitor

The 2B Technologies Model 202 O_3 Monitor™ provides accurate and precise measurements of ozone ranging from 1 ppb to 100 ppm with a precision of 1 ppbv by absorption of ultraviolet radiation (at 254 nm). The amount of radiation absorbed is directly related to the concentration of the compound. The Ozone Monitor™ is simple to operate and has a fast response time. The O_3 monitor was placed in a temperature-controlled environmental enclosure (Figure 2-3 shows the environmental enclosure at Nampa). An 8-ft Teflon sampling line was used to draw air to the monitor. Particle contamination was eliminated by a Teflon filter which was changed frequently

(weekly or bi-weekly) by site operators. Since these monitors are not federal equivalent methods, two inter-comparison studies were carried out at St. Lukes. The effort included a field comparison among the four instruments to evaluate the inter-instrument response and repeatability and a direct comparison with the FRM monitor. However, the FRM monitor at St. Lukes failed to pass an audit test during the first inter-comparison study and was not operational during the second effort.

2.3 Tethered-balloon measurements

Tethered balloon soundings were obtained at the Ann-Morrison Park near downtown Boise on August 9. 10, 14, and 15. A total of 35 vertical meteorological profiles and 16 ozone profiles during the course of this study was collected. Table 2-5 shows the profile numbers obtained each day and the daily hours of observations.

Table 2-5 Summary of vertical profile measurements in August 2007

Date	Total Number of profiles	Number of ozone profiles	Sunrise	Profiles Started	Profiles Ended	Sunset
8/9/2007	8	4	6:43 AM	8:36 AM	2:59 PM	8:58 PM
8/10/2007	6	3	6:44 AM	7:08 AM	12:30 PM	8:56 PM
8/14/2007	13	9	6:48 AM	7:28 AM	8:30 PM	8:50 PM
8/15/2007	8	0	6:49 AM	7:01 AM	10:58 AM	8:49 PM

Ann-Morrison Park is approximately 3.25 miles north of Boise International airport (BOI) (Lat: 43.61319 Lon. -116.2211at an elevation of about 2,675 feet (815 m) above mean sea level). The 145 acre Park is nestled along the Boise River and is covered with grass and bordered by tall trees. A small parking lot is located near the balloon launch site about 30 meters from the site that has the potential to hold about 80 or 90 cars although no more than 20 cars were parked in the lot at any time during measurements. A large water fountain feature is located 150 meters to the south. The grass surrounding the site was irrigated daily which caused the ground to be saturated in the morning and moist the duration of the day. Crescent Rim Drive borders the park to the west and is approximately 400 meters from the site. The business district of Boise lies at the northern side of the Boise River. Americana Blvd, a fairly busy four-lane arterial that connects downtown to the southwestern part of Boise, runs at a distance of 220 meters west of the site

The tethered balloon is part of the Vaisala TT12 DigiCORA Tethersonde System and holds 318 cubic feet (9 cubic meters) of helium. The balloon's dimensions are approximately 16 feet (5.2 m) long and 7.5 feet (2.3 m) in diameter. It is capable of lifting about 12 pounds (5.45 kg). The balloon is constructed of 3 mil bright orange film material and is attached to an electric winch by a braided line with a manufacture's rated test strength of 240 pounds. The winch and electronics were powered by a small gasoline generator that was located 100 feet away and toward the parking lot. The tethered balloon system was used with a manufacturer supplied automatic deflation device and was programmed to let helium at the 700 mb pressure altitude in case of an accidental release. The tethersonde was normally attached to the tetherline approximately 10 meters below the balloon to avoid wind flow interference from it. When flying an ozonesonde, we attached it immediately below the tethersonde because of a short data cable.

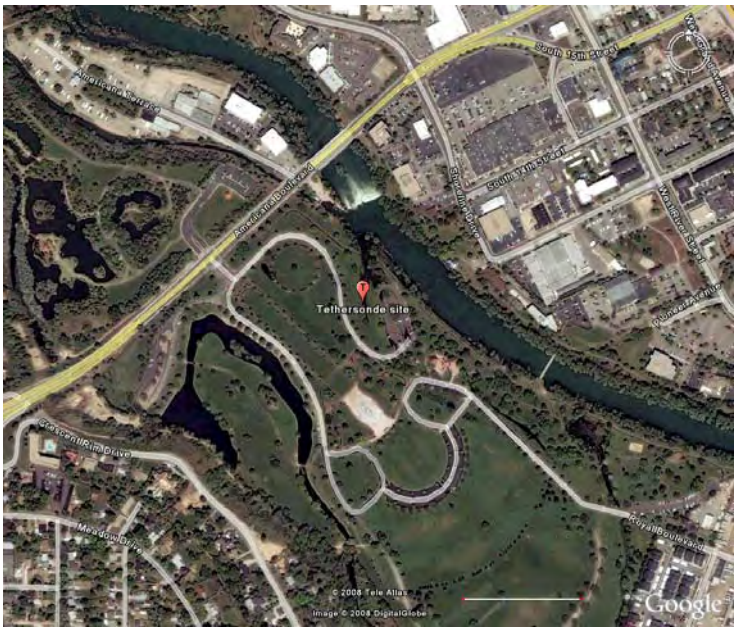

Figure 2-4 Location of the balloon launch area with respect to the park

Mr. Scott Pitzer acquired permission from the City of Boise as well as obtained a waiver from the Federal Aviation Agency (FAA) to operate the balloon. The FAA waiver required us to operate the balloon no more than 3,000 feet above ground level (900 meters) at this site. The FAA waiver had a stipulation that requires us to operate from sunrise to sunset each day. The observed sunrise actually occurred a few minutes after this due to the mountainous terrain to the east of Boise.

The daily routine of operations started around 6 am each day. The balloon was operated in the vertical profile mode where it was slowly lifted and lowered by the winch while collecting data. Ascent/descent rates ranged from 0.25 to 0.5 m/s depending on the purpose and payload. We carefully monitored the wind speed at the height of the balloon since the manufacturer recommends its safe operation at speeds less than 10 m/s. This threshold wind speed was surpassed in the late mornings and early afternoons, causing the termination of operations for the day. Preparation of ozonesondes required 2-3 hours of work prior to deployment on the balloon. Because of this procedure, ozonesondes were not employed in vertical profile measurements until around 10 am.

2.4 Data completeness

Table 2-6 shows the days for which there were less than fifteen (15) valid hourly measurements for O_3, NO_x, PM_{10}, $PM_{2.5}$, CO and meteorological data in a day (x). For VOCs, an "incomplete day" statuwas assigned for days with fewer than ten (10) valid measurements. For vertical profile measurements with the tethered-balloon system, only days with successful launches of the system and collection of data are marked (✓). Failures of O_3 and NO_x instruments at ITD and St. Lukes were associated with inability to meet calibration and audit specifications. Incomplete VOC datasets were frequently due to instrument failures associated with gas consumption. Loss of O_3 data at the four supplemental sites was due to broken pumps and failed attempts to collect

and initiate the data collection during site visits. Overall, complete datasets for O_3 and its precursors were mostly concentrated in August and September 2007.

Table 2-6 Data completeness for each parameter [(x) indicates the days for which there were less than 15 valid hourly measurements for O_3, NO_x, PM_{10}, $PM_{2.5}$, CO and meteorological data and less than 10 valid measurements for VOCs; (✓) indicated the days with successful launches of the tethered balloon].

	O_3							**NO & NO2**		**VOC**		**PM_{10}**		**$PM_{2.5}$**					**CO**	**Meteorology**		
	St. Lukes	ITD	Whitney	Parma	Nampa	White Pine	Mountain View	ITD	St. Lukes	ITD	St. Lukes	Nampa	Boise	St. Lukes	Parma	Nampa	White Pine	Mountain View	Boise	Fairgrounds	Warm Springs	Vertical profiles
7/1/2007	x	x						x	x	x	x					x	x		x			
7/2/2007	x	x						x	x	x	x					x	x		x			
7/3/2007	x	x						x	x	x	x					x	x		x			
7/4/2007	x	x						x	x		x					x	x		x			
7/5/2007	x	x						x	x		x					x	x		x			
7/6/2007	x	x						x	x	x						x	x		x			
7/7/2007	x	x						x	x	x						x	x		x			
7/8/2007	x	x						x	x	x			x			x	x		x			
7/9/2007	x	x						x	x	x					x	x	x		x			
7/10/2007	x	x						x	x	x					x	x			x			
7/11/2007	x	x						x	x	x						x			x			
7/12/2007	x	x						x	x							x			x			
7/13/2007	x	x						x	x						x	x	x		x			
7/14/2007	x	x						x	x						x	x			x			
7/15/2007	x	x						x	x	x					x	x			x			
7/16/2007	x	x						x	x	x	x				x	x			x			
7/17/2007	x	x						x	x		x				x	x			x			
7/18/2007	x	x						x	x		x					x			x			
7/19/2007	x	x						x	x						x	x			x			
7/20/2007	x	x						x	x		x					x			x			
7/21/2007	x	x						x	x		x				x	x			x			
7/22/2007	x	x						x	x						x	x			x			
7/23/2007	x	x						x	x						x	x			x			
7/24/2007	x	x						x	x							x			x			
7/25/2007	x	x						x	x						x	x			x			
7/26/2007	x	x						x	x						x	x			x			
7/27/2007	x	x						x	x						x				x			
7/28/2007	x							x							x				x			
7/29/2007	x							x							x				x			
7/30/2007	x							x							x				x			
7/31/2007	x							x							x				x			

8/1/2007									x			x			x				x			
8/2/2007									x			x			x				x			
8/3/2007									x			x			x				x			
8/4/2007									x										x			
8/5/2007									x										x			
8/6/2007									x						x				x			
8/7/2007									x						x				x			
8/8/2007									x	x					x				x			
8/9/2007									x	x					x				x			✓
8/10/2007		x	x						x						x				x			✓
8/11/2007		x	x						x						x		x		x			
8/12/2007		x	x						x						x				x			
8/13/2007		x	x						x						x				x			
8/14/2007		x	x		x				x						x				x			✓
8/15/2007		x	x		x				x						x				x			✓
8/16/2007					x					x					x				x			
8/17/2007					x					x					x				x			
8/18/2007					x					x					x				x			
8/19/2007					x													x	x			
8/20/2007					x										x	x			x			
8/21/2007					x						x				x	x			x			
8/22/2007					x						x								x			
8/23/2007					x										x				x			
8/24/2007					x	x										x			x			
8/25/2007						x				x					x	x			x			
8/26/2007						x				x					x	x			x			
8/27/2007						x				x	x				x	x			x			
8/28/2007						x					x					x	x		x			
8/29/2007						x					x					x			x			
8/30/2007						x										x			x			
8/31/2007						x										x	x		x			
9/1/2007				x		x										x			x			
9/2/2007						x									x	x			x			
9/3/2007						x									x	x			x			
9/4/2007						x									x	x			x			
9/5/2007						x									x	x			x			
9/6/2007				x		x								x	x	x	x		x			
9/7/2007						x								x	x	x	x					
9/8/2007						x								x	x	x	x					
9/9/2007						x				x				x	x	x	x					
9/10/2007						x				x					x	x						
9/11/2007						x				x					x							
9/12/2007										x				x	x							
9/13/2007															x							
9/14/2007															x							

9/15/2007															x						
9/16/2007															x						
9/17/2007															x		x				
9/18/2007														x	x	x	x				
9/19/2007															x		x				
9/20/2007									x						x						
9/21/2007									x	x											
9/22/2007				x					x	x	x										
9/23/2007				x						x									x		
9/24/2007				x						x											
9/25/2007				x																	
9/26/2007				x																	
9/27/2007				x																	
9/28/2007				x															x		
9/29/2007				x															x		
9/30/2007				x														x	x		

2.5 Data Validation and Database Development

The Central Database (CD) was created to produce a system that is straightforward and easy for users to obtain data. Microsoft ACCESS was used as the major tool for the development of the CD. Each partner was responsible for reviewing and validating their collected data based on their procedures.

Table 2-7 Name and description of the CD components

Name	Description
VOC_Level0	VOC data as they were provided by VOCTEC Inc.
VOC_Level1	VOC data modified to match the format of the database. Values from blank, calibrations and tests were excluded.
NAAQS_Level1	O_3, NO, NO_2, CO, PM_{10} and $PM_{2.5}$ data modified ro match the format of the database. QA/QC controls were included.
Meteorology_Level1	Wind speed and direction, temperature, relative humidity, solar radiation, and barometric pressure data modified to match the format of the database.
OzoneSuppl_Level0_5min	O_3 data (5-min) from supplemental sites. Values from blank, calibrations and tests were not flagged.
OzoneSuppl_Level1_5min	O_3 data (5-min) from supplemental sites. Values from blank, calibrations and tests were flagged.
OzoneSuppl_Level1_1hr	O_3 data from supplemental sites averaged on an hourly basis (12:01-13:00 as 12:00). Values from blank, calibrations and tests were flagged
Balloon_Profiles_Level1	Vertical profiles and O_3 data using the tethered balloon on August 2007
CollocationOzoneSuppl_Jun07_Level0_5min	O_3 data (5-min) from intercomparison test on June 2007. Values from blank, calibrations and tests were not flagged.
CollocationOzoneSuppl_Jun07_Level1_5min	O_3 data (5-min) from intercomparison test on June 2007. Values from blank, calibrations and tests were flagged.

CollocationOzoneSuppl_Jun07_Level1_1hr	O_3 data from from intercomparison tests on June 2007 averaged on an hourly basis (12:01-13:00 as 12:00). Values from blank, calibrations and tests were flagged
CollocationOzoneSuppl_Oct07_Level0_5min	O_3 data (5-min) from intercomparison test on October 2007. Values from blank, calibrations and tests were not flagged.
CollocationOzoneSuppl_Oct07_Level1_5min	O_3 data (5-min) from intercomparison test on October 2007. Values from blank, calibrations and tests were flagged.
CollocationOzoneSuppl_Oct07_Level1_1hr	O_3 data from from intercomparison tests on October 2007 averaged on an hourly basis (12:01-13:00 as 12:00). Values from blank, calibrations and tests were flagged

The format of VOC_Level1 database is as follows:

Site# (1-2); Date; Time; 1,2,3-Trimethylbenzene; 1,2,4-Trimethylbenzene; 1,3,5-Trimethylbenzene; 1-Butene; 1-Hexene; 1-Pentene; 2,2,4-Trimethylpentane; 2,3,4-Trimethylpentane; [2,3-Dimethylbutane/2-Methylpentane/Isoprene/3-MethylPentane]; [2,3-Dimethylpentane/2-Methylhexane/3-Methylhexane/Methylcyclohexane]; 2,4-Dimethylpentane; 2-[2-Dimethylbutane/c2Pentene]; [2-Methylheptane/3-Methylheptane]; Acetylene; Benzene; [Cis-2-Butene/Isopentane]; Ethylbenzene; Isobutane; [Isopropylbenzene/Npropylbenzene]; [m-Xylene/p-Xylene/Acetone]; nButane; nDecane; nHeptane; [n-Hexane/Cyclohexane]; n-Nonane; n-Octane; [n-Pentane/Cyclopentane]; o-Xylene; Propane; Propylene; Styrene; Toluene; Trans-2-Butene; Trans-2-Pentene; m,p-ethyltoluene

Data from the Air Quality Monitoring Network are reported as follows:

Site# (1-8), Date; Time; O3Conc; O3Flag; NOConc; NOFlag; NO2Conc; NO2Flag; PM10TEOMConc; PM10TEOMFlag; PM25TEOMConc; PM25TEOMFlag; COConc; COFlag

Data from the meteorological towers are reported as follows:

Site# (9-10), Date; Time; Wind_Speed; WS_VC; Wind_direction; WD_VC; Temperature; T_VC; Relative_Humidity; RH_VC; Solar_radiation; SR_VC; Pressure; P_VC

where VC is void code for invalid cases.

Data from the supplemental O_3 monitors should be reported as follows:

Site# (4-7); Date; Time; O3Conc; Error

The following numbers were assigned to each site:

ITD:1; St.Lukes:2; Whitney: 3; Parma: 4; Nampa: 5; White Pine:6; Mountain View: 7; Boise_PM10/Eastman: 8; Fairground Met Tower: 9; Warm Springs: 10

Date was expressed as *mm/dd/yyyy*
Time was be expressed as *hh:mm* (0:00-23:00) local time
O_3, NO, NO_2, CO and VOC concentrations are in *ppbv*
PM_{10} and $PM_{2.5}$ mass concentrations are in $\mu g\ m^{-3}$
Wind speed in $m\ s^{-1}$
Wind direction in *degrees* clockwise from north
Temperature in ^oC

Relative humidity in *%*
Barometric pressure in *mbar*
Solar radiation in $W\ m^{-2}$

The format of balloon profiles database is as follows:

Parameter	**Description**
Date	Local date in dd/mm/yyyy
Time	Local time in hh:mm:ss
Press_hPa	Atmospheric pressure in hecto Pascals
Press_hPa_VC	Atmospheric pressure in hPa validation code
T_C	Atmospheric temperature in C
T_C_VC	Atmospheric temperature in C validation code
RH	Relative Humidity in percent
RH_VC	Relative Humidity validation code
Alt_m	Altitude above ground level in meters
Alt_m_VC	Altitude above ground level in meters validation code
WS_mps	Wind speed in meters per second
WS_mps_VC	Wind speed in meters per second validation code
WD	Wind direction, clockwise from north
WD_VC	Wind direction, clockwise from north validation code
Batt_v	Tethersonde battery level of 9 volt battery
Batt_v_VC	Tethersonde battery level of 9 volt battery validation code
Theta_C	Potential temperature in C
Theta_C_VC	Potential temperature in C validation code
Dewpt_C	Dew point temperature in C
Dewpt_C_VC	Dew point temperature in C validation code
SpecHum	Specific humidty, unitless
SpecHum_VC	Specific humidty, unitless validation code
MixRat_g/kg	Water vapor mixing ration in g/kg
MixRat_g/kg_VC	Water vapor mixing ration in g/kg validation code
O3_ppb	Ozone concentration in ppbv
O3_ppb_VC	Ozone concentration in ppbv validation code
O3Curr_uA	Ozone sampler current in micro amps
O3Curr_uA_VC	Ozone sampler current in micro amps validation code
O3Temp	Ozone sampler cell temperature in C
O3Temp_VC	Ozone sampler cell temperature in C validation code
descripion	Status of sounding, either profile up or down

2.6 Quality assurance and control tests

Measurements of O_3, NO/NO_2, PM_{10}, $PM_{2.5}$, CO and meteorological parameters have been subject to quality provisions as they are described in the QAPP for the Air Quality Monitoring Network. VOC measurements have been evaluated by VOCTEC Inc. This section provides only the results of quality control checks for the 2B ozone monitors. Two intercomparison campaigns

were conducted on June 25-26, 2007 and on October 12-13, 2007. During the first intercomparison period, the FRM ozone monitor at St. Lukes failed to pass the calibration and audit tests, so no measurements were retrieved. During the second period, the FRM O_3 monitor in St.Lukes was not operational. DEQ switched on the instrument to collect ozone data; however no QA/QC checks were performed. The instrument was successfully audited in late September.

Table 2-8 Estimated %bias AND %CV of O_3 monitors

	Parma	Nampa	White Pine	Mountain View
%Precision	6	5	4	9
% Bias	-19	-15	17	-5
% CV	26	22	14	18

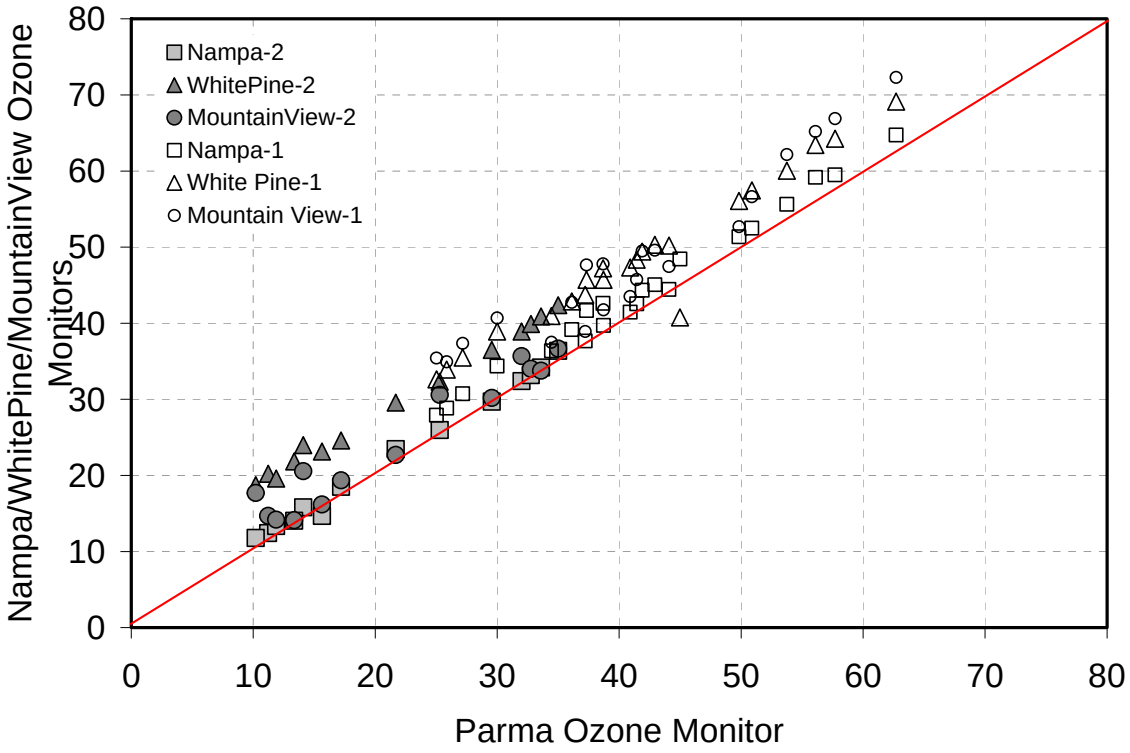

Figure 2-5 Scatter plot of O_3 concentration using "Nampa", "White Pine" and "Mountain View" monitors vs. O_3 concentrations measured by "Parma" monitor during the first (open symbols) and second (grey-filled symbols) intercomparison periods

Only data collected during daytime by FRM and 2B monitors were used to evaluate the response of 2B monitors. Precision, bias and %CV were computed for the second set of inter-comparison (Table 2-8). To compensate for the absence of data from FRM monitors during the first intercomparison period, the correlations between the four 2B monitors were analyzed to address the repeatability and consistency of portable ozone measurements and provide estimates of bias.

Both the precision and bias are within the goals defined for this study. These results indicated that the readings between the instruments were comparable and consistent between each other. Similar conclusions can be drawn from the analysis of %CV. The relatively high %bias for

"Parma" and "White Pine" ozone monitors may be related to the replacement of the pump at the end of the monitoring campaign that may affect "zero" values; however the impact was negligible for ambient concentrations.

Figure 2-5 illustrates the associations between the portable monitors for both test periods. Table 2-9 and Table 2-10 show the correlations and the regression coefficients between the four portable monitors. Both the correlation and regression coefficients showed very good agreement between the monitors at the beginning and end of the monitoring campaign. Taking into account, that there were no serious problems associated with the performance of the detector, the portable O_3 monitors showed remarkable consistency and repeatability. Note that these measurements cannot be used to determine compliance with NAAQS as they were not certified as FRM or FEM methods.

Table 2-9 Correlation coefficients between the four monitors during the intercomparison studies

	June 2007			October 2007		
	Nampa	White Pine	Mountain View	Nampa	White Pine	Mountain View
Parma	0.993	0.969	0.958	0.996	0.997	0.970
Nampa		0.962	0.980		0.997	0.971
White Pine			0.971			0.972

Table 2-10 Regression coefficients of O_3 measurements in Nampa, White Pine and Mountain View against O_3 measurements in Parma using the 2B portable monitors

	R	Slope	Intercept
Nampa	0.9925	1.0191	1.0990
White Pine	0.9781	0.93897	9.1572
Mountain View	0.9551	1.0809	2.4400

2.7 Supplementary datasets

2.7.1 Air Mass Trajectories

Backward trajectories with a resolution of one hour and going back eight days were generated for Boise at 1 hour intervals using the NOAA HYSPLIT trajectory model (Draxler and Hess, 1997) and Eta Data Assimilation System (EDAS) meteorological fields as inputs. Starting heights for both sites were 100 m, 200 m, 500 m, 1000 m, 1500 m, 2000 m and 3000 m above ground level. The residence time defined as the fraction of the total time of backtrajectories that the airmass was over a given area of 0.25 degree latitude by 0.25 degree longitude was computed.

2.7.2 Wildland Fire Episodes

Wildland fire activity in western United States and Canada for the monitoring period was retrieved from the National Interagency Fire Center (www.nifc.gov). The locations of fire episodes were obtained using data collected by both TERRA MODIS and AQUA MODIS

satellites and processed as a cooperative effort between the USDA Forest Service Remote Sensing Applications Center, NASA-Goddard Space Flight Center and the University of Maryland (Remote Sensing Applications Center; www.fs.fed.us/eng/rsac/index.html).

2.7.3 Road Construction and Pavement Activities

DEQ contacted and obtained from Ada County Highway District (ACHD) information regarding construction and maintenance activities during the monitoring period. Maintenance activities include chip sealing and maintenance paving while documented construction activities involved major capital projects.

2.7.4 Surface weather maps and smoke plume

Weather maps, modeled plume of smoke from wildland fires and GOES-11 satellite remote sensing maps were obtained from the Unisys Weather (http://weather.unisys.com/index.html). Navy Research Laboratory (http://www.nrlmry.navy.mil/aerosol/) and NOAA/NASA (http://www.osei.noaa.gov/Events/Fires/US_Northwest/), respectively.

3. Results

This section contains a synopsis of air quality and meteorological data obtained during the course of the study. In addition, auxiliary datasets of air mass backward trajectories, wildland fires and road construction and maintenance activities are included. The data are delineated in the form of summary tables and time series plots.

3.1 Synopsis of measurements

3.1.1 O_3 concentrations in primary and supplemental sites

Descriptive statistics of O_3 hourly mixing ratios are presented in Table 3-1. Figure 3-1 and Figure 3-2 show the box plots of hourly and 8-hr ozone concentration in the seven monitoring locations. The boxes represent the 25%, 50% (median) and 75% percentiles, and whiskers show the 5% and 95% percentiles. The open squares show the mean value. For all locations, hourly ozone concentrations were significantly lower than 120 ppbv, the 1-hour ozone standard that is only applicable for the fourteen 8-hour ozone non-attainment Early Action Compact (EAC) Areas. With respect to the newly revised 8-hr ozone standard, ozone levels exceeded the current standard three days at the White Pine (WHP), five days Whitney (WHT) locations, and once at Idaho Transportation Dept., two at Whitney (WHT) and one at St. Lukes (STL)). The exceedances were observed on July 6, 2007 (WHT), July 14, 2007 (WHT and WHP), July 27-28, 2007 (WHT and WHP) and August 1, 2007 (all sites). It is noteworthy to mention that similar trends were observed for the other sites (for which a 2B portable monitor was used) and that the exceedances were observed at the sites that are located in the southeast end of the Treasure Valley. Figure 3-3 - Figure 3-5 show the time series of O_3 at Idaho Transportation Dept (ITD), St. Lukes (STL) and Whitney (WHT) sites. Variations of hourly O_3 concentrations at Parma, Nampa, Mountain View and White Pine supplemental sites are illustrated in Figure 3-6 through Figure 3-9. Hourly O_3 levels at all sites ranged from a few ppbv during the nighttime to 83 ppbv at St. Lukes, 91 ppbv at ITD and 104 ppbv at Whitney, with average concentrations of 27 ppbv at ITD, 32 ppbv at St. Lukes and 30 ppbv at Whitney. For the supplemental sites, O_3 levels ranged from a few ppbv during the nighttime to 80 ppbv at Parma and 99 ppbv at White Pine. The average levels from July 1, 2007 to September 30, 2007 between the four sites varied from 28 ppbv at Mountain View to 37 ppbv at White Pine. The highest O_3 mixing ratios were measured at Whitney on July 14, 2007, while the highest O_3 levels at ITD and St. Lukes were recorded on August 1, 2007. The highest O_3 measurements at Nampa, Mountain View and White Pine were observed on August 1, 2007. For Parma, the highest measurement was obtained on July 14, 2007. During this day, O_3 levels were among the highest at Nampa, Mountain View and White Pine.

Table 3-1 Descriptive statistics of hourly O_3 concentrations at primary sites

Site	n	Mean	Median	σ	Max
Idaho Transportation Dept.	1726	27	24	19	91
St. Lukes	1440	32	31	19	83
Whitney	2096	30	27	22	104
Parma	1726	29	30	16	80
Nampa	1925	30	30	17	91

White Pine	1757	37	34	18	99
Mountain View	2096	28	29	19	87

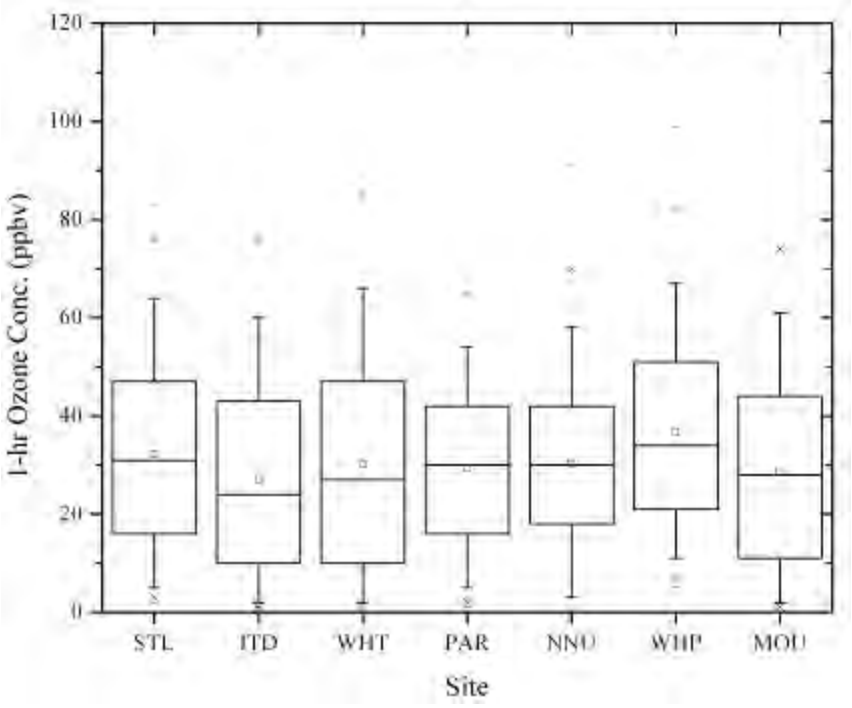

Figure 3-1 Box plots of hourly O_3 concentrations at ITD, St.Lukes, Whitney, Parma, Nampa, White Pine and Mountain View

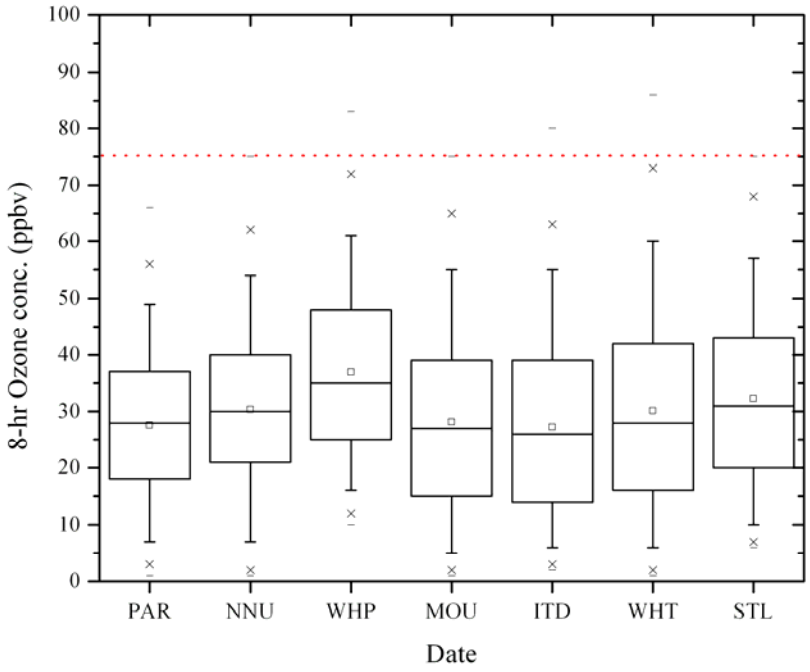

Figure 3-2 Box plots of 8-hr O_3 concentrations at ITD, St.Lukes, Whitney, Parma, Nampa, White Pine and Mountain View [The existing and proposed 8-hr NAAQS are represented by the red dotted and blue solid lines, respectively]

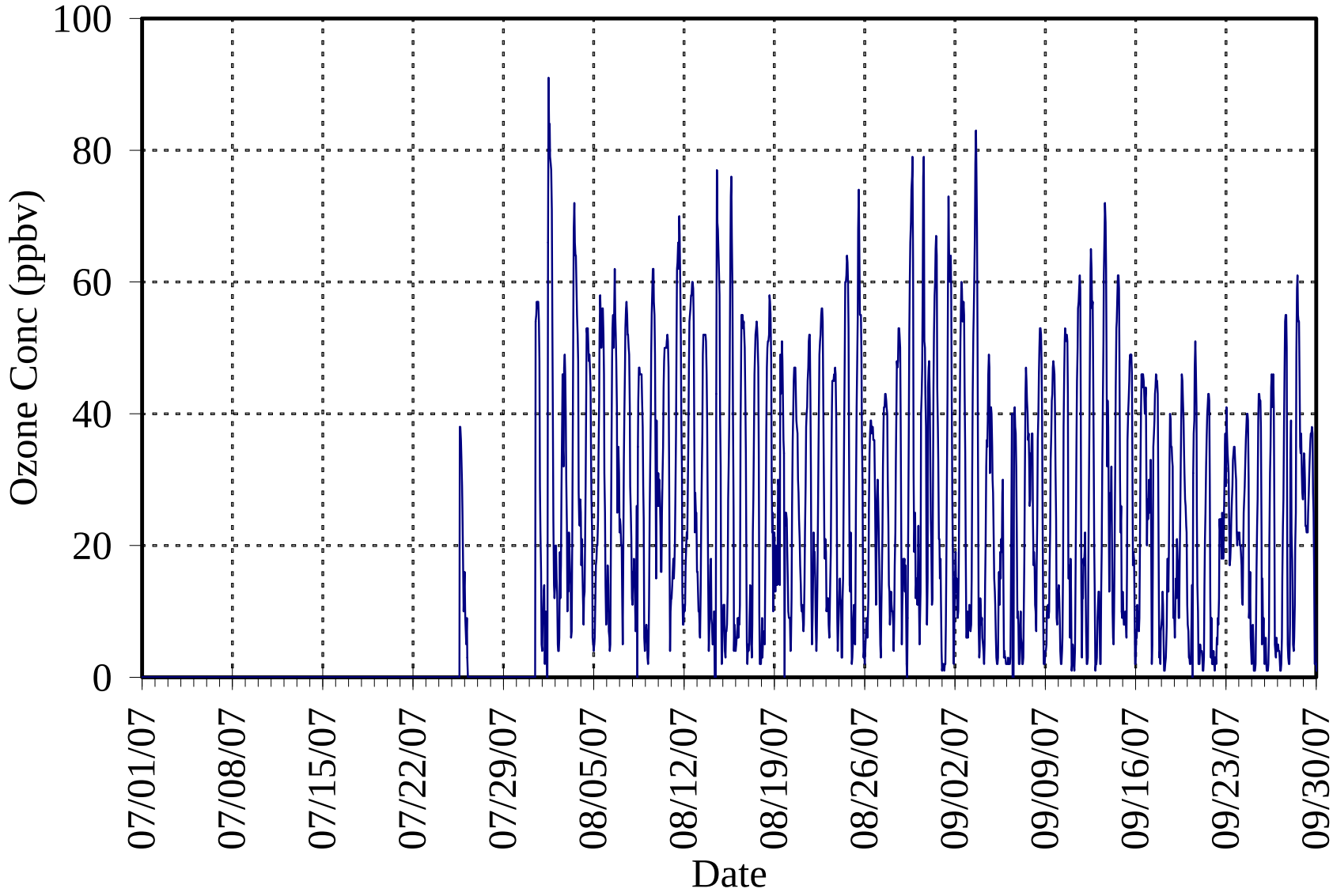

Figure 3-3 Times series of O_3 (in ppbv) at ITD

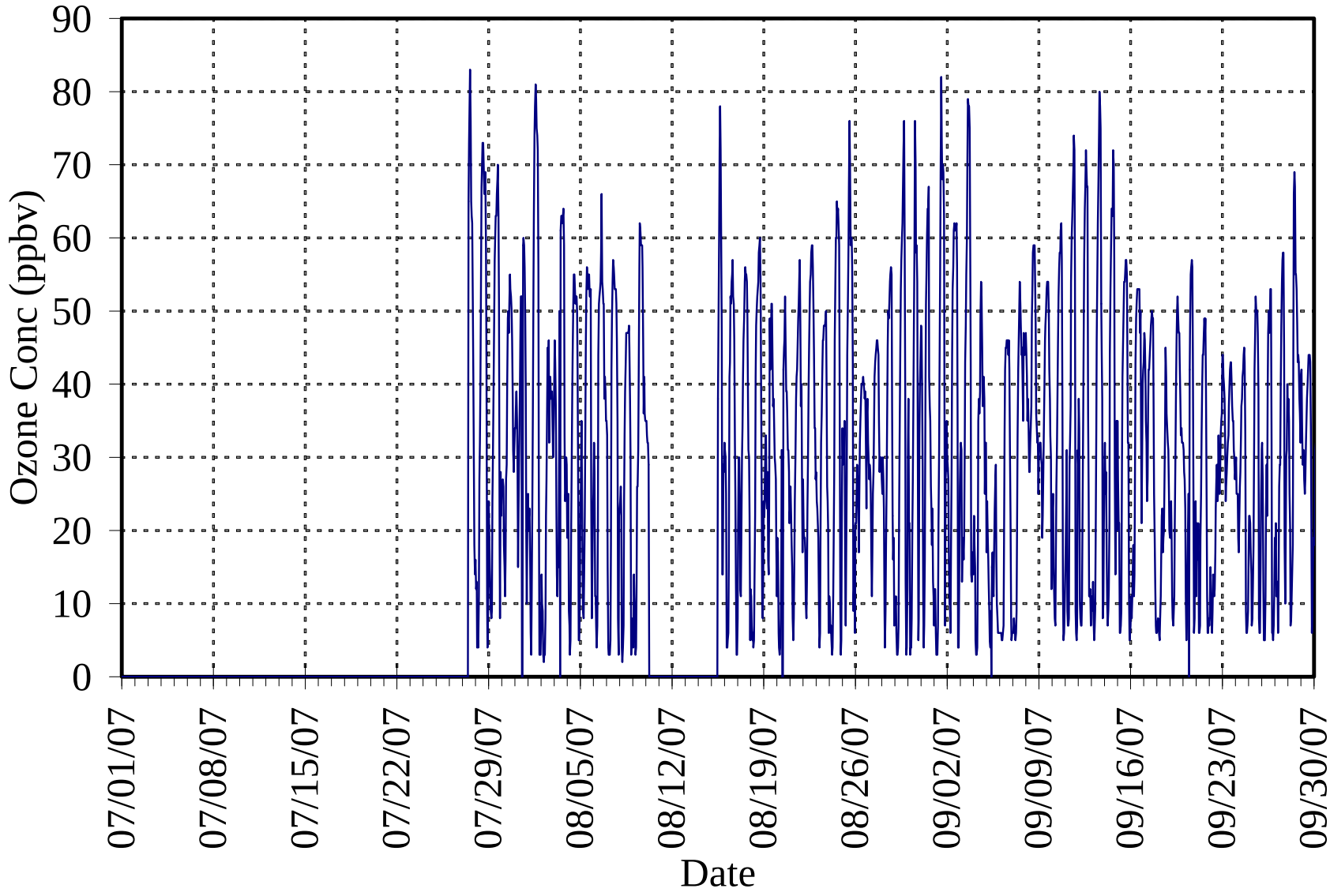

Figure 3-4 Times series of O_3 (in ppbv) at St. Lukes

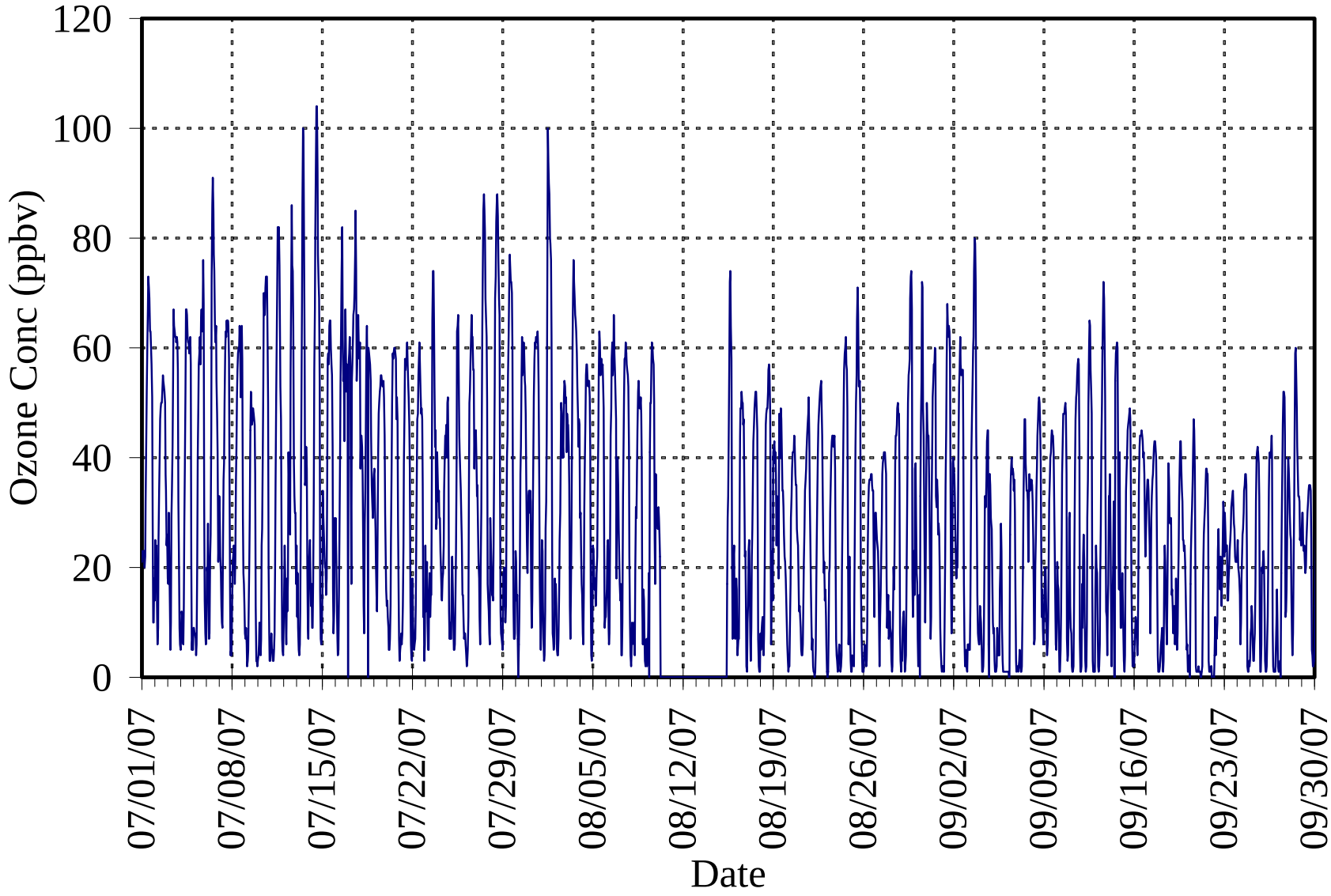

Figure 3-5 Times series of O_3 (in ppbv) at Whitney

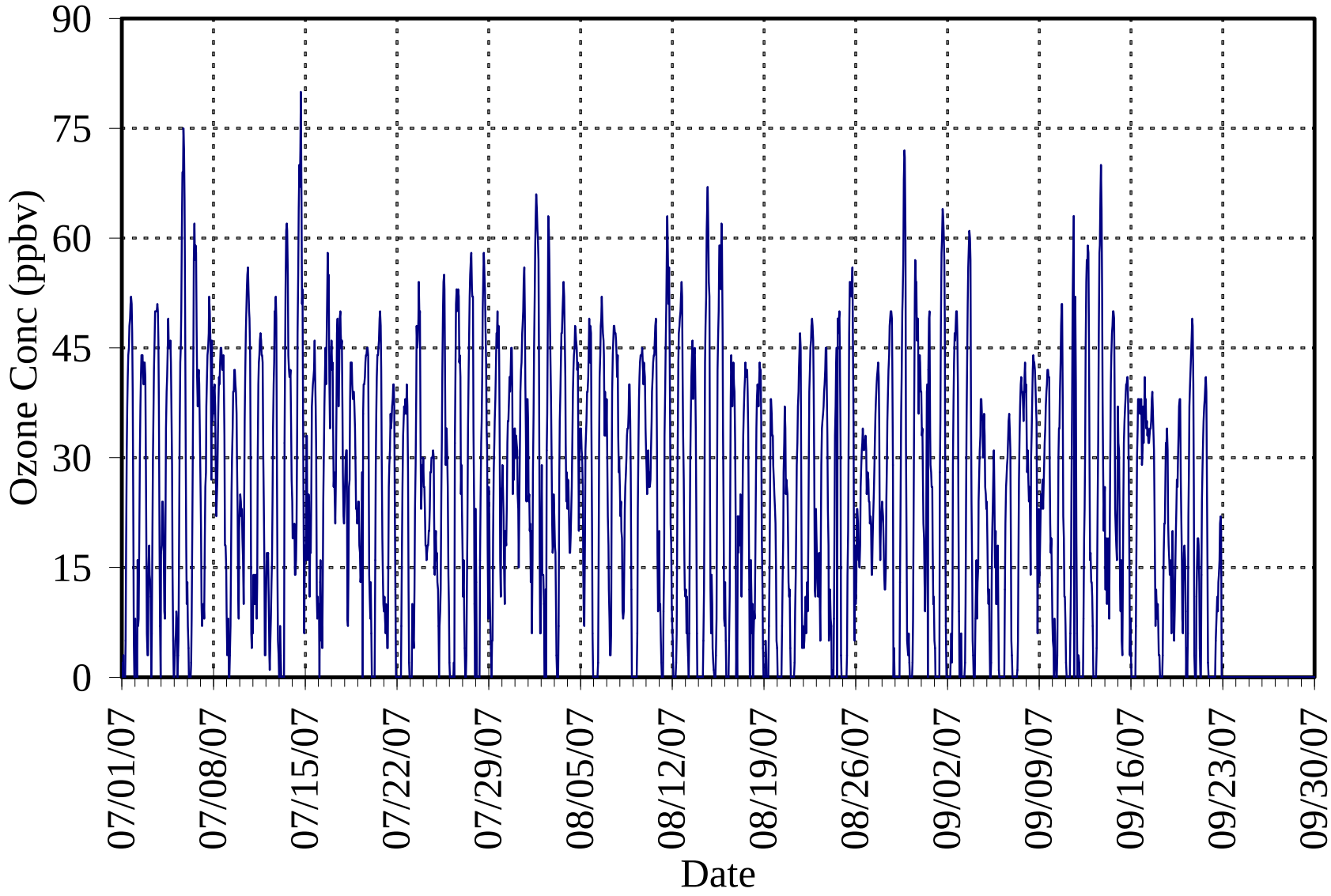

Figure 3-6 Times series of O_3 (in ppbv) at Parma. Non-FRM.

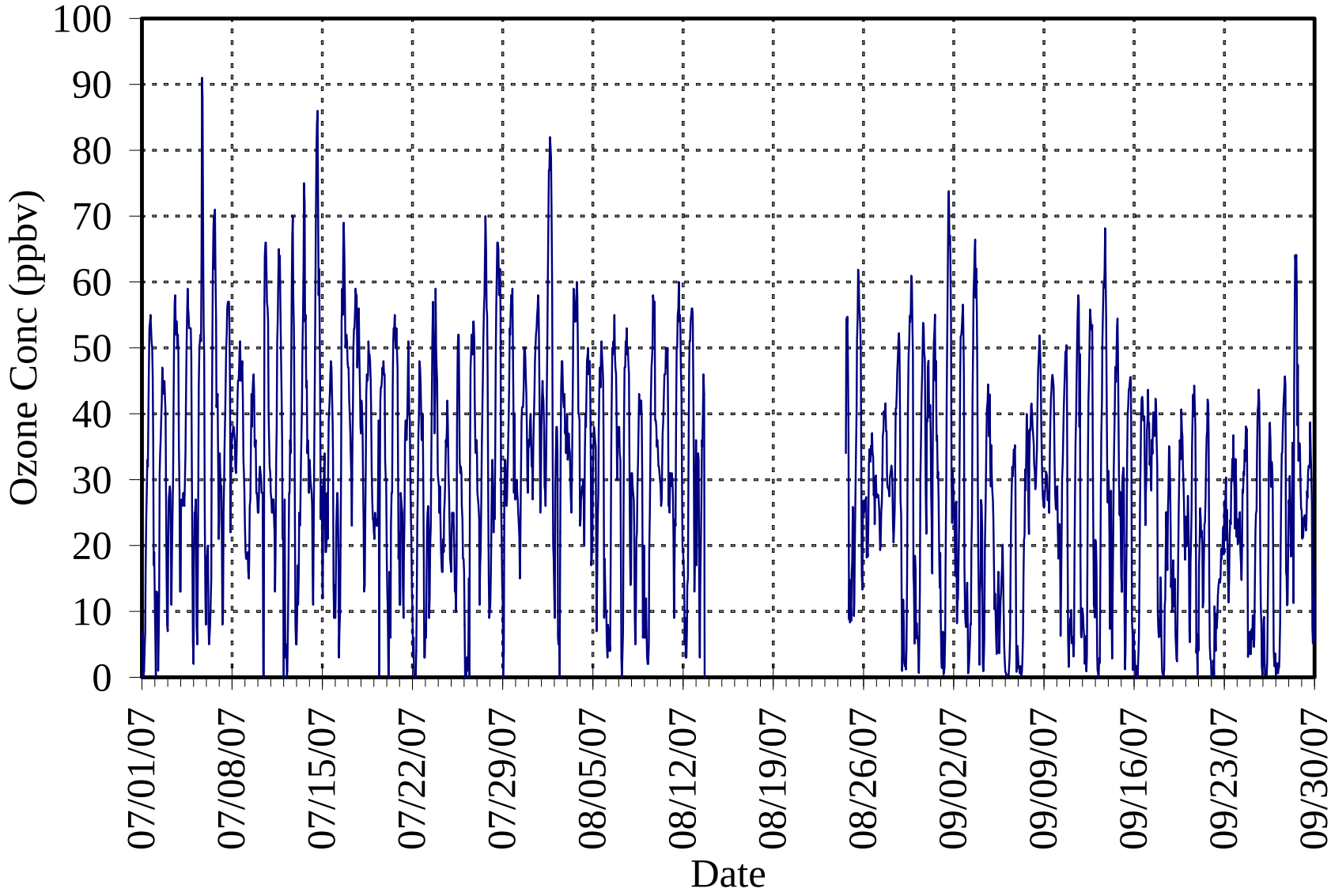

Figure 3-7 Times series of O_3 (in ppbv) at Northwestern Nazarene University at Nampa. Non-FRM.

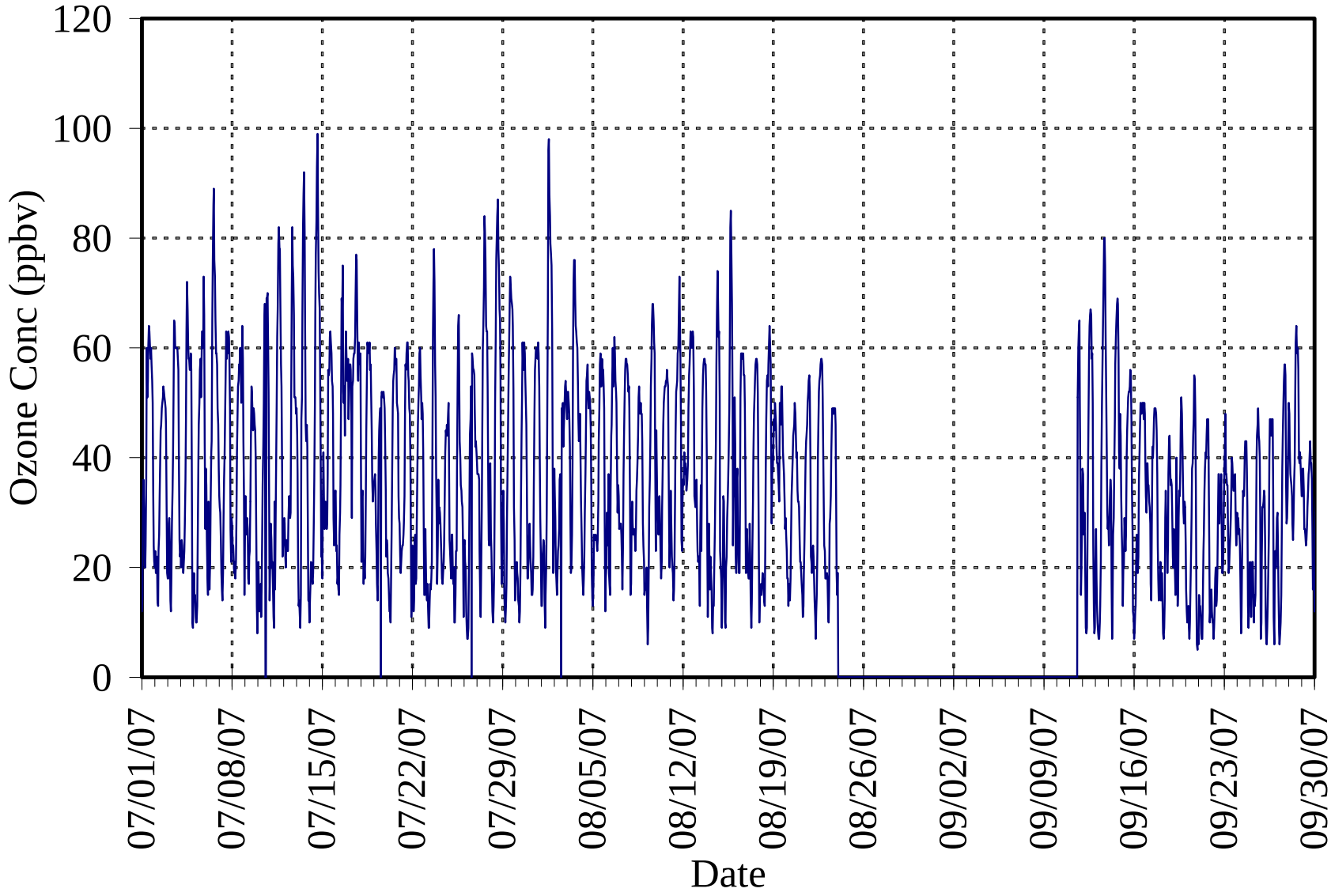

Figure 3-8 Times series of O_3 (in ppbv) at White Pine Elementary School. Non-FRM.

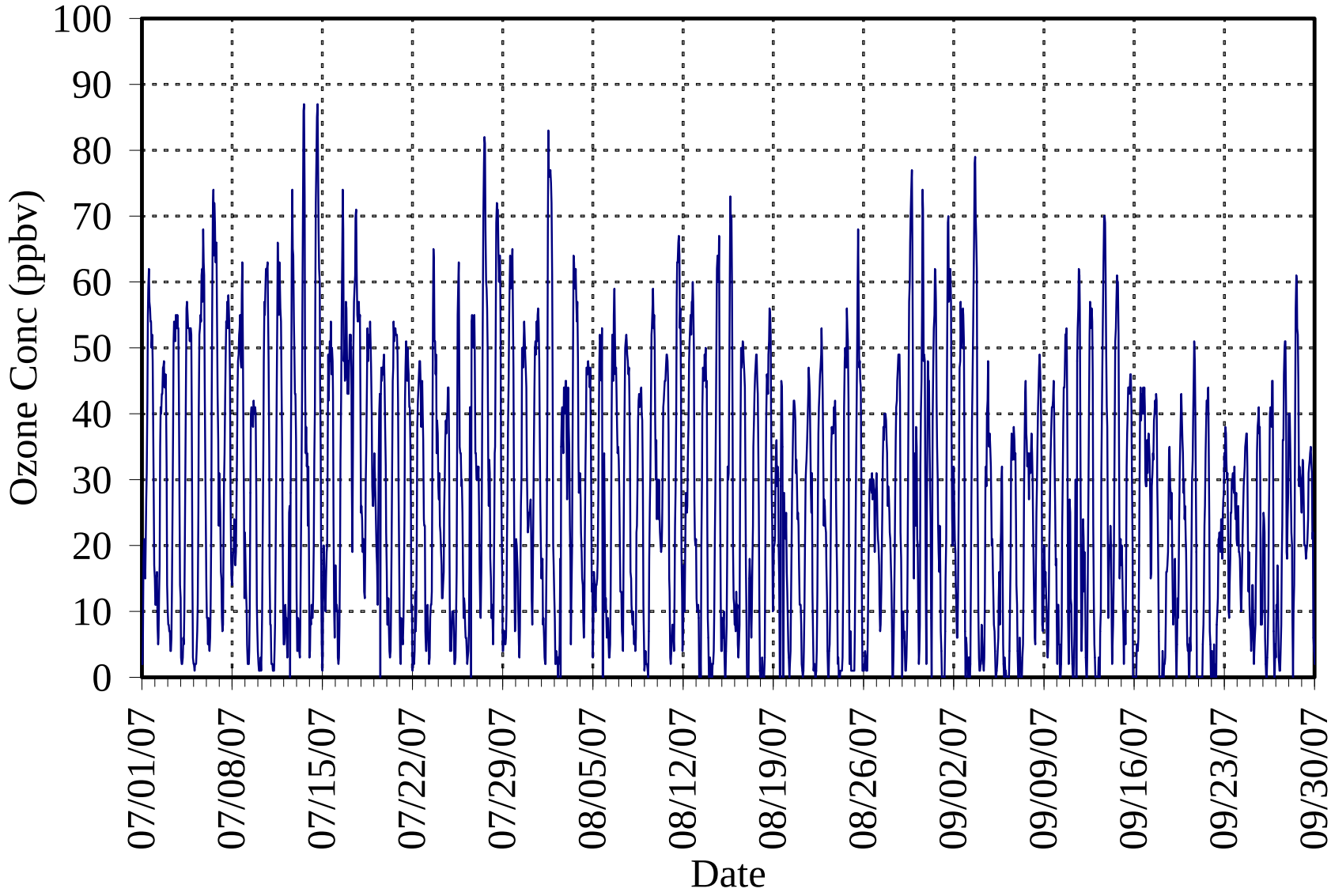

Figure 3-9 Times series of O_3 (in ppbv) at Mountain View Elementary School. Non-FRM.

3.1.2 Volatile organic compounds and nitrogen oxides at ITD and St. Lukes

Table 3-2 and Table 3-3 present the mean, median, standard deviation and 1-hour maximum concentrations of alkanes, alkenes/alkynes, and aromatic hydrocarbons measured at ITD and St. Lukes sites. In total, forty-eight compounds were identified: twenty-two aliphatic saturated hydrocarbons (from propane (C_3H_8) to *n*-decane ($C_{10}H_{22}$)), three cyclic saturated hydrocarbons (cyclopentane, cyclohexane and methyl-cyclohexane), seven *n*-alkenes (from butene to hexene), two alkynes (acetylene and propylene), thirteen aromatic hydrocarbons (from benzene to propylbenzene) and one oxygenate (acetone, co-eluted with xylenes).

Figure 3-10 to Figure 3-15 show the variations of selected alkanes, alkenes and aromatic hydrocarbons at the two locations. The 1-hour mean concentration ranged from 0.1 ppbv (for *n*-decane at St.Lukes) to 93.62 ppbv (for propane at Idaho Transportation Dept). The highest 1-hour concentrations were measured for propane (up to 15.4 ppmv) and acetylene (3.9 ppmv) at ITD. VOCs concentrations followed a log-normal distribution (as it is diagnosed by the difference between mean and median) that was influenced by the high-end outliers, especially for the more volatile compounds (e.g. propane/acetylene). For the vast majority of individual compounds, concentrations of VOCs measured at ITD were up to ten times higher than those measured at St. Lukes. Concentrations of o-xylene data were inconsistent with other aromatic VOCs during the period 7/8 – 7/15 at St. Lukes. Although the integration program correctly found this very large peak at the retention time of o-Xylene, it almost certainly is caused by-co-eluting compound. Further investigation of these days by VOCTEC Inc. may identify the origin of the discrepancy.

Table 3-2 Descriptive statistics of concentrations (in ppbv) of alkanes, alkenes/alkynes and aromatic hydrocarbons measured at ITD

	n	Mean	Median	σ	Max
Alkanes					
Propane	1199	93.62	1.46	715.51	15345.26
n-Butane	1203	5.57	2.57	14.82	248.66
iso-Butane	1184	2.54	1.22	8.51	179.71
n-Pentane/Cyclopentane	804	2.21	1.35	3.97	73.77
cis-2-Butene/*iso*-Pentane	1157	4.33	2.46	7.64	136.94
2,3-Dimethylbutane/*iso*- and *anteiso*-Pentane/Isoprene,	1086	1.24	0.43	3.56	43.41
n-Hexane/Cyclohexane	1146	0.96	0.4	2.25	33.25
2-2-Dimethylbutane/*cis*-2-Pentene	nd				
n-Heptane	963	0.58	0.33	1.42	24.68
2,4-Dimethylpentane	1168	1.29	0.5	4.78	147.96
2,3-Dimethylpentane/i*so*- and *anteiso*-Hexane/ methyl-Cyclohexane	1089	1.47	0.53	3.92	39.32
n-Octane	1021	0.81	0.14	5.38	160.67

	n	Mean	Median	σ	Max
Iso- and *anteiso*-Heptane,	899	0.21	0.09	0.87	19.76
2,2,4-Trimethylpentane	995	0.92	0.42	1.98	43.75
2,3,4-Trimethylpentane	916	0.37	0.11	0.99	12.74
n-Nonane	1075	0.26	0.15	1.03	25.95
n-Decane	476	0.24	0.14	0.41	6.90
Alkenes and Alkynes					
Acetylene	1168	43.27	2.01	251.73	3908.08
Propylene	652	0.77	0.48	1.49	24.88
1-Butene	824	0.62	0.2	2.97	76.61
trans-2-Butene	630	0.69	0.26	2.14	30.38
1-Pentene	740	0.64	0.36	1.77	31.73
trans-2-Pentene	1154	1.45	0.51	4.23	111.75
1-Hexene	968	0.60	0.25	4.16	126.68
Aromatic hydrocarbons					
Benzene	1167	1.13	0.58	2.08	19.91
Toluene	1208	4.15	2.95	5.1	57.11
m- and *p*-Xylene/acetone	1206	3.32	2.94	3.93	90.26
o-Xylene	1213	1.49	1.03	1.74	27.85
1,2,3-Trimethylbenzene	586	0.16	0.08	0.46	7.54
1,2,4-Trimethylbenzene	460	0.17	0.08	0.49	7.68
1,3,5-Trimethylbenzene	650	0.13	0.08	0.35	6.05
Ethylbenzene	1158	0.69	0.25	2.01	55.44
m,p-Diethyltoluene	nd				
Styrene	380	0.11	0.08	0.09	0.96
n-propyl/*iso*-propylbenzene	1096	0.5	0.26	0.83	12.96

Table 3-3 Descriptive statistics of concentrations (in ppbv) of of alkanes, alkenes/alkynes and aromatic hydrocarbons measured at St.Lukes

	n	Mean	Median	σ	Max
Alkanes					
Propane	1360	1.23	0.22	8.04	90.5
n-Butane	1299	1.1	0.43	2.42	37.8
iso-Butane	1287	0.47	0.35	0.78	17.59
n-Pentane/Cyclopentane	1348	0.44	0.21	0.73	9.28
cis-2-Butene/*iso*-Pentane	1326	1.1	0.5	2.04	29.65
2,3-Dimethylbutane/*iso*- and *anteiso*-Pentane/Isoprene,	1211	0.33	0.18	0.44	4.44
n-Hexane/Cyclohexane	1013	0.26	0.14	0.32	3.5
2-2-Dimethylbutane/*cis*-2-Pentene	1315	0.22	0.09	0.53	9.73
n-Heptane	1389	0.11	0.09	0.14	2.25
2,4-Dimethylpentane	1101	0.14	0.06	0.27	4.55
2,3-Dimethylpentane/i*so*- and *anteiso*-Hexane/	1256	0.33	0.15	0.48	5.03

	n	Mean	Median	σ	Max
methyl-Cyclohexane					
n-Octane	1100	0.15	0.03	1.1	33.96
Iso- and *anteiso*-Heptane,	1323	0.19	0.04	0.59	11.77
2,2,4-Trimethylpentane	1113	0.67	0.08	2.18	25.72
2,3,4-Trimethylpentane	1303	0.2	0.05	1.2	31.25
n-Nonane	959	0.17	0.04	1.18	34.02
n-Decane	657	0.1	0.06	0.11	1.4
Alkenes and Alkynes					
Acetylene	1236	2.85	0.38	19.75	331.15
Propylene	1341	0.49	0.36	0.59	10.78
1-Butene	1186	0.24	0.07	1.08	27.86
trans-2-Butene	1277	0.18	0.06	0.68	15.08
1-Pentene	1120	0.2	0.05	0.7	15.08
trans-2-Pentene	1137	0.17	0.08	0.37	7.59
1-Hexene	967	0.05	0.02	0.21	5.38
Aromatic hydrocarbons					
Benzene	1355	0.30	0.18	0.36	4.92
Toluene	1379	0.93	0.57	1.24	23.17
m- and *p*-Xylene/acetone	1392	0.79	0.63	0.66	7.62
o-Xylene	1363	0.55	0.2	1.26	16.76
1,2,3-Trimethylbenzene	nd				
1,2,4-Trimethylbenzene	841	0.13	0.04	0.48	3.71
1,3,5-Trimethylbenzene	840	0.25	0.05	0.76	5.18
Ethylbenzene	1212	0.24	0.1	1.02	25.05
m,p-Diethyltoluene	789	0.31	0.11	1.89	51.22
Styrene	1054	0.22	0.04	1.77	45.86
n-propyl/*iso*-propylbenzene	1239	0.14	0.08	0.23	4.2

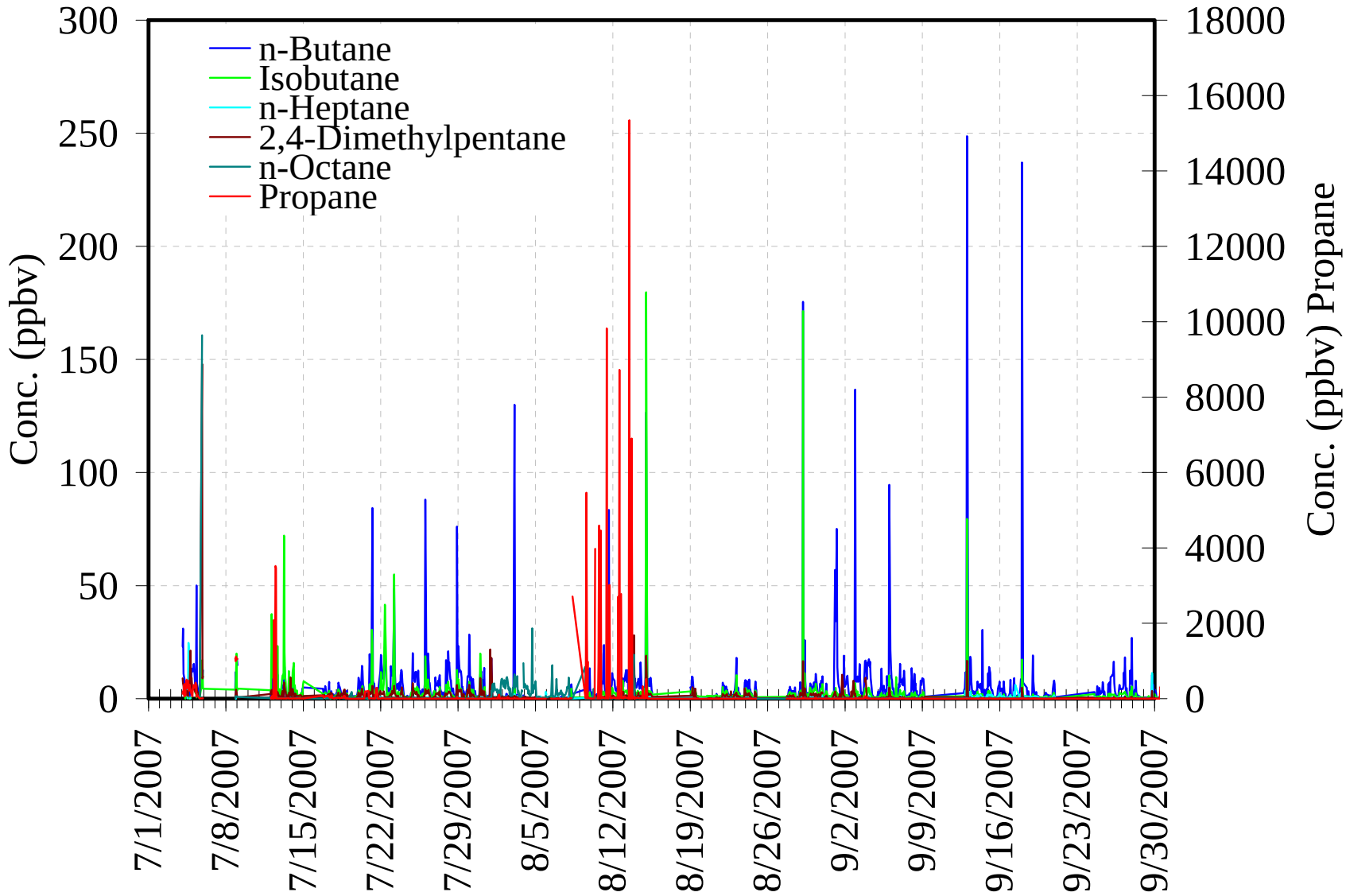

Figure 3-10 Times series of alkanes (in ppbv) at ITD

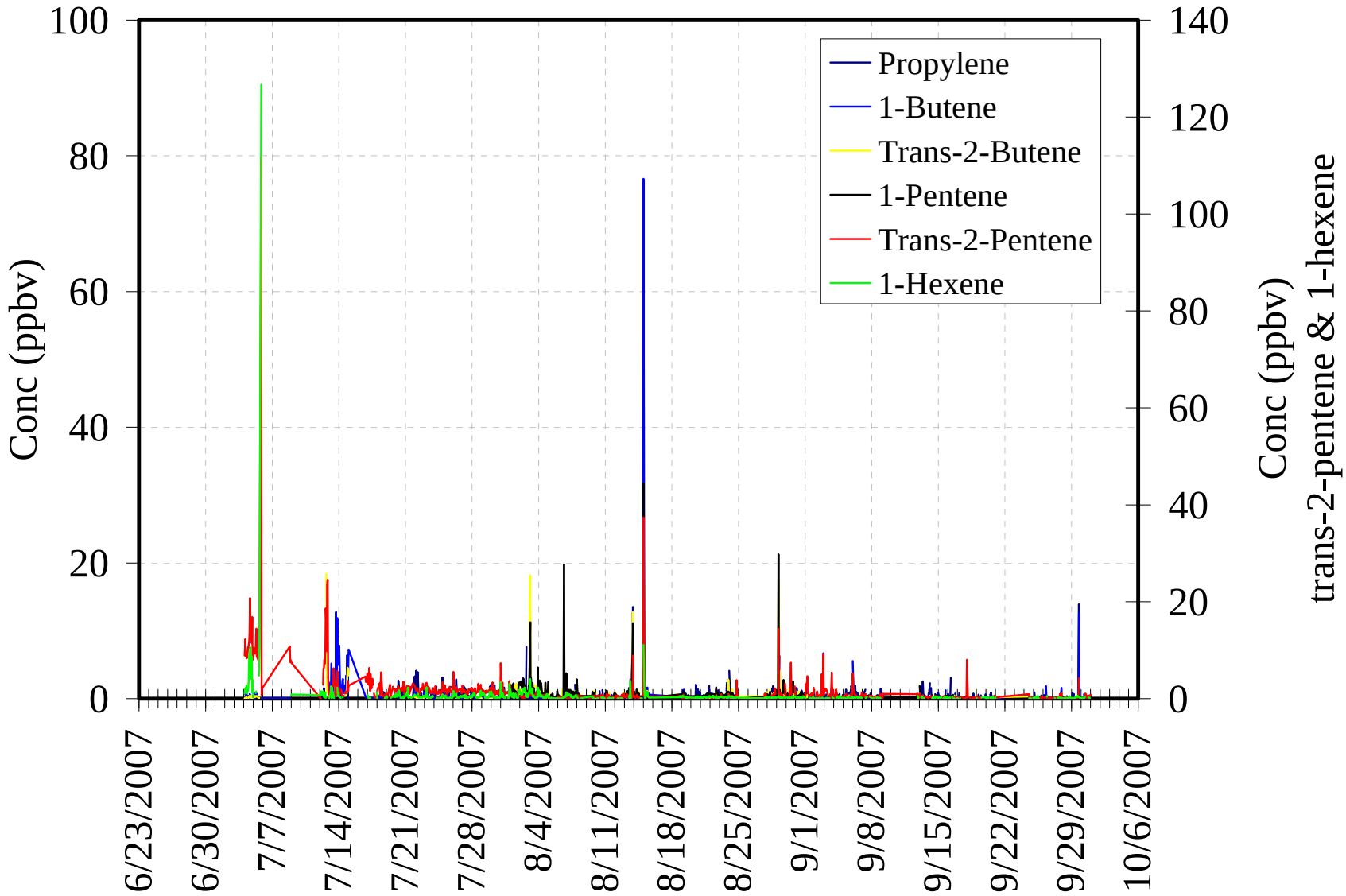

Figure 3-11 Times series of *n*-alkenes (in ppbv) at ITD

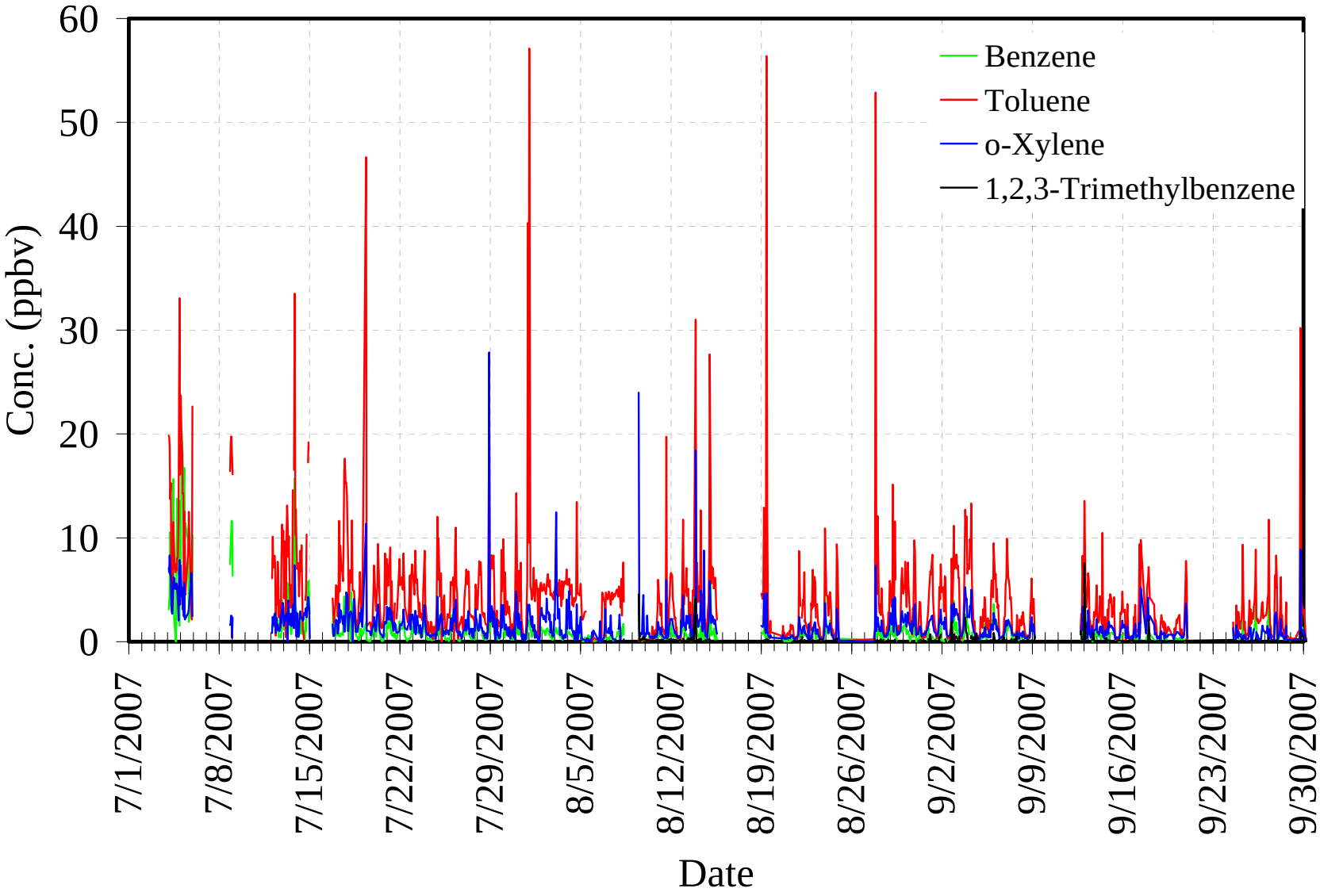

Figure 3-12 Times series of aromatic hydrocarbons (in ppbv) at ITD

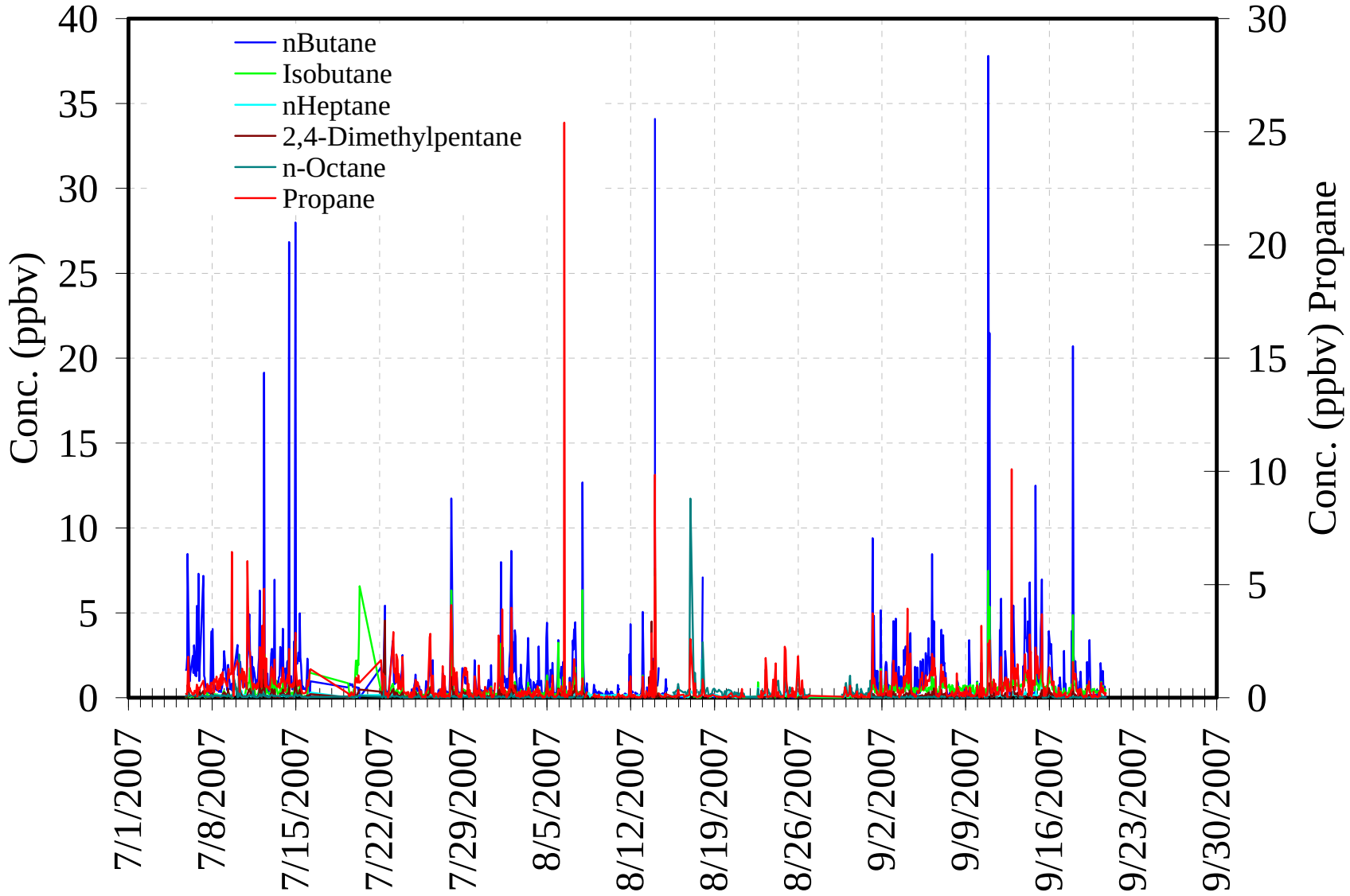

Figure 3-13 Times series of alkanes (in ppbv) at St. Lukes

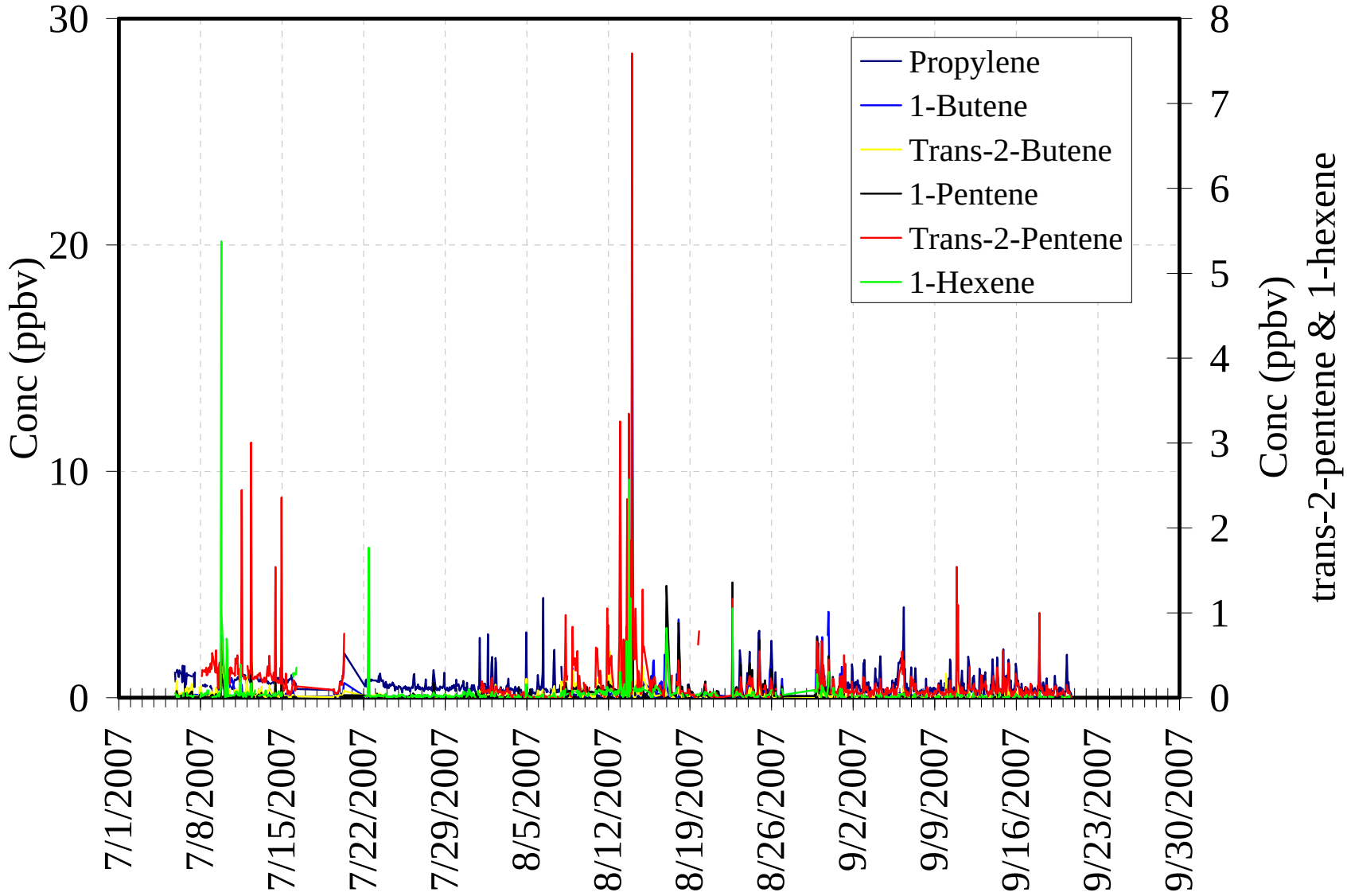

Figure 3-14 Times series of *n*-alkenes (in ppbv) at St. Lukes

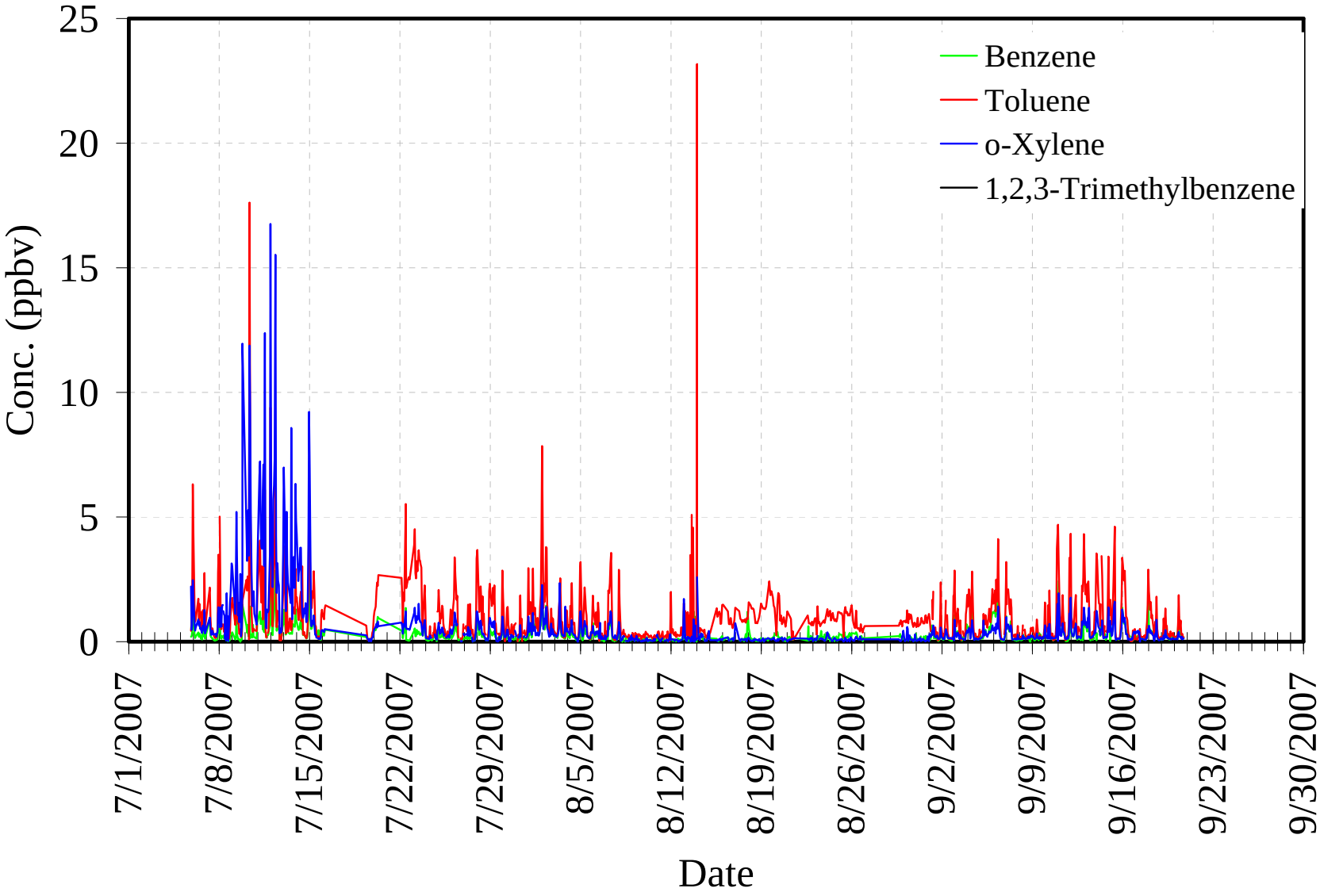

Figure 3-15 Times series of aromatic hydrocarbons (in ppbv) at St. Lukes

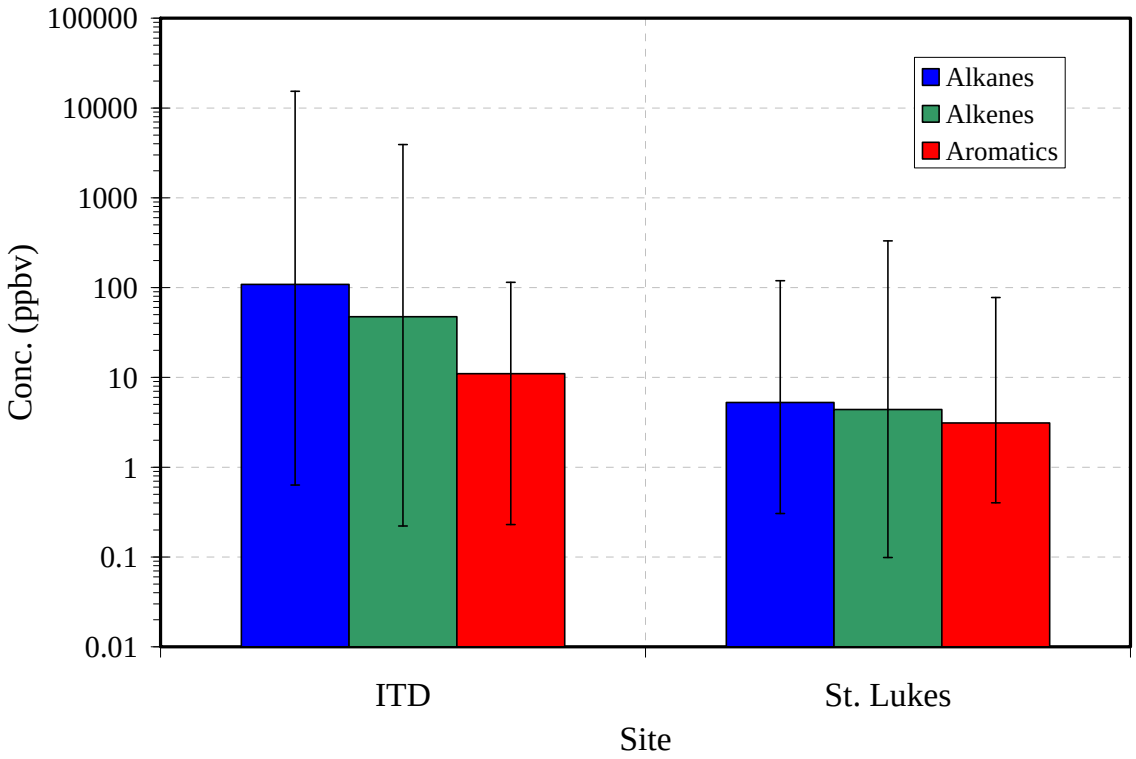

Figure 3-16 Median concentrations of alkanes, alkenes and aromatic hydrocarbons measured at St. Lukes and ITD for the monitoring period

The median concentration of each compound group is illustrated in Figure 3-16. Note that the scale in the concentration axis (y-axis) is logarithmic. Alkanes and alkenes were the predominant compound classes at ITD representing on average about 95% of VOCs (108.6 ppbv for alkanes and 47.3. ppbv for alkenes). Aromatic hydrocarbons accounted for about 13.0 ppbv at ITD. A different pattern was observed at St. Lukes. The concentrations of the three compound classes were comparable (5.3 ppbv for alkanes, 4.4 ppbv for alkenes and 3.1 ppbv for aromatic hydrocarbons). The relative contributions of each compound group represent a conservative estimate since other compounds such as ethane, ethene and monoterpenes were not identified by PFGC.

3.1.3 Nitrogen oxides at ITD and St. Lukes sites

Table 3-4 shows the descriptive statistics of hourly NO and NO_2 concentrations at the ITD and St. Lukes sites. The variation of nitrogen oxides is also depicted in Figure 3-17 and Figure 3-18. Nitrogen oxides were measured during August and September, 2007. At ITD, NO levels varied from a few ppbv to 92 ppbv with an average of 10 ppbv, while NO_2 concentrations ranged from 0 to 30 pppbv with a mean value of 4 ppbv. Higher NO and NO_2 levels were measured in September as compared to August. For St. Lukes, NO concentrations were as high as 192 ppbv with a mean value of 18 ppbv, while no detectable amounts of NO_2 were observed. With the exception of high NO concentrations in late July, daily NO levels did not vary significantly over the monitoring period.

Table 3-4 Descriptive statistics of hourly NO and NO_2 concentrations (in ppbv) at ITD and St. Lukes

	n	Mean	Median	σ	Max
ITD					
NO	1466	10	7	10	92
NO_2	1466	4	2	4	30
St. Lukes					
NO	1162	18	10	20	192
NO_2	Not detected				

The daily variation of NO and NO_2 at the two sites is plotted in Figure 3-19. The patterns are characterized by periods of two-three days with 24-hr NO concentrations higher than 20 ppbv at St. Lukes followed by a drastic decrease to 2-5 ppbv for a couple of days from the beginning of August till mid-September. Similar patterns were also observed at ITD but NO levels were significantly lower than those measured at St. Lukes. These patterns may be related to weather regimes that favor the formation of temperature inversion layers, resulting in the accumulation of emitted pollutants in the boundary layer. The relationships between nitrogen oxides and local meteorology will be discussed later.

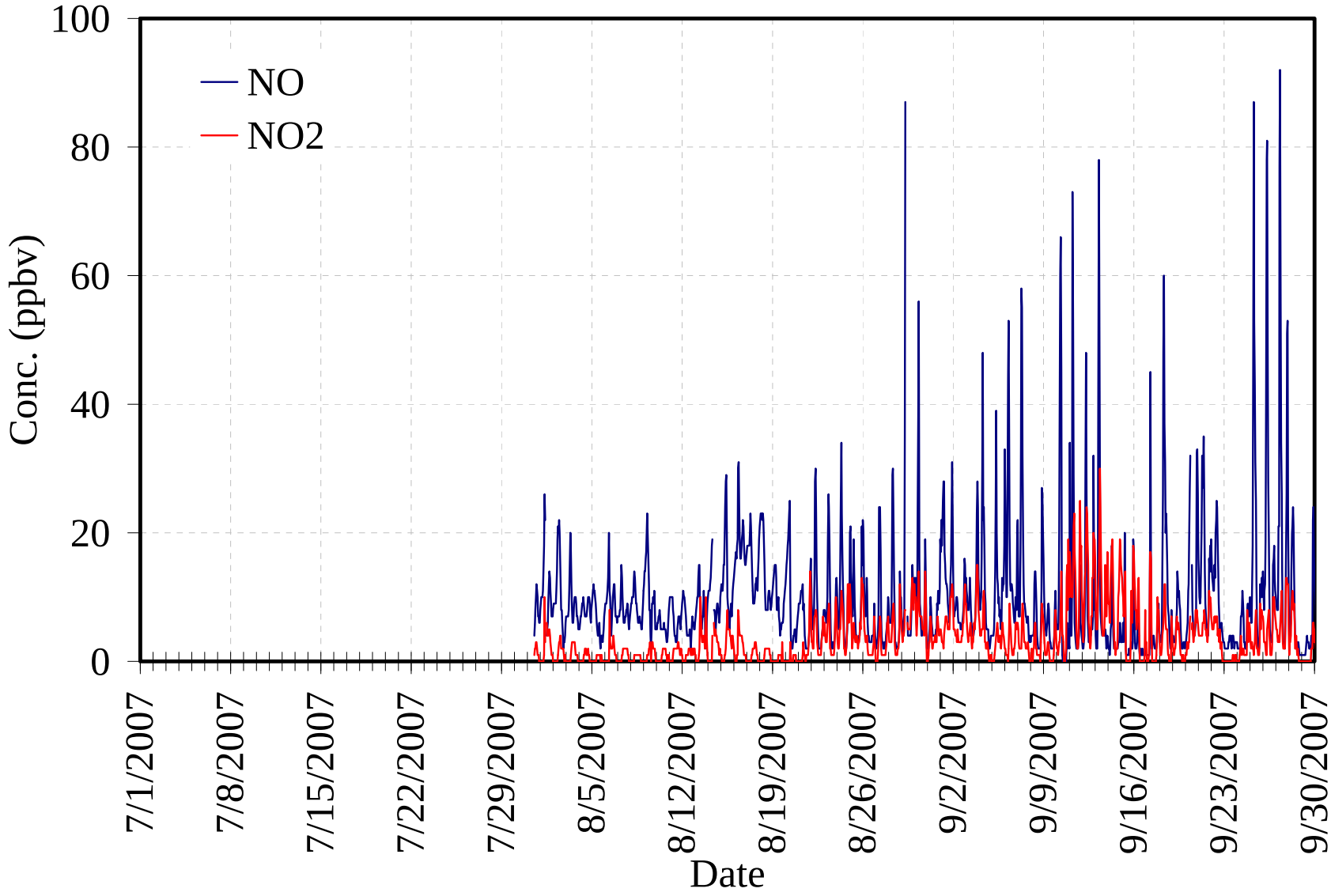

Figure 3-17 Times series of NO and NO_2 (in ppbv) at ITD

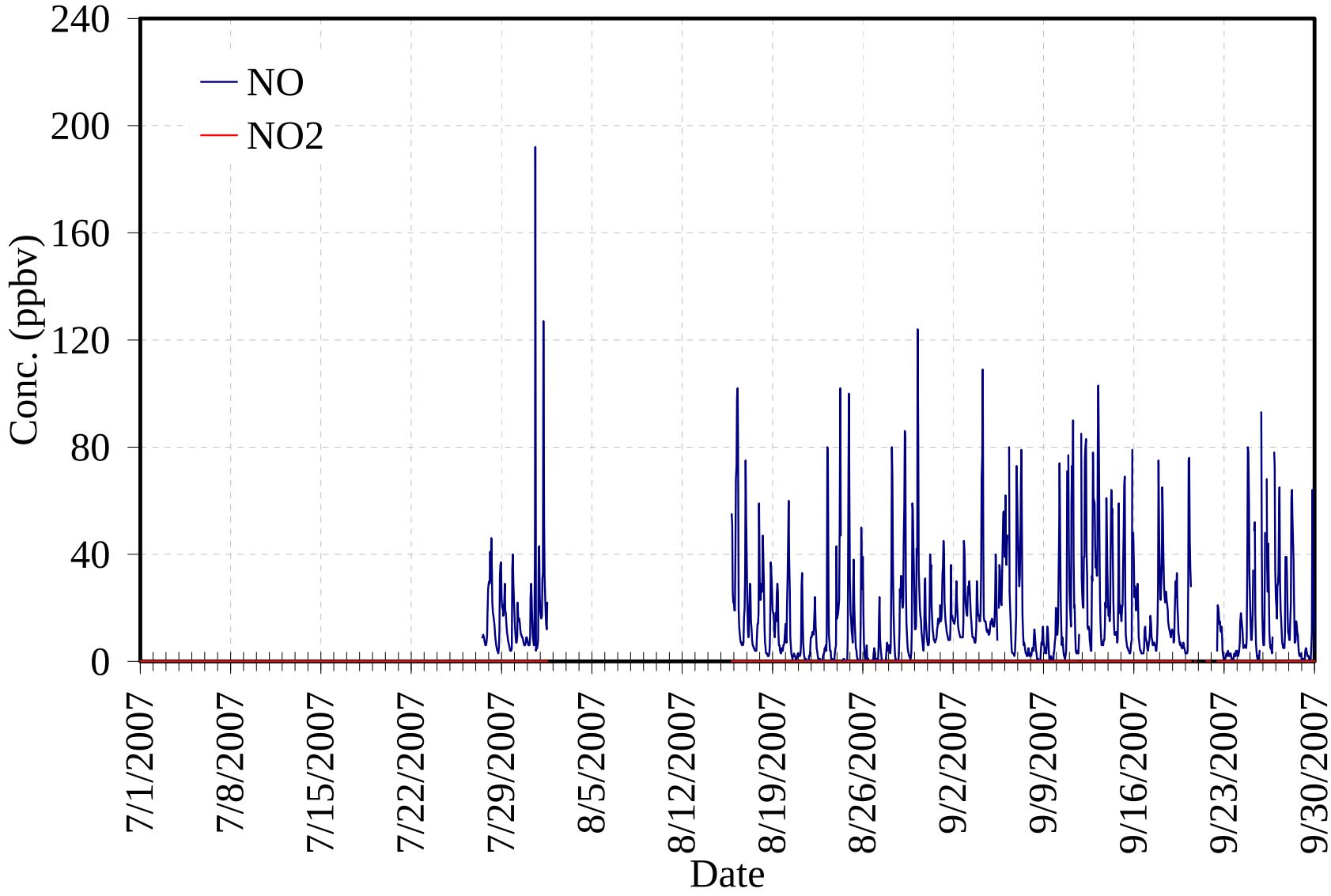

Figure 3-18 Times series of NO and NO_2 (in ppbv) at St. Lukes

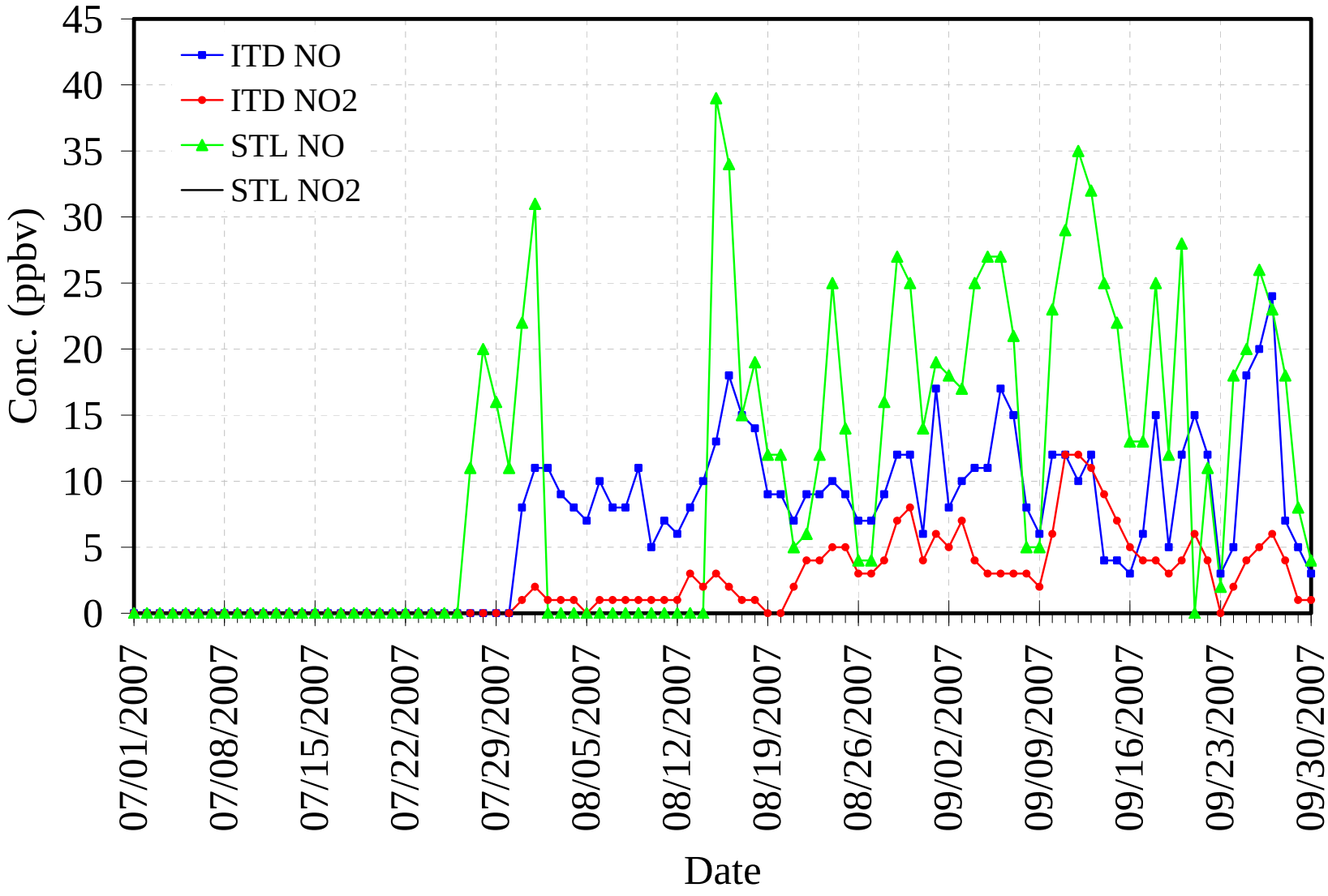

Figure 3-19 Daily NO and NO_2 concentrations at ITD and St. Lukes

3.1.4 Meteorological parameters at Boise and STL

Variations of hourly data for each meteorological parameter are presented in Figure 3-20 through Figure 3-30. Descriptive statistics of hourly data are also presented in Table 3-5. In general, meteorological conditions were described by mild temperatures and relatively humid conditions. Wind conditions were variable with low NW winds in the afternoon (noon to 7:00 pm) and SE winds otherwise. Ambient temperature, relative humidity and barometric pressure did not vary substantially between the two sites.

Table 3-5 Descriptive statistics of hourly meteorological data

	n	Mean	Median	σ	Max
Boise Fairgrounds					
Wind Speed (m s^{-1})	2206	2.1	1.7	1.5	10.0
Temperature (^{o}C)	2197	21.9	21.5	7.7	39.8
Rel. Humidity (%)	2199	41	39	21	96
Solar Radiation (W m^{-2})	2206	206	60	248	775
Pressure (mbar)	2186	920	920	3	934
Warm Springs					
Wind Speed (m s^{-1})	2208	1.5	1.1	1.3	8.8
Temperature (^{o}C)	2200	22.0	21.8	7.9	39.5
Rel. Humidity (%)	2196	48	46	25	96
Solar Radiation (W m^{-2})	2189	208	43	274	937
Pressure (mbar)	2208	919	919	3	932

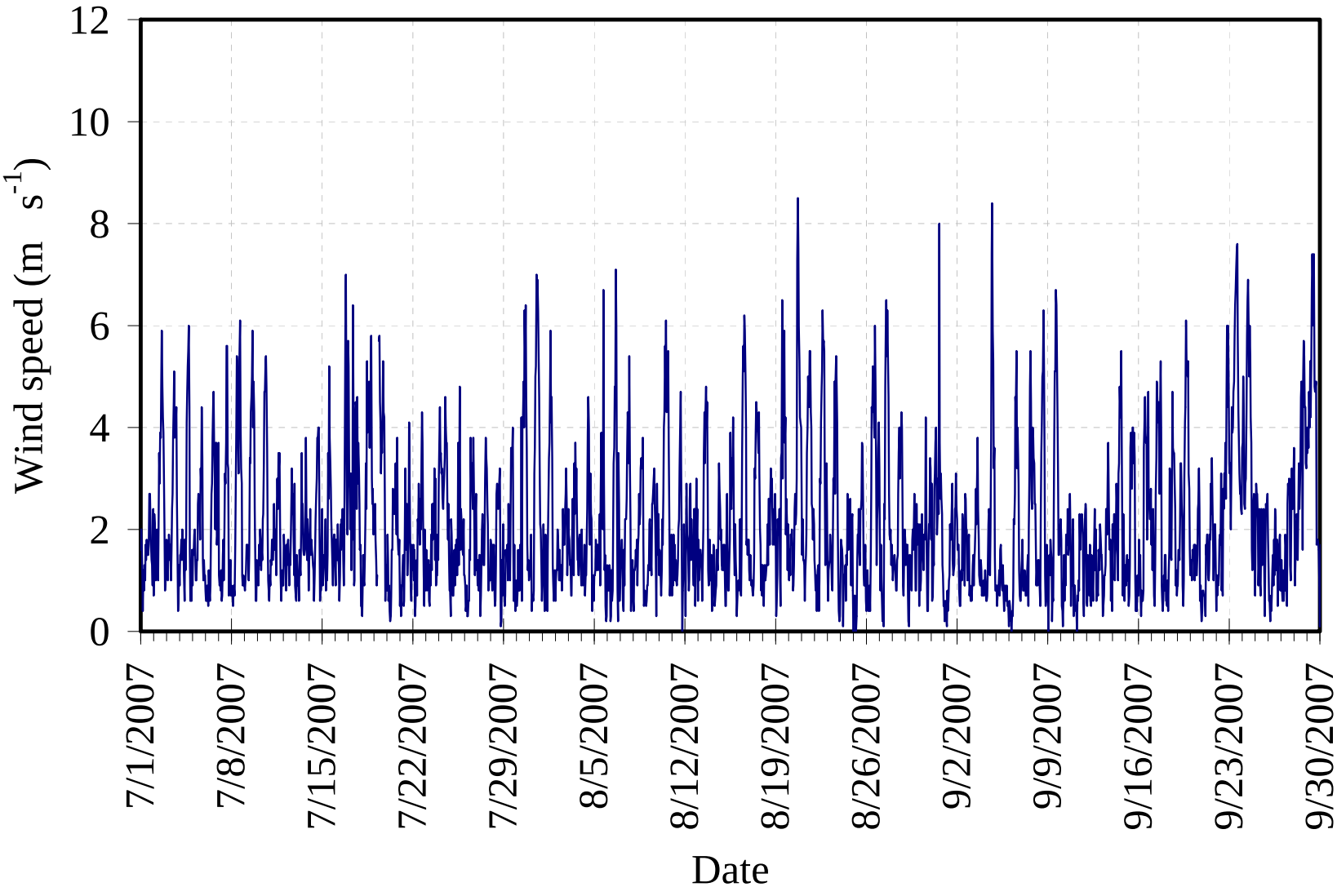

Figure 3-20 Wind speed (in m s^{-1}) at Boise Fairgrounds

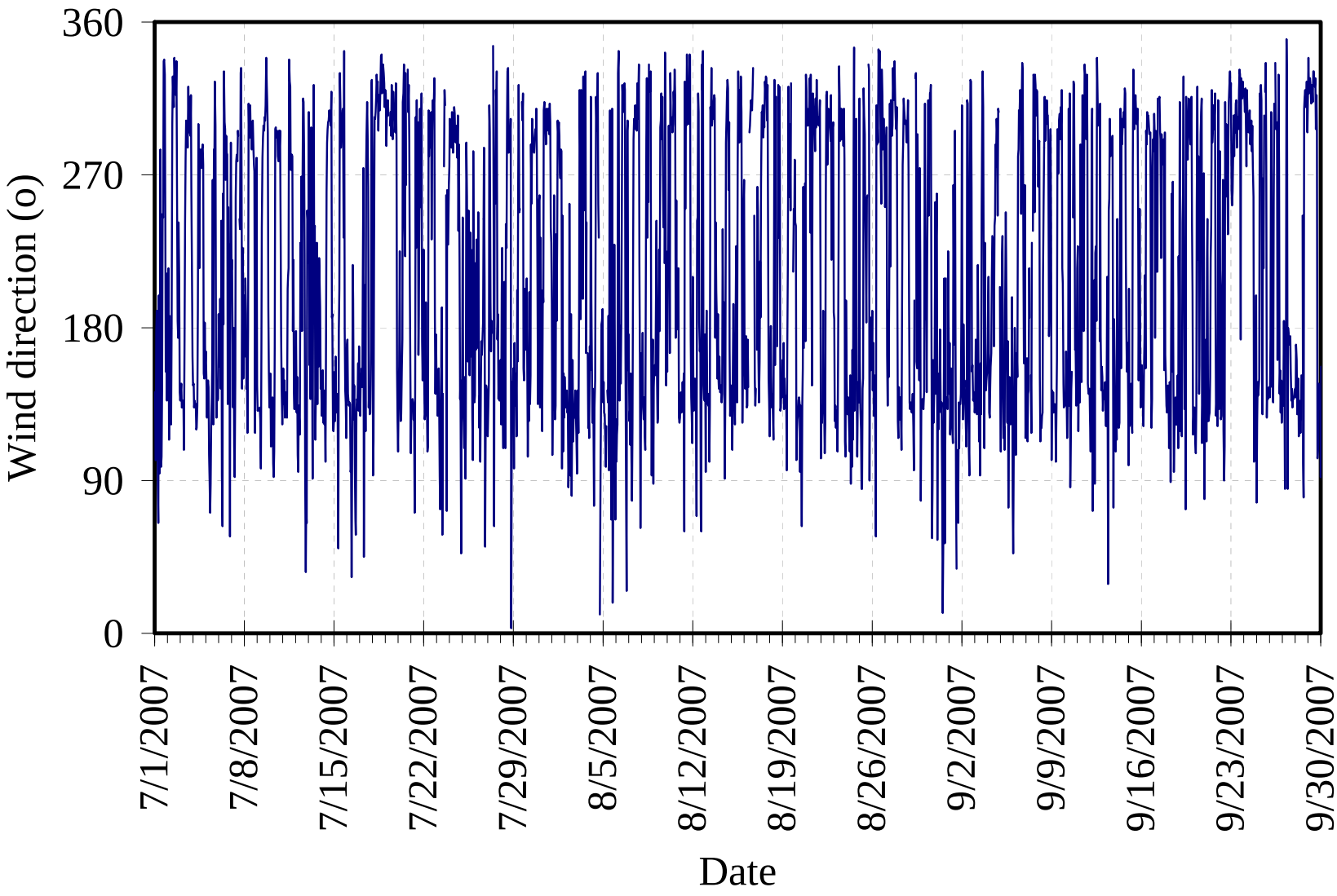

Figure 3-21 Wind direction (in degrees) at Boise Fairgrounds

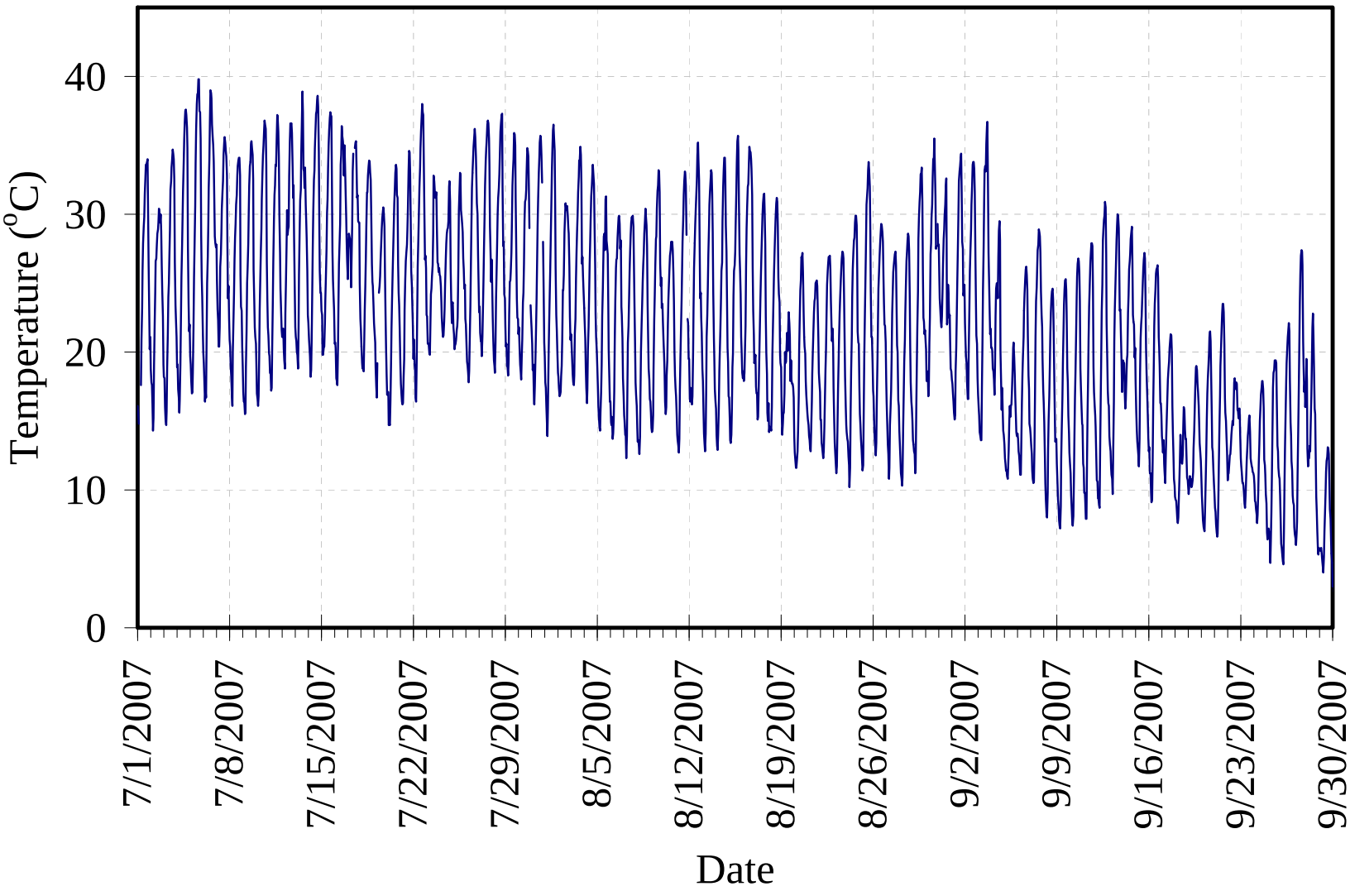

Figure 3-22 Ambient temperature (in °C) at Boise Fairgrounds

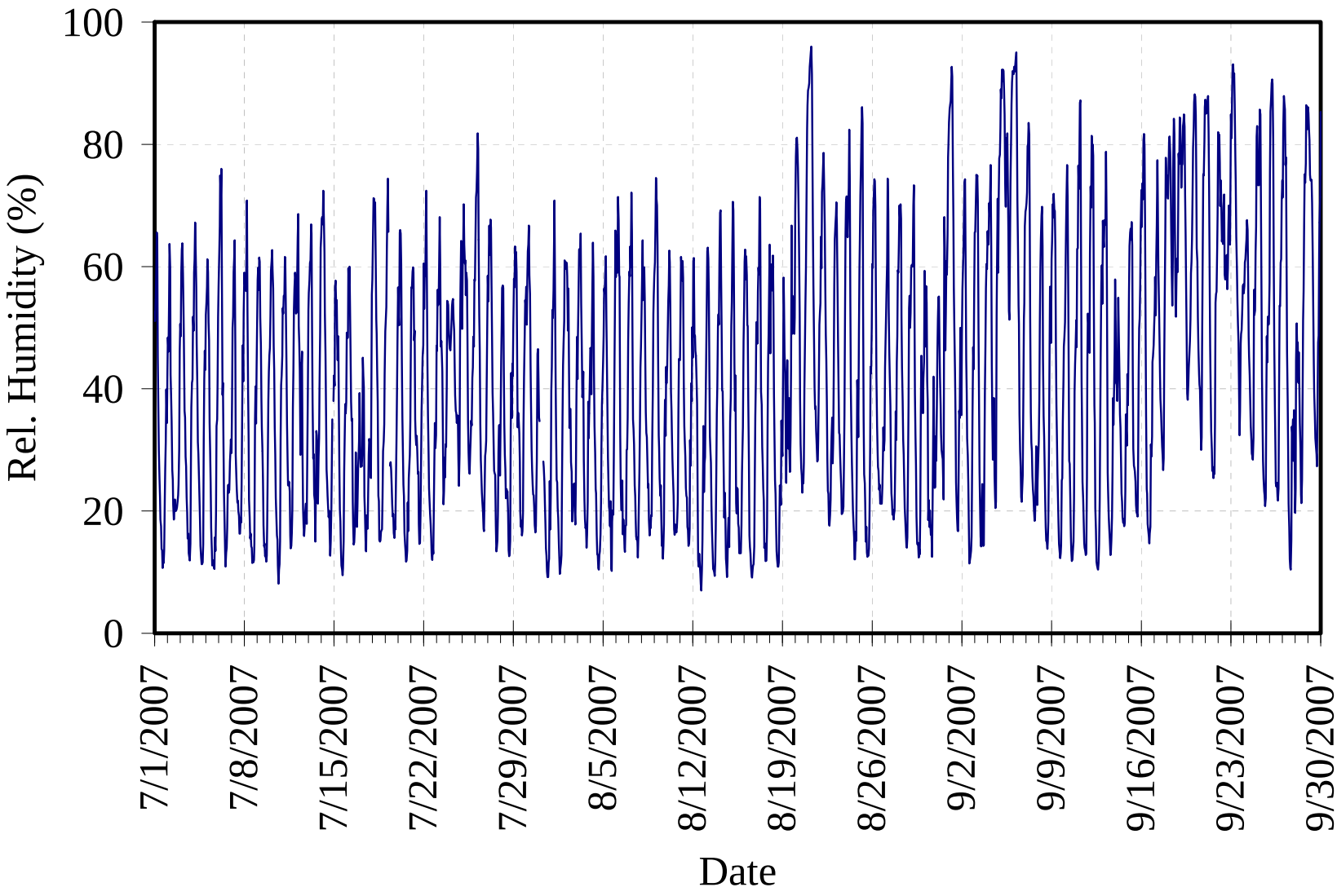

Figure 3-23 Ambient relative humidity (in %) at Boise Fairgrounds

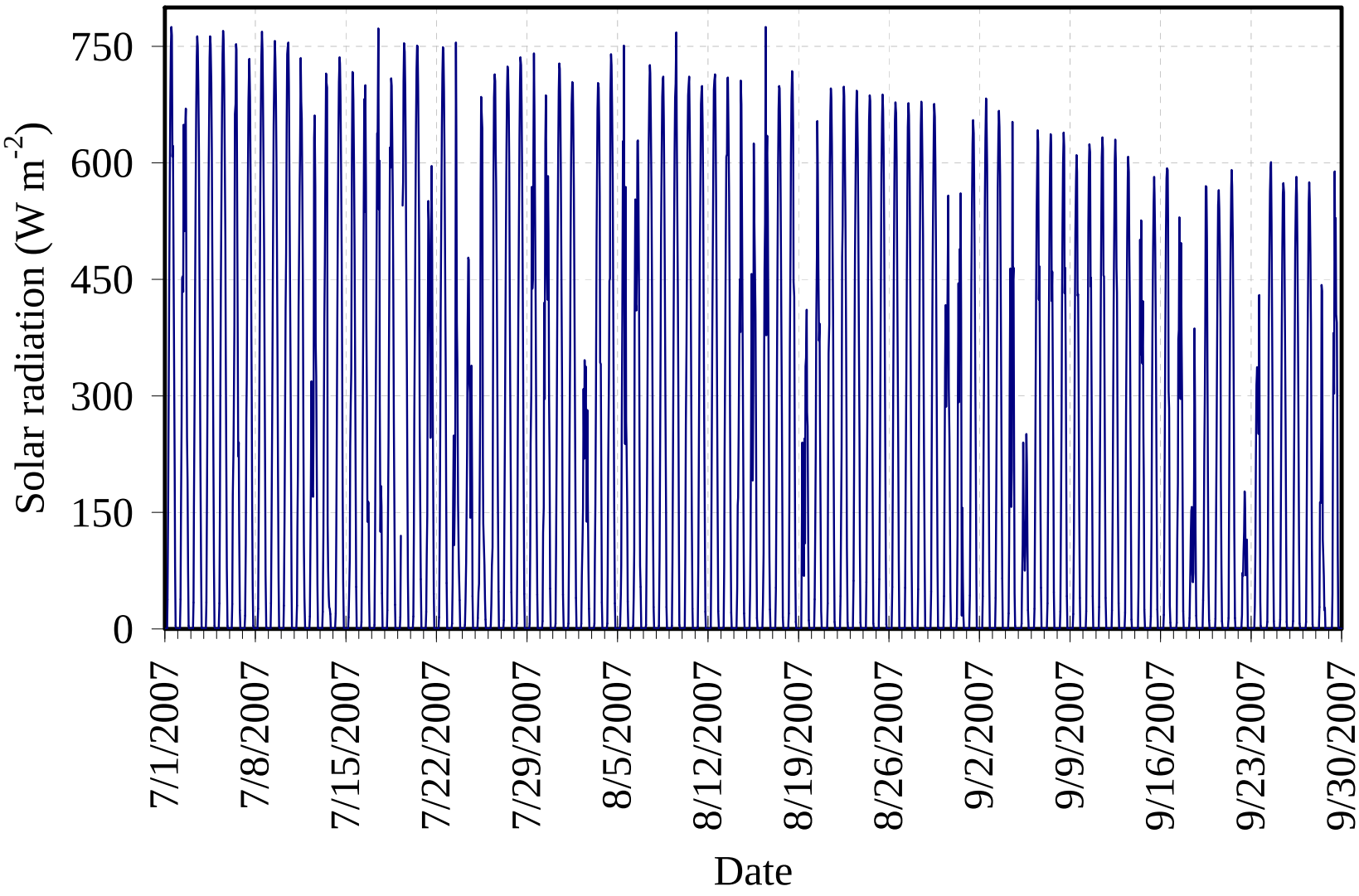

Figure 3-24 Incoming solar radiation (in W m^{-2}) at Boise Fairgrounds

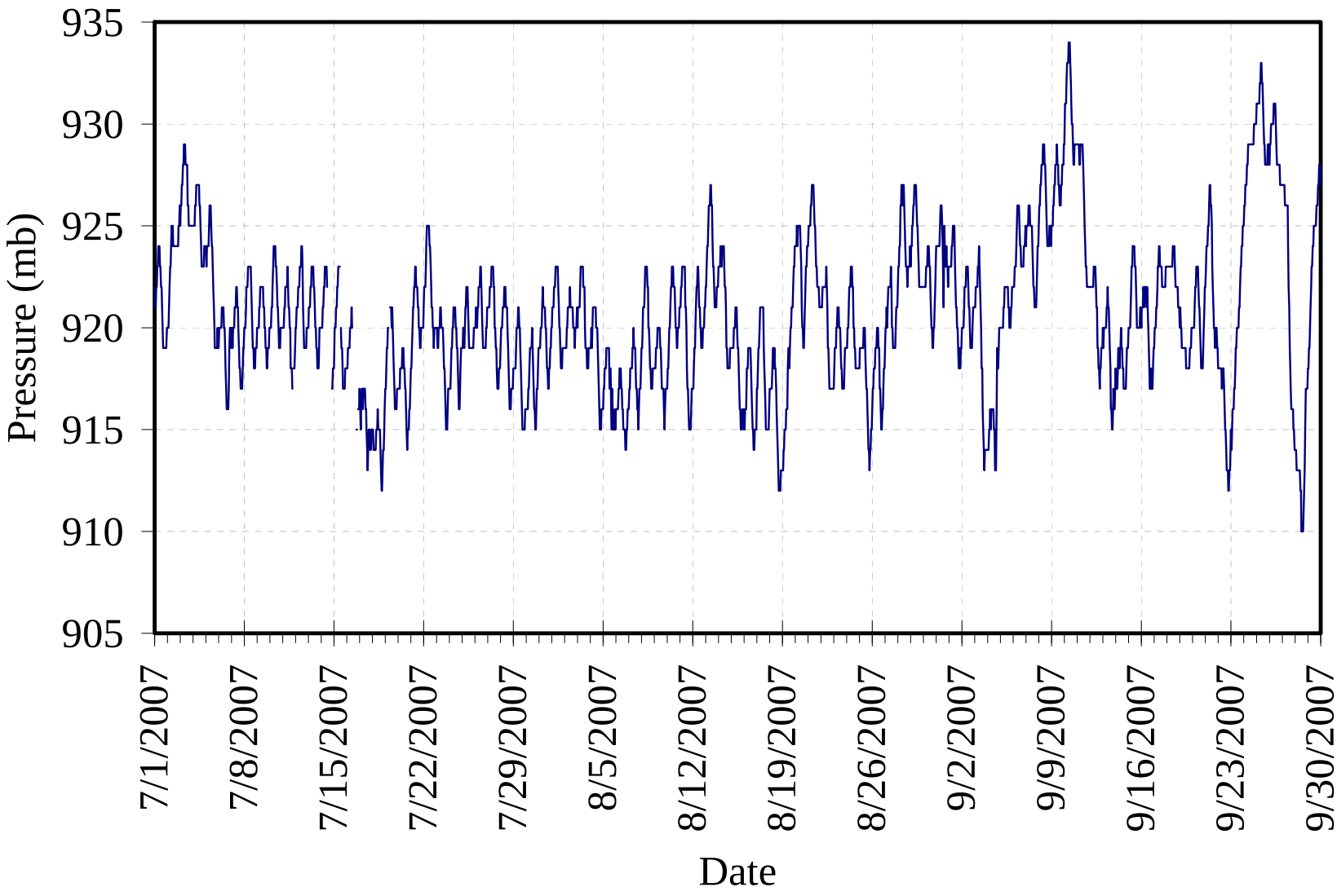

Figure 3-25 Barometric pressure (in mbar) at Boise Fairgrounds

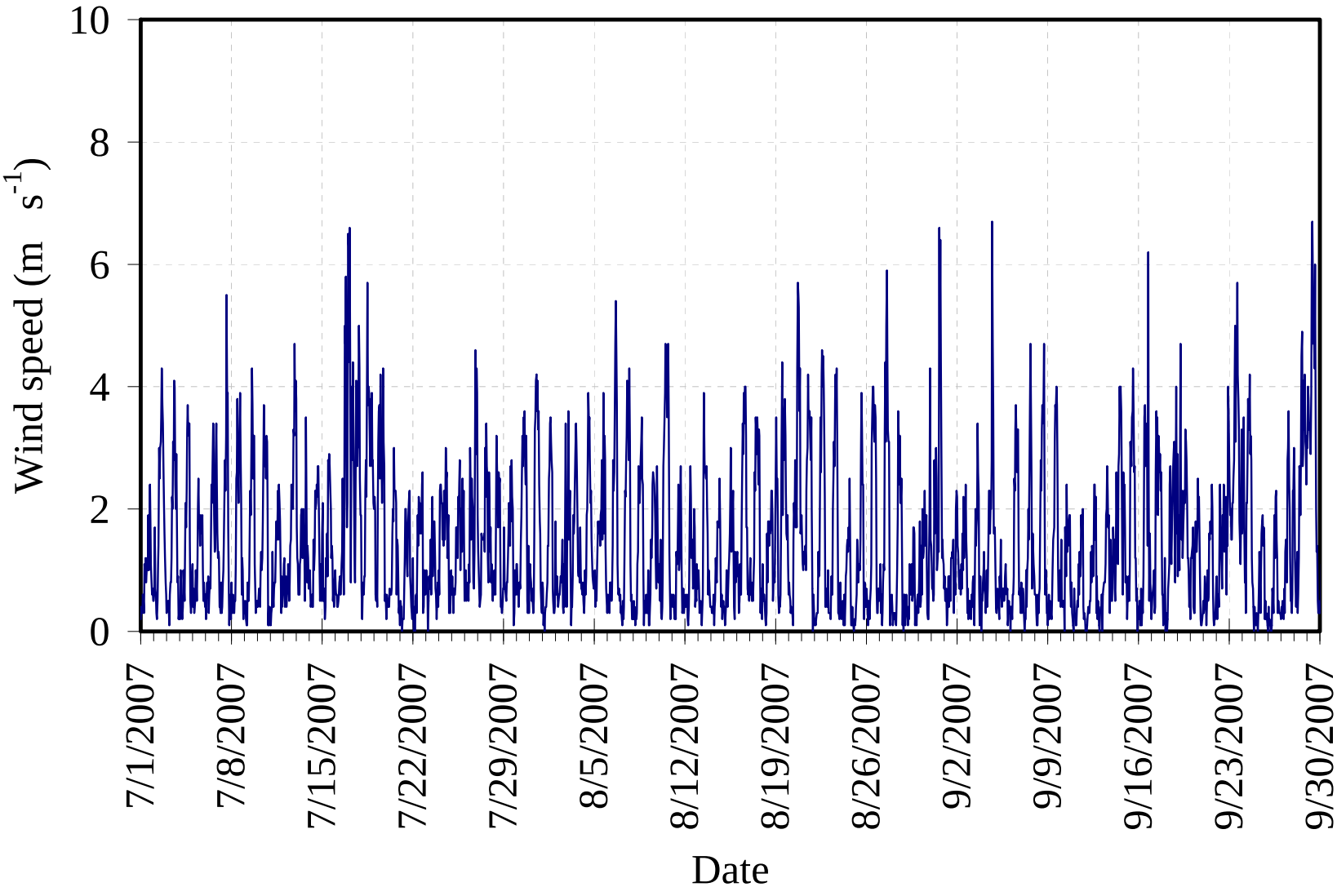

Figure 3-26 Wind speed (in m s^{-1}) at Warm Springs

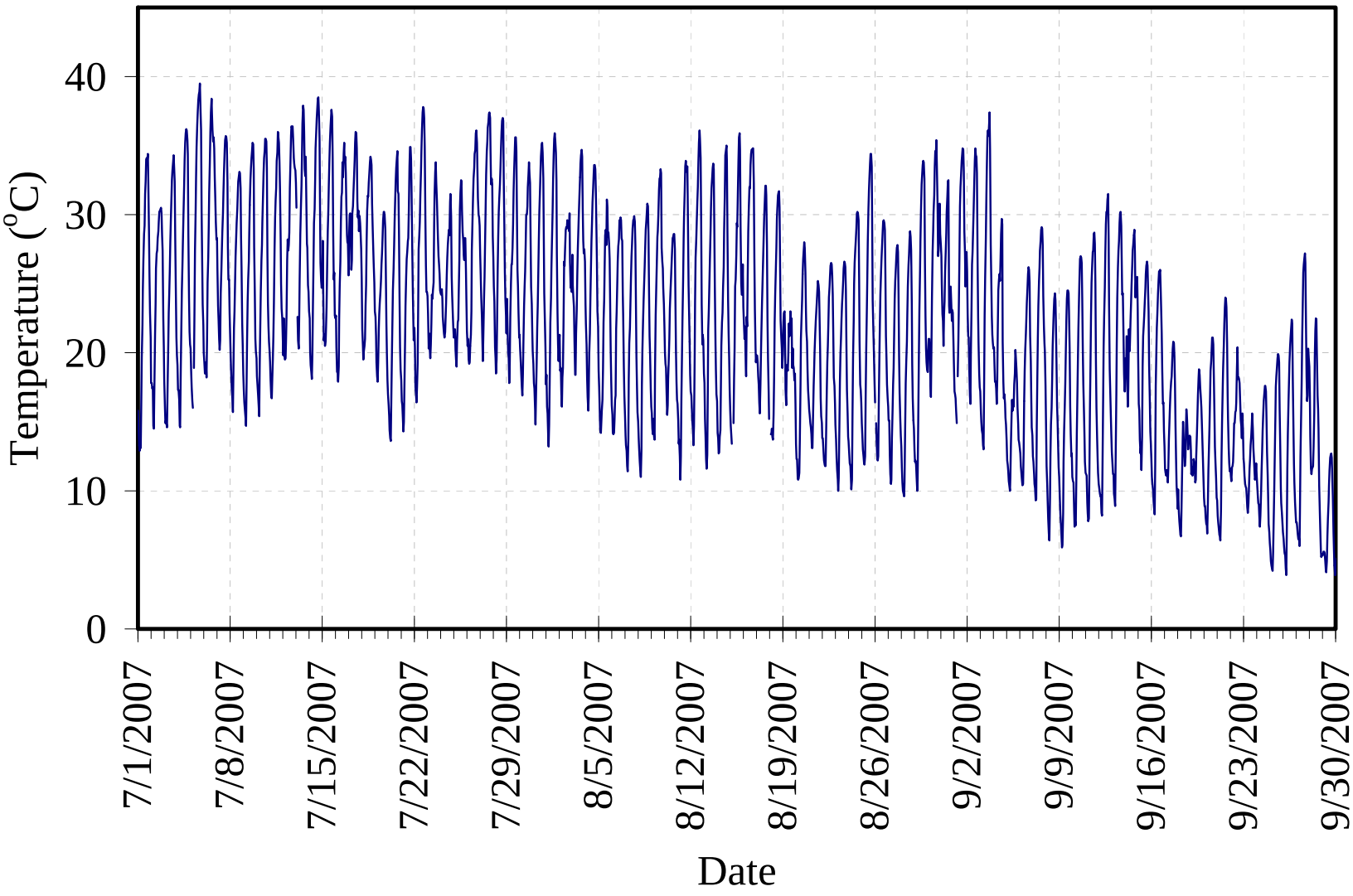

Figure 3-27 Ambient temperature (in °C) at Warm Springs

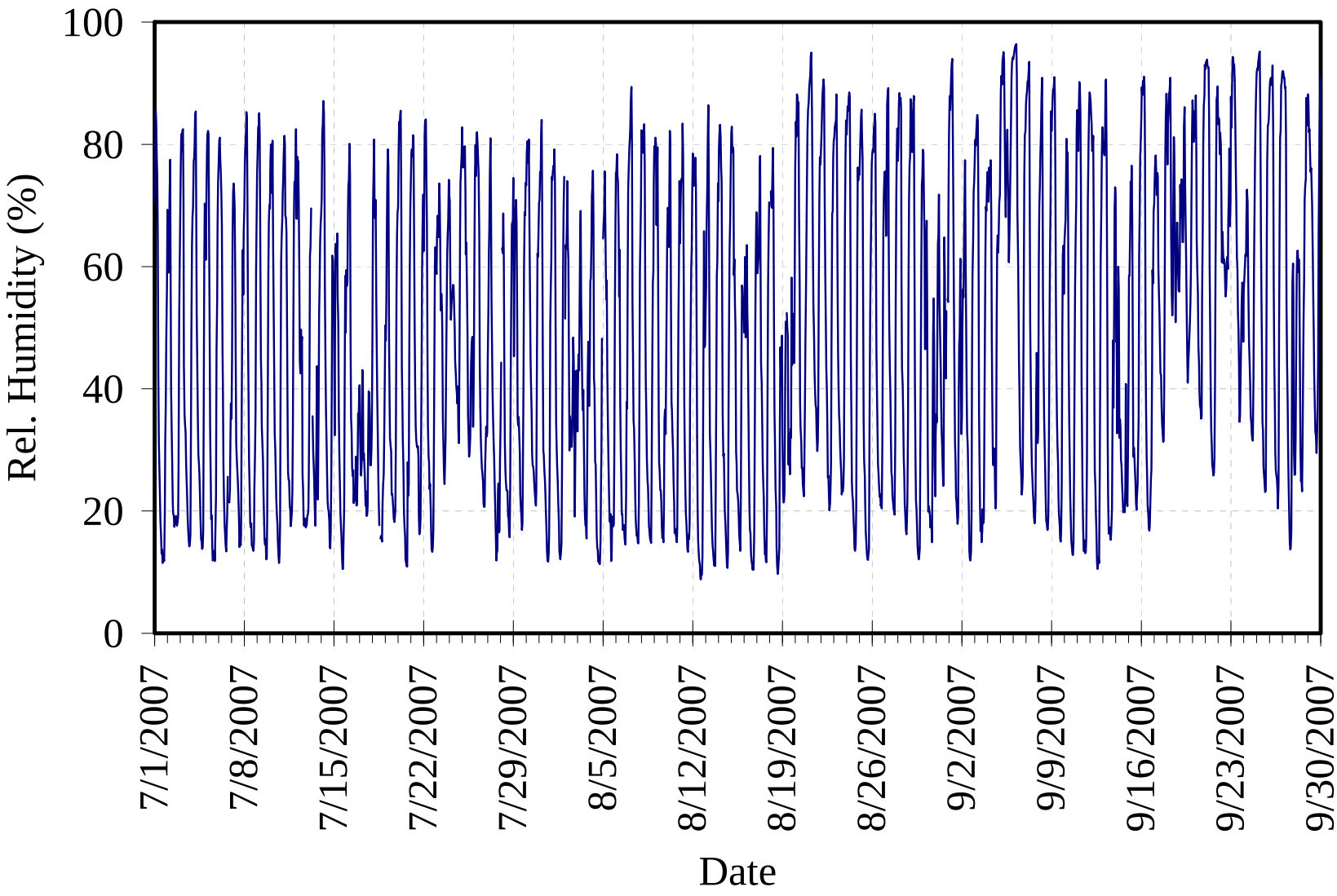

Figure 3-28 Ambient relative humidity (in %) at Warm Springs

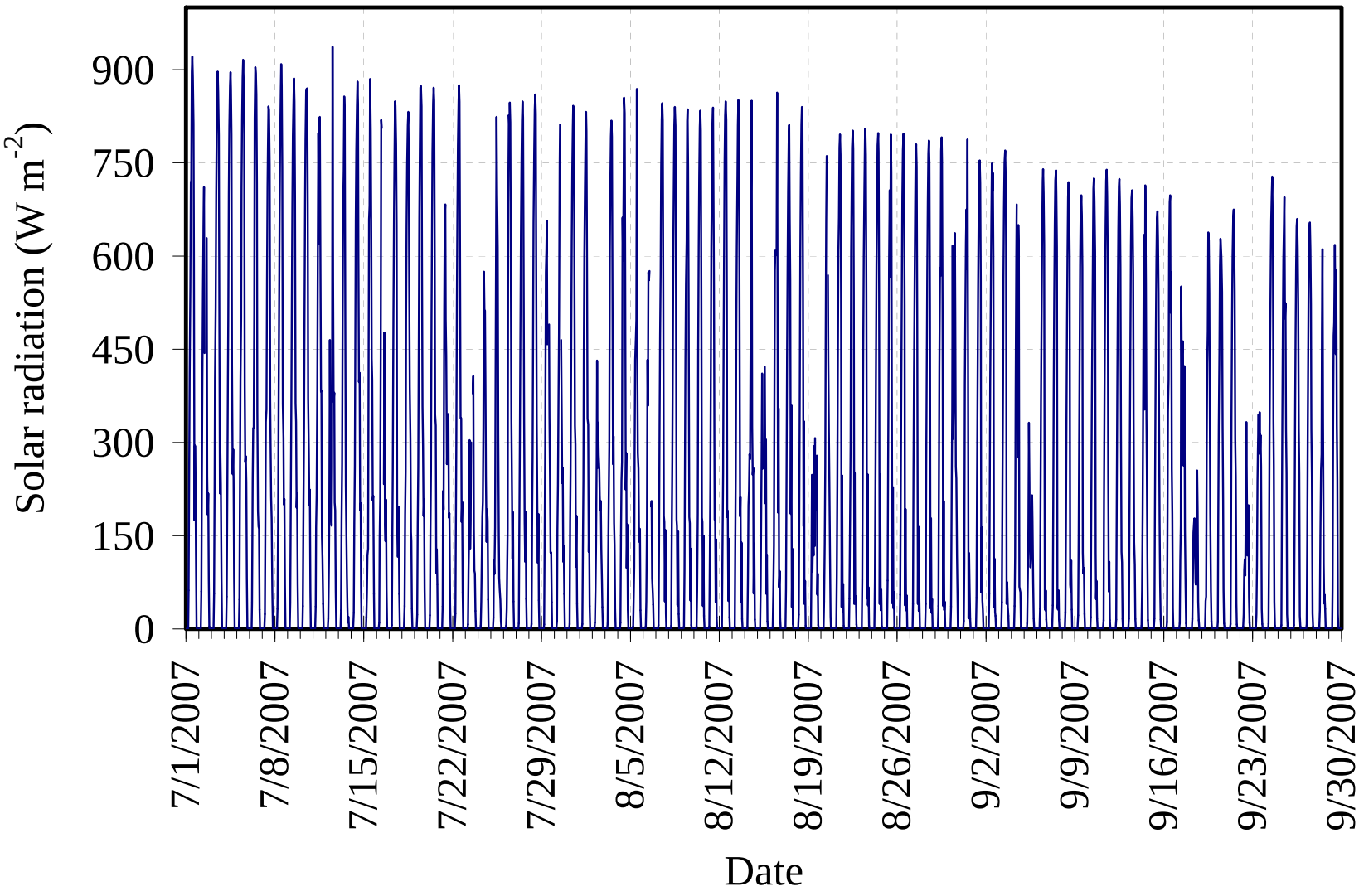

Figure 3-29 Solar radiation (in W m^{-2}) at Warm Springs

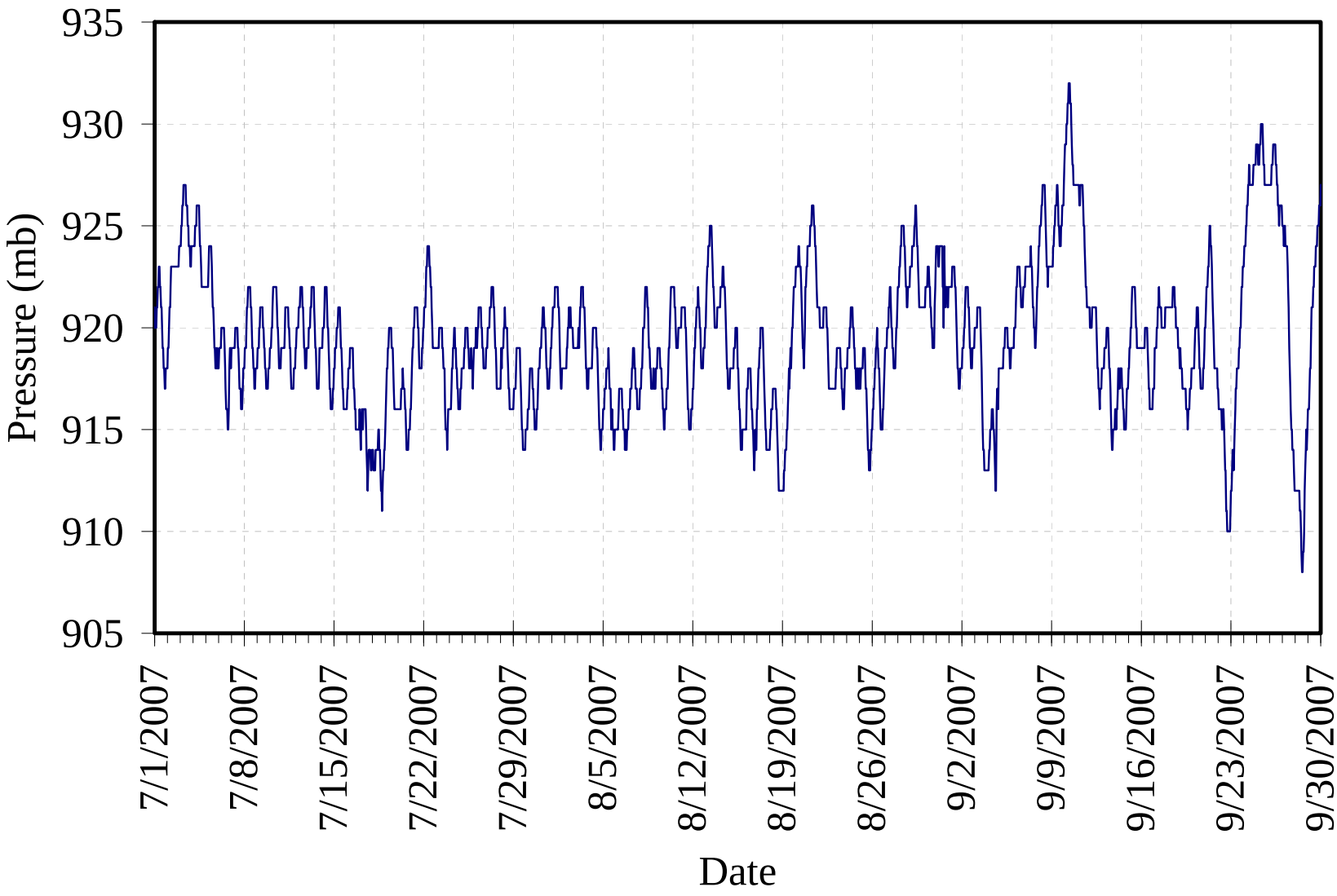

Figure 3-30 Barometric pressure (in mbar) at Warm Springs

3.1.5 Vertical profiles

The following section summarizes results from the balloon profile measurements during the study.

August 9, 2007 profiles: This was our first day of operations at the park and as a result took a little longer to set up than the remaining days. Conditions during this day were typical of a calm summer day with no clouds and cool morning temperatures. Convective development and the smoke from Idaho fires were well to the north during the sample day. Upper air winds were from the southwest during this day pushing smoke plumes away from the valley. The first profile indicated an inversion just above 330 meters above the ground. This inversion lasted for several more hours but weakened due to the quickly warming surface. Some interesting observations of the evolution of this inversion can be seen in the figure below. From the first sounding, the inversion base height doubled to about 630 meters by 1 pm. By afternoon, the inversion appeared to be above 700 m and lapse rates were very close to the adiabatic rate at 1 °C per 100 meters. Since the park was heavily irrigated we commonly observed high relative humidity near the ground each morning. Aloft, humidity remained in the 30% range below the inversion and decreased to around 10 to 15% above it.

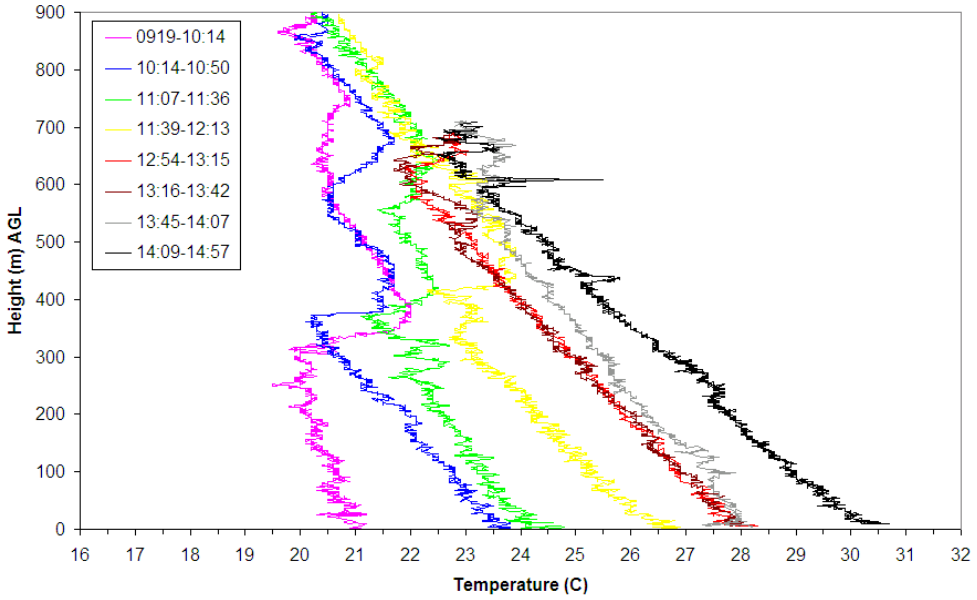

Figure 3-31 August 9, 2007 temperature profiles

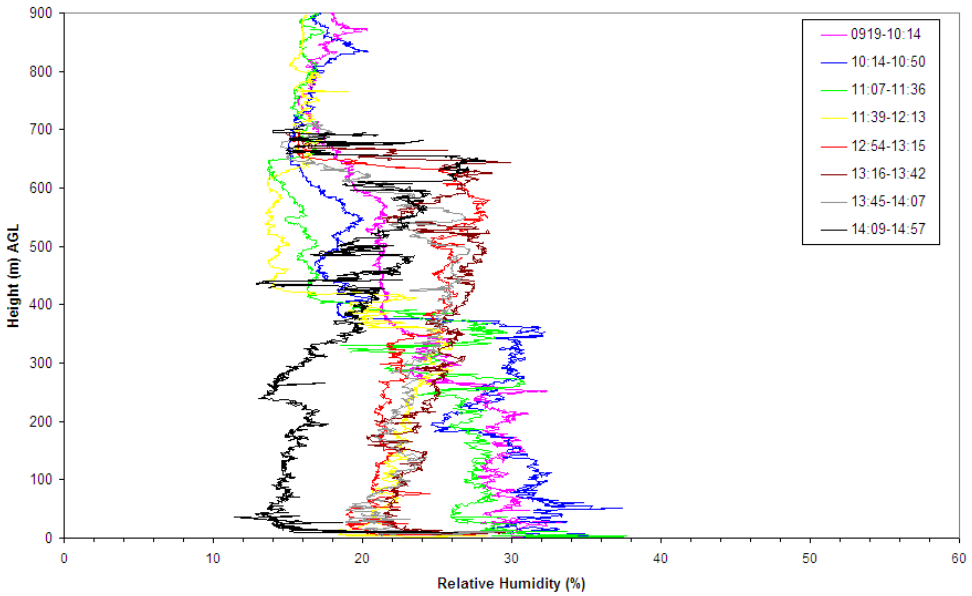

Figure 3-32 August 9, 2007 relative humidity profiles

Winds were light and varied from zero to 3 to 4 m/s throughout the day. Figure 3-33 below shows the wind speed profiles smoothed using a fast Fourier transform (FFT) method. During the first sounding, the wind speeds increased to about 5 m/s up to the inversion height. Above the inversion height, wind speeds decreased rapidly to 2-3 m/s. While we were not sampling at the time, a cold front passed through the area bringing in high winds but very little precipitation.

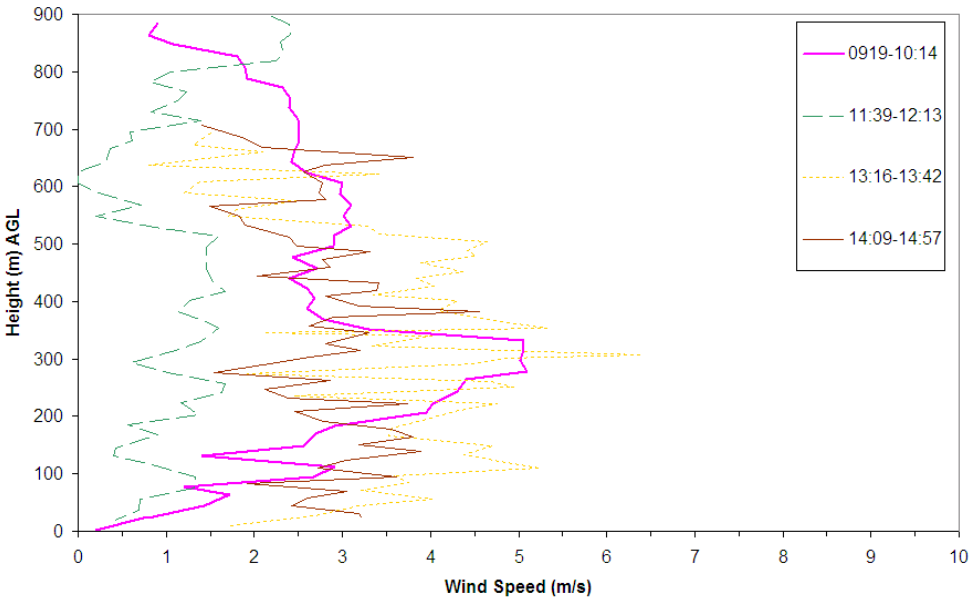

Figure 3-33 August 9, 2007 wind speed profiles

Ozone profiles showed little variation in the afternoon from the ground up to 700 meters. Although included in the plot, the 12:54 to 13:15 sounding showing high concentrations near the ground is suspect due to possible equipment failure.

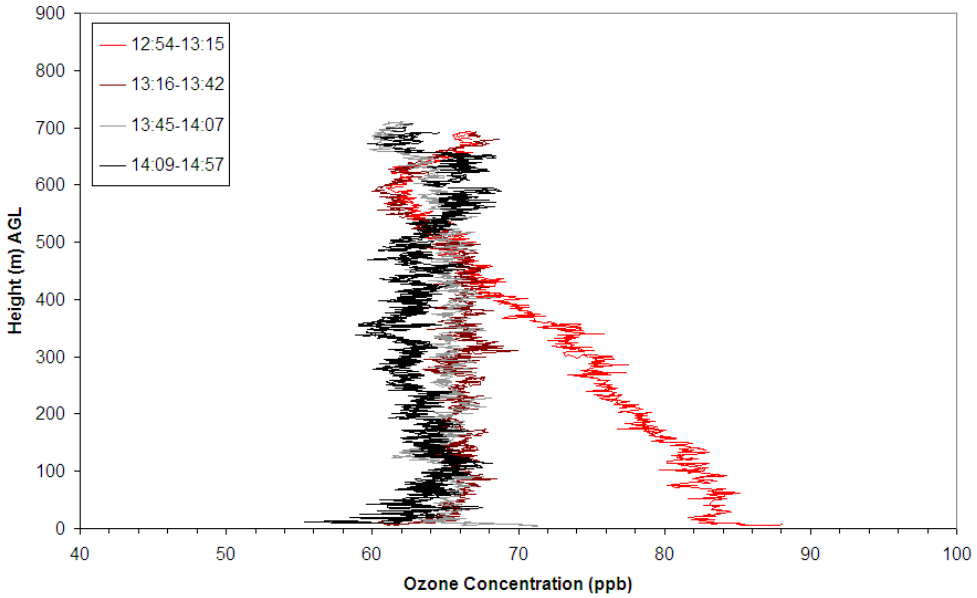

Figure 3-34 August 9, 2007 ozone concentration profiles. Note 12:54 – 13:15 sounding is suspect.

August 10, 2007 profiles: A cold front moved through the area overnight reducing morning temperatures several degrees from the previous day. An upper level trough passed through during the day bringing breezier conditions. Patchy high level clouds dominated the morning but by the afternoon it was sunny. A very weak low level inversion was observed at around 100 meters above the ground. This inversion was short-lived and disappeared by 8 am. Another stronger inversion was evident at around 375 meters. Measurements were terminated at around 12 pm due to high winds

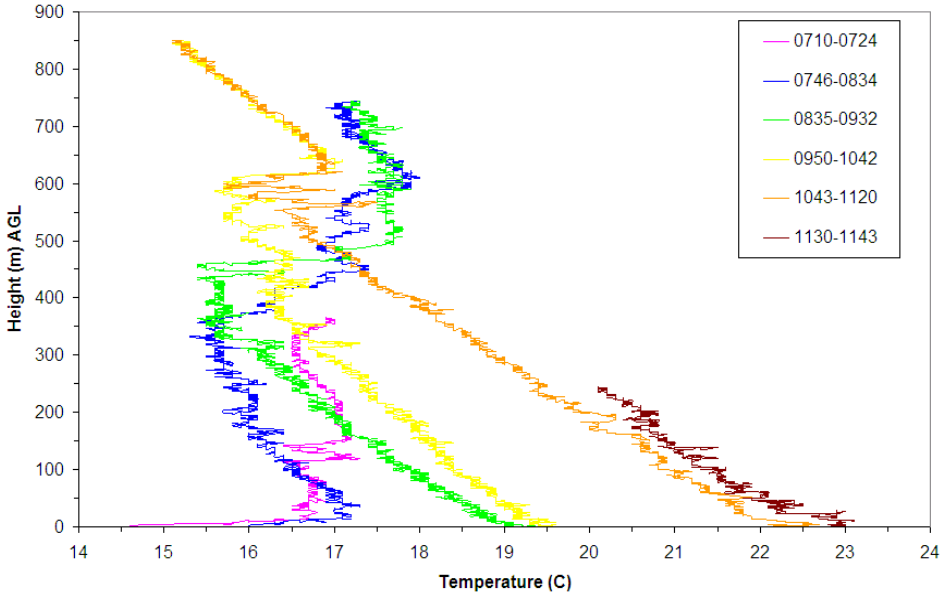

Figure 3-35 August 10, 2007 temperature profiles

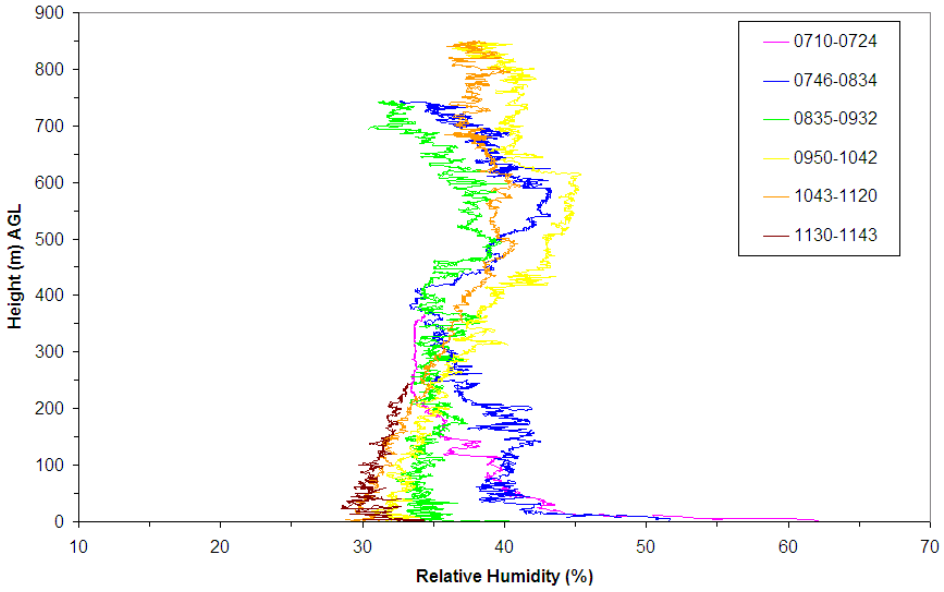

Figure 3-36 August 10, 2007 relative humidity profiles

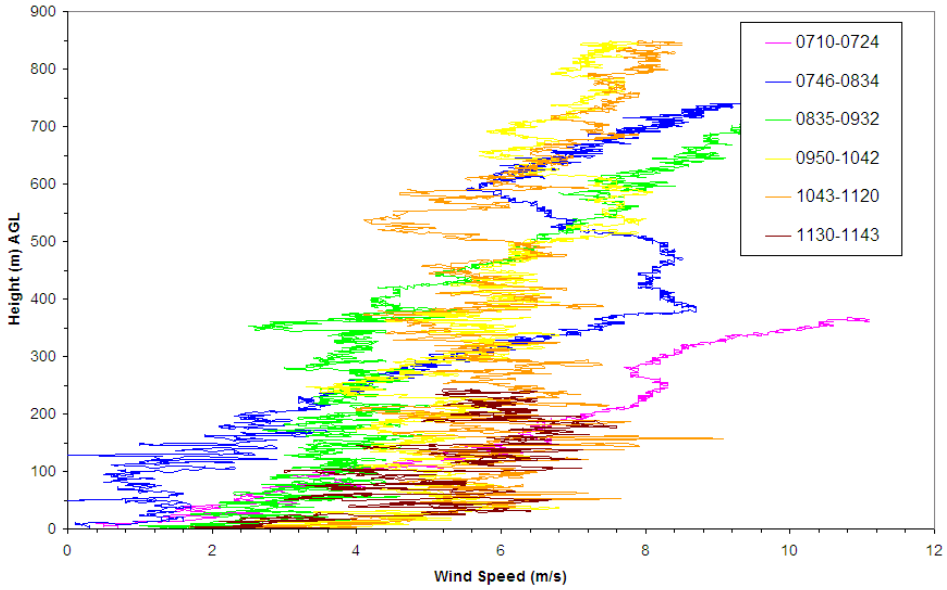

Figure 3-37 August 10, 2007 wind speed profiles

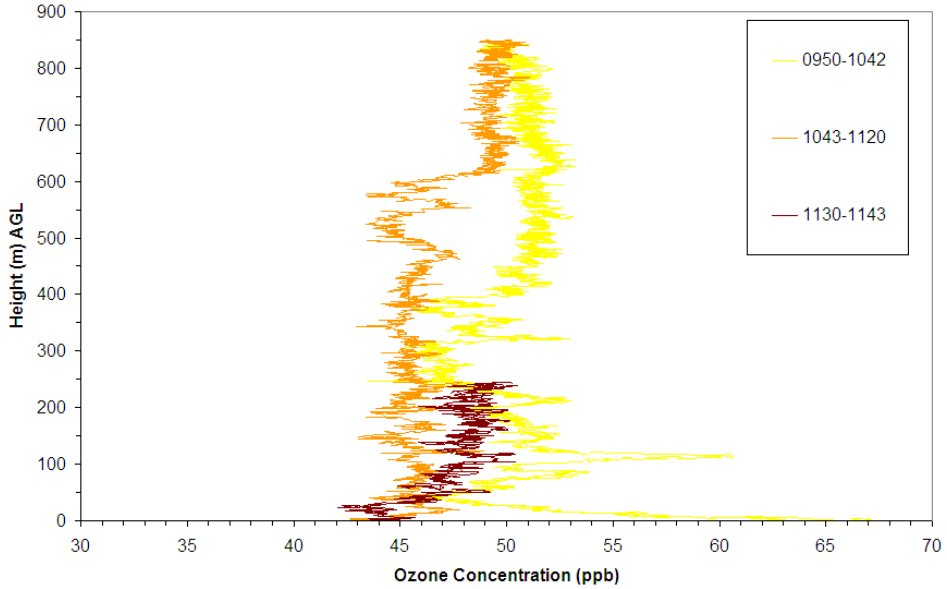

Figure 3-38 August 10, 2007 ozone profiles

Relative humidity profiles showed little variation compared to the previous day and varied between 30 and 40 percent over most of the boundary layer. Figure 3-36 shows the windy conditions during this day. The first profile had to be terminated at around 350 meters due to winds above 10 m/s. It is interesting to note that winds at the surface were calm while winds just 300 meters aloft were blowing at over 10 m/s or higher. As expected, ozone concentrations showed very little variations in height during this day. The early sounding had the highest concentrations but quickly tapered off to around 50 ppb for the remaining profiles.

August 14, 2007 profiles: Aloft winds were from the southwest keeping smoke from the mountains well to the north of the study area. The morning started off with cool surface

temperatures but quickly warmed up in the afternoon. Forecasted high for Boise was predicted to be 36° C (97° F). The maximum temperature at the BOI airport reached 36° C (97° F). By 6:30 pm the surface temperature reached 34° C (93° F) at the site. Surface temperatures quickly cooled in the late afternoon. The early morning profile showed a deep stable lapse rate to a height around 700 meters AGL. The airport radiosonde at 12 UTC (5 am) also observed a similar profile. A small inversion appeared during the 8:30 to 9:43 am profile at a height of 300 m AGL.

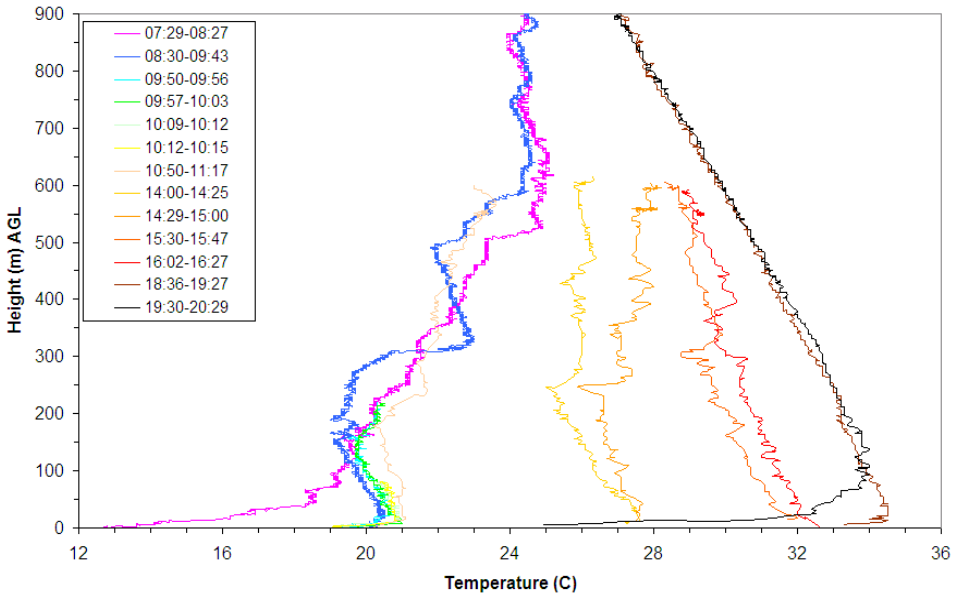

Figure 3-39 August 14, 2007 temperature profiles

Humidity remained very low aloft with increasing levels near the ground from local effects. The late afternoon (7:30 PM) sounding indicated the lowest humidity nearing 4 % due to the warm temperatures (33° C) at that height.

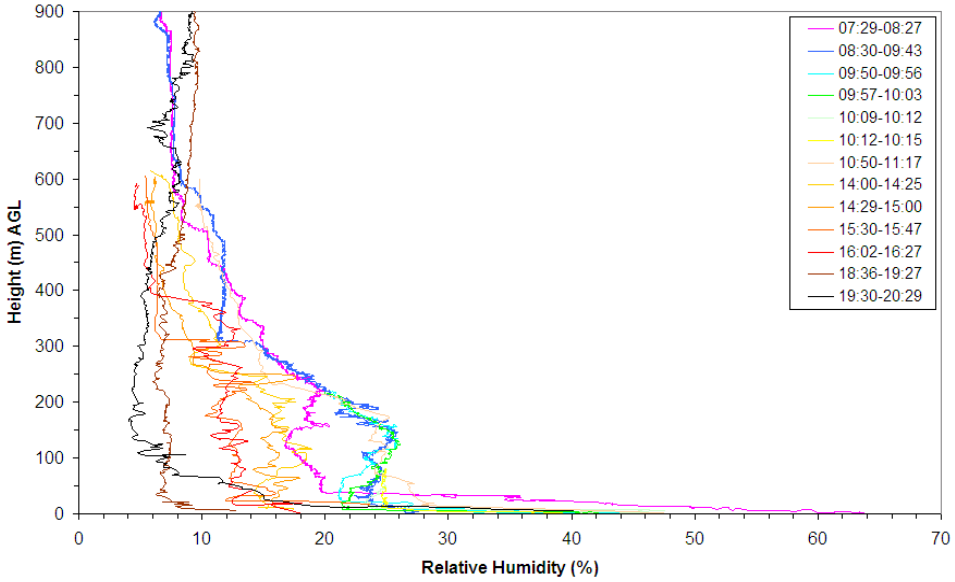

Figure 3-40 August 14, 2007 relative humidity profiles

Wind speeds remained low most of the day but picked up during late afternoon and into the evening hours. The 8:30 to 9:43 am sounding indicated a jet at 330 meters at the height of the inversion layer's base.

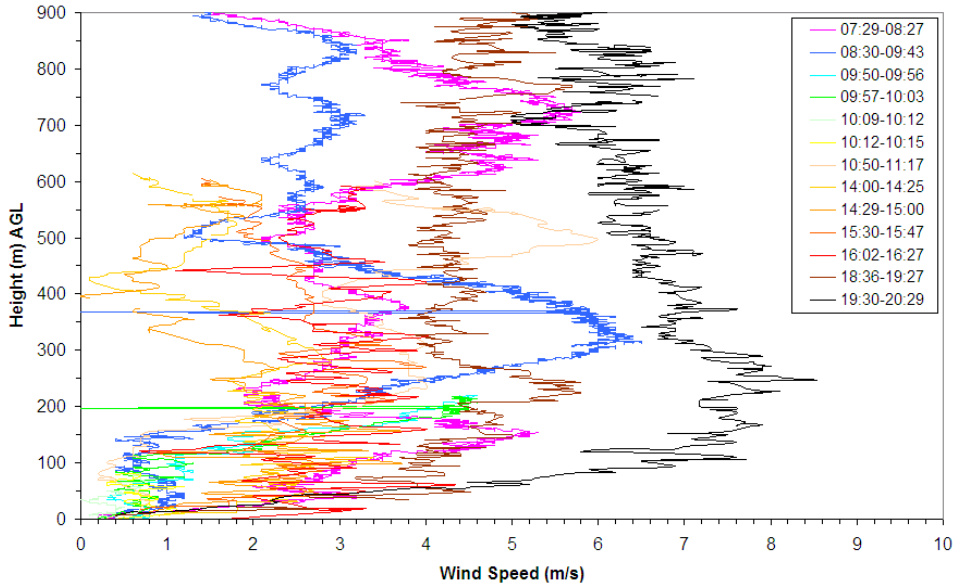

Figure 3-41 August 14, 2007 wind speed profiles

Ozone concentration profiles were collected and showed an increase in ozone as a function of height during the lowest 100 meters. Aloft ozone concentrations tended to merge around 60 ppb around 600 meters.

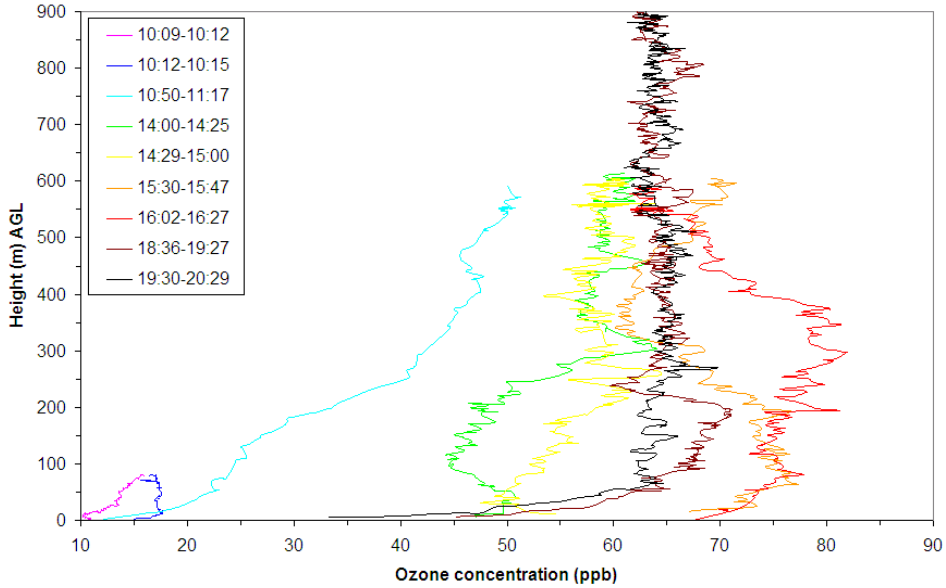

Figure 3-42 August 14, 2007 ozone concentration profiles

August 15, 2007 profiles: A warming trend continued from the previous day with a forecasted high temperature of 38° C (100° F) for Boise. Unfortunately we had to terminate flights due to a request from the Boise air traffic control to do so because they had to reroute flights over our airspace. Thus, we ended the tethersonde flights for this project after the 10:25 to 10:57 am profile. Based on the profiles in the morning the temperatures were heading toward the forecasted high of (38 C).

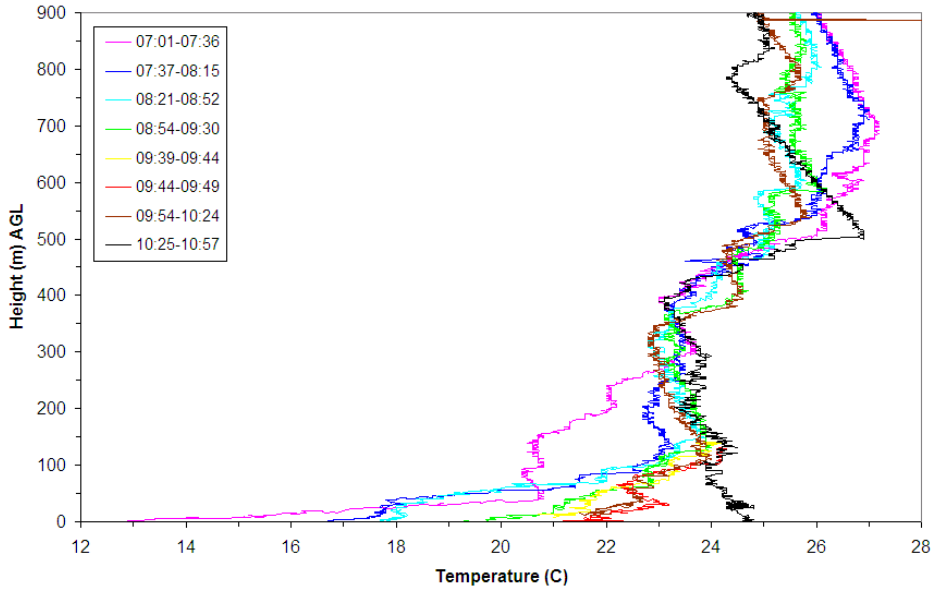

Figure 3-43 August 15, 2007 temperature profiles

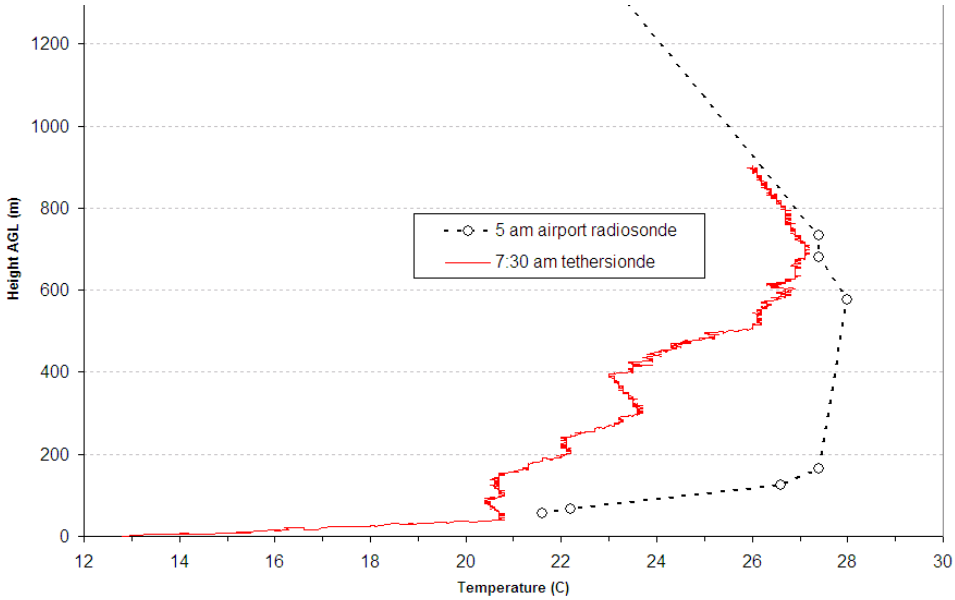

Figure 3-44 August 15, 2007 temperature profiles with the tethered-balloon and from the airport radiosonde

The first morning profile showed a pattern similar to the previous day although two degrees warmer. To compare the airport radiosonde measurement at 5 am with the 7:30 am tethersonde profile, Figure 3-44 shows them side by side. Even though the tethersonde profile was taken two hours later, the profile was overall cooler than the airport sounding at the lower levels particularly below 600 meters. The two profiles agreed above 700 meters AGL.
Humidity profiles are very similar throughout the morning on this day as shown in the figure below. The wind speed profiles show the most interesting structure over the course of the day. Early in the morning the peak wind speed appears at 400 m but quickly increases again above 600 m. In the late morning, wind speeds peak around 400 and 600 m.

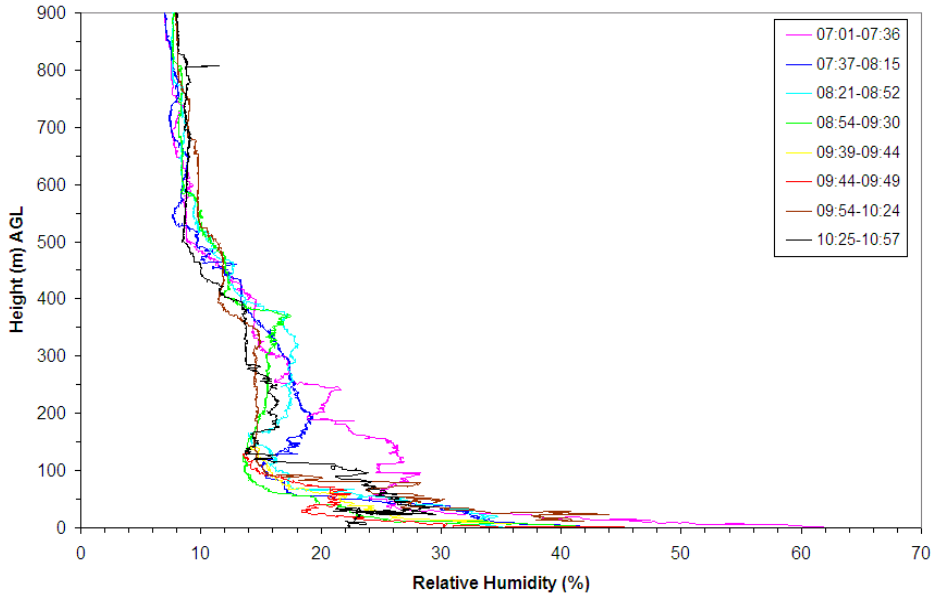

Figure 3-45 August 15, 2007 relative humidity profiles

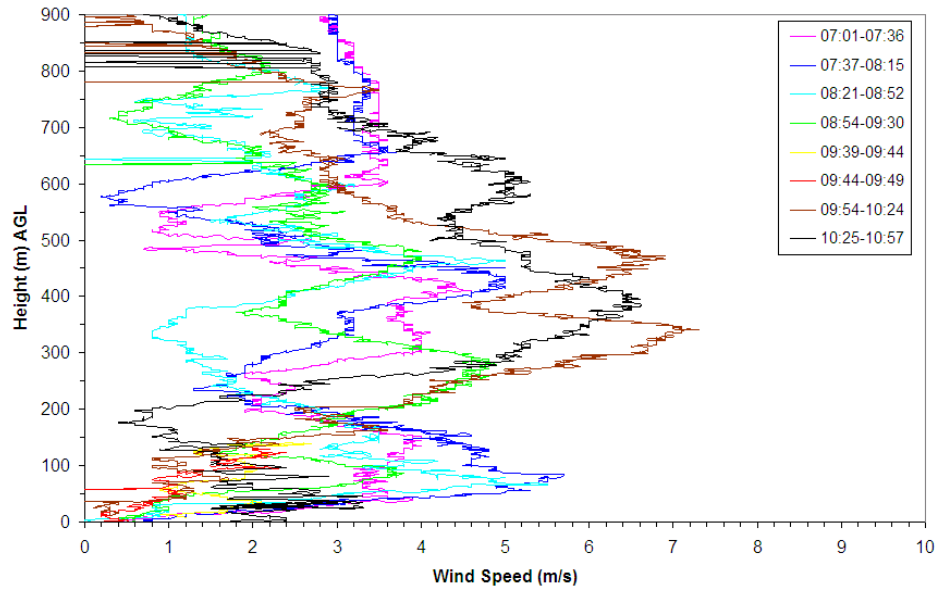

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Figure 3-46 August 15, 2007 wind speed profiles

3.1.6 Supplementary air quality parameters

The concentrations of PM_{10}, $PM_{2.5}$ and CO were measured at several sites during the study. Table 3-6 shows the hourly mean, median, st.deviation and maximum concentrations for the study. The mean 1-hr PM_{10} mass concentrations were comparable at the Nampa and Boise sites. As for $PM_{2.5}$, mean 1-hour concentrations varied from 11.1 μg m^{-3} at Parma to 15.9 μg m^{-3} at Mountain View. The highest 1-hour PM_{10} and $PM_{2.5}$ mass concentrations were measured at Nampa and Mountain View, respectively, on July 4, 2007 (22:00 to midnight), probably due to the use of fireworks.

Table 3-6 Descriptive statistics of PM_{10}, $PM_{2.5}$ and CO

	Mean	Median	σ	Maximum
PM_{10} (in μg m^{-3})				
Boise (BOI)	38.2	32.3	35.4	731.6
Nampa (NNU)	39.7	32.9	39.8	930.1
$PM_{2.5}$ (in μg m^{-3})				
St. Lukes (STL)	13.8	11.1	18.3	537.6
Parma (PAR)	11.1	8.6	8.9	65.8
Nampa (NNU)	13.6	11	10.6	76.0
White Pine (WHP)	13.8	11.4	11.7	96.5
Mountain View (MOU)	15.9	12.3	29.8	827.9
CO (in μg m^{-3})				
Boise (BOI)	0.53	0.50	0.35	3.8

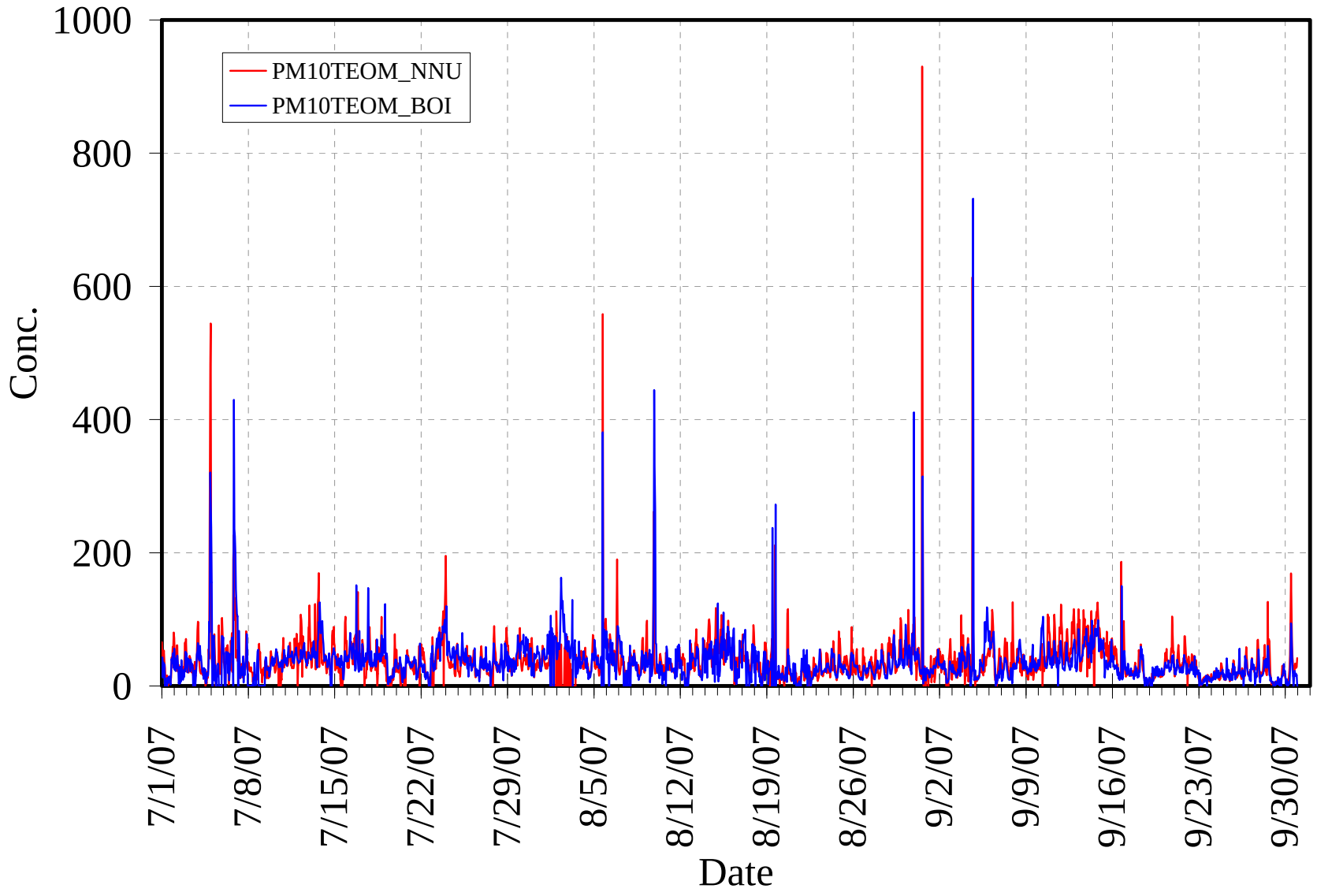

Figure 3-47 Times series of PM_{10} mass (in µg m^{-3}) at Nampa (NNU) and Boise (BOI)

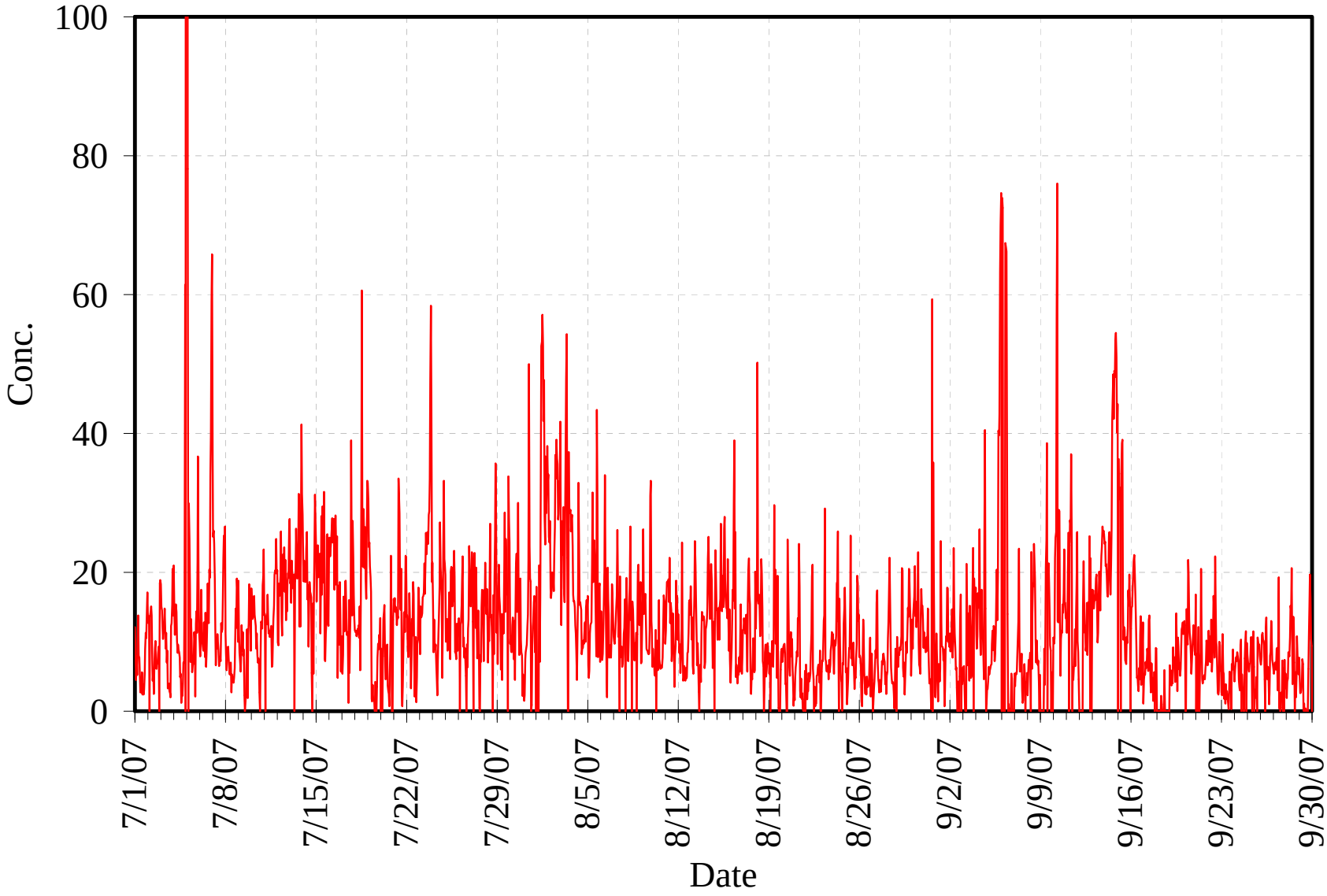

Figure 3-48 Times series of $PM_{2.5}$ mass (in µg m^{-3}) at St. Lukes

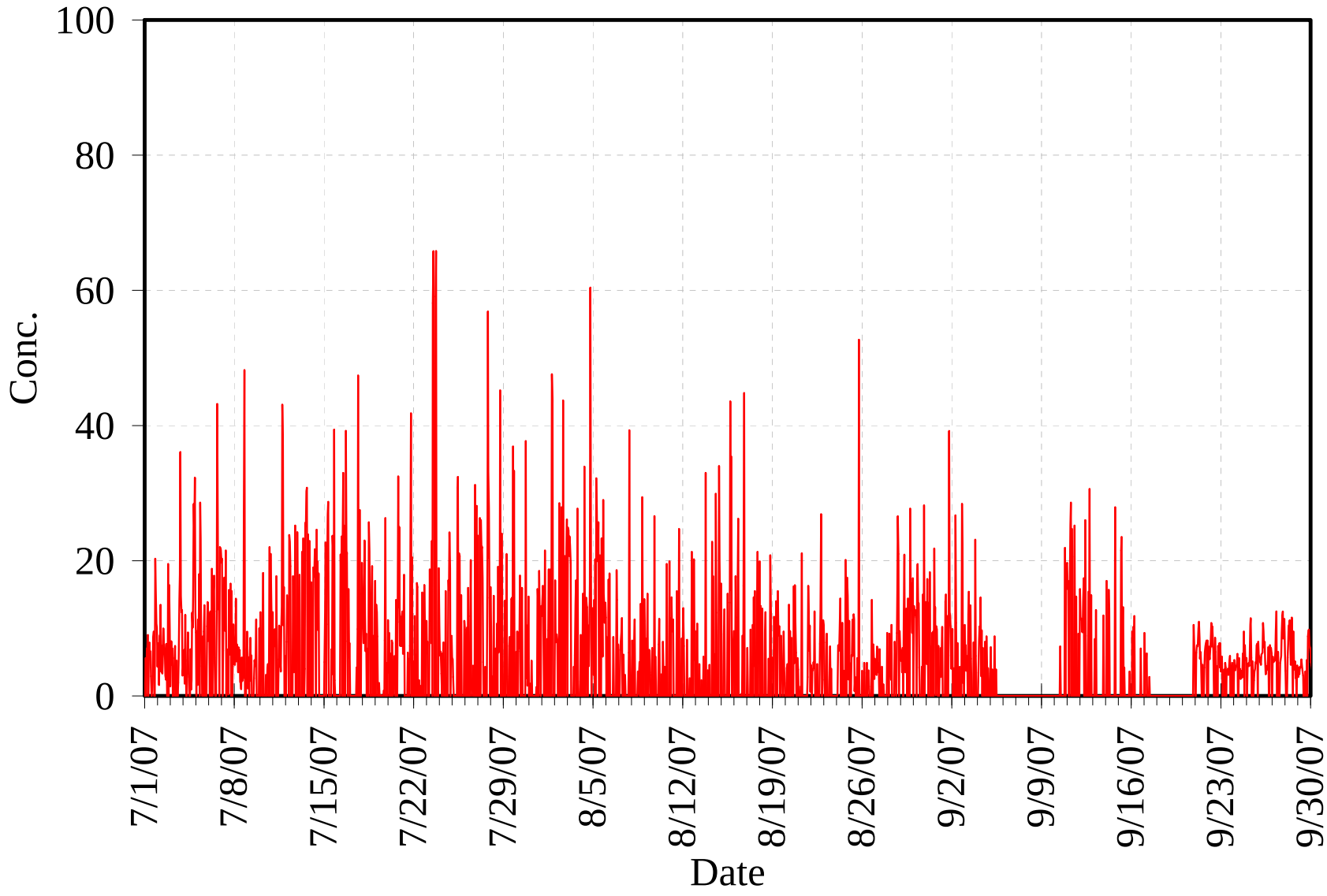

Figure 3-49 Times series of $PM_{2.5}$ mass (in µg m^{-3}) at Parma

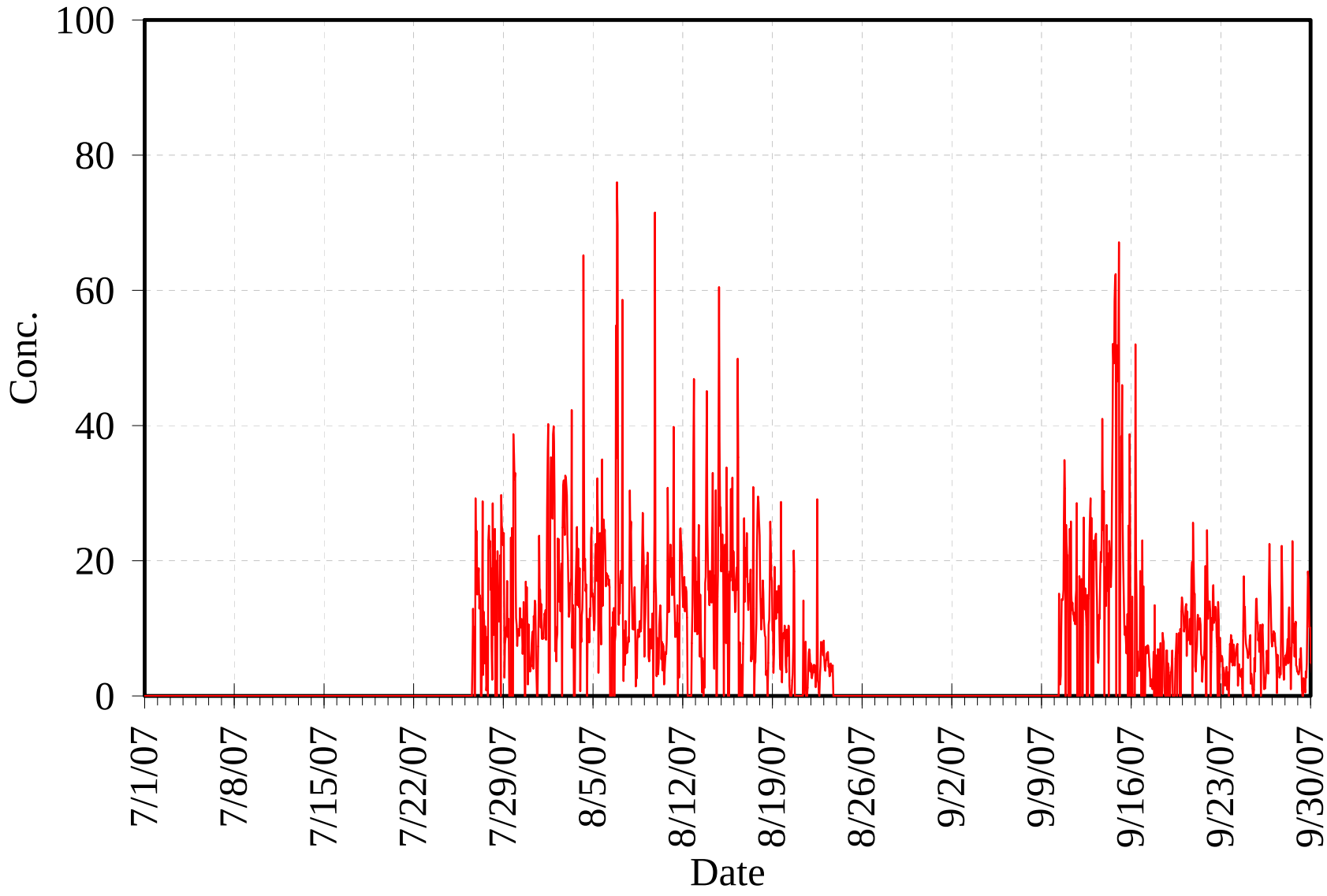

Figure 3-50 Times series of $PM_{2.5}$ mass (in µg m^{-3}) at Nampa

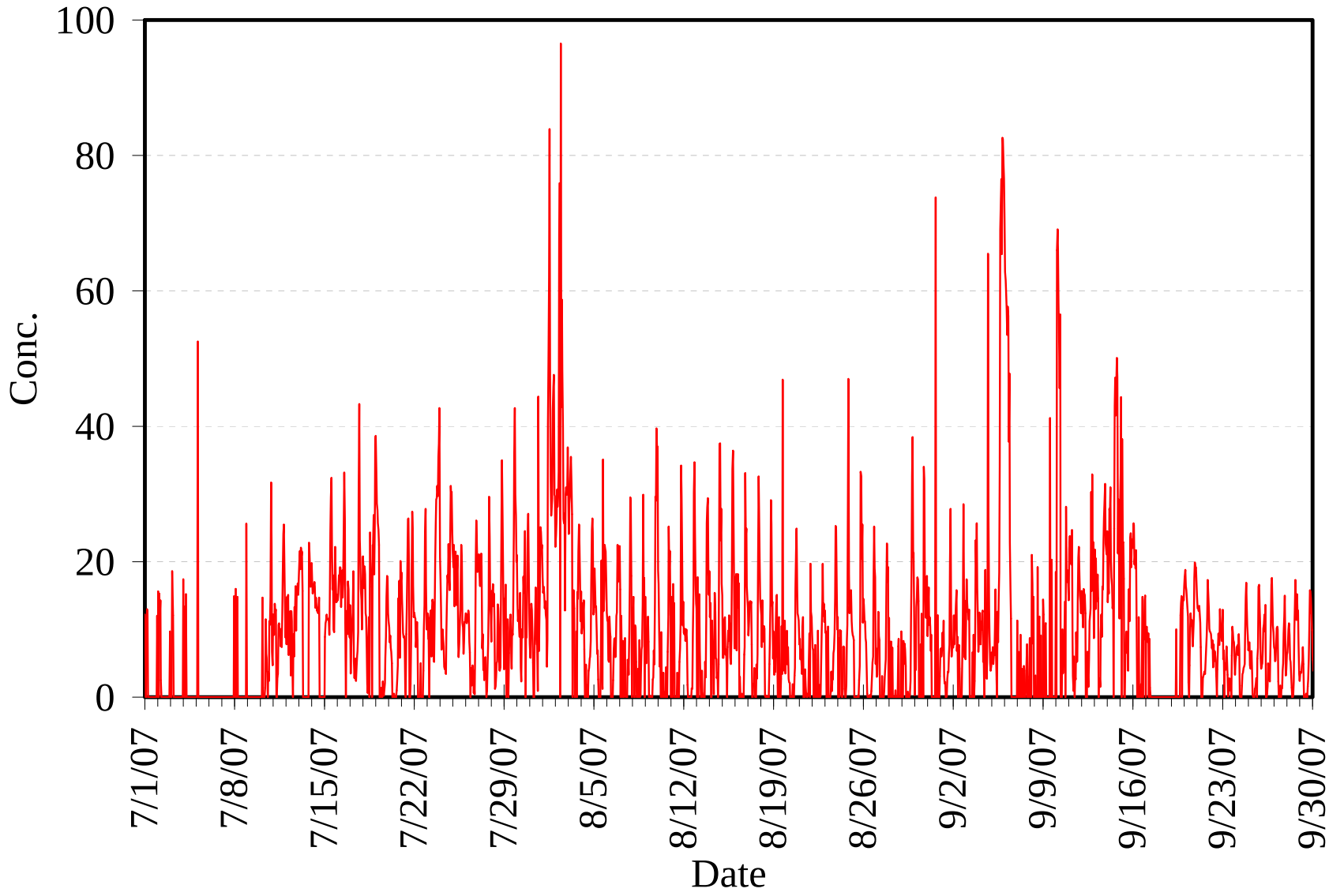

Figure 3-51 Times series of $PM_{2.5}$ mass (in µg m^{-3}) at White Pine

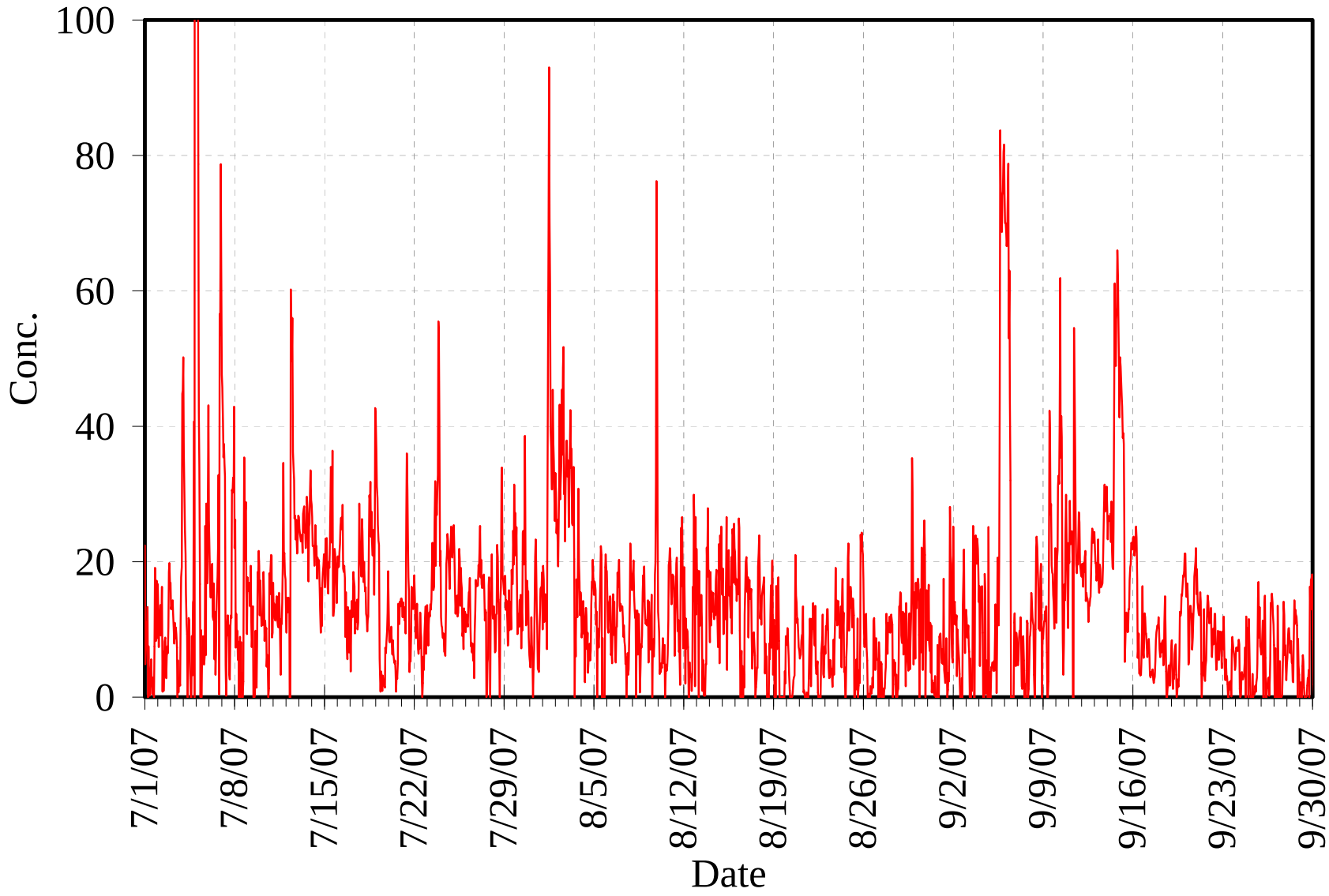

Figure 3-52 Times series of $PM_{2.5}$ mass (in µg m^{-3}) at Mountain View

3.1.7 Wildland fires

Fire episodes in Idaho and surrounding states including California were examined to determine the impact of aloft plume transport on ground ozone concentrations in the Treasure Valley. The summary windland fire episodes for each state are presented in Table 3-7. Detailed information for wildland fires including the cause, date of origin and size of burned area (more than 1000 acres) are presented in Appendix A. Data are retrieved from the Incident Information System (www.inciweb.org).

Table 3-7 Summary of wildland fires in Idaho and surrounding states from July 1, 2007 to September 31, 2007

State	Number of fires	Burnt area (in acres)
Idaho	26	2,113,227
Nevada	16	512,012
Oregon	21	454,728
Washington	12	172,739
California	18	421,924
Montana	22	549,933

Approximately half of the burned area in Idaho was incurred during three large fires in Twin Falls (Myrphy Complex Wildland Fire) from July 16 to August 2, 2007 (653,100 acres), two fires in Payette (East Zone Complex Wildland Fire, started on July 7, 2007; 300,022 acres), and Boise (Cascade Complex Wildland Fire, started on July 17, 2007; 302,376 acres) National Forests. The majority of wildland fires in Idaho (including the three largest fires) were initiated by lightning. About 500,000 acres of wildland was also burned in eleven fires in northern Nevada (north of Interstate-80 corridor) and near the Nevada/Idaho Stateline. Frequent but smaller in size wildland fires in the surrounding states of Oregon, Washington and western Montana consumed about 1,000,000 acres. Wildfires in California usually occur in late fall following dry Santa Ana winds. During the monitoring period, a large wildland fire incident (Zaca) near Santa Barbara caused by human activities lasted more than a month (July 4-September 2) and burned 240,207 acres.

Figure 3-53 shows the cumulative data of thermal anomalies caused by fire incidents as they were detected by Terra and Aqua MODIS satellites during the monitoring period. The size of the aggregating cells is 0.25 degrees per side. These results indicate that emissions from wildland fires just north of Treasure Valley, northern Nevada, west Montana, and parts of Oregon may affect patterns and concentrations levels of precursors of ozone.

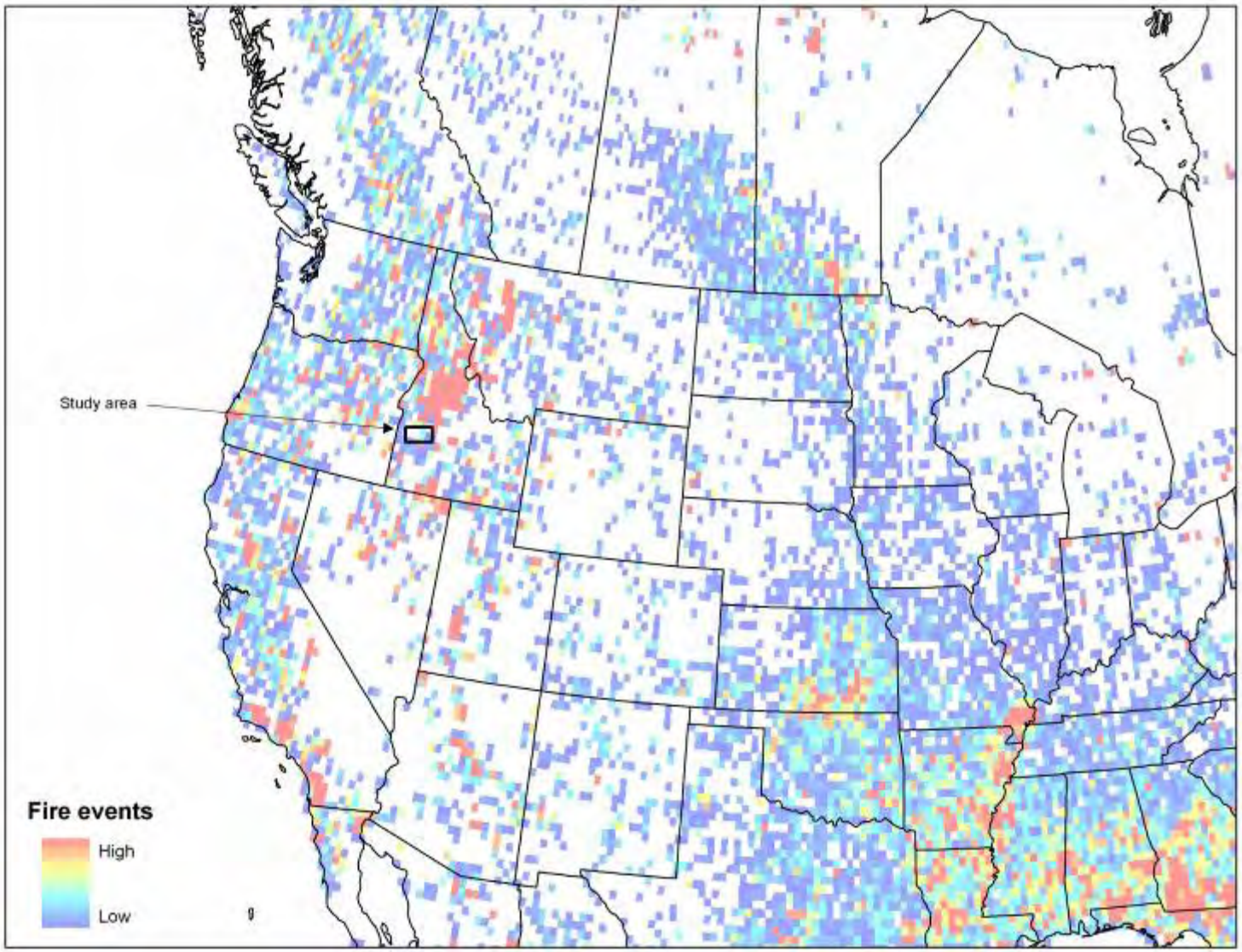

Figure 3-53 Cumulative Terra and Aqua MODIS fire and thermal anomalies generated from MODIS near real-time data for the monitoring period. The size of the grid cells is 0.25 degrees per side.

3.1.8 Air mass trajectories

The paths of air masses arriving in Boise at eight different elevations (100, 200, 500, 1000, 1500, 2000, 2500 and 3000 m) for each hour during the entire monitoring period were utilized to compute the cell residence times of air masses as an indicator of possible contribution of upwind sources to ozone precursors. Figure 3-54 - Figure 3-61 show the spatial variation of residence times at different elevations. These maps show clear differences between air masses near the ground as compared to those at higher elevations. More specifically, trajectories at 100, 200 and 500 m originated often from northeast Oregon, traveled through the Columbia River Gorge (on the border or Oregon and Washington states), and followed the I-84 corridor prior to their arrival in Treasure Valley. Trajectories originating from northern California and west Montana also appeared to arrive in Treasure Valley but less frequently. On the other hand, air masses at higher elevations covered a larger geographical area and were not as influenced by topographic restrictions. Air mass transport at 1000m and higher followed summer weather patterns, with a relatively constant flow from southwest to northeast. Thus, trajectories at higher elevations originated from southern California and spent significant time over central California and northern Nevada. These distinctions indicated that air masses aloft may have substantially different compositional characteristics as compared to near-ground air masses.

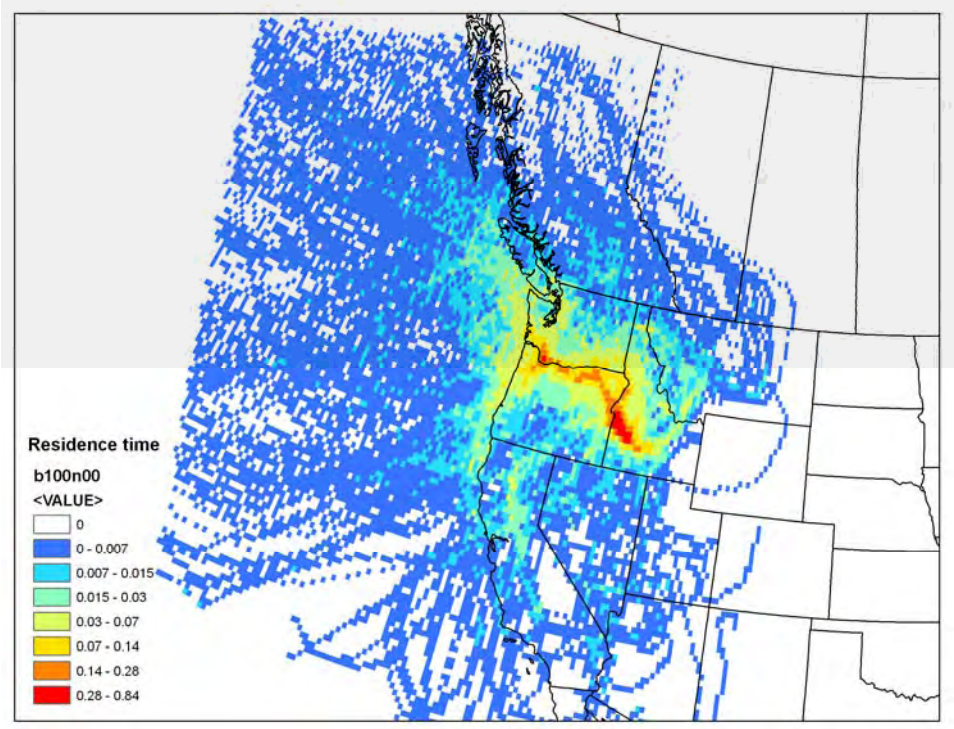

Figure 3-54 Residence time of air mass arriving in Boise at 100m

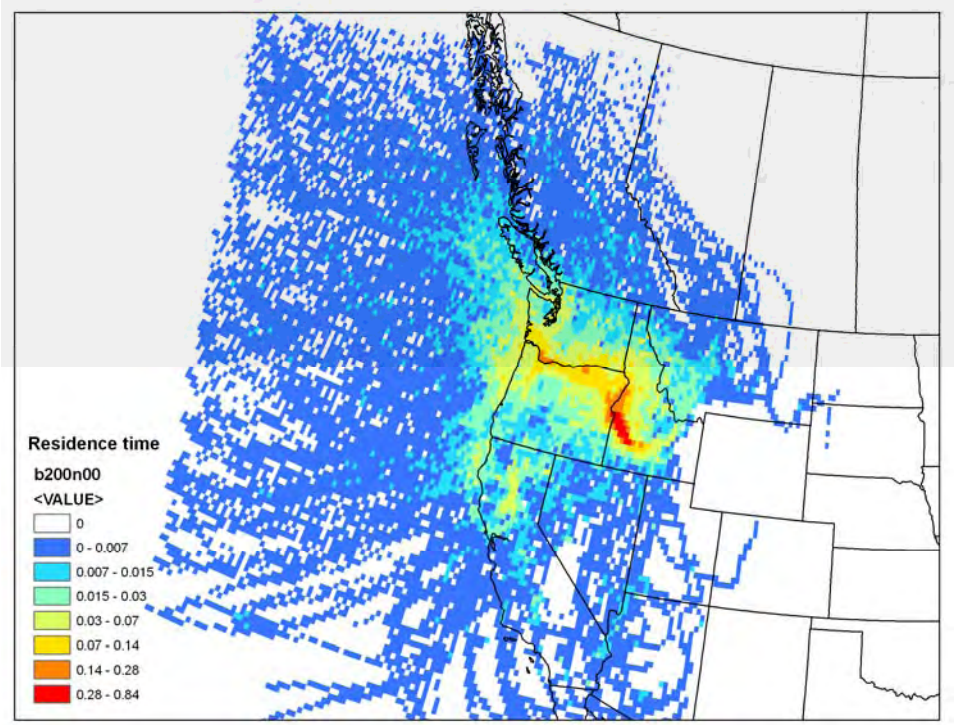

Figure 3-55 Residence time of air mass arriving in Boise at 200m

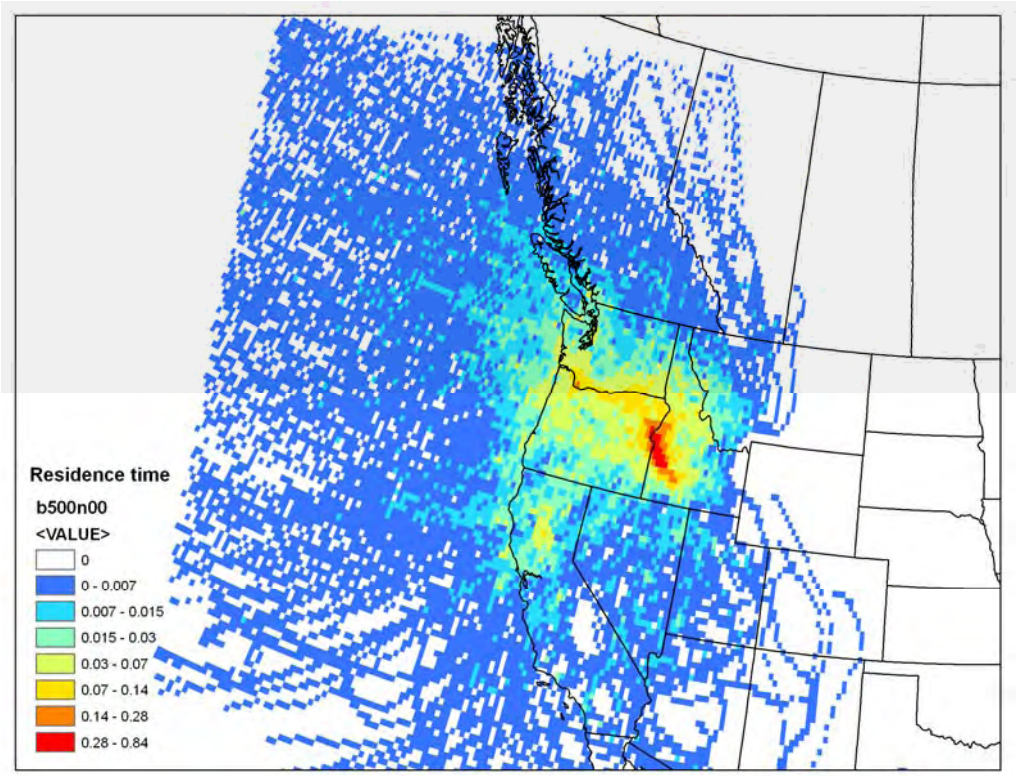

Figure 3-56 Residence time of air mass arriving in Boise at 500m

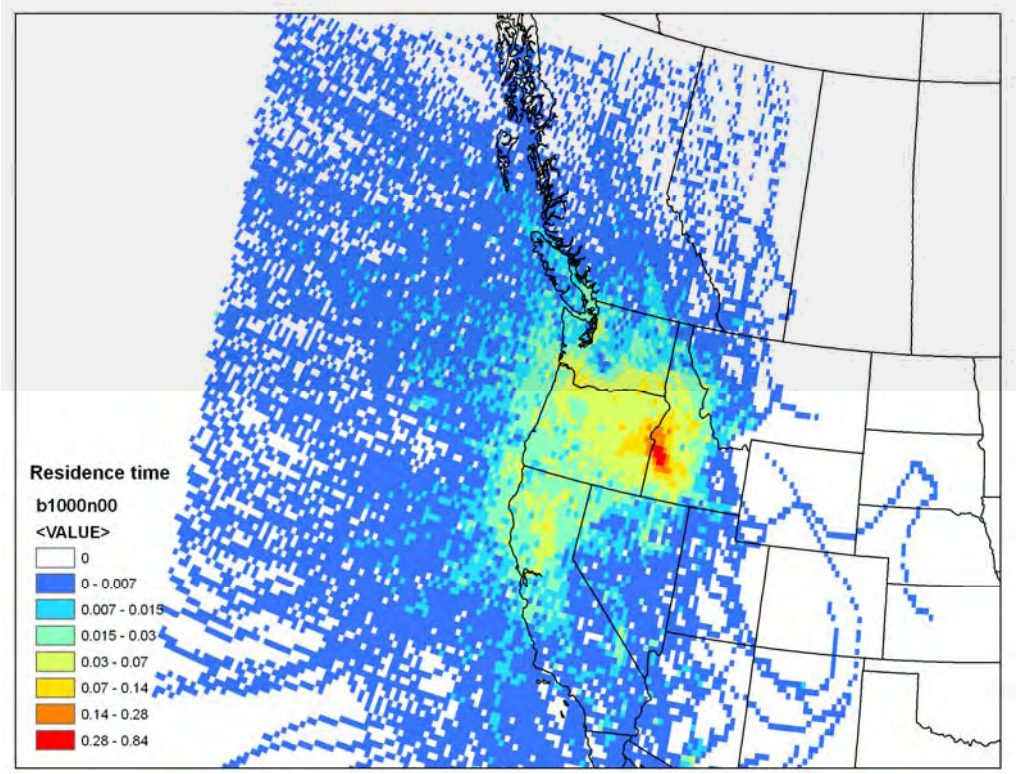

Figure 3-57 Residence time of air mass arriving in Boise at 1000m

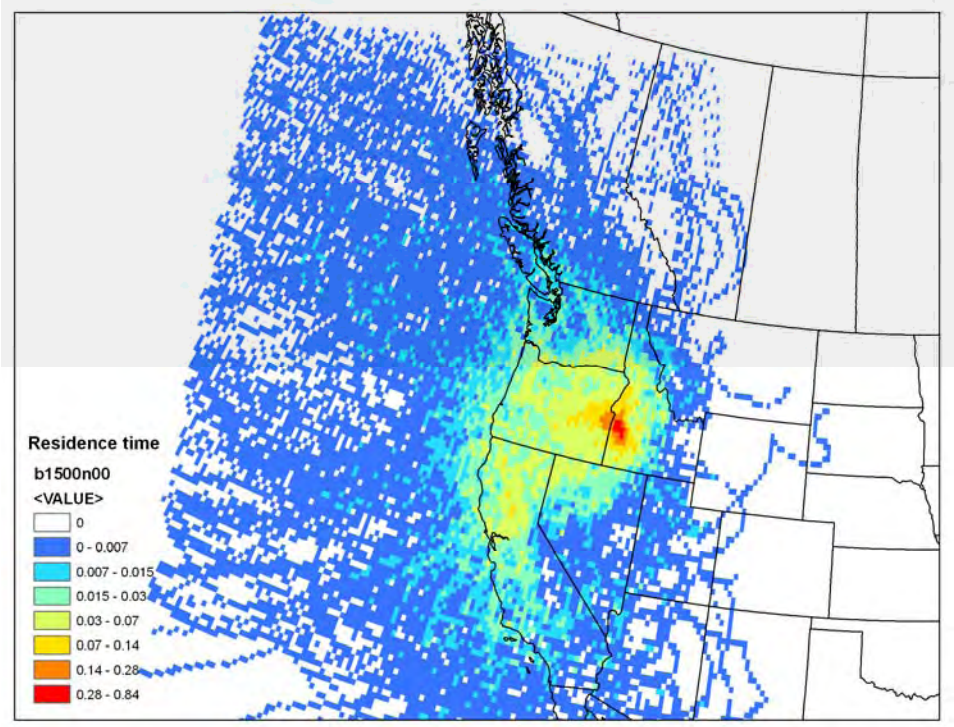

Figure 3-58 Residence time of air mass arriving in Boise at 1500m

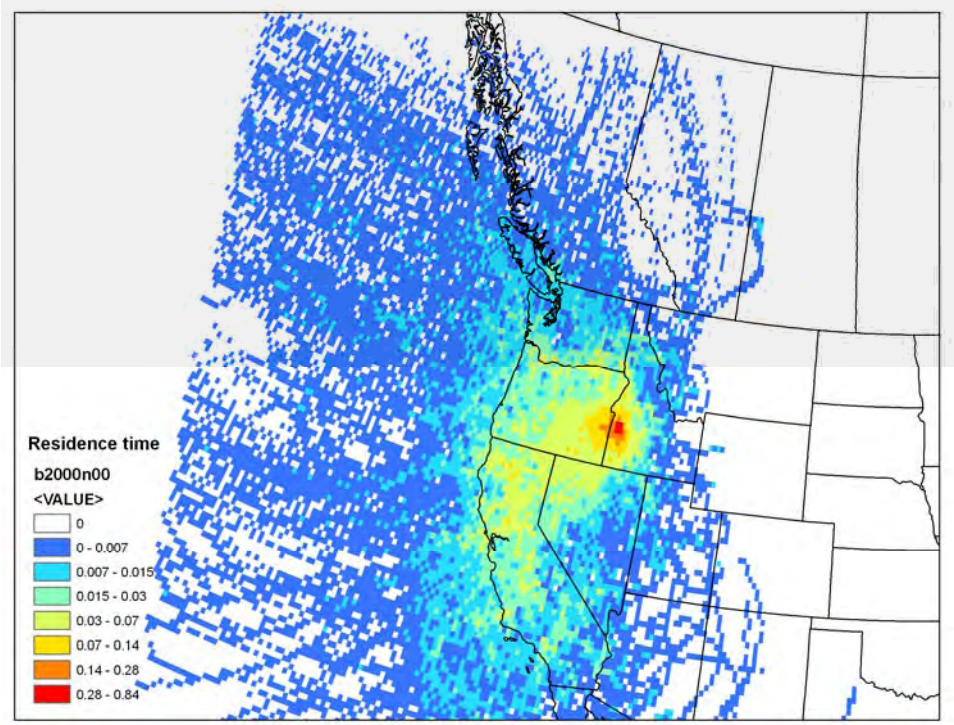

Figure 3-59 Residence time of air mass arriving in Boise at 2000m

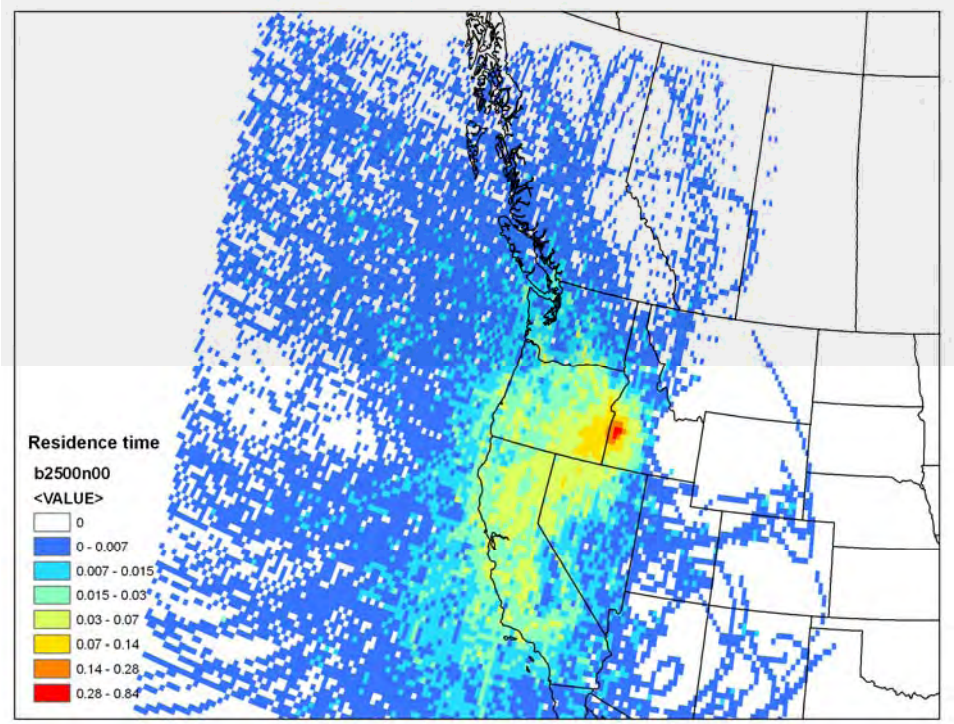

Figure 3-60 Residence time of air mass arriving in Boise at 2500m

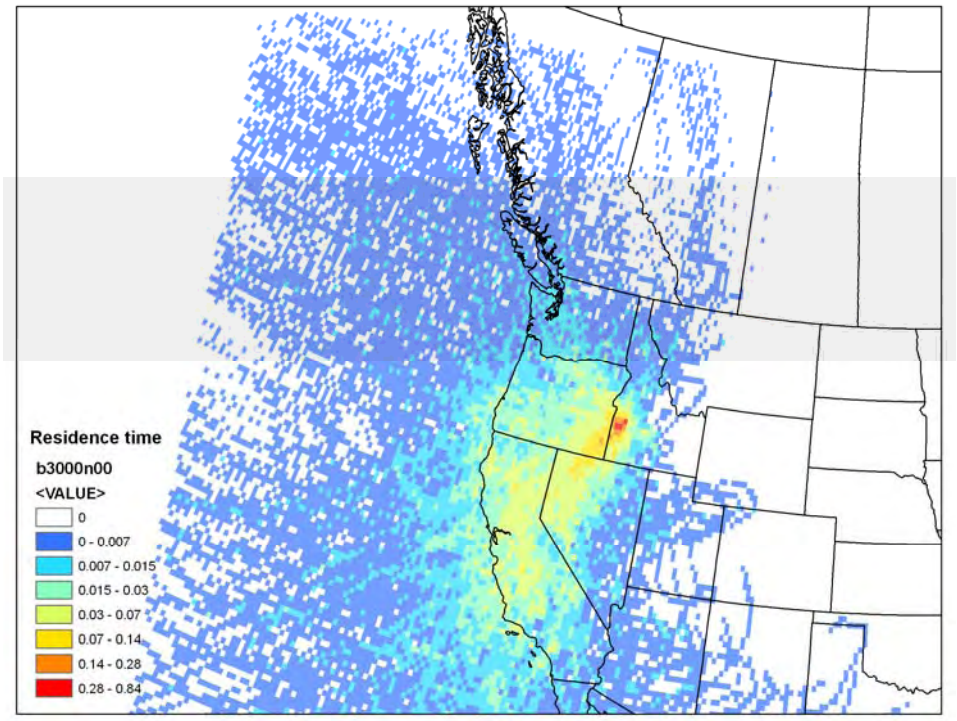

Figure 3-61 Residence time of air mass arriving in Boise at 3000m

3.1.9 Pavement

Several road construction and maintenance activities took place in Ada County during the study. A major project that was extended to Canyon County included the pavement of I-84. Other construction tasks included paving activities at Overland Rd, Ustick Rd, Vista Rd and Locust Grove Rd. Table 3-8 shows the dates and the locations of maintenance and construction activities in Ada County. Maintenance activities occurred in Zones A3, A4 and B3 during the study. Figure 3-62. shows the boundaries of the three zones and the locations of air quality sites. Zone A4 covers the region between Lake Hazel Rd. on the south, Locust Grove on the east, Ustick Rd. on the north and McDermott Rd. on the west. Zone A3 covers the area between Lake Hazel Rd. on the south, Five Mile Rd. on the east, Fairview Rd. on the north and Locust Drive Rd. on the west. The St. Lukes monitoring site is located in Zone A3. Zone B3 encompasses communities within the Boise river and State Street on the south, the Ada county line on the northeast, Hwy 21 on the southeast and Harrison Blvd/Bogus Basin on the west. The two meteorological towers and the Boise downtown CO and PM_{10} monitors are located on the edges of Zone B3. Chip sealing was the most frequent maintenance activity (44 days) primarily in zones A3 and A4. ACHD paved roads in Zone B3 for seven days in late September.

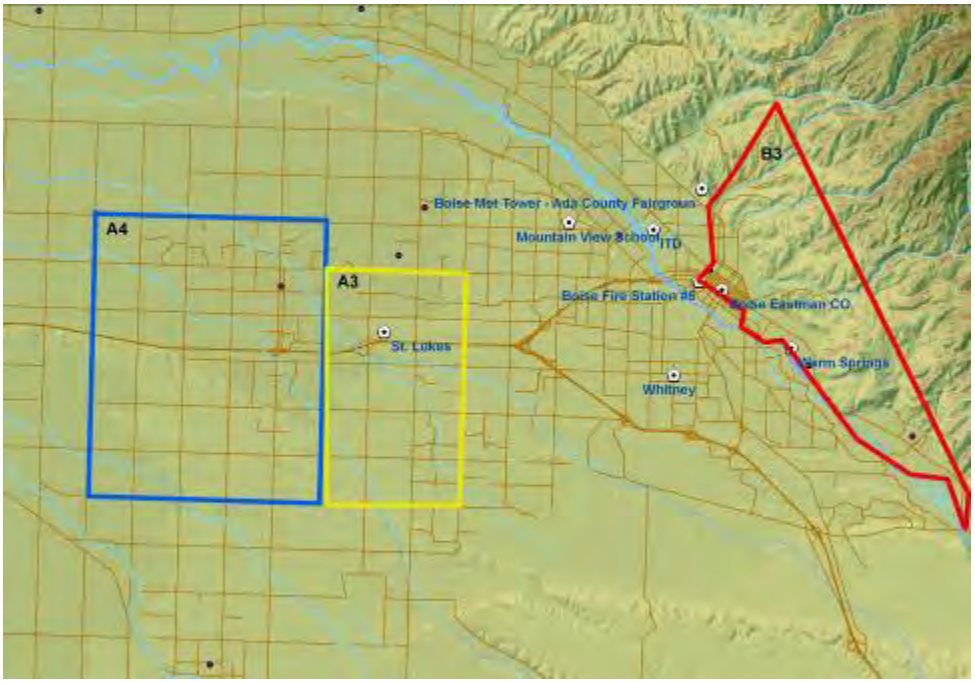

Figure 3-62 Map showing Maintenance Zones A3, A4 and B3

Table 3-8 2007 Maintenance chip sealing and paving. and major construction work dates and areas

Date	Maintenance ChipSealing	Paving	Construction
7/2/2007	A3,B3		NightWork: Bottom lift on South side of Overland (Linder to Stoddard)
7/3/2007	A3,B3		NIghtWork: Bottom lift on South side of Overland and Linder; Paving mainline (RT) on Overland between Topaz and Cloverdale
7/6/2007			Paving Locust Grove Mainline
7/7/2007			Paving Locust Grove Mainline
7/9/2007	A3,B3		Paving Locust Grove Mainline
7/10/2007	A3,B3		
7/11/2007	A3,B3		
7/12/2007	A3,B3		
7/13/2007	A3		
7/16/2007	B3		
7/17/2007	A3,B3		
7/18/2007	A3,B3		
7/19/2007	A3,B3		
7/20/2007	B3		Paving Locust Grove Mainline
7/22/2007	A3		
7/23/2007	A3,B3		
7/24/2007	A3,B3		Ustick
7/25/2007	A3,B3		Paving Vista
7/26/2007	B3		DayWork: Bottomo lift of South side of Overland

			(between Stoddard and Meridien); Paving Vista Rd
7/27/2007	B3		Ustick
7/29/2007	A3,B3		
7/30/2007	A3,B3		Paving Vista
7/31/2007	A3,B3		
8/1/2007	B3		Paving Vista
8/2/2007	B3		
8/3/2007	B3		
8/5/2007	A3,B3		
8/6/2007	A3,B3		
8/7/2007	A3,B3		
8/8/2007	A3,B3		
8/9/2007	B3		
8/12/2007	A3		
8/13/2007	B3		
8/14/2007	B3		
8/15/2007	B3		
8/16/2007	B3		DayWork: Bottom lift on Stoddard Rd
8/18/2007			Ustick
8/20/2007	B3		
8/21/2007	B3		
8/22/2007	B3		
8/23/2007	B3		
8/26/2007	B3		
8/27/2007	B3		
8/28/2007	A3,B3		
8/29/2007	B3		
8/30/2007	A3		
9/4/2007			Paving Overland mainline (LT) between Topaz and Cloverdale
9/5/2007			Paving Overland approaches and side streets (LT/RT) between Topaz and Cloverdale
9/10/2007	A3		
9/11/2007			Put down 140 Ton on Approrettus
9/12/2007			Finished the business Approrettus
9/17/2007		B4	
9/18/2007		B4	
9/20/2007		B4	
9/24/2007		B4	
9/25/2007		B4	
9/26/2007		B4	Ustick
9/27/2007		B4	Finished Bottom lift on North half of Overland (started on 6/22/2007); Started Top lift from Meridian to Stoddard
9/28/2007			Ustick; Top Lift on Overland
9/29/2007			Top Lift on Overland

4. Discussion

The results of the monitoring campaign have been analyzed to:

(i) investigate of the relationships between O_3, its precursors (VOCs and NO_x) and meteorological regimes;

(ii) determine the spatial and temporal patterns of ozone;

(iii) determine the characteristics of high ozone days (days with O_3 mixing ratio higher than the 80^{th} percentile at a given site) as compared to typical ozone days (days with O_3 mixing ratio between the 45^{th} and 55^{th}-percentiles at a given site) and;

(iv) evaluate the impact of wildland fires and road pavement activities on ozone precursors.

4.1 Irradiated O_3-VOC-NO_x mixtures and local meteorology

Figure 4-1 and Figure 4-2 show the average diurnal variations of O_3, NO, NO_2 and selected VOCs at ITD and St. Lukes, respectively. For VOCs, the median values were computed, because of the log-normal distribution and to minimize the influence of outliers. Nighttime O_3 mixing ratios were about 12-15 ppbv, followed by a moderate decrease to about 8 ppbv in early morning (6:00 – 7:00) caused by the increased emissions of NO and NO_2 during the early morning commute. O_3 mixing ratios grew rapidly during morning and early afternoon, reaching a maximum at around 16:00-17:00. Then, O_3 declined till midnight and maintained low concentrations (less than 15 ppbv) overnight. The decline in the evening is the combined outcome of increased NO emissions during the evening commute and the absence of solar radiation.

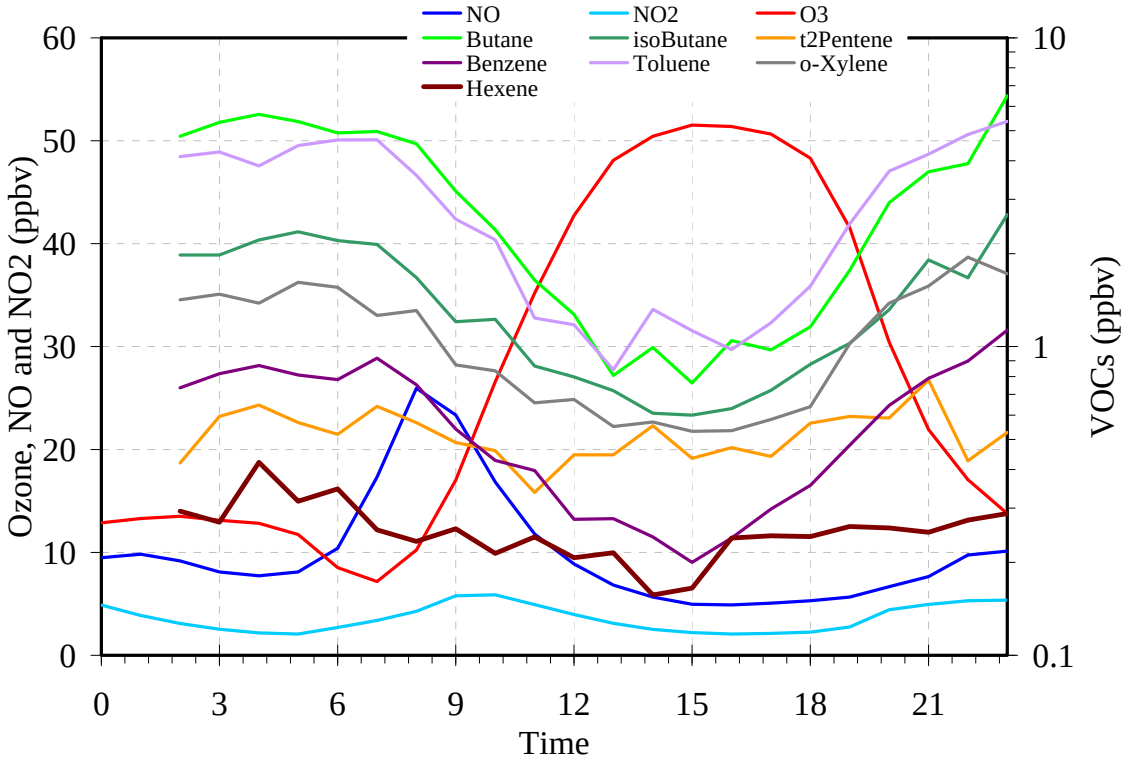

Figure 4-1 Diurnal variation of average ozone, NO, NO_2, and median *n*-butane, isobutene, *trans*-2-pentene, 1-hexene, benzene, toluene and *o*-xylene at ITD

The precursors (NO, NO_2 and VOCs) followed an opposite diurnal profile. For NO, concentrations increased rapidly in early morning, reaching their maximum levels at 7:00 (St.Lukes) or 8:00 (ITD) because of traffic emissions during the morning rush hours (6:00-9:00). Then, NO levels decreased progressively until early afternoon. The minimum NO concentration was measured at 18:00 (at St. Lukes) and 16:00 (at ITD). Nighttime NO increased to 10-30 ppbv. A similar pattern was also observed for NO_2, but the maximum concentration was observed at around 9:00-10:00, while nighttime levels where comparable to those observed in morning. Elevated nighttime NO_2 concentrations are due to the NO_x titration reaction (4). For both sites, the profiles of O_3 and NO_x are comparable to those observed in urban areas (see Figure 4-3).

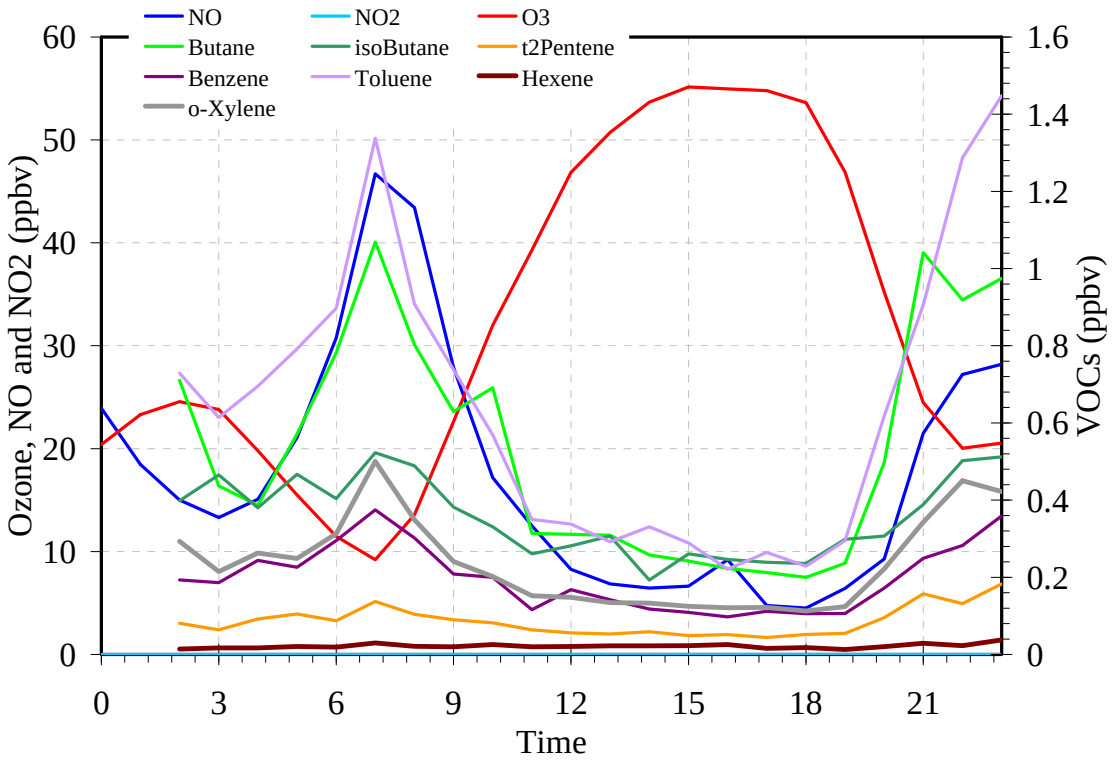

Figure 4-2 Diurnal variation of average ozone, NO, NO_2, and median *n*-butane, isobutene, *trans*-2-pentene, 1-hexene, benzene, toluene and *o*-xylene at St. Lukes

For VOCs, the diurnal pattern followed a trend similar to NO with lower concentrations during daytime as compared to those measured at night, but with a few significant differences for specific compounds and between the two sites. VOCs react with atmospheric oxidants including O_3, and $OH^{\cdot}$ and $NO_3^{\cdot}$ radicals. The kinetics of the reactions of different subgroups of VOCs with atmospheric oxidants determines their atmospheric lifetime and thus, their significance in tropospheric chemistry and oxidation capacity. Table 4-1 shows the estimated lifetimes for typical compounds of each VOC subgroup (alkanes, alkenes, alkynes, aromatic and oxygenated). For all subgroups, reactions with $OH^{\cdot}$ radicals are more significant than other oxidants. Ozone and nitrate radicals also play a significant role on the tropospheric reactivity of alkenes.

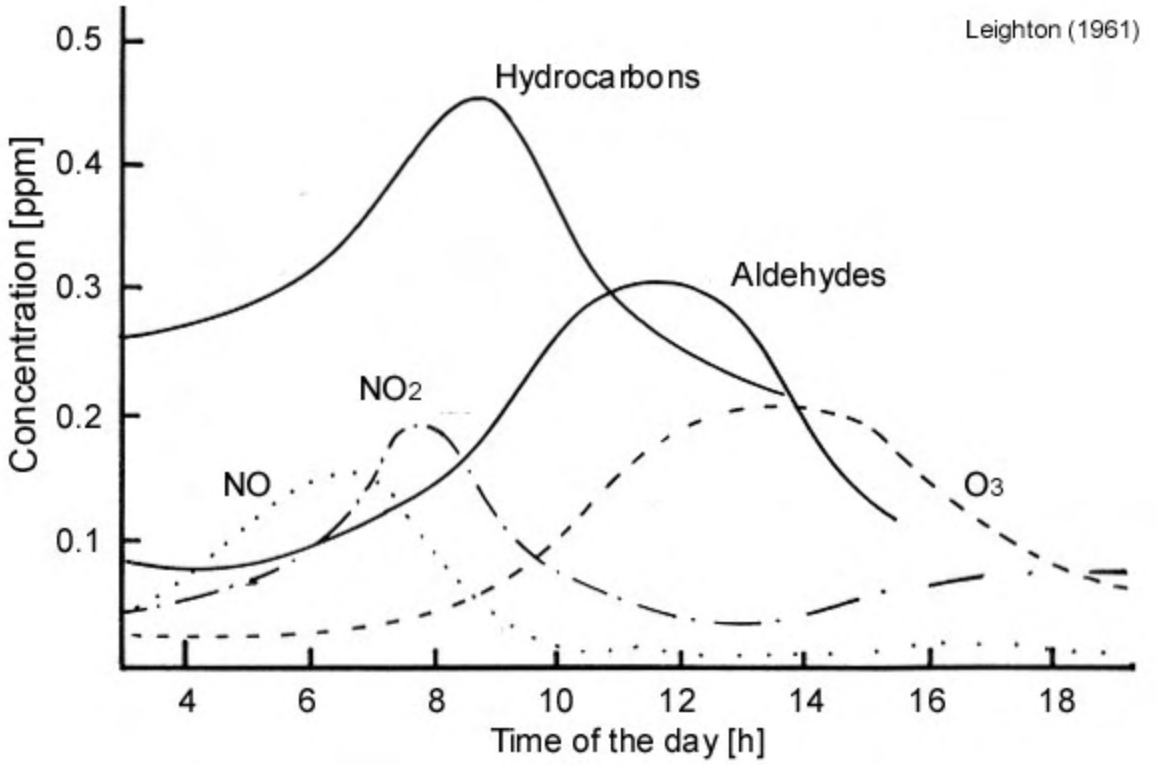

Figure 4-3 Typical variation of nitrogen oxides, hydrocarbons, carbon monoxide and ozone in urban photochemical smog episodes (Leighton, 1961)

Table 4-1 Estimated lifetimes of VOCs in the troposphere at typical atmospheric concentrations

	$OH^{\cdot}$ radical (1×10^6 cm^{-3})	**O_3 (100 ppbv)**	**$NO_3^{\cdot}$ radical (50 pptv)**	**Cl (1×10^4 cm^{-3})**
n-Butane	5 days	> 1300 yr	205 days	5 days
Trans-2-Butene	4.3 h	36 min	35 min	~ 4 days
Acetylene	14 days	> 400 days	> 188 days	~22 days
Toluene	2 days	> 400 days	138 days	20 days
Formaldehyde	1.2 days	> 463 days	16 days	16 days

Table 4-2 presents the rate constants of the VOCs measured in this study with OH radicals. Note that the higher reaction rates suggest effective removal of the organic compound by OH radicals. With the exception of acetylene, the values of rate constants indicate that alkenes react faster than aromatic hydrocarbons followed by alkanes.

Table 4-2 Rate constants of oxidation by OH radical of VOCs measured in this study

Compound			**k (10^{-12} cm^3 mol^{-1} s^{-1}) at 298 K**		
Alkanes		**Alkenes and Alkynes**		**Aromatic hydrocarbons**	
Propane	1.12	Acetylene	0.90	***Benzene***	***1.2***
n-Butane	***2.44***	Propylene	5.9	***Toluene***	***6.0***

Compound	k (10^{-12} cm^3 mol^{-1} s^{-1}) at 298 K					
iso-Butane	***3.7***	Isoprene	101	m-Xylene	23.6
n-Pentane	4.0	*cis*-2-Butene	56.4	p-Xylene	14.3
iso-Pentane	5.3	1-Butene	31.4	***o-Xylene***	***13.7***
	5.4		64.0	1,2,3-	32.7
anteiso-Pentane		trans-2-Butene		Trimethylbenzene	
	5.8		31.4	1,3,5-	57.5
2-2-Dimethylbutane,		1-Pentene		Trimethylbenzene	
2,3-Dimethylbutane;	5.8	*cis*-2-Pentene	65	Ethylbenzene	7.1
2,3-Dimethylpentane	3.4	**trans-2-Pentene**	**67**	n-Propylbenzene	6.0
2,2,4-Trimethylpentane	3.6	***1-Hexene***	***37***	Isopropylbenzene	6.5
n-Hexane,	5.45				
n-Heptane	7.0				
n-Octane	8.7				
n-Nonane	10.0				
n-Decane	11.2				
Cyclopentane	5.02				
Cyclohexane	7.21				
Methyl-cyclohexane	10				

Referring to Figure 4-1 and Figure 4-2, concentration levels of alkanes and aromatic hydrocarbons decreased progressively (at different rates) as O_3 increased in the morning. The minimum VOC concentrations were measured at around 13:00-16:00 pm. VOC levels increased in the evening similarly to the NO diurnal pattern. This indicated that a large fraction of alkanes and aromatics are associated with the evening commute activities, suggesting that VOCs are directly emitted from gasoline and diesel-powered vehicles. The concentrations of these organic compounds remained relatively stable throughout the nighttime because of the extremely slow reactions of alkanes and aromatic hydrocarbons with $NO_3^{\cdot}$ radicals ($k_{butane\text{-}NO3}$=4.59 10^{-17} cm^3 mol^{-1} s^{-1}; $k_{toluene\text{-}NO3}$=6.8 10^{-17} cm^3 mol^{-1} s^{-1}). Even under certain conditions in which concentrations of $NO_3^{\cdot}$ radicals (400 ppt) are three orders of magnitude higher than of $OH^{\cdot}$ concentrations (~0.4 ppt), the removal of alkanes and aromatic hydrocarbons by $NO_3^{\cdot}$ is not anticipated to be significant. As for alkenes, their concentrations were substantially lower than those of alkanes with no significant differences between day and night. This indicated that alkenes undergo continuous oxidation, by $OH^{\cdot}$ radicals and O_3 in the daytime and, by $NO_3^{\cdot}$ radicals at night. The rates of reactions of alkenes with $OH^{\cdot}$ radicals are typically up to ten times higher than those of alkanes. At the same time, while rate constants of alkenes with $NO_3^{\cdot}$ radicals span about six orders of magnitude, they are up to five orders of magnitude higher than those of alkanes and aromatic hydrocarbons. As a result, reaction of alkenes with $NO_3^{\cdot}$ radicals is expected to be a major removal pathway of alkenes at night. This reaction scheme also contributes to the removal of NO. The by-products of the alkenes- $NO_3^{\cdot}$ radicals reactions include polyfunctional organic compounds that can include more than one nitro group and may be responsible for the "missing NO_y" (where NOy equals the sum of all reactive oxidized nitrogen species). Since $NO_3^{\cdot}$ radicals react very quickly with NO, a moderate decrease of NO concentrations may be observed at night, consistent with the diurnal pattern of NO at both ITD and St. Lukes.

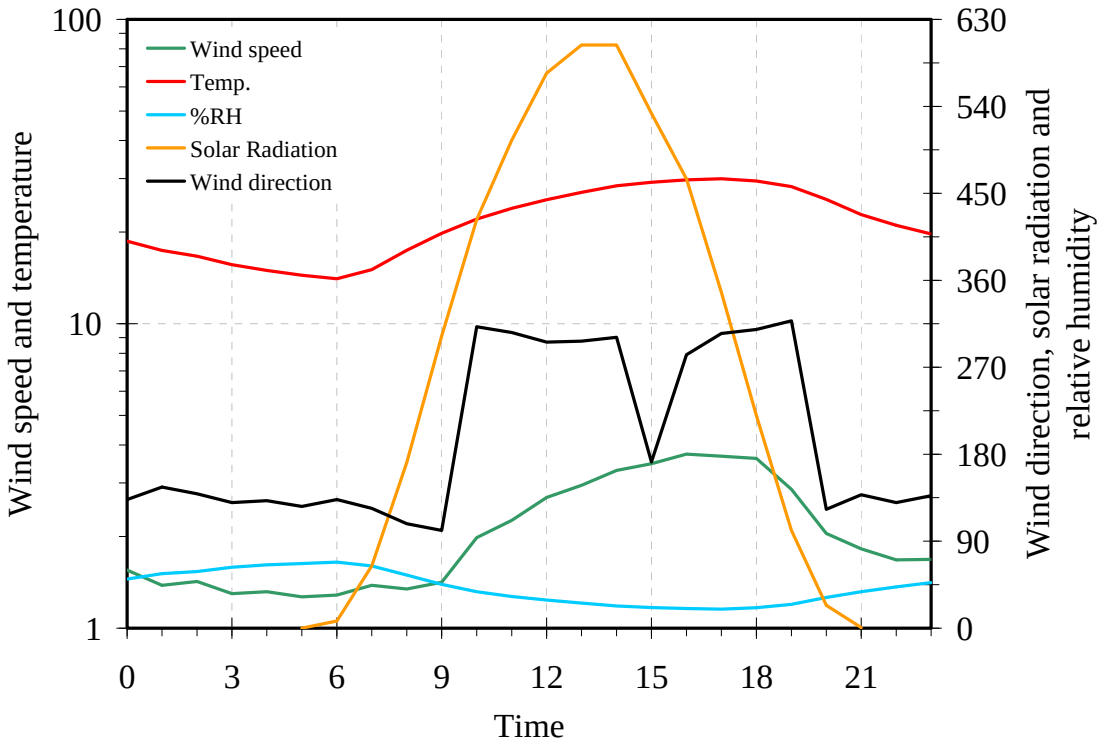

Figure 4-4 Diurnal variation of wind conditions (wind direction (in degrees) and wind speed (m s^{-1})), temperature (in ^{o}C), relative humidity (%) and solar radiation (W m^{-2}) at Boise Fairgrounds

Local meteorology and weather patterns are also important parameters in the chemistry of O_3 as they determine to a large extent the spatial and temporal patterns of ozone and precursor concentrations. Solar radiation is a driving force for the initiation of photo-oxidation reactions. Temperature is another indicator of the incoming solar radiation. Wind speed and direction provide information on the local air circulation. Changes in wind speed and direction may also provide indications of the intrusion of aloft O_3 during daytime. Water vapor is an important factor in photochemical processes both directly as a source of $OH^{\cdot}$ radicals, and indirectly through the formation of secondary organic aerosol that influence the ultraviolet actinic flux (Duenas et al., 2002).

Figure 4-4 shows the diurnal variation of meteorological conditions in Boise. As anticipated, the profiles of temperature and solar radiation track very well. In general, wind direction changes from the southeast during nighttime to the northwest during daytime as wind speed increased from 1.5 to 4 m s^{-1}. Table 4-3 shows the correlation matrix for meteorological parameters, O_3, NO_x and selected VOCs. The hourly average concentrations for ozone and its precursors (median was calculated for VOCs) for selected ranges of wind speed and direction, temperature and relative humidity are shown in Table 4-4 - Table 4-7. O_3 showed moderate positive correlations with wind speed, while negative correlations were computed for NO_x and VOCs. The average O_3 concentration increased for winds originating from the north and west sectors at all sites, while the opposite was observed for NO_x and VOCs. The O_3 concentrations increased progressively with the wind speed (from 1.0 to 4.0 m s^{-1}) and remained stable for wind speeds higher than 4.0

m s^{-1}. The concentrations of NO, NO_2 and VOCs decreased steadily with increasing wind speeds. This pattern indicated that intrusion of O_3 from upper layers is more prevalent as the wind speed increases and reduces the stability of the boundary layer. O_3 in the upper layers is most likely originated from upwind sources. The mixing of surface air with upper air also contributes to the faster dispersion of local NO_x and VOCs.

Table 4-3 Correlations of O_3, NO_x and selected VOCs withmeteorological parameters ([a] significant at 0.05 level; [b] not significant; all other significant at 0.01 level)

	Wind speed	Temperature	Relative humidity	Solar radiation
ITD				
O_3	0.398	0.791	-0.792	0.570
NO	-0.377	-0.365	0.440	-0.140
NO_2	-0.378	-0.108	0.148	-0.088
n-Butane	-0.240	-0.083[a]	0.159	-0.191
Isobutane	-0.247	0.009	0.127	-0.168
trans-2-Butene	-0.120[a]	0.085[b]	-0.025[b]	-0.043[b]
1-Hexene	-0.029[b]	0.096[a]	-0.045[b]	-0.022[b]
Benzene	-0.142	0.084[a]	0.045 [b]	-0.143
Toluene	-0.210	0.051 [b]	0.059 [b]	-0.256
o-Xylene	-0.204	0.119	0.025	-0.143
St.Lukes				
O_3	0.365	0.749	-0.782	0.553
NO	-0.361	-0.353	0.469	-0.291
n-Butane	-0.191	-0.075[a]	0.170	-0.163
Isobutane	-0.149	-0.311	0.260	-0.208
trans-2-Butene	-0.102	-0.049[b]	0.075[a]	-0.126
1-Hexene	0.026[b]	0.092[a]	-0.073[b]	0.054[b]
Benzene	-0.263	-0.157	0.294	-0.213
Toluene	-0.273	-0.105	0.265	-0.184
o-Xylene	-0.122	0.091	0.058[b]	-0.022[b]

Table 4-4 Concentrations of O_3 and its precursors for different segments of wind direction ([a]not significant; all other significant at 0.01 level)

	315-45	45-135	135-225	225-315
O_3				
O_3 (ITD)	39	18	18	37
O_3 (St. Lukes)	44	22	23	42
O_3 (Whitney)	42	20	21	42
O_3 (Parma)	39	20	23	37
O_3 (Nampa)	39	24	24	39
O_3 (White Pine)	46	28	29	46
O_3 (Mountain View)	40	19	20	39
Precursors				

NO	8	11	12	8
NO_2	2	4	4	3
n-Butane	1.234	3.467	4.824	1.366
Isobutane	0.765	1.544	1.952	0.910
trans-2-Pentene[a]	0.355	0.540	0.561	0.517
1-Hexene[a]	0.232	0.275	0.238	0.221
Benzene	0.312	0.752	0.845	0.339
Toluene	1.487	3.905	4.132	1.775
o-Xylene	0.532	1.339	1.398	0.713
St. Lukes				
NO	6	25	25	9
n-Butane	0.200	0.730	0.750	0.280
Isobutane	0.296	0.434	0.407	0.261
trans-2-Pentene[a]	0.049	0.088	0.103	0.063
1-Hexene[a]	0.016	0.021	0.024	0.020
Benzene	0.100	0.300	0.200	0.100
Toluene	0.260	0.870	0.870	0.350
o-Xylene	0.109	0.266	0.299	0.147

Table 4-5 Concentrations of O_3 and its precursors for selected ranges of wind speed ([a]not significant; all other significant at 0.01 level)

	< 1.0	1.0 – 2.0	2.0 – 4.0	> 4.0
O_3				
O_3 (ITD)	13	22	37	43
O_3 (St. Lukes)	20	27	42	45
O_3 (Whitney)	15	25	43	46
O_3 (Parma)	18	25	37	41
O_3 (Nampa)	19	28	39	42
O_3 (White Pine)	25	31	48	50
O_3 (Mountain View)	15	24	40	42
Precursors				
Idaho Transportation Dept.				
NO	14	11	7	5
NO_2	5	4	3	1
n-Butane	6.096	3.582	1.209	0.714
Isobutane	2.040	1.702	0.714	0.615
trans-2-Pentene[a]	0.671	0.556	0.446	0.446
1-Hexene[a]	0.262	0.274	0.210	0.218
Benzene	0.903	0.723	0.306	0.243
Toluene	4.530	3.688	1.549	0.831
o-Xylene	1.571	1.304	0.647	0.471
St. Lukes				
NO	27	20	12	5
n-Butane	0.910	0.620	0.250	0.180
Isobutane	0.469	0.367	0.247	0.314

trans-2-Pentene[a]	0.097	0.088	0.057	0.054
1-Hexene[a]	0.021	0.022	0.022	0.017
Benzene	0.300	0.200	0.100	0.100
Toluene	0.930	0.760	0.310	0.200
o-Xylene	0.341	0.265	0.129	0.103

The dependence of O_3 concentrations on ambient temperature is well documented. As anticipated, O_3 showed a significant correlation with temperature. The highest O_3 concentrations (> 50 ppbv) were measured for temperatures higher than 30°C. O_3 levels decreased drastically as temperatures decreased to 10°C. In contrast, there were significant differences among the precursors. NO concentrations decreased at higher temperatures, while NO_2 did not show any significant variation with temperature. As for VOCs, concentrations increased as temperatures decreased to 10-20°C, but they dropped for temperatures lower than 10°C.

Table 4-6 Concentrations of O_3 and its precursors for selected ranges of temperature ([a]not significant; all other significant at 0.01 level)

	> 10	10 – 20	20 - 30	> 30
O_3				
O_3 (ITD)	10	16	39	59
O_3 (St. Lukes)	19	21	42	62
O_3 (Whitney)	11	15	35	62
O_3 (Parma)	15	17	31	47
O_3 (Nampa)	14	20	33	53
O_3 (White Pine)	21	25	40	62
O_3 (Mountain View)	13	15	33	56
Precursors				
Idaho Transportation Dept.				
NO	12	12	7	8
NO_2	3	4	3	3
n-Butane	2.824	4.210	1.691	1.463
Isobutane	0.973	1.592	1.080	0.828
trans-2-Pentene[a]	0.128	0.413	0.530	1.404
1-Hexene[a]	0.138	0.250	0.250	0.216
Benzene[a]	0.370	0.681	0.492	0.407
Toluene	1.905	3.824	2.512	2.345
o-Xylene	0.464	1.356	0.912	1.111
St. Lukes				
NO	22	22	11	9
n-Butane	0.250	0.610	0.360	0.360
Isobutane	0.519	0.466	0.286	0.182
trans-2-Pentene[a]	0.053	0.086	0.065	0.084
1-Hexene[a]	0.008	0.021	0.023	0.032
Benzene	0.200	0.200	0.200	0.100
Toluene	0.410	0.790	0.550	0.340
o-Xylene	0.140	0.238	0.166	0.199

O_3 showed a significant negative correlation with relative humidity. The highest O_3 concentrations (higher than 40 ppbv) were recorded during dry conditions (less than 40%). For extremely humid conditions (higher than 80%), average O_3 concentrations were low. Concentrations of NO_x and VOCs increased as relative humidity increased to about 80%, but dropped slightly for more humid conditions. This may be explained by the scavenging of NO, NO_2 and VOC by water droplets.

Table 4-7 Concentrations of O_3 and its precursors for selected ranges of relative humidity ([a]not significant; all other significant at 0.01 level)

	< 40	40 - 60	60 - 80	> 80
O_3				
O_3 (ITD)	42	16	11	9
O_3 (St. Lukes)	46	22	17	16
O_3 (Whitney)	46	18	11	8
O_3 (Parma)	38	18	14	12
O_3 (Nampa)	42	22	16	11
O_3 (White Pine)	50	26	20	21
O_3 (Mountain View)	42	16	10	11
Precursors				
Idaho Transportation Dept.				
NO	7	12	12	14
NO_2	3	4	4	3
n-Butane	1.405	4.860	4.974	4.358
Isobutane	0.886	1.994	1.835	1.245
trans-2-Pentene[a]	0.545	0.597	0.443	0.323
1-Hexene[a]	0.223	0.322	0.270	0.167
Benzene	0.414	0.878	0.735	0.545
Toluene	2.006	4.399	4.063	3.134
o-Xylene	0.775	1.383	1.376	0.637
St. Lukes				
NO	10	24	26	23
n-Butane	0.290	0.660	0.750	0.690
Isobutane	0.243	0.395	0.508	0.491
trans-2-Pentene[a]	0.059	0.100	0.094	0.069
1-Hexene[a]	0.025	0.022	0.015	0.011
Benzene	0.100	0.200	0.300	0.300
Toluene	0.360	0.860	0.920	0.700
o-Xylene	0.142	0.300	0.287	0.198

These relationships indicated the existence of two distinct meteorological conditions in Treasure Valley that affect the boundary layer and transport within the valley. As the sun rises, the heating of the surface by incoming solar radiation warms the air near the surface which becomes unstable and begins to rise. As a result, the height of the boundary layer increases as does the wind speed, reaching their maxima in late afternoon. This accelerates the dispersion of surface

ozone precursors as well as the mixing of O_3 from upper layers. At the same time, changes in wind direction trigger air to move from the northwest of the valley to the southeast, accumulating pollutants in the southeast end of the valley. In evening and night, the cooling of the surface triggers an opposite trend with low wind speed, descent of the boundary layer, and change in wind direction. This results in the development of a near-ground inversion layer. These conditions favor the accumulation of ozone precursors emitted in the evening and early morning within the shallow near-ground layer.

4.2 O_3 accumulation

The O_3 mixing ratio measured at a given location is the outcome of contributions from the background, regional and long-range transport, penetration of stratospheric O_3 (rarely) and local photochemistry of biogenic and anthropogenic precursors. While the relative importance of these processes varies substantially, it has been recognized that photochemistry is the most important O_3 formation pathway in urban areas. As mentioned, the chemistry involving NO_x, radicals and VOCs to form O_3 is quite complex and non-linear. On the other hand, a large number of field, laboratory and modeling studies have provided significant insights into the process of irradiated O_3/NO_x/VOC mixtures and how changes in NO_x and VOCs will influence the formation (or destruction) of O_3. To analyze the impact of NOx and VOCs, the following three parameters are defined:

- NO-O_3 crossover time, tNO=O3, is the time of the day where NO and O_3 diurnal profiles intersect. Before this, O_3 concentrations reflect the carryover from nighttime. After the crossover, little NO is available For O_3 titration. The NO-O_3 crossover time defines also the end of the inhibition period, in which O_3 is destructed by NO in early morning.
- O_3 accumulation time, tO3_acc, is the time at which O_3 reaches its maximum concentration
- Accumulation rate is defined as follows:

$$\text{Acc.Rate} = \frac{[O_3]_{tO3\_acc} - [O_3]_{tNO=O3}}{tO3\_acc - tNO = O3}$$

where $[O_3]_{tNO=O3}$ and $[O_3]_{tO3\_acc}$ are the O_3 concentrations at NO-O_3 crossover and O_3 accumulation times, respectively.

As shown in Figure 4-5, the NO-O3 crossover occurred at the same time at both the IDT and St. Lukes sites, although, previous studies showed that inhibition ends earlier at downwind sites and for lower NO emissions [ITD is downwind of St.Lukes, and NO levels at ITD are lower than those measured at St.Lukes (Table 3-4)] (Fujita et al. 2003a). The O_3 accumulation rate was slower at St. Lukes but lasted longer as compared to the O_3 production at ITD, yielding comparable ozone levels.

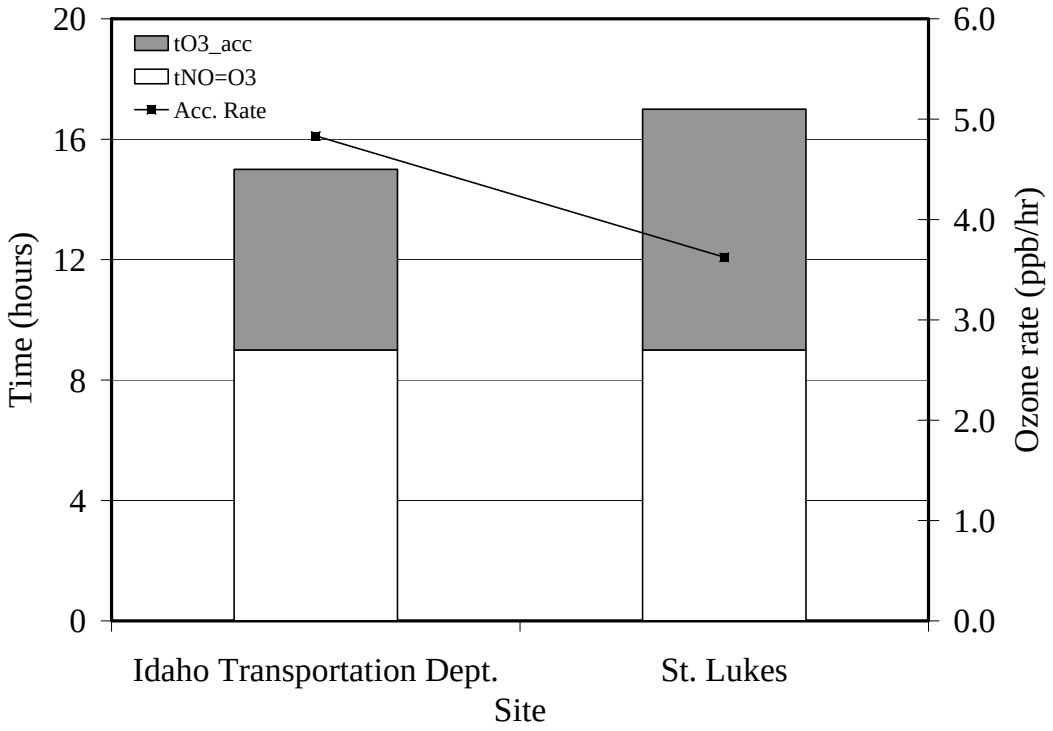

Figure 4-5 Duration and rate of ozone accumulation at ITD and St. Lukes

The differences in accumulation duration and time are reflected in the values of VOC/NO_x ratio (ITD: 30.1 ± 6.8; St.Lukes; 3.6 ± 1.1) and they indicate that O_3 formation at ITD is limited by NO_x while at St. Lukes, it is limited by VOCs. Table 4-8 presents the mean NO_x (in ppbv) and VOC (in ppbC) concentrations as well as the mean VOC/NO_x ratio between 8:00 and 19:00. The high VOC/NO_x ratios explain the faster formation of O_3 at ITD, however, it shuts down earlier than St.Lukes. This occurs because of the rapid consumption of NO by $HO_2^{\cdot}$ (reaction scheme 3) (note that NO levels in St. Lukes are lower than those measured in ITD). Hydroperoxy radicals ($HO_2^{\cdot}$) is produced from the oxidation of VOC with $OH^{\cdot}$. These reactions result also in the formation of NO_2, that was detected at ITD.

Table 4-8 Mean VOC/NO_x ratios and NO_x and VOC concentrations during daytime (8:00 – 19:00)

	ITD	**St. Lukes**
	Mean ± St.error	*Mean ± St.error*
NO_x (ppbv)	13 ± 1	13 ± 1
VOC (ppbC)	186 ± 36	10 ± 1
VOC/NO_x	30.1 ± 6.8	3.6 ± 1.1

4.3 Spatial and temporal variation

The purpose of this section is to determine the spatial and temporal characteristics of ozone and its precursors using a set of data analysis tools. These include:

- the Pearson correlation coefficient (r) to determine whether there is a uniform temporal profile (concentrations decrease or increase simultaneously). Pearson's correlation reflects the degree of linear relationship between two variables. It was calculated on an hourly basis as follows:

$$r = \frac{1}{n} \cdot \sum \left(\frac{X_i - \overline{X}}{s_x} \right) \left(\frac{Y_i - \overline{Y}}{s_y} \right)$$

Where $\frac{X_i - \overline{X}}{s_x}$, X_i, s_x, $\frac{Y_i - \overline{Y}}{s_y}$, $\overline{Y}$ and s_y are the standard errors, and population mean and standard deviation of X and Y populations. High (>0.70) correlation coefficients values indicate a positive linear relationship between variables, while negative values suggest a strong anti-correlation.

- the absolute (ΔC) and the relative difference ($\%\Delta C/Ref$) of 24-hr paired concentration differences between two sites. The relative difference was computed as the percentage of the absolute concentration difference to the reference site concentration. For the needs of this study, we used Parma (PAR) as a reference site for O_3 because of its upwind location with respect to the other sites in the Treasure Valley. The St. Lukes site is used as the reference monitor for NO_x and VOCs. Positive values indicate that ozone concentrations at the site were higher than those measured at Parma. The relative difference was also computed and analyzed on an hourly basis. Median absolute and relative differences provided an indication of systematic differences between the sites, whereas site-to-site variation was quantified using the standard deviation
- The coefficient of divergence (COD) was used to assess the spatial uniformity of measurements with respect to the concentration levels. The COD was estimated as follows:

$$COD = \sqrt{\frac{1}{p} \cdot \sum_{i=1}^{p} \left(\frac{C_{ij} - C_{ik}}{C_{ij} + C_{ik}} \right)^2}$$

where p is the total number of paired measurements, and C_{ij} and C_{ik} are the measured concentrations at the reference and comparison sites on the i-th day, respectively. The COD was computed using 24-hr concentrations at Parma for the reference values. COD values vary from 0 to 1, with COD values close to unity being indicative of strong spatial variation.

4.3.1 O_3

Table 4-9 shows the correlation coefficients of hourly O_3 measurements among the seven sites. The correlation coefficient values were high, from 0.815 to 0.938, indicating that O_3 concentrations followed almost identical temporal profiles. Figure 4-6 shows the hourly variation of O_3 at all sites.

Table 4-9 Pearson correlation coefficients of 1-hr ozone measurements at the sites

	ITD	STL	WHT	PAR	NNU	WHP
STL	0.908					
WHT	0.936	0.913				
PAR	0.854	0.861	0.833			
NNU	0.853	0.873	0.867	0.853		
WHP	0.920	0.896	0.946	0.816	0.815	
MOU	0.941	0.921	0.939	0.843	0.823	0.938

The amplitude, defined as the difference between maximum and minimum O_3 concentrations, ranged from 35 and 37 ppbv for Parma and Nampa up to 49 ppbv for Whitney (42 ppbv for White Pine, 43 ppbv for Mountain View, 44 ppbv for ITD and 46 ppbv for St. Lukes). These deviations (between Parma/Nampa and the other sites) were caused by very low nighttime/early morning O_3 levels at ITD, St. Lukes, Mountain View and Whitney as compared to those measured at Parma and Nampa. White Pine O_3 levels were consistently higher than the other sites, with a minimum concentration of 17 ppbv (that was 5-10 ppbv higher than those measured at all other sites).

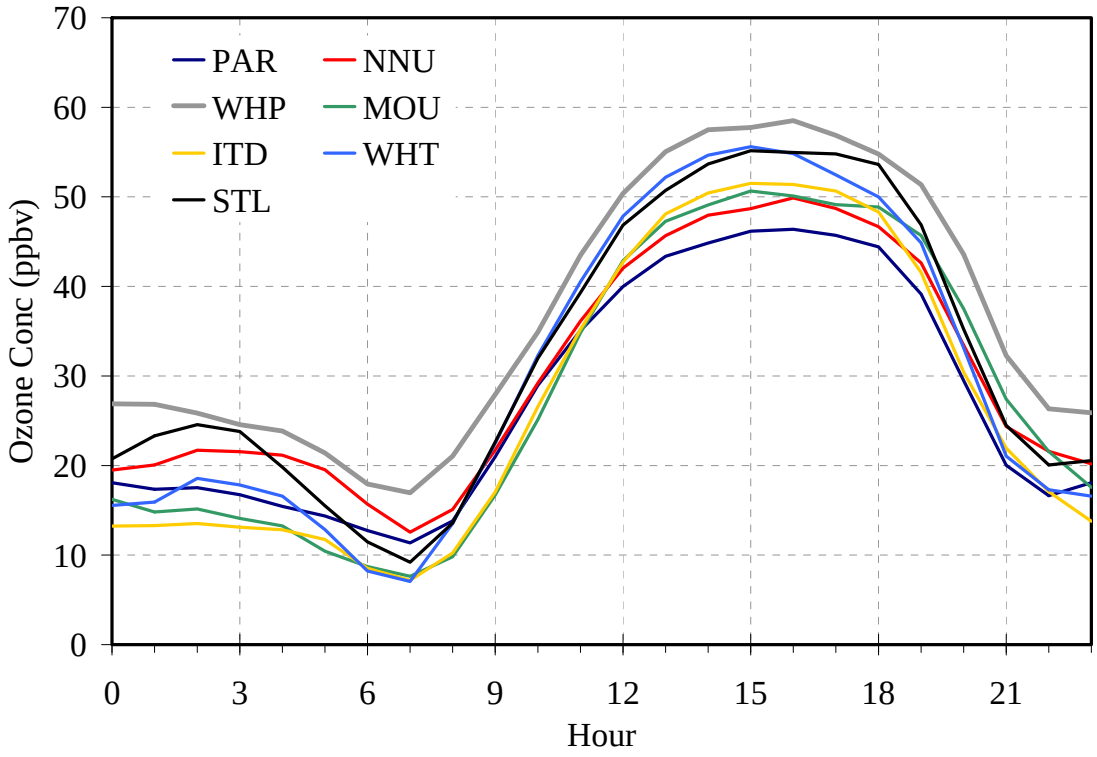

Figure 4-6 Average hourly O_3 concentrations at all sites

Table 4-10 Absolute (ΔC) and relative (%ΔC/Ref) differences (Median and standard deviation) and COD values of daily concentration of O_3 at each site. Reference site: Parma.

	ΔC		%ΔC/Ref		
	Median	**σ**	**Median**	**σ**	**COD**
Idaho Transportation Dept.	-0.9	4.7	-4%	16%	0.057

St. Lukes	3.1	5.4	13%	19%	0.078
Whitney	1.3	6.6	5%	22%	0.112
Nampa	2.5	5.9	8%	19%	0.083
White Pine	8.3	5.9	27%	22%	0.167
Mountain View	-0.3	4.8	-1%	16%	0.057

Table 4-10 shows the distribution (median and standard deviation) of the 24-hour absolute (ΔC) and relative differences (%ΔC/Ref), between measurements at ITD, St. Lukes, Whitney, Nampa, White Pine, Mountain View and Parma (reference). In general, median ΔC values were low, indicating a rather uniform spatial pattern in the valley on a day-to-day basis. High 24-hour O_3 ΔC values were more commonly associated with increased O_3 concentration levels. This was more pronounced for White Pine (see Table 3-1) where O_3 levels were about 27% higher than those measured at Parma. The rather uniform spatial pattern of daily ozone concentrations was demonstrated by the low COD values (Table 4-10). The analysis of the site-to-site variation of O_3 concentrations, expressed by the standard deviation of %ΔC/Ref values, suggested common characteristics for ITD and Mountain View (sites located close to each other and near downtown Boise), Whitney and White Pine (sites located on the southeast end of the valley) and Nampa and St.Lukes (sites located upwind of Boise, but with significant mobile sources). However, overall, the differences between these three groups of sites were relatively small.

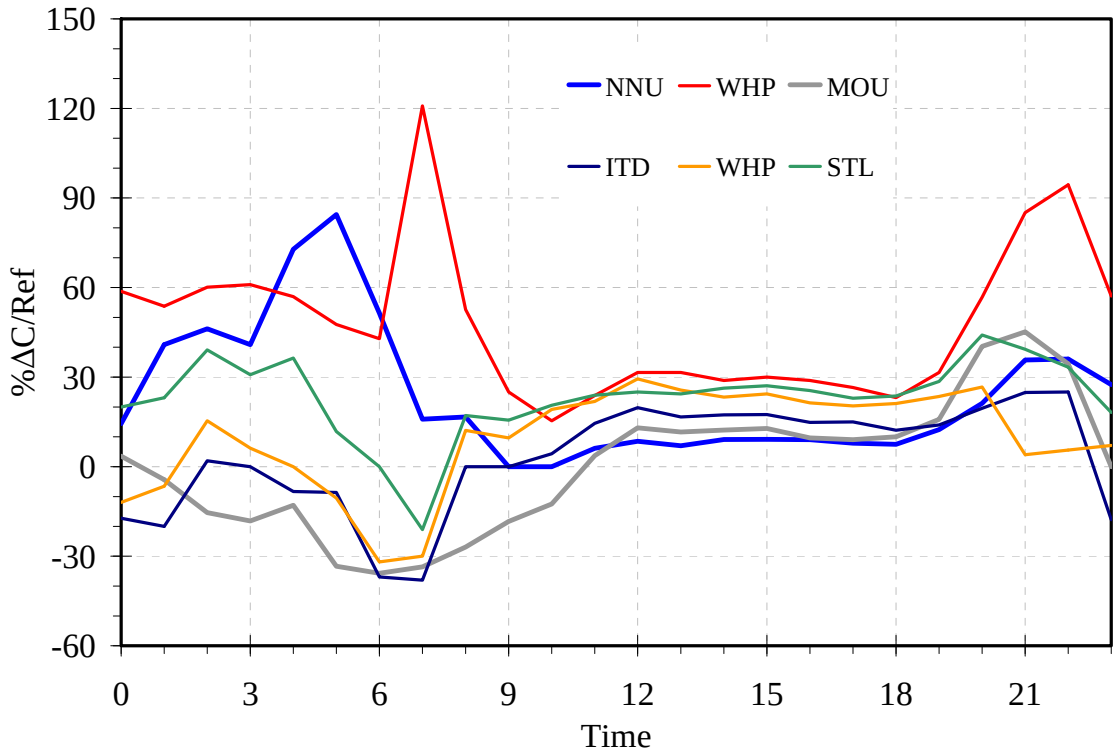

Figure 4-7 Diurnal profile of the relative difference

To further examine temporal differences between the sites, we plotted the relative difference as a function of the time of day for each site (Figure 4-7). There are two well-defined regimes. The first one, from 10:00 to 19:00, is characterized by relatively constant (0-30%) and comparable

relative differences for all sites. The second regime encompasses the hour from 21:00 till 8:00. The relative differences were quite variable and site-dependent with two peaks (for most of the sites) in the early morning (6:00-7:00) and late in the evening (20:00 - 22:00). These patterns indicate that (a) during daytime, photochemistry and local transport within the valley results in relatively uniform ozone levels and; (b) destruction of ozone in nighttime and early morning (by NO_x) is non-uniform, exhibiting significant site-to-site variability. This is further supported by the diurnal variation of wind condition (direction and speed) and incoming solar radiation (Figure 4-4). Overall, wind conditions were characterized by low speed winds from the south at nighttime and in the early morning. As solar radiation increase in early morning triggering the formation of OH radicals and reactions with NO_x and VOCs, winds tend to blow from the northwest. This change in wind direction facilitates transport from the northwest (Parma) to the southeast (Whitney and White Pine).

4.3.2 NO_x and VOCs

Table 4-11 shows the correlation coefficient of hourly NO and NO_2 measurements between the two sites. The correlation coefficient values were lower than 0.5 indicating poor temporal correlation. Figure 4-8 shows the hourly variation of NO and NO_2 at both sites.

Table 4-11 Pearson correlation coefficients of 1-hr NO and NO_2 measurements at the sites

	Idaho Transportation Dept	
	NO	NO_2
Idaho Transportation Dept. NO_2	0.312	
St. Lukes NO	0.473	0.377

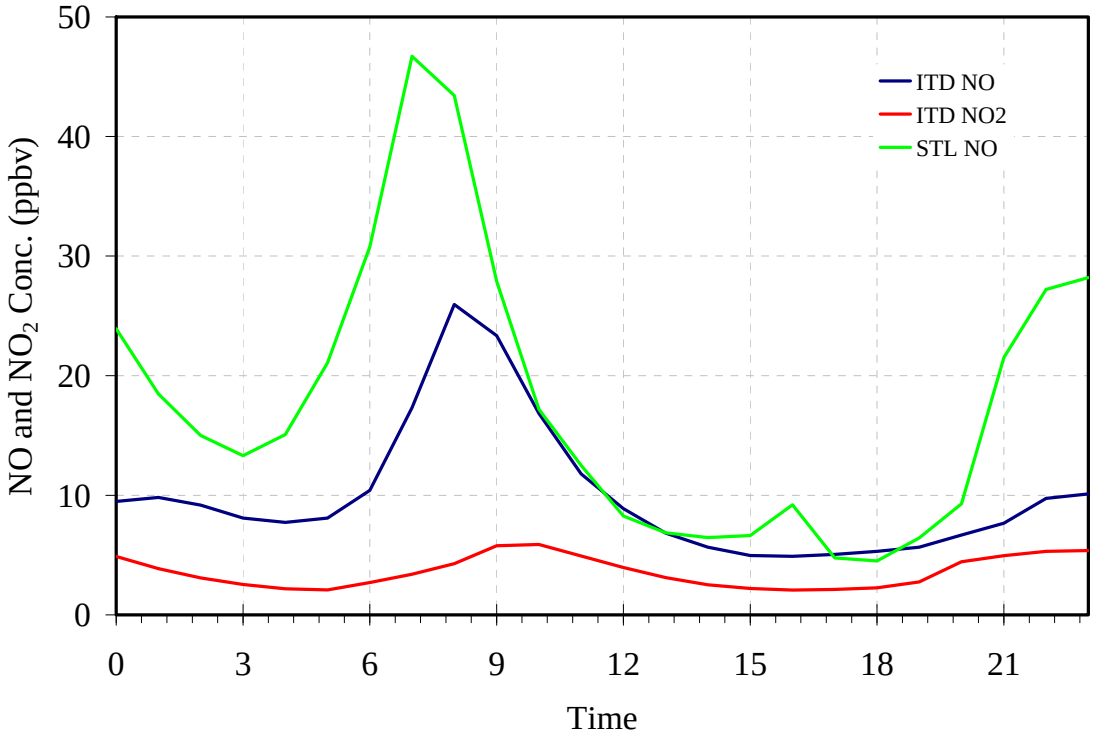

Figure 4-8 Hourly NO and NO_2 concentrations

The diurnal profiles follow a bimodal trend with two local maxima in the early morning and early evening that are associated with commuter traffic. NO at St.Lukes reached its maximum concentration one hour earlier as compared to ITD. NO_2 also followed a bimodal trend with the first local maximum observed at 9:00-10:00 a.m. This delay (compared to NO) was due to the time required to form NO_2 from VOC oxidation (reaction scheme 3 in Section 1.2). Table 4-12 shows the distribution (median and standard deviation) of the 24-hour absolute (ΔC) and relative differences (%ΔC/Ref) and COD values between measurements at ITD and St. Lukes (reference). Negative values of absolute and relative differences indicated that St. Lukes concentrations were lower than those measured at ITD at the same time of day. This variability was further supported by the high COD values and the site-to-site variation of NO concentrations, expressed by the standard deviation of %ΔC/Ref values (Table 4-12).

Table 4-12 Absolute (ΔC) and relative (%ΔC/Ref) differences (Median and standard deviation) and COD values of daily concentration of NO

	ΔC		%ΔC/Ref		
	Median	**σ**	**Median**	**σ**	**COD**
Idaho Transportation Dept.	-7.5	7.9	-43%	44%	0.832

Very high relative differences (~ -30%) were observed during early morning (5:00-9:00) and evening (17:00-22:00) as compared to noon and early afternoon (Figure 4-9). The differences between the two sites were primarily caused by traffic emissions. When wind conditions favored transport and mixing, NO measurements were comparable at the two sites (See Figure 4-4 for comparison).

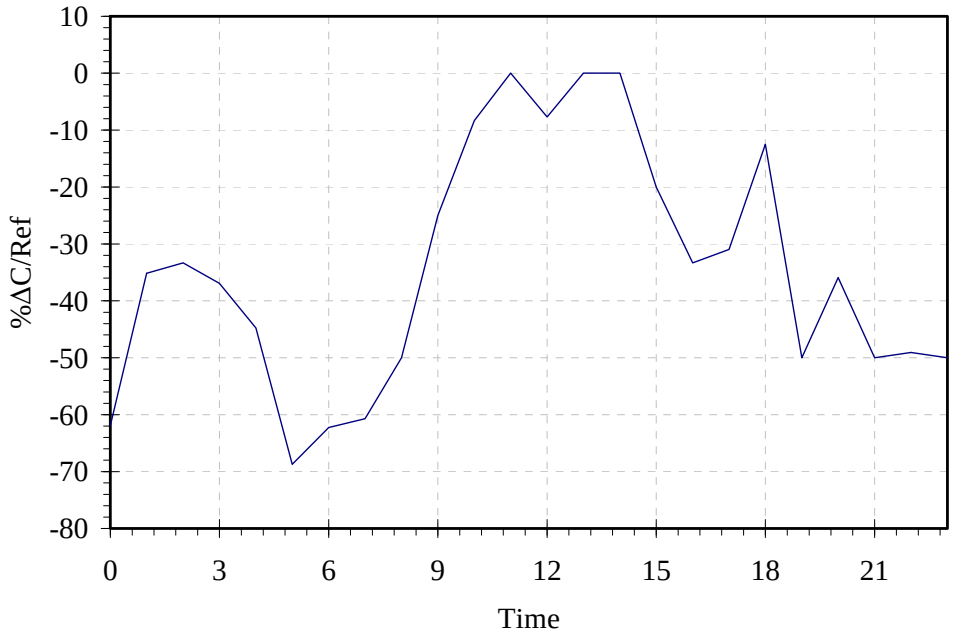

Figure 4-9 Relative differences in NO concentrations between the St Lukes (reference) and ITD sites.

Figure 4-10 and Figure 4-11 show the diurnal variation of selected VOCs at ITD and St. Lukes. Table 4-13 shows the correlation coefficient measurements, the distribution (median and standard deviation) of the 24-hour absolute (ΔC) and relative differences (%ΔC/Ref) and COD values between measurements at ITD and St. Lukes (as the reference) for VOCs. The correlation coefficients were low for all VOCs indicating that there were significant differences between the two sites. The highest correlations were computed for 1,2,4-trimethylbenzene, benzene, toluene, *n*-heptane, 2,3-Dimethylbutane/*iso*-&*anteiso*-Pentane/Isoprene and *m*-&*p*-Xylene/acetone. Most of these compounds are associated with vehicle emissions.

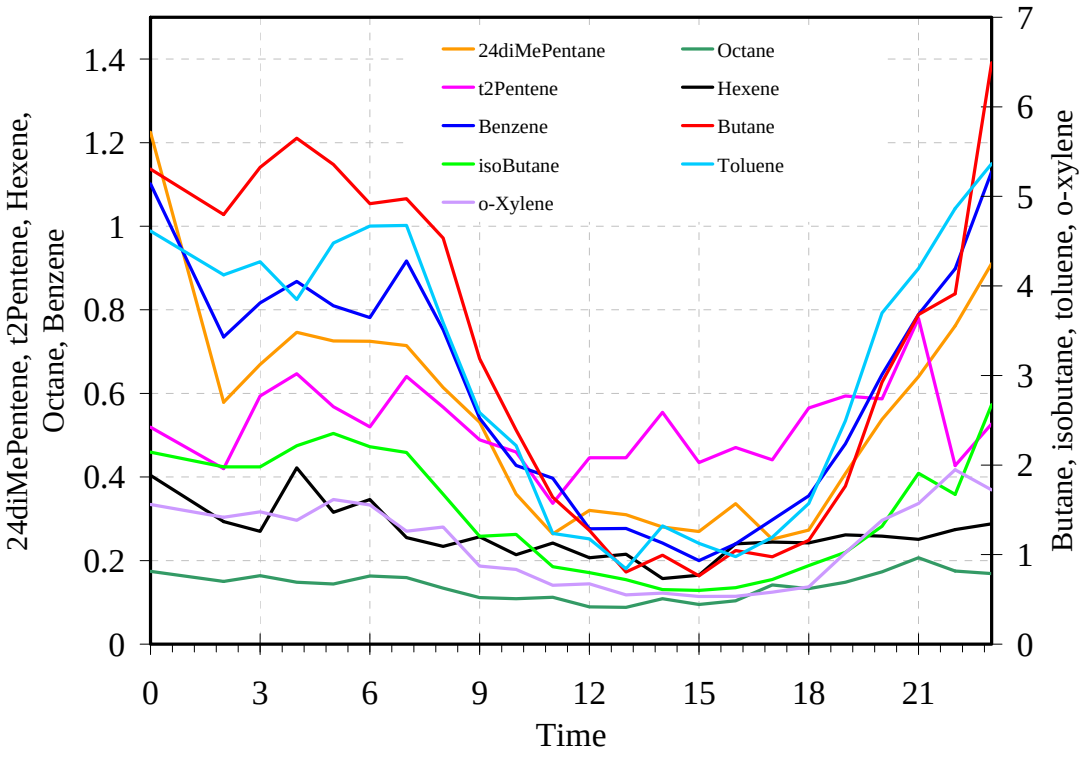

Figure 4-10 Diurnal variation of selected VOCs at ITD

Median ΔC values were moderate-to-high, indicating strong spatial differences between the two sites on a day-to-day basis. The high COD values and the site-to-site variation, expressed by the standard deviation of %ΔC/Ref values, provide strong evidence of the spatial variability of VOCs within the Treasure Valley. Note that COD values are higher than 1 because concentrations differences between the sites are quite frequently as high as one order of magnitude. The relative difference as a function of the time of day for each site is shown in Figure 4-12. In general, most of the VOCs (e.g. benzene, octane, hexene) showed lower variation during daytime. Given the large number of VOCs and the varieties of their sources, this evidence supports the assertion that spatial and temporal patterns are heavily influenced by emissions from nearby sources.

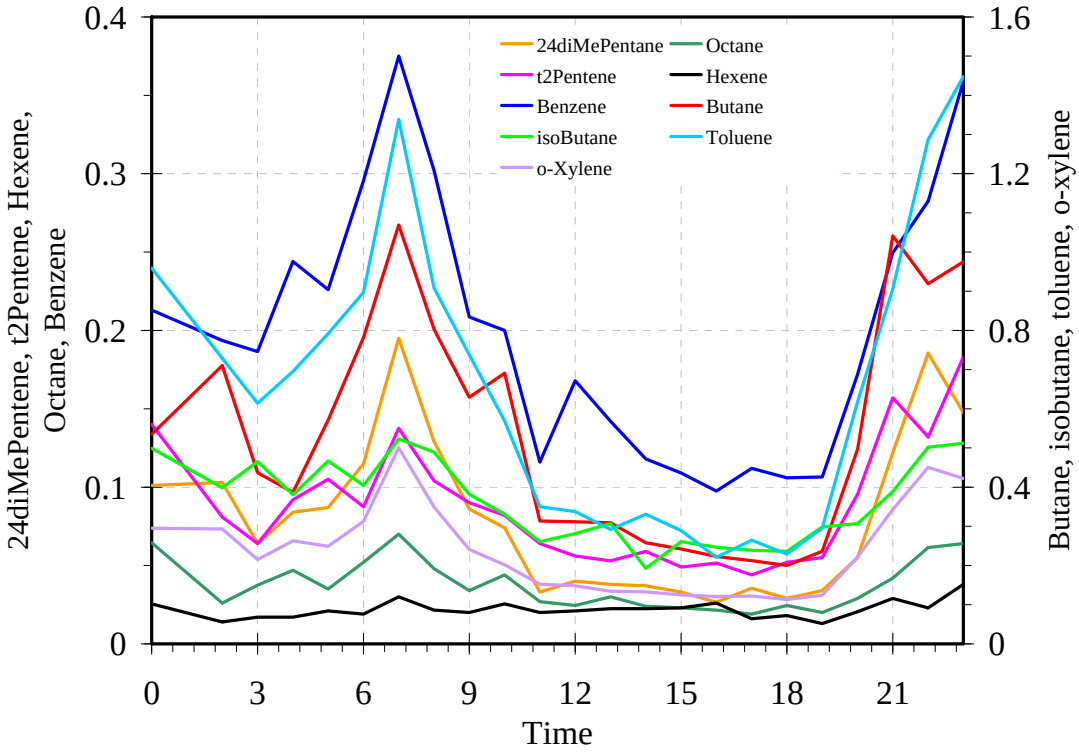

Figure 4-11 Diurnal variation of selected VOCs at St. Lukes

Table 4-13 Pearson correlation coefficients, absolute (ΔC) and relative (%ΔC/Ref) differences (Median and standard deviation) and COD values of VOCs measured at ITD and St. Lukes

	R	ΔC		%ΔC/Ref		COD
		Median	*σ*	*Median*	*σ*	
Alkanes						
Propane	0.030	1.22	311.1	431	328335	4.41
n-Butane	0.086	3.52	4.76	702	2849	4.60
iso-Butane	-0.007	1.30	3.25	325	6227	3.84
n-Pentane/Cyclopentane	0.134	1.62	1.32	517	582	3.31
cis-2-Butene/*iso*-Pentane	0.141	2.81	3.36	370	5820	3.64
2,3-Dimethylbutane/*iso*- and *anteiso*-Pentane/Isoprene,	0.224	0.32	1.25	135	1298	2.62
n-Hexane/Cyclohexane	0.091	0.35	0.94	223	491	2.82
n-Heptane	0.205	0.25	0.38	291	410	3.04
2,4-Dimethylpentane	0.017	0.61	1.79	668	2014	4.45
2,3-Dimethylpentane/*iso*- and *anteiso*-Hexane/ methyl-Cyclohexane	0.037	0.31	1.56	164	2095	2.89
n-Octane	-0.005	0.09	7.58	369	7635	3.99
Iso- and *anteiso*-Heptane,	0.052	0.02	0.37	52	741	2.34
2,2,4-Trimethylpentane	-0.057	0.35	3.05	271	2217	3.93
2,3,4-Trimethylpentane	-0.017	0.05	0.73	74	1300	2.35

n-Nonane	0.081	0.12	0.74	272	4631	3.23
n-Decane	0.078	0.10	0.22	122	333	1.37
Alkenes and Alkynes						
Acetylene	0.120	2.04	337.5	355	50372	4.18
Propylene	0.073	0.13	0.73	34	906	1.20
1-Butene	0.019	0.20	1.38	314	1810	3.31
trans-2-Butene	0.089	0.04	1.31	77	1414	2.26
1-Pentene	-0.005	0.20	0.70	350	1950	2.83
trans-2-Pentene	0.135	0.31	1.78	445	853	3.46
1-Hexene	0.040	0.21	3.37	1060	9366	5.23
Aromatic hydrocarbons						
Benzene	0.243	0.47	2.10	230	741	2.65
Toluene	0.282	2.56	3.27	339	445	3.40
m- and *p*-Xylene/acetone	0.226	2.20	1.92	284	584	3.27
o-Xylene	0.129	0.87	0.86	324	737	3.39
1,2,4-Trimethylbenzene	0.502	0.04	0.10	78	236	1.03
1,3,5-Trimethylbenzene	0.063	0.01	0.28	36	160	1.32
Ethylbenzene	0.103	0.11	1.20	118	431	1.96
Styrene	0.045	0.06	0.07	246	265	1.68
n-propyl/*iso*-propylbenzene	0.109	0.20	0.50	290	616	3.19

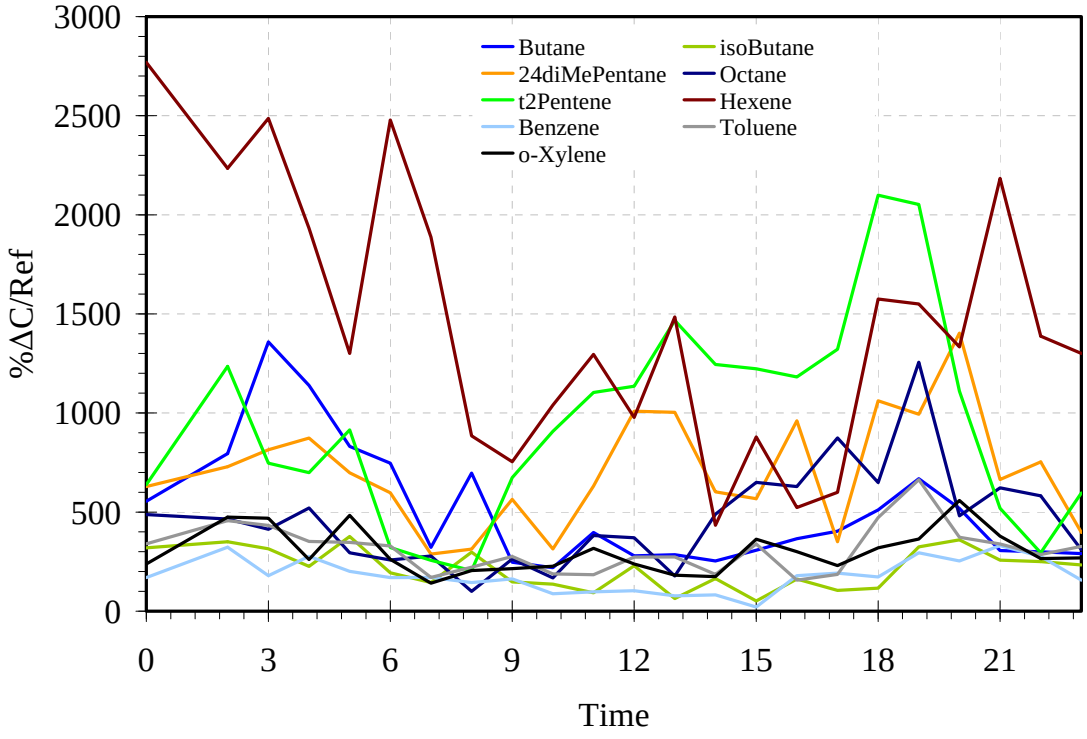

Figure 4-12 Diurnal profile of the relative differencebetween St Lukes (reference) and ITD in VOC concentrations.

4.4 Weekday/Weekend variations

Previous studies in California and elsewhere showed that there were significant differences in O_3 and its precursors between weekdays and weekends. The so-called "weekend O_3 effect" refers to higher O_3 concentrations during weekends despite lower NO_x and VOC levels. The California Air Resources Board (CARB) examined the causes of the weekend effect, including, (a) NO_x reduction; (b) NO_x timing; (c) carryover near ground; (d) carryover aloft; (e) increased weekend emissions and: (f) increased sunlight. From the analysis of data collected for over 20 years, carryover near ground and increased weekend emissions were excluded. Carryover aloft may be important only for specific episodes that are related to regional or long-range transport but not for the weekend effect. Reductions of NO_x emissions during weekends appeared to be the most important factor that causes the weekend effect. Details of this report can be found in Heuss et al., 2003 and Fujita et al., 2003a.

Figure 4-13 shows the day-of-week trends of average maximum O_3 concentrations for all sites in the Treasure Valley. O_3 concentrations were lowest on Sundays at all sites. In general, they increased through the week and peaked on Saturdays. Figure 4-14 and Figure 4-15 show the variation of mean NO_x concentrations at 4:00-5:00 am (to determine the overnight carryover), 7:00-8:00 (to determine the levels of NO_x associated with traffic emission during morning commute) and 15:00-16:00 (to assess the consumption of NO_x by photochemistry at ITD and St. Lukes. Similarly, Figure 4-16 and Figure 4-17 show the variation of total VOCs. Total VOCs (in ppbC) are calculated as:

$$\text{VOC in ppbC} = \sum \left(\frac{\text{Carbon Atoms} \cdot 12.001}{\text{MW}} \right) \cdot C_{voc}$$

where MW and C_{VOC} are the molecular weight and the concentration of each compound. For peaks associated with more than one compound, the MW and the structure of the compounds were comparable, thus the mean of the ratios of the number of carbon atoms by the molecular weight is used. Note that the computed total VOCs in ppbC was calculated using only the compounds determined by PFGC. More volatile (e.g. ethane, ethene) and biogenic hydrocarbons were not determined during this study. As a result, the estimated VOCs in ppbC represents a low-end estimate.

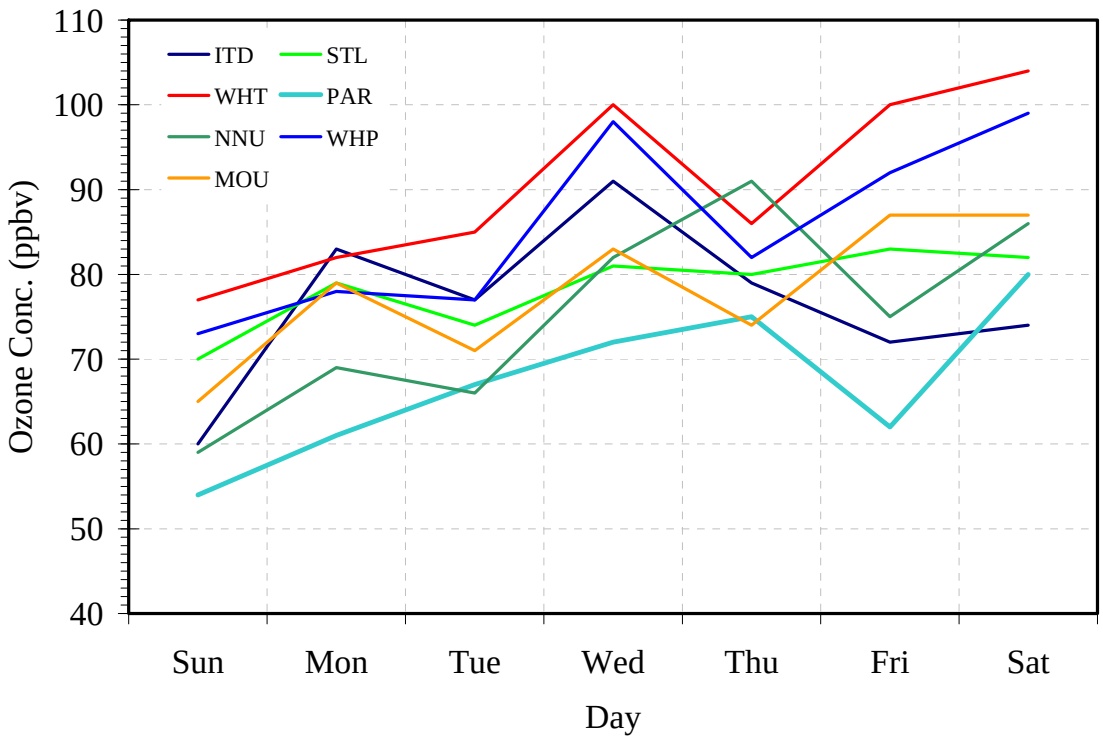

Figure 4-13 Day-of-week patterns of hourly maximum O_3 concentrations at ITD, St. Lukes, Whitney, Parma, Nampa, White Pine and Mountain View

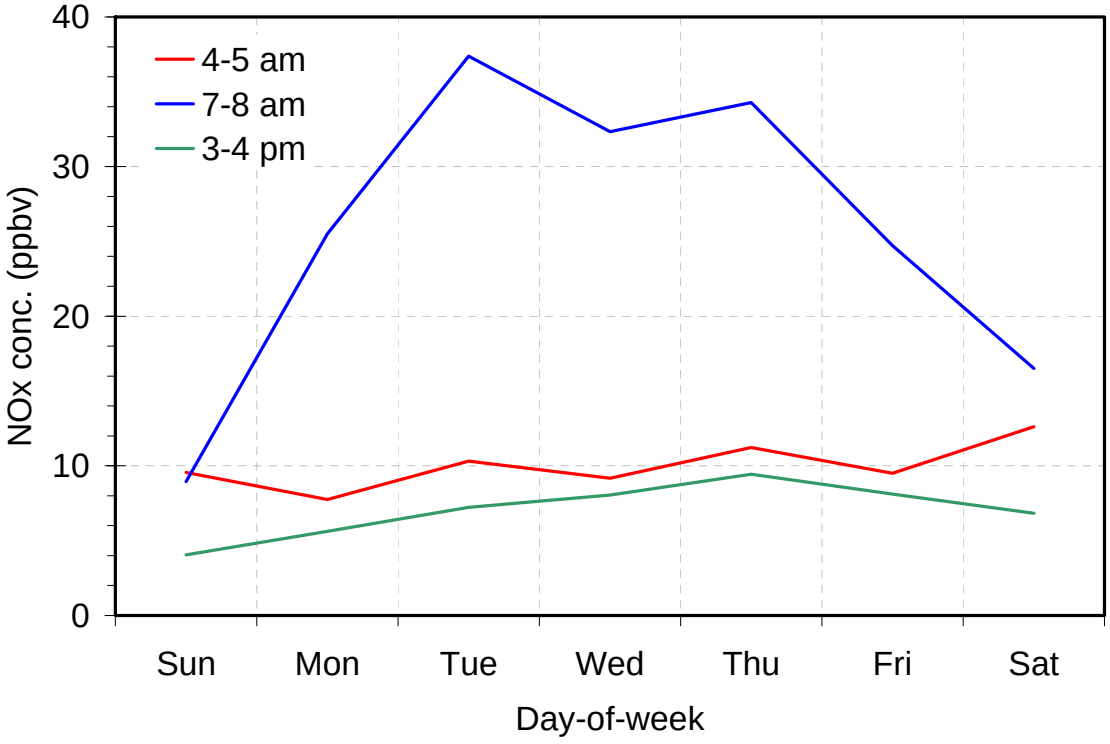

Figure 4-14 Day-of-week patterns of mean NO_x at 4:00-5:00, 7:00-8:00, 15:00-16:00 pm at ITD

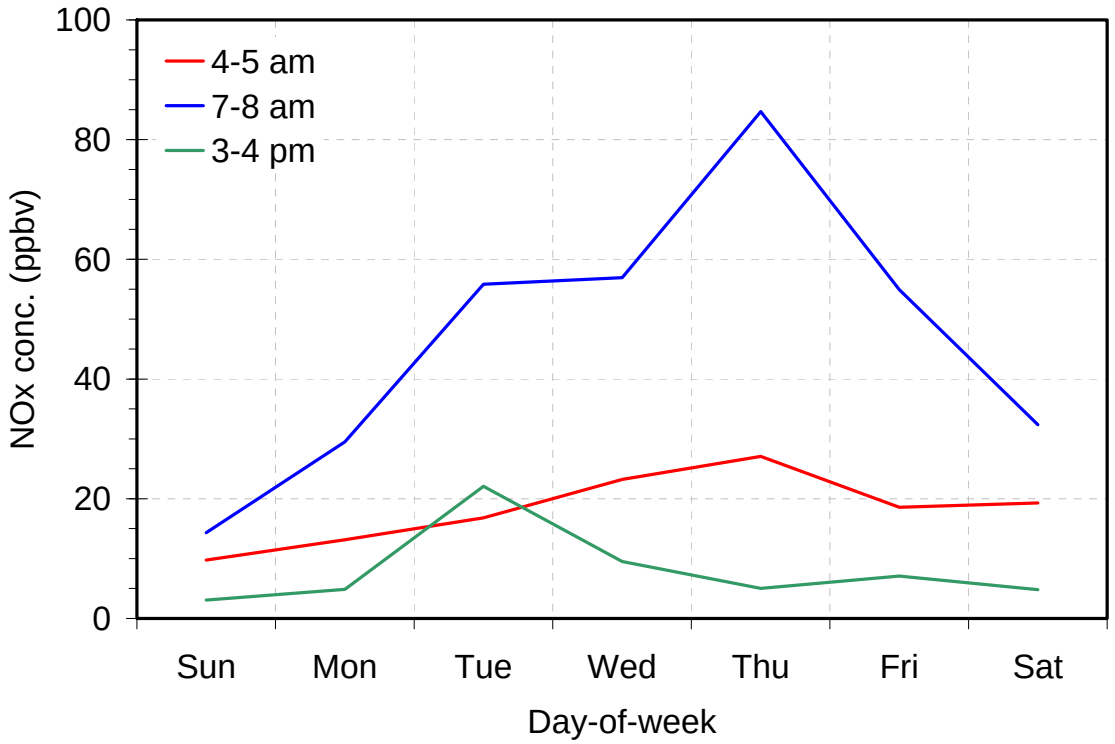

Figure 4-15 Day-of-week patterns of mean NO_x at 4:00-5:00, 7:00-8:00, 15:00-16:00 pm at St. Lukes

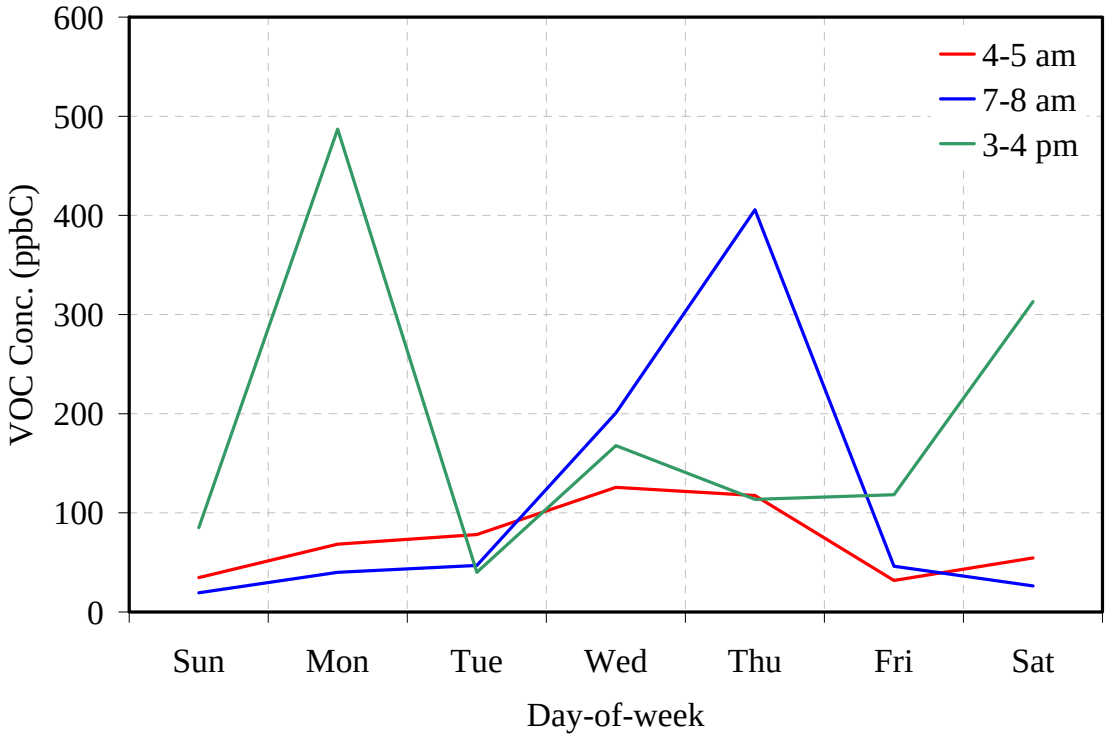

Figure 4-16 Day-of-week patterns of mean VOC at 4:00-5:00, 7:00-8:00, 15:00-16:00 pm at ITD

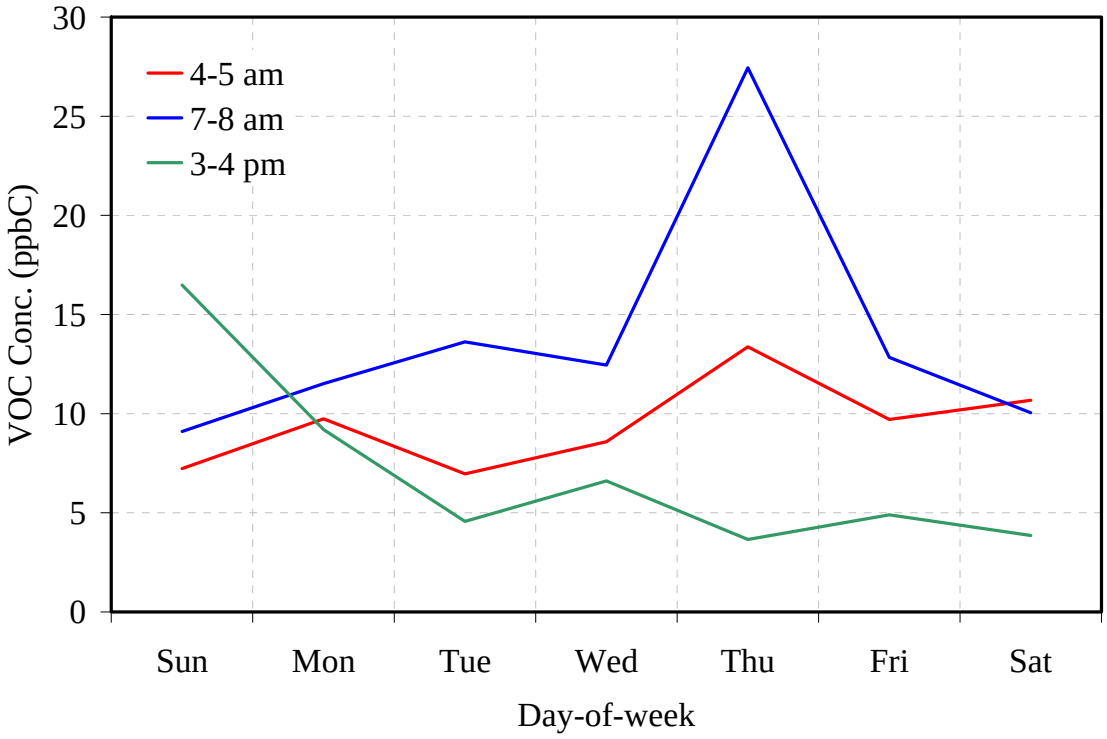

Figure 4-17 Day-of-week patterns of mean VOC at 4:00-5:00, 7:00-8:00, 3:00-4:00 at St. Lukes

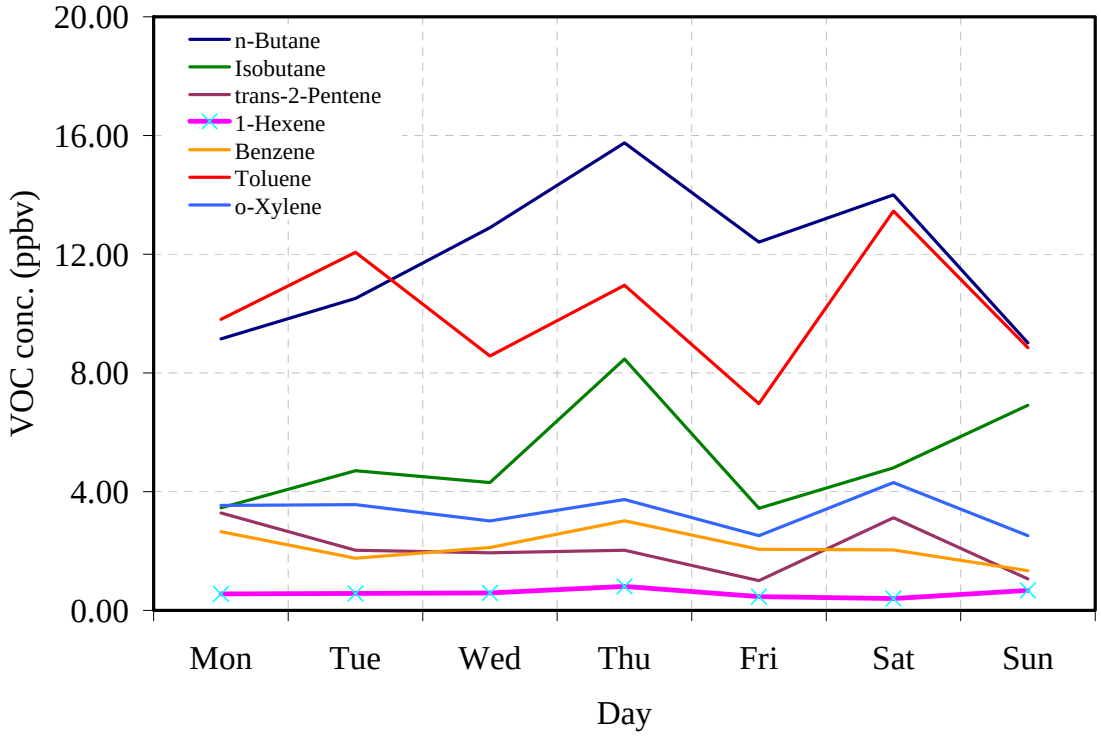

Figure 4-18 Day-of-week variation of median maximum concentrations of selected VOCs at ITD

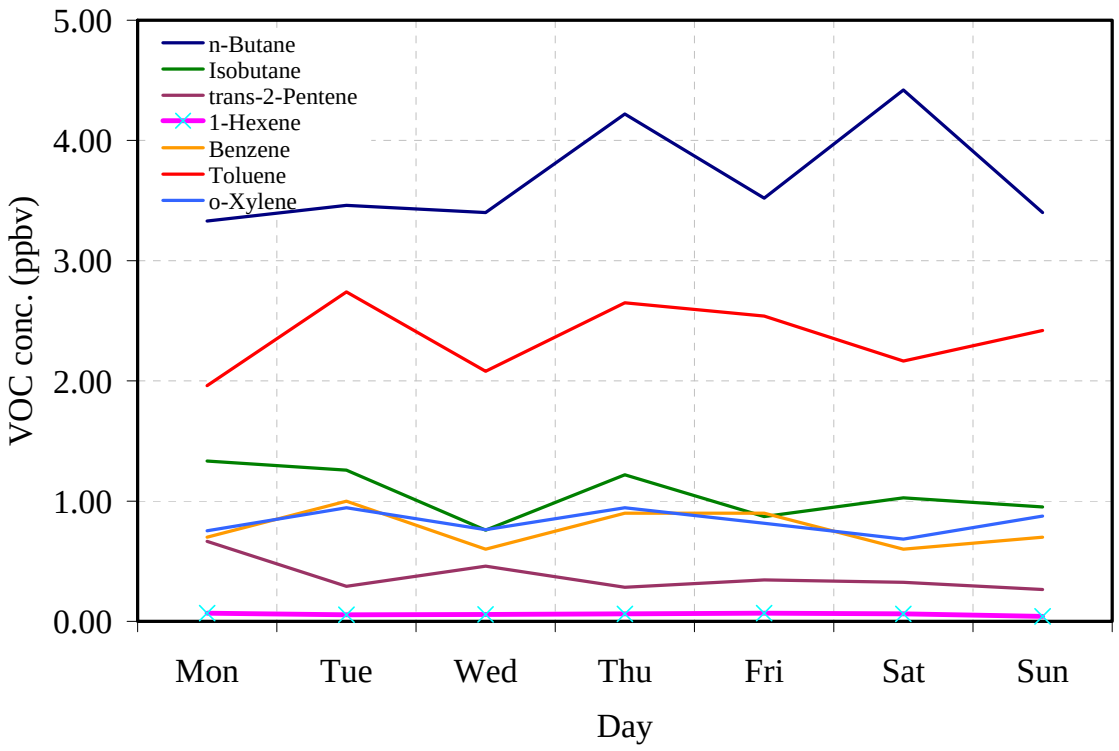

Figure 4-19 Day-of-week variation of median maximum concentrations of selected VOCs at St. Lukes

The amount of NO_x carryover was about 10 ppbv at ITD for all days and varied from 10 to 20 ppbv at St. Lukes. As for VOCs, the overnight carryover was about 100 ppbC at ITD and only 10 ppbC at St.Lukes. Mean NO_x levels during morning hours (7:00-8:00) during weekend days are two-four times lower than those measured during weekdays. As a result, the O_3 inhibition period, defined as the O_3 titration time by NO, ends earlier on weekends. NO_x levels in the early afternoon were substantially lower than the overnight carryover at both sites. A less clear pattern was observed for VOCs because it is composed of a range of organic compounds with different reaction rates. (Figure 4-18 and Figure 4-19). The levels of selected alkanes, alkenes and aromatic hydrocarbons did not change systematically between weekdays and weekends.

Figure 4-20 show the diurnal variations of NO and O_3 on Thursdays and Sundays. NO and O_3 on Thursday followed the typical profiles for urban areas, as described previously. The tNO=O3 crossover was observed at about 10:00 am, while O_3 accumulated for about 5 hours. Sunday NO levels did not increase in the morning due to reduced traffic. As a result, O_3 formation was not inhibited. The lower accumulation rate observed on Sundays was offset by the longer accumulation period, resulting in O_3 levels comparable to Thursdays. O_3 reached its highest concentration at 16:00. The day-of-week variation of the morning crossover, accumulation and accumulation rate are presented in Figure 4-21 and Figure 4-22. The inhibition period (destruction of nighttime carryover O_3 by NO in the morning) ends one hour earlier on Saturdays and virtually never starts on Sundays at both sites. O_3 accumulation ends later Monday-Wednesday, but the accumulation rates are higher Thursday - Saturday. Lower NO emissions are responsible for the faster end of the inhibition period at St. Lukes as compared to ITD.

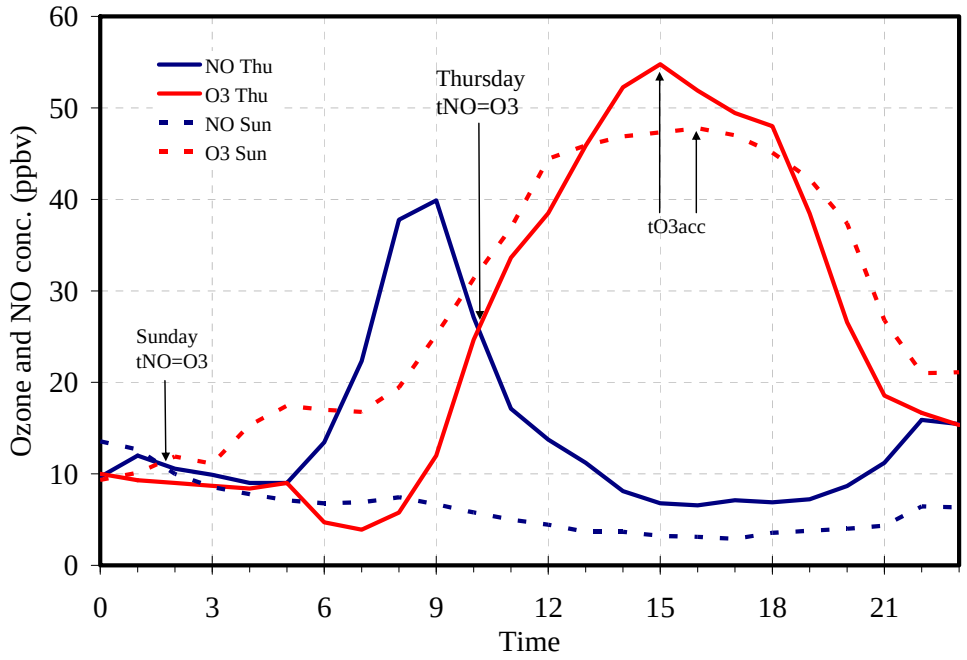

Figure 4-20 Diurnal variation of average maximum O_3 and NO concentration on Thursdays and Sundays at St. Lukes

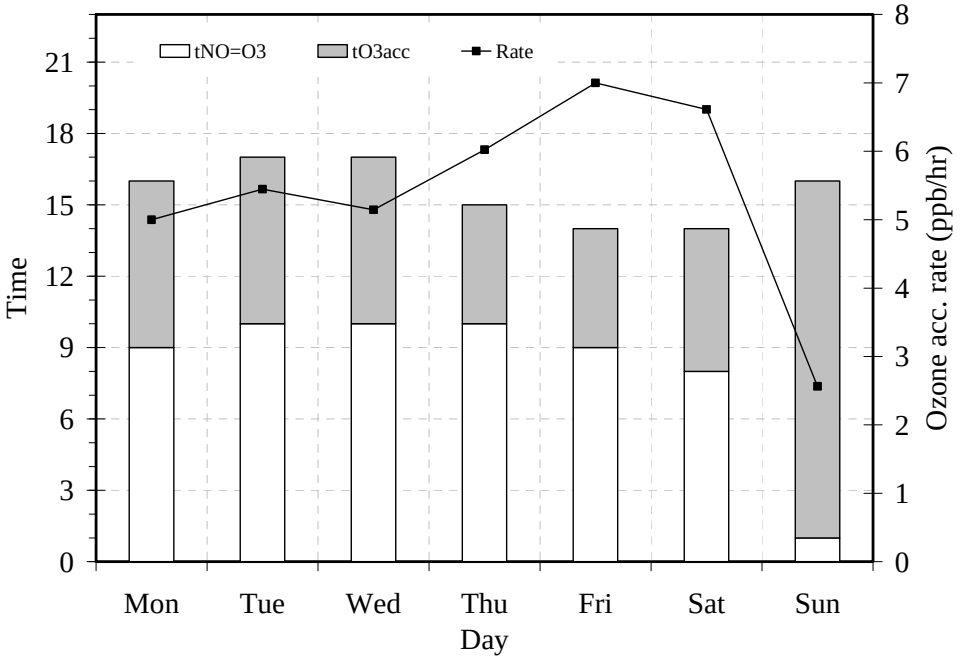

Figure 4-21 Duration and rate of ozone accumulation at ITD during weekdays and weekends

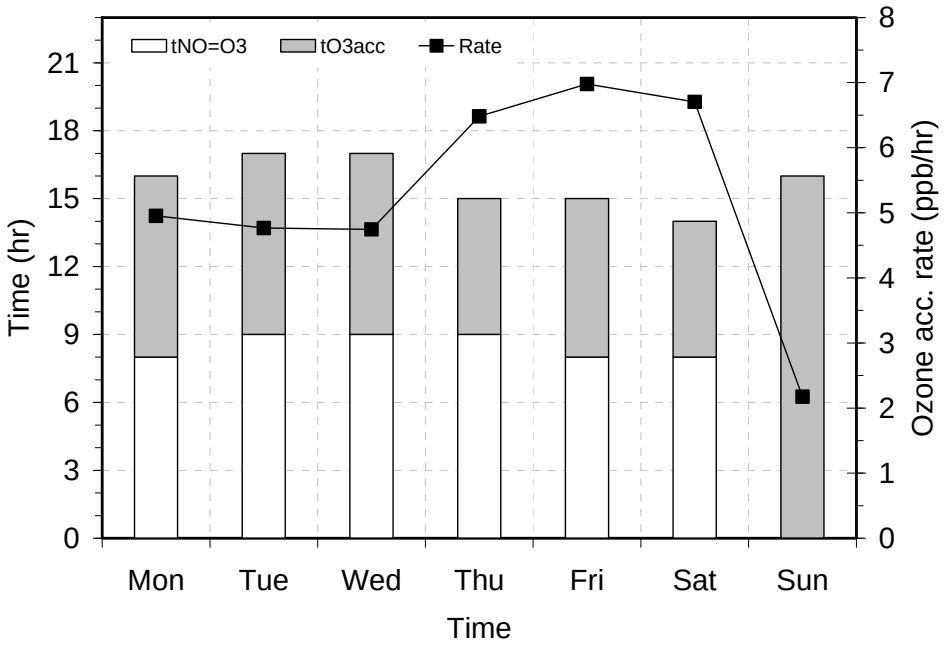

Figure 4-22 Duration and rate of ozone accumulation at St.Lukes during weekdays and weekends

Comparison of weekday/weekend patterns of O_3, NO_x and VOCs showed that O_3 levels on weekends were comparable (but not higher) to those measured on weekdays even though levels of precursors (NO_x) were significantly lower than on weekdays. This was the embodiment of the "weekend O_3 effect" in the Treasure Valley.

The 2005 updated emissions inventories for Idaho (based on NEI 2002) showed that NO_x emissions were 112,811 tons/year with on- and off-road mobile sources being the most important contributors (~50%) [*DEQ*, 2005] (Figure 4-23). Emissions of biogenic VOCs are not included here, but they usually represent a large fraction of VOC emissions (up to 50%). Estimated VOC emissions were about 180,763 tons/year. Analysis of VOC emission by sector showed that area source asphalt paving operations contribute about 40% of VOCs to the atmosphere, while mobile emissions account for 32.5% (Figure 4-24). Considering the chemistry of irradiated VOC/NO_x mixtures:

- at NO_x-limited conditions, lowering VOC emissions (assuming that NO_x remain constant) has no impact, while reduced NO_x emissions will slow O_3 formation.
- at VOC-limited conditions, reduced VOC emissions yield lower rates of radical formation while reductions in NO_x increase the formation rate of O_3. Under these conditions, concurrent changes in emissions of both NO_x and VOC may, at best, counterbalance changes in O_3 concentrations.

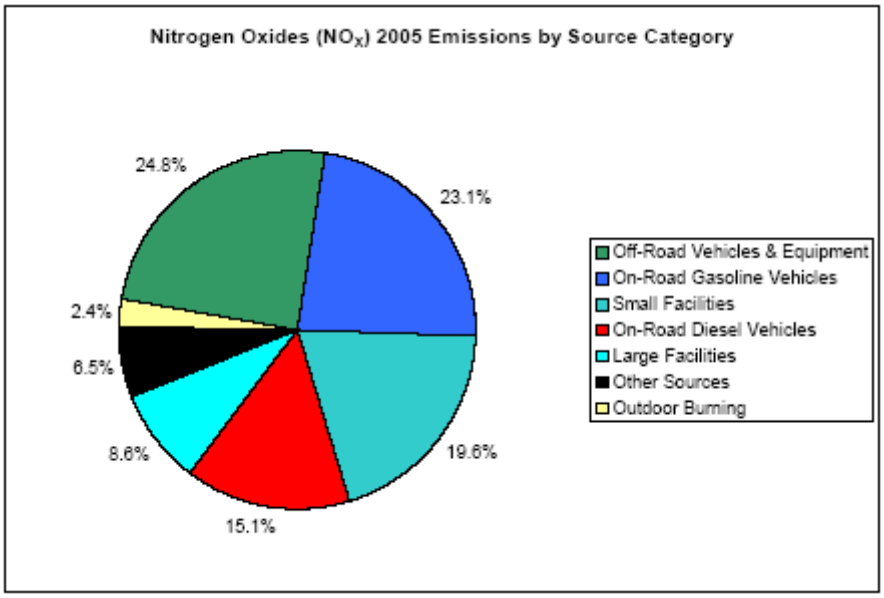

Figure 4-23 Emissions of NO_x by source category in 2005

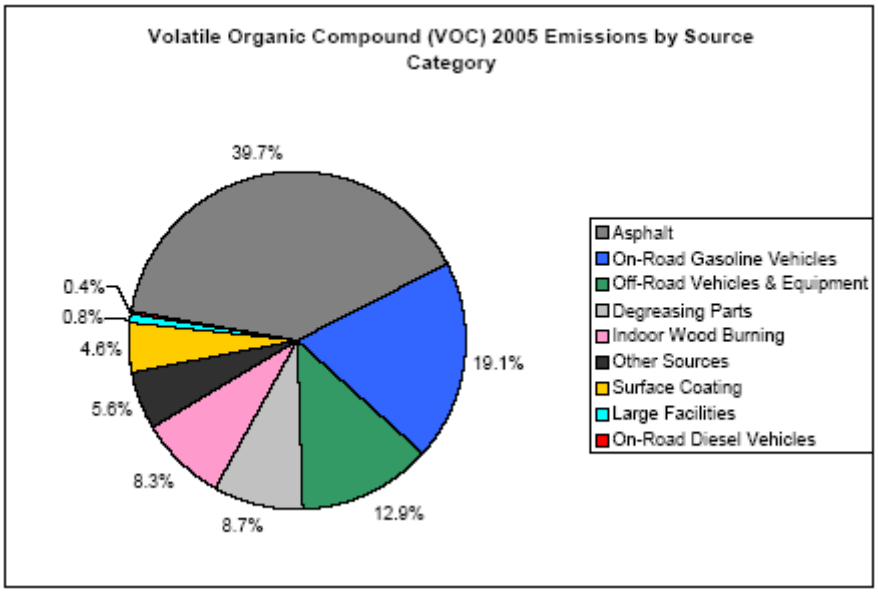

Figure 4-24 Emissions of VOCs by source category in 2005. Biogenic emissions are not included

The VOC/NO_x ratio during the daytime (6:00 – 16:00) at ITD and St. Lukes is shown in Figure 4-25. These results indicated that NO_x and VOCs were the limiting factors at the ITD and St. Lukes sites, respectively. On Sundays, the VOC/NO_x ratio at St. Lukes was substantially higher than 5.5, indicating NO_x-limited conditions. Because of the differences between the two sites, changes in NO_x and VOCs emissions may decrease O_3 levels at one location but increase them (at least temporarily) at the other. For example, reduction of NO_x emissions (assuming VOC emissions remain constant) in Ada and Canyon counties would decrease O_3 levels at ITD but increase them at St. Lukes. If VOC emissions are reduced, especially from open source areas (and NO_x remains unchanged), St.Lukes would likely exhibit lower O_3 levels, but no changes

would be observed at ITD, unless VOC reductions are very substantial. It is clear that efforts to reduce O_3 levels will require reductions in both VOC and NO_x emissions at different rates. The outcomes of this study as well other studies, indicate that the first step should include significant reductions of VOC emissions in the near future and moderate reductions of NO_x emissions over time. In a previous study in Treasure Valley, Stockwell et al., (2003) determined that reductions in the emission rates of volatile organic compounds were found to be most effective in reducing secondary inorganic aerosol concentrations while reductions in nitrogen oxide emission rates would be expected to increase aerosol concentrations. This response of aerosol formation rates was due to the effects of the nitrogen oxide and volatile organic compound emission rates on the concentration of hydroxyl radical mixing ratios, which is also a controlling factor for summertime ozone chemistry.

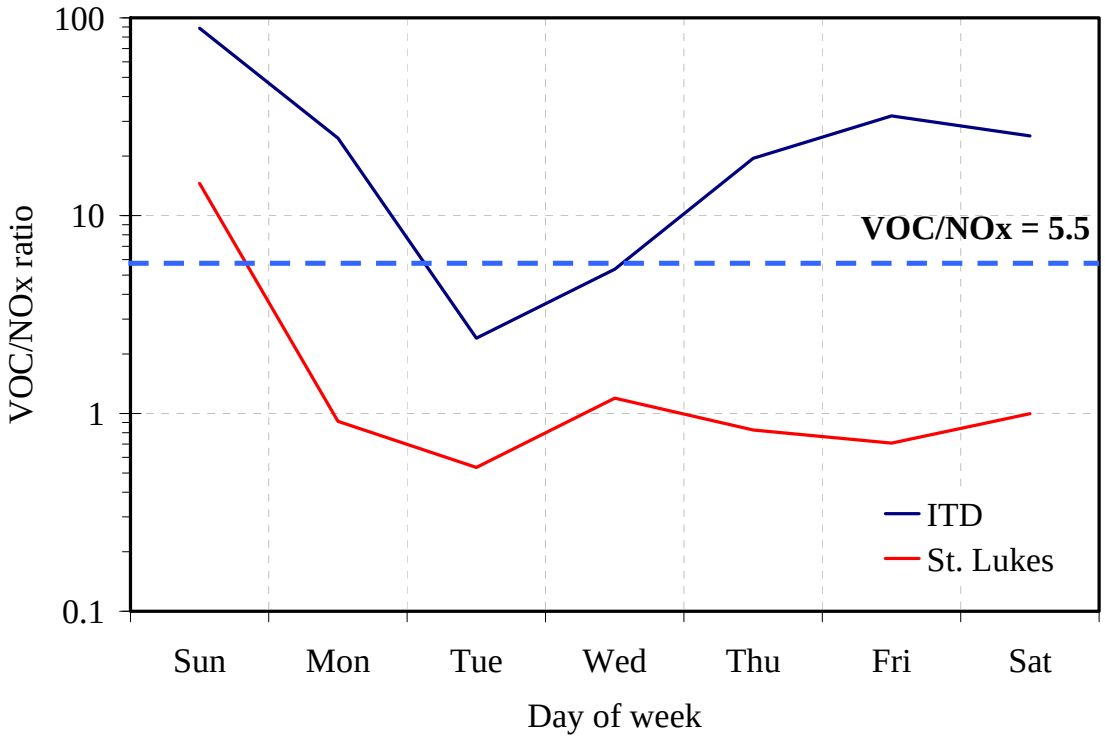

Figure 4-25 Day-of-week variation of mean VOC/NO_x ratio at ITD and St.Lukes

4.5 Classification of ozone events

The analysis of exposure, epidemiological and controlled studies summarized in 40 CFR Part 50 (2007) suggested that there is substantial evidence of health responses to ozone concentrations higher than 60 ppbv, while recent studies showed reduced lung function and respiratory-related symptoms at lower concentrations for healthy individuals and anticipated that these outcomes may be more severe for asthmatic patients.

Figure 4-26 shows the percentage cumulative occurrences of 8-h maximum O_3 concentrations at the monitoring sites [for each day, the maximum 8-hour ozone concentration was used]. Less than 30% of days showed 8-hour maximum concentrations lower than 35 ppbv. It has been

previously observed that the 5th percentile of measurements in background urban locations provide a good estimate of the background conditions for the measurement period (Van Dingenen, 2004). The computed 5th percentiles of 8-h maximum ozone concentrations measured in this study were: ITD: 35 ppbv; St.Lukes: ppbv; Whitney: 31 ppbv; Parma: 30 ppbv; Nampa: 32 ppbv; White Pine: 38 ppbv and Mountain View: 32 ppbv, with a mean value of 33 ppbv. These concentrations most likely represent conditions when ozone levels not directly attributable to anthropogenic emissions of VOCs, CO and NO_x. While analysis of the relationships between ozone and its precursors at background conditions may provide useful information on the chemistry at remote locations, the outcomes may not be applicable to urban areas and for events of high ozone that can pose health risks to susceptible groups and/or the general population. For this reason, the characteristics of high ozone days will be determined and compared against the typical ozone days in the Treasure Valley. The definitions for high and typical ozone days are:

- **high ozone** (Type-A) calendar days in which the 8-h maximum ozone concentration was equal or higher than the 80th percentile of the cumulative frequencies of 8-h maximum concentrations at this site. Note that the 80th percentile is determined on a site-by-site basis, thus it varies among the sites (upper grey box in Figure 4-26).
- **Typical ozone** (Type-B) calendar days in which the 8-h maximum ozone concentration was between the 40th and 60th percentiles of the cumulative frequencies of 8-h maximum concentrations at this site (middle grey box in Figure 4-26).

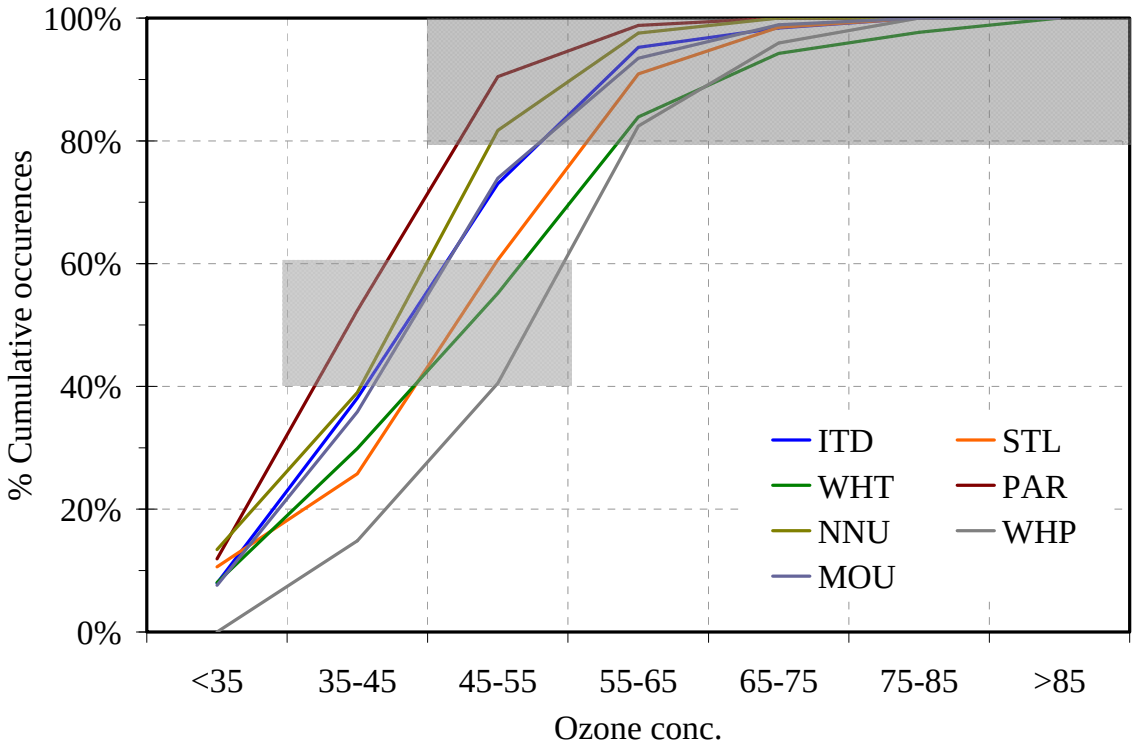

Figure 4-26 Percentage cumulative occurrences of 8-h maximum ozone concentrations at the primary and supplemental sites during the monitoring period

Table 4-14 shows the 40th, 60th and 80th percentile values of 8-h maximum O_3 concentrations for each day as well as the classification of calendar days as typical or high ozone days. A total of

thirty (30) calendar days (98 site-days) are identified as high ozone episodes for at least one site and forty-eight(48) calendar days (98 site days) are classified as typical ozone days. Most of the high ozone days (20 of 30) were observed at more than three sites, with the concentrations at the other sites still being comparatively high. This indicates the occurrence of an event in the valley. Of the 48 typical ozone days, only one-third were observed at more than three sites at the same time. A large fraction of high and typical ozone days occurred simultaneously and/or consecutively at multiple sites. More specifically:

a) High ozone days - TypeA:
   - A five-day period at Whitney, Parma (except 7/11/2007 and 7/12/2007), Nampa, White Pine, and Mountain View (ITD and St. Lukes did not report data) on 7/10/2007 to 7/14/2007
   - A three-day period at Whitney, Parma, Nampa, White Pine, and Mountain View (ITD and St. Lukes did not report data) on 7/27/2007 to 7/29/2007 [Parma and Nampa on 7/29 are not classified as having a high ozone day]
   - A two-day period at Whitney, Parma, Nampa, White Pine, and Mountain View (ITD and St. Lukes did not report data) on 7/5/2007-7/6/2007
   - Six one-day periods at ITD, St. Lukes, Whitney, Parma, Nampa, White Pine, and Mountain View on 8/01/2007, 8/03/2007, 8/29/2007, 9/01/2007, 9/03/2007 and 9/13/2007.

b) Typical ozone days - TypeB:
   - Two four-day periods at several sites from 7/18/2007 to 7/21/2007 and from 8/04/2007 to 8/07/2007
   - Three one-day periods at several sites on 8/10/2007, 8/13/2007 and, 8/22/2007.

Table 4-14 Classification of typical (green) and high (yellow) ozone days and the 8-h maximum ozone concentration for each site

Date	ITD	St. Lukes	Whitney	Parma	Nampa	White Pine	Mountain View
40th percentile	*45*	*46*	*49*	*43*	*45*	*55*	*46*
60th percentile	*52*	*52*	*57*	*46*	*50*	*58*	*52*
80th percentile	*56*	*61*	*63*	*50*	*55*	*62*	*57*
7/1/2007			66	48	51	60	56
7/2/2007			52	43	43	51	45
7/3/2007			63	49	54	61	53
7/4/2007			63	45	55	61	54
7/5/2007			65	63	64	61	60
7/6/2007			76	54	62	74	68
7/7/2007			62	46	54	60	54
7/8/2007			60	43	47	57	53
7/9/2007			48	39	41	48	40
7/10/2007			69	52	62	67	59
7/11/2007			71	45	58	71	58
7/12/2007			63	43	54	65	57
7/13/2007			72	53	58	72	62
7/14/2007			86	66	71	81	74
7/15/2007			61	41	43	58	49

Date	ITD	St. Lukes	Whitney	Parma	Nampa	White Pine	Mountain View
7/16/2007			62	49	59	58	57
7/17/2007			70	46	55	66	61
7/18/2007			59	40	47	59	51
7/19/2007			54	43	46	51	46
7/20/2007			58	46	52	56	52
7/21/2007			57	37	42	57	47
7/22/2007			53	37	42	53	44
7/23/2007			57	48	50	59	52
7/24/2007			44	29	35	45	40
7/25/2007	38		51	45	41	49	45
7/26/2007			59	50	51	55	53
7/27/2007		75	77	53	59	71	69
7/28/2007		70	79	50	62	77	67
7/29/2007		64	70	45	54	68	61
7/30/2007		51	57	40	46	56	50
7/31/2007	56	56	61	49	54	59	53
8/1/2007	80	75	85	60	75	83	75
8/2/2007	41	40	49	50	43	51	41
8/3/2007	63	62	68	49	57	68	60
8/4/2007	50	52	54	45	47	52	47
8/5/2007	54	54	58	44	47	56	49
8/6/2007	54	55	58	47	50	56	51
8/7/2007	53	54	57	46	50	56	49
8/8/2007	45	46	50	35	40	49	42
8/9/2007	56	57	56	43	52	62	52
8/10/2007	50	33		45	47	54	47
8/11/2007	63	0		54	54	61	61
8/12/2007	58	0		49	53	61	55
8/13/2007	51	0		43	45	55	47
8/14/2007	64	0		58		61	55
8/15/2007	58	61	54	56		64	56
8/16/2007	52	52	48	40		57	48
8/17/2007	51	52	48	40		55	45
8/18/2007	53	55	52	40		58	50
8/19/2007	43	45	42	32		47	38
8/20/2007	43	45	40	29		45	38
8/21/2007	46	49	44	40		50	40
8/22/2007	52	55	50	45		55	46
8/23/2007	45	47	42	41		48	39
8/24/2007	59	61	56	47	49		49
8/25/2007	60	63	58	52	55		52
8/26/2007	38	40	36	32	34		29

Date	ITD	St. Lukes	Whitney	Parma	Nampa	White Pine	Mountain View
8/27/2007	41	44	39	39	39		38
8/28/2007	49	52	46	47	47		46
8/29/2007	67	64	63	59	55		65
8/30/2007	56	58	53	50	48		54
8/31/2007	57	55	52	40	46		52
9/1/2007	61	69	60	58	64		61
9/2/2007	56	60	56	46	52		52
9/3/2007	68	69	66	53	60		67
9/4/2007	42	44	35	35	40		38
9/5/2007	20	19	14	22	17		19
9/6/2007	39	45	37	32	32		35
9/7/2007	40	47	39	39	38		37
9/8/2007	48	55	46	41	46		43
9/9/2007	44	51	42	40	43		40
9/10/2007	50	56	46	42	45		47
9/11/2007	53	64	52	50	49	60	56
9/12/2007	54	64	54	51	51	61	52
9/13/2007	59	68	59	57	59	68	61
9/14/2007	55	63	57	46	47	62	55
9/15/2007	46	53	45	39	42	52	44
9/16/2007	44	52	43	37	39	49	42
9/17/2007	43	47	40	36	39	46	39
9/18/2007	33	35	29	28	27	37	28
9/19/2007	39	47	36	32	35	41	36
9/20/2007	42	51	36	43	38	45	40
9/21/2007	38	45	34	37	35	43	38
9/22/2007	35	39	27	21	24	38	33
9/23/2007	33	40	30		31	37	32
9/24/2007	36	40	33		34	38	34
9/25/2007	37	47	36		36	42	35
9/26/2007	41	46	38		33	44	39
9/27/2007	44	49	41		40	49	42
9/28/2007	51	57	48		54	56	50
9/29/2007	35	41	33		32	38	32
9/30/2007	47	47	43		41	49	45

The conditions associated with each event are described in Appendix B. For each event, NRL NAAPS particulate smoke concentrations (as an indicator of the wildland fire smoke plume) and surface weather maps (at 12:00Z time for each day) were utilized. In addition, backward trajectories at 500m and 2500m, and the location of wildland fires for the entire duration of the event are plotted

Based on the analysis of prevailing weather conditions, air mass trajectories, occurrence of wildland fires and maintenance/construction activities in Ada County, the impact of emissions from wildfires and/or pavement activities for each ozone event was characterized as strong, moderate, low or absent. Table 4-15 identifies the contributions of wildland fires and road activities for each Type-A and Type-B ozone event. Strong evidence of wildfires smoke was determined for A2-A5 events, and B1 and B2. Events B1 and B2 occurred after high O3 events due to the passage of a new front through the Treasure Valley which disturbed the stagnant conditions. Four Type-A events (A6-A9) exhibited moderate association with wildfires and four events (A1 and B3-B5) did not show any inputs from wildfires. Given the limited information on the magnitude of maintenance and construction activities, a moderate and low degree of contribution was allocated to emissions from these activities.

Table 4-15 Contributions of wildland fires and pavement activities on high (Type A) and typical (Type B) O_3 events

Episode	Wildland fires	Pavement activities
A1 (July 4-5, 2007)	Absent	Moderate
A2 (July 10-14, 2007)	Strong	Moderate
A3 (July 27-29, 2007)	Strong	Moderate
A4 (August 1, 2007)	Strong	Low
A5 (August 3, 2007)	Strong	Low
A6 (August 29, 2007)	Moderate	Low
A7 (September 1, 2007)	Moderate	Low
A8 (September 3, 2007)	Moderate	Low
A9 (September 13, 2007)	Moderate	Low
B1 (July 18-21, 2007)	Strong	Moderate
B2 (August 4-7, 2007)	Strong	Low
B3 (August 10, 2007)	Absent	Low
B4 (August 13, 2007)	Absent	Low
B5 (August 22, 2007)	Absent	Low

Table 4-16 - Table 4-19 show the levels of O_3, its precursors, meteorological conditions and air quality conditions during high (A-events) and typical (B-events) O_3 events, respectively. Because of the definition of high and typical O_3 days, mixing ratios of O_3 during A-events were higher than those measured during B-events. The differences were more pronounced for 1-hr maximum O_3 levels as compared to the daily average O_3 concentrations, because of the low mixing ratios during nighttime. O_3 levels for A2-A5 events (strong indications of fire smoke) appeared to be somewhat higher than those measured for A6-A9 events.

Table 4-16 Mean and maximum ozone concentrations in Treasure Valley for the high (A1-A9) and typical (B10-B14) ozone days

Episode	Parma	Nampa	White Pine	Mountain View	ITD	Whitney	St. Lukes
A1	30|80	37|86	41|99	31|87		36|104	
A2	***31|58***	***37|70***	***43|87***	***37|82***		***41|88***	***41|83***
A3	***34|75***	***35|91***	***42|89***	***34|74***		***39|91***	
A4	***35|66***	***49|82***	***44|98***	***37|83***	***38|91***	***41|100***	***39|81***

A5	***33|54***	***43|60***	***50|76***	***39|64***	***36|72***	***48|76***	***39|64***
A6	40|72	26|60		31|77	35|79	29|74	30|76
A7	40|64	31|73		38|70	27|73	28|68	33|82
A8	32|61	30|66		35|79	33|83	31|80	40|79
A9	35|70	31|68	36|80	42|70	30|72	28|72	34|80
B1	***28|50***	***32|55***	***38|61***	***31|54***		***36|64***	
B2	***32|52***	***32|55***	***37|62***	***28|59***	***31|62***	***34|66***	***33|66***
B3	32|49	36|50	38|56	33|49	35|52	27|31	33|35
B4	25|46	28|46	35|58	26|50	28|52		
B5	24|49		33|58	24|53	29|56	25|54	35|59
A-episodes	34|66	35|72	42|88	36|76	33|78	35|83	36|77
B-episodes	28|49	32|41	36|59	28|53	30|55	30|53	33|53

Differences between A- and B-events were also observed for NO and NO_2 (ITD: NO 8 ppbv for B-events and 12 ppbv for A-events; St. Lukes: NO 6 ppbv for B-events and 24 ppbv for A-events). A complicated pattern was observed for VOC, which showed extremely high VOC levels during B3 and B4 events at ITD. During A-events, the highest VOC levels were measured for the A2 and A3 episodes for both sites. Comparison of ozone precursors for A-type events showed that smoke-dominated the A2-A5 events experienced higher VOC concentrations, while higher NO (and NO_2) concentrations were measured for A6-A9 events. With respect to meteorological conditions, A-events were associated with lower wind speeds (mean of 1.7 m s^{-1}) and relatively higher temperature and relative humidity.

Table 4-17 Mean NO, NO_2 and VOCs concentrations in Treasure Valley for the high (A1-A9) and typical (B1-B5) ozone days

		ITD		St. Lukes	
Episode	**NO**	**NO_2**	**VOC**	**NO**	**VOC**
A1			382		20
A2			***39***	***17***	***9***
A3			***401***		***15***
A4	***11***	***2***	***103***	***31***	***13***
A5	***9***	***1***	***49***	***.***	***8***
A6	12	7	71	27	9
A7	16	6	46	19	10
A8	10	7	59	17	8
A9	12	11	48	33	10
B1			***186***		***9***
B2	***8***	***1***	***17***		***12***
B3	5	1	592		4
B4	8	3	1310		14
B5	9	4	24	6	10
A-episodes	12	6	133	24	11
B-episodes	8	2	426	6	10

Table 4-18 Mean wind speed, temperature and relative humidity in Treasure Valley (Boise Fairgrounds site) for the high (A1-A9) and typical (B1-B5) ozone days

Episode	Wind speed	Temperature	Relative humidity
A1	1.9	27.7	38
A2	***1.7***	***27.4***	***37***
A3	***2.0***	***28.5***	***34***
A4	***2.1***	***24.9***	***34***
A5	***1.9***	***25.9***	***39***
A6	1.5	22.0	39
A7	1.3	24.2	55
A8	1.5	24.2	43
A9	1.6	20.1	41
B1	***2.3***	***24.9***	***37***
B2	***2.0***	***22.8***	***35***
B3	2.9	22.5	35
B4	2.2	23.2	32
B5	2.7	19.9	45
A-episodes	1.7	25.0	40.1
B-episodes	2.4	22.7	36.8

Table 4-19 Mean $PM_{2.5}$ and PM_{10} concentrations in Treasure Valley for the high (A1-A9) and typical (B1-B5) ozone days

Episode	$PM_{2.5}$					PM_{10}	
	St. Lukes	Parma	Nampa	White Pine	Mountain View	Boise	Nampa
A1	17.0	14.9	.	13.2	19.8	46.8	48.5
A2	***15.9***	***16.9***	***16.4***	***13.1***	***15.9***	***36.0***	***35.6***
A3	***41.2***	***13.7***	***.***	***52.5***	***58.8***	***79.7***	***65.3***
A4	***33.3***	***17.3***	***21.7***	***30.0***	***32.8***	***65.4***	***37.5***
A5	***27.4***	***19.2***	***18.1***	***22.3***	***24.6***	***47.0***	***38.5***
A6	10.7	10.9	.	12.2	11.0	39.4	52.3
A7	9.1	10.7	.	7.5	8.5	27.0	24.8
A8	10.2	9.7	.	13.0	13.0	27.8	36.3
A9	18.6	11.0	19.6	16.1	21.2	53.1	70.0
B1	**14.1**	**11.8**	**.**	**14.1**	**14.3**	**34.0**	**31.8**
B2	**13.9**	**15.2**	**18.0**	**11.8**	**12.0**	**46.8**	**48.7**
B3	8.8	7.2	8.8	12.3	9.2	37.3	29.3
B4	11.5	9.8	14.0	12.9	11.6	35.7	41.1
B5	6.0	7.0	5.1	8.8	7.2	25.2	21.0
A-episodes	20.4	13.8	19.0	20.0	22.8	46.9	45.4
B-episodes	10.9	10.2	11.5	12.0	10.9	35.8	34.4

5. Conclusions and Recommendations

A study to address the formation of O_3 in Treasure Valley was carried out from July 1, 2007 to September 30, 2007. Ozone, nitrogen oxides and speciated VOCs were monitored at two locations, the Idaho Transportation Department (ITD) and St. Lukes Hospital. Ozone was also measured at sites in Whitney, Parma, Nampa, Mountain View and White Pine. The height of the boundary layer and vertical profiles of ozone were measured on four days using a tethered-balloon system. Supplemental data were obtained to assist in the analysis effort. Those datasets included meteorological and air quality data from the IDEQ monitoring network, air mass backward trajectories using the NOAA HYSPLIT model at several different elevations, the locations, durations, and associated burned areas of wildland events, satellite images for viewing the areal coverage of smoke plumes from wildfires, surface weather maps, model results for regional smoke aerosol concentrations, and road maintenance activities as documented by the Ada County Highway District (ACHD).

Hourly O_3 levels at all sites ranged from minimum nighttime values of a few parts per billion by volume (ppbv) to 83 ppbv at St. Lukes, 91 ppbv at ITD, 104 ppbv at Whitney, 80 ppbv at Parma, 91 ppbv at Nampa, 87 ppbv at Mountain View and 99 ppbv at White Pine. At ITD, NO hourly levels varied from a few ppbv to 92 ppbv with an average of 10 ppbv, while NO_2 concentrations ranged from 0 to 30 ppbv with a mean value of 4 ppbv. At St. Lukes, the maximum 1-hour NO concentration was 192 ppbv and the mean was 18 ppbv; no detectable amounts of NO_2 were measured at St Lukes. Forty-eight organic compounds were identified including twenty-two aliphatic saturated hydrocarbons, three cyclic saturated hydrocarbons, seven *n*-alkenes, two alkynes, thirteen aromatic hydrocarbons and one oxygenate. VOC levels at ITD were up to one order of magnitude higher than those measured at St. Lukes. The highest hourly concentrations were measured for propane (15 parts per million by volume, ppmv) and acetylene (3.9 ppmv) at ITD. Alkanes and alkenes were the predominant compound classes at ITD representing on average about 95% of VOCs. Aromatic hydrocarbons accounted for about 13.0 ppbv at ITD and about 4 ppbv at St. Lukes. In general, despite differences in emission patterns for O_3 precursors, there was very little site-to-site variation in daytime O_3 mixing ratios among the seven sites examined.

Over the diurnal cycle, O_3 mixing ratios increased rapidly from a few ppbv during the nighttime hours starting in the morning (~8:00) through the early afternoon. The O_3 concentrations peaked late in the afternoon (~16:00) and then gradually declined in evening (starting at ~18:00). The precursors (NO, NO_2, and VOCs) generally followed an opposite diurnal pattern with the lowest concentrations measured during the daytime, while ozone levels were at their highest. NO and some VOC mixing ratios exhibited an early morning peak and an early evening gradual climb. This is consistent with the expectation that elevated concentrations of nitrogen oxides and VOCs are associated with traffic emissions during early morning and evening commute hours. For NO_2, elevated nighttime concentrations were likely due to the NO_x titration reaction. Alkanes and aromatic hydrocarbon mixing ratios remained relatively constant throughout the nighttime because removal of alkanes and aromatic hydrocarbons by $NO_3^{\cdot}$ radicals is quite slow. The progression of the mixing ratios of nitrogen compounds, VOCs, and ozone over the diurnal cycle was consistent with that observed in other urban areas.

The day-of-week trends of O_3, NO_x and VOCs mixing ratios in the Treasure Valley showed the presence of a "weekend O_3 effect", in which O_3 concentrations remain high on weekends despite decreases in emissions of precursors due to reduced motor vehicle activities. The weekend effect is caused by the shorter inhibition period on weekends because of the decrease in early morning emissions of NO_x, allowing for a longer accumulation time of O_3 (albeit at lower rates) compared to weekdays. In the Treasure Valley, the weekend effect is reflected in comparable O_3 levels throughout the week. This provides some initial guidance for the direction of O_3 control strategies in the Treasure Valley. The VOC/NO_x ratio indicates that the O_3 –limiting factor at ITD is the NO_x , but that the limiting factor at St. Lukes is the VOC concentration except on Sundays when St Lukes exhibits NO_x-limited conditions.

The weather conditions, regional transport as well as local activities were examined for days on which more than three sites were identified as "high" or "typical" O_3 days. Nine high and five typical O_3 events were identified spanning in length from one to five days. High O_3 days were regularly associated low surface wind speeds and stagnant conditions. For four the of the "high O_3" events (mostly in July and early August), there was substantial evidence that smoke plumes from wildland fires in Payette and Boise National Forest as well as from southern Idaho, northern Nevada and California were impacting air quality in the Treasure Valley. These events lasted for at least a couple of days and exhibited high 1-hr maximum O_3 mixing ratios and high VOC concentrations but low NO_x levels. During these events, $PM_{2.5}$ levels in Treasure Valley were consistently higher than 15 $\mu g\ m^{-3}$. Four "high O_3" events (in late August and September) showed moderate or little impact from wildfire smoke. These events were associated with higher NO_x and lower VOC levels and $PM_{2.5}$ levels lower than 15 $\mu g\ m^{-3}$. Hourly O_3 levels were slightly lower than those measured for "high O_3" days when smoke was present. A "high O_3" event in early July (July 5-6, 2007) may have been associated with the use of fireworks on July 4th, 2007 that can trigger the formation of ozone through the dissociation of molecular oxygen at lower wavelengths (Arun et al., 2001). No specific association was uncovered between road maintenance operations and high O_3 levels.

Overall, factors that affect O_3 mixing ratios in the Treasure Valley include local emissions, regional fires, and local air circulation. Regional fires occur on an episodic basis and are associated with high PM and VOC levels. The contribution of local emissions (mobile, point and area sources) is more constant and associated with regular activities such as motor vehicle traffic. While emissions of O_3 precursors are variable, both spatially and temporally, O_3 mixing ratios across the valley are fairly uniform with slightly higher levels observed at sites in the more southeastern. Analysis of the observed "weekend O_3 effect" showed that efforts to reduce O_3 levels should focus on the reduction of VOC emissions while continuing to monitor NO_x emissions. Fortunately, this is in-line with findings from an earlier modeling effort (Stockwell et al., 2003) that examined the formation of secondary aerosols in the Treasure Valley. That work indicated that reduction of VOC emissions would decrease the formation of secondary aerosols while reduction of NO_x emissions would increase the amount of secondary aerosol in the Treasure Valley. Very large NO_x emission rate reductions would be required before reductions occur in aerosol formation. Kuhns et al. (2003) found that production of particulate ammonium nitrate was limited by the formation of HNO3 due to the large amounts of NO_x and NH_3 available in Treasure Valley. The formation of HNO_3 and therefore aerosol formation rates follow the same sensitivities as HO and HO_2 radicals to NO_x and VOC emission rates.

An explicit, discernible relationship was not found between road maintenance activities and O_3 mixing ratios because these activities are widespread and continuous during the summer. However, a recent VOC emission inventory for the Treasure Valley (DEQ, 2005) indicated that asphalt operations were responsible for about 40% of the VOC emissions. Given that controlling VOC emissions appears to be the most promising starting point for a long term ozone control strategy, it may be desirable to accurately determine the contribution of summertime road paving operations to VOC concentrations in the Treasure Valley and, if necessary, mitigate VOC emissions from those activities.

Given the variation of ozone and its precursors in Treasure Valley, the existing monitoring network at St. Lukes and ITD location describe adequately the typical urban environment; however, further expansion will substantially improve the spatial coverage and provide detailed information of the instantaneous effect of NO_x and VOCs on local photochemistry. Expansion may include:

(a) the operation of an ozone monitoring site in a location upwind of Boise MSA (similar to Parma or Middleton) and at a site in the southeast part of the valley (similar to White Pine or Whitney)
(b) each of the four monitoring sites may also be equipped with monitor for NO_x, total non-methane hydrocarbons (NMHC) and CO.

Taking into account the significant role of the mixture of VOCs and NO_x in ozone chemistry, it will be essential to characterize emissions (primarily VOCs) from chipsealing and road maintenance activities and evaluate the relative contribution of on/off road mobile sources, road maintenance and wildland fires on high ozone events. Efforts may also include characterization of the spatial variation of NO_x and VOCs emissions that will identify real-time emissions and provide a unique high-resolution input for modeling applications.

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7. Appendixes

Appendix A. Characteristics of wildland fires in Idaho and surrounding states during the monitoring period

Appendix B. Analysis of high and typical ozone episodes

Appendix C. Applicability of tethered-balloon measurements

Appendix A. Characteristics of wildland fires in Idaho and surrounding states during the monitoring period

Incident	Location	Date of Origin	Containment Day	Cause	Size (acres)	Fuel involved
				Idaho		
Boundary Junction	Pierce	8/10/2007	11/1/2007	Lightning	5,100	Subalpine fir with a shrub understory.
Bridge	Lowell	7/25/2007	11/1/2007	Lightning	42,250	Predominantly timber (litter and understory) and brush.
Moose Creek	Pierce	8/4/2007	9/3/2007	Lightning	37,708	Timber litter and understory; used for resource benefit
Chief Parrish	Banks	9/3/2007	9/9/2007	Human	3,690	Timber, grass and brush. Fuel model 2
Grays Creek	Indian Valley	8/30/2007	9/10/2007	Lightning	24,900	2 Timber (grass and understory) 5,8,9, & 10
Red Bluff	Challis	7/17/2007	9/30/2007	Lightning	60,143	The Red Bluff fire is currently burning in spruce, fir, litter and understory.
Shower Bath	Challis	8/1/2007	9/30/2007	Lightning	59,909	sub-alpine fir and lodge pole pine mix with heavy dead and down fuel.
Papoose	North Fork	7/10/2007	n/a	Lightning	19,520	n/a
Clear Sage	Salmon	7/14/2007	9/30/2007	Lightning	20,566	Cheat grass and Underbrush
Trapper Ridge	Idaho City	7/17/2007	n/a	Lightning	20,159	Timber litter and understory; Fuel Models 8, 9, 10; Used for Resource benefit
Black Pine 2	Malta	7/6/2007	8/1/2007	Lightning	73,000	Grass,sagebrush, pinyon pine/juniper
Castle Rock	Ketchum	8/16/2007	9/3/2007	Lightning	48,520	Heavy timber with a lot of dead standing and down, brush, grass and aspen stands. Sagebrush and grass on south-facing slopes. Douglas fir and subalpine fir on north facing slopes. Rolling terrain with discontinuous timber on both north and south slopes.
Chimney Complex	Lewiston	7/13/2007	8/17/2007	Lightning	51,000	2 Timber (Timber with grass understory)Over area of the fire a mixture of

Incident	Location	Date of Origin	Containment Day	Cause	Size (acres)	Fuel involved
						timber and grassy areas are involved.
Myrphy Complex	Twin Falls	7/16/2007	8/2/2007	Lightning	653,100	Brush, grass, with a mix of Juniper. Slick Spot Peppergrass and other sensitive plant species,and numerous cultural sites.
Tongue Complex	Silver City	7/6/2007	7/24/2007	Lightning	46,680	Juniper, sagebrush and grass.
Boulder Creek	Silver City	7/6/2007	7/16/2007	Lightning	4,350	Grass, sage, and juniper.
Warm Springs	Weiser	7/6/2007	7/11/2007	Lightning	23,760	Tall grass (2.5 feet)
Landmark Complex	Yellow Pine	8/8/2007	n/a	Lightning	47,270	Subalpine fir; lodgepole pine (litter and understory)
East Zone Complex	Payette NF	7/07/2007	n/a	Lightning	300,022	Fir, lodgepole pine, spruce and Ponderosa pine with discontinuous understory.
Poe Cabin	White Bird	7/18/2007	10/12/2007	Lightning	58,522	2 Timber (grass and understory); 10 Timber, heavy down and dead
Middle Fork Complex	NE Garden Valley	7/17/2007	8/17/2007	Lightning	17,280	10 Timber (litter and understory). FBPS 8, 10 - timber and brush.
Cow Creek	Farfield	n/a	8/16/2007	Lightning	5,292	Grass, Sagebrush, and Douglas Fir
Cascade Complex	Boise NF	7/17/2007	n/a	Lightning	302,376	Fuel Models 8 and 10; Isolated smoldering and burning of large fuels
Krassel WFU Complex	Payette NF	6/17/2007	n/a	Lightning	85,700	Timber, litter and understory and grasses as well as past fire areas with dead and down. Bug kill is present throughout the Complex.
Rattlesnake	Nez Perce NF	7/13/2007	n/a	Lightning	102,000	Model 10 (TIMBER) higher elevation slopes and 2 / 1 (Grass and Timber) lower slopes along the Salmon River
				Nevada		
Mendive	Wildhorse Reservoir	7/17/2007	7/21/2007	Lightning	3,000	Sage, grass, and pinion juniper
Telegraph	Ely	7/18/2007	n/a	Lightning	1,588	n/a

Incident	Location	Date of Origin	Containment Day	Cause	Size (acres)	Fuel involved
Winecup Complex	Wells	7/17/2007	7/27/2007	Lightning	163,767	Grass, sage brush, and pinyon/juniper Minimal fire behavior with some smoldering.
Cathedral	Ely	7/18/2207		Lightning	3,847	Pinyon-juniper, sagebrush and grasses.
Hepworth Complex	Wells	7/16/2007	7/25/2007	Lightning	58,427	Grass, Sagebrush, Pinyon/Juniper, Mountain Mahognay, Aspen
Hawken	Humboldt - Toiyabe NF	7/16/2007	7/23/2007	Construction activities	2,710	Smoldering, few smokes. Grass, sagebrush, mountain mahogany & moving up into larger timber.
Tippets	Ely	7/18/2007	7/25/2007	Lightning	3,510	Pinyon Juniper, sagebrush and grasses
Red House Complex	Carlin	7/17/2007	7/26/2007	Lightning	71,340	Sage,grass understory and scattered Pinyon Juniper
Willow Creek Ridge	Elko	7/17/2007		Lightning	5,100	Sage, pinion, and grass understory
Bob's Flat 3	Carlin	7/17/2007	7/20/2007	Lightning	8,000	Sage and grass understory
Highway 93 Complex	Jackpot	7/6/2007	7/15/2207	Lightning	80,629	Sage, Cheat grass, and pinyon juniper
Adrian	Carson City	7/6/2007	7/12/2007	Lightning	14,009	n/a
Thomas	Winnemuca	7/6/2007	7/11/2007	Lightning	18,334	Grass, sagebrush and juniper.
Tungsten	Imlay	7/6/2007	7/11/2007	Lightning	61,951	brush grass and brush
Barth	Carlin	7/6/2007	7/7/2007	Lightning	15,000	Sagebrush and grass; Erratic fire behavior, winds 40-50 mph; Structures lost due to fast moving, wind driven fire
Oregon						
GW Fire	Black Butte Ranch	8/31/2007	9/11/2007	Lightning	7,357	10 Timber (litter and understory) Fuel models 10 & 11
Otter Creek	Dale	8/15/2007	9/9/2007	Lightning	3,039	10 Timber (Litter and understory); Fire and Lodgepole stands, heavy dead and down throughout in Wilderness. Creeping and smoldering.

Incident	Location	Date of Origin	Containment Day	Cause	Size (acres)	Fuel involved
Irish Spring	Ironside	8/17/2007	9/1/2007	Under Investigation	47,930	Brush (2 feet), Sage and Grass with timber stringers; Creeping and smoldering, with isolated single and group tree torching in the interior.
Ukiah Complex	Ukiah	8/15/2007	8/23/2007	Lightning	4,764	Fuel Models 1, 2, 8, 9, and 10
Battle Creek	Joseph	7/14/2007	8/25/2007	Lightning	79,209	Timber (litter and understory)
WSA Lightning Complex	Warm Springs	7/12/2007	8/20/2007	Lightning	13,047	10 Timber (litter and understory) Also fuel models 5 & 8.
Juniper Reservoir	Juntura	7/13/2007	7/25/2007	Lightning	29,000	Dormant Brush and Hardwood Slash
Highway 9	Simancho	8/16/2007	8/16/2007	Human	1,288	2 Timber (grass and understory)/ Fuel models 1, 2, & 10; Light smoke from burning of deep fuels.
Trout Meadows	Granite	8/3/2007	8/20/2007	Lightning	3,890	Lodgepole pine with heavy dead and down concentrations, area is intermixed with grass meadows.
Shelton Fire	Fossil	8/2/2007	8/9/2007	Under Investigation	2,726	Fuel Type 2 Timber (grass & understory; Fuel Type 2 & 10 (grass, brush & timber)
Coleman/Juniper Complex	Crane	8/5/2007	8/12/2007	Lightning	10,053	1 short grass (1 foot). Fuel models 1 and 6.
Calamity Complex	Seneca	7/6/2007	7/16/2007	Lightning	2,276	Timber, grass understory
Egley Complex	Riley	7/6/2007	7/22/2007	Lightning	140,360	Timber, timber litter and understory, plantation trees, grass and brush vegetation
Monument Complex	Monument	7/13/2007	7/31/2007	Lightning	54,000	Timber (litter and understory). Pine, mixed conifer, juniper, and grass. Fuel models 2, 6, and 10 are present in various areas.
Fossil Creek	Dayville	7/12/2007	7/21/2007	Lightning	3,270	Short grass, juniper, sage, minor amounts of

Incident	Location	Date of Origin	Containment Day	Cause	Size (acres)	Fuel involved
						timber
Cottonwood Creek	Wallowa	7/13/2007	7/21/2007	Lightning	8,100	Grass, timber, brush and some slash
Ball Point	Dufur	7/12/2007	7/21/2007	Lightning	1,237	10 Timber (litter and understory); Additional fuel models 2 and 11 present.
Barlett Mountain	Drewsey	7/6/2007	7/12/2007	Lightning	32,312	sagebrush, grass, and juniper
Round Top Butte	Riley	7/5/2007	7/8/2007	Human	9,870	sage brush, grass, and juniper
				Washington		
Rattlesnake Creek	Yakima	8/6/2007	10/29/2007	Lightning	1,700	n/a
Manila Creek	Keller	9/10/2007	9/17/2007	Under Investigation	26,805	Mixture of grass and heavy timber.
Domke Lake Complex	Chelan	8/5/2007	n/a	Lightning	11,900	Mixed conifer with extensive insect kill. Some areas with grass understory and brush.
South Omak Lake	Omak	8/30/2007	9/5/2007	Human	10,500	2 Timber (Grass and Understory) Currently grass, shrub, with scattered timber.
Wautoma	Benton City	8/16/2007	n/a	Under Investigation	67,000	Short and tall grasses and sage.
Tunk Grade	Omak	7/14/2007	7/21/2007	Lightning	15,540	Grass, brush, and scattered pine.
Horse Heaven Complex	Prosser	7/13/2007	7/18/2007	Lightning	28,575	Grass, Juniper and sagebrush Fuel models 1 and 6
Little Chopaka	Loomis	7/7/2007	7/14/2007	Under Investigation	4,428	grass, scattered timber and heavy ground litter.
Easy Street	Wenatchee	7/8/2007	7/10/2007	Human Caused	5,209	Tall Grass (Fuel Model 3)
California						
Grouse	Golden	8/27/2007	n/a	Lightning	1,022	Brush, timber

Incident	Location	Date of Origin	Containment Day	Cause	Size (acres)	Fuel involved
Butler 2	Trout Wilderness Big Bear Lake	9/14/2007	9/20/2007	Under Investigation	14,039	Grass, Brush, and Timber.
Moonlight	Moonlight Valley	9/3/2007	9/15/2007	Under Investigation	65,000	Heavy timber & slash.
Pine	Pine Valley	9/12/2007	9/16/2007	Illegal Campfire	2,170	n/a
Elk Complex	Happy Camp Range District	7/10/2007	10/30/2007	Lightning	17,684	10 Timber (litter and understory). Mature heavy timber overstory with brush understory, large quantities of dead fuels and snags.
North	Santa Clara-Mojave Rivers	9/2/2007	n/a	Under Investigation	2,200	Chaparral,Grass, Brush and Light Timber
Zaca	Santa Barbara	7/4/2007	9/2/2007	Human Caused	240,207	n/a
Wallow	Hayfork	8/29/2007	9/3/2007	Under Investigation	1,440	timber, fuel model 10 timeber (litter and understory). heavy accumulations of dead and down material and brush within the burned area of the Friendly Fire 1987.
Fletcher	Davis Creek	7/10/2007	7/19/2007	Lightning	8,121	Timber (Jeffrey and Ponderosa pine, white fir, juniper) and grass
China-Back	Yreka	7/10/2007	7/19/2007	Lightning	2,906	Timber
Inyo Complex	Independence and Big Pine	7/6/2007	n/a	Lightning	35,176	Brush, timber, mountain mahogany, timber, and grass
Antelope Complex	Antelope Lake Recreational Area	7/5/2007	7/13/2007	Lightning	22,902	All vegetation in the area is extremely dry. The fire area includes mature timber, mixed conifers, brush and dead vegetation

Incident	Location	Date of Origin	Containment Day	Cause	Size (acres)	Fuel involved
Angora	Lake Tahoe	6/24/2007	7/2/2007	Illegal Warming Fire	3,100	Heavy Timber with large dead and down component
Goldledge	Kernville	6/3/2007	7/8/2007	Shooting	4,196	Annual grass, low shrubs,chaparral and chamise at lower elevations. Fire has burned into live oak, Jeffrey pine and mixed conifer forest.
				Montana		
Ahorn	Augusta	7/11/2007	n/a	Lightning	52,505	Lodgepole pine and spruce interspersed with old fire scars with considerable standing dead trees.
Fool Creek	Choteau	6/28/2007	n/a	Lightning	60,038	Lodgepole pine and spruce interspersed with old fire scars with considerable standing dead trees.
WH Complex	Mill Creek	8/9/2007	10/8/2007	Lightning	28,600	10 Timber (litter and understory); Fuel models 8 and 10; burning in lodgepole, subalpine fir and Douglas-fir forest;
Sawmill	Missoula	7/31/2007	n/a	Lightning	67,490	Heavy timber, litter, and understory with grass on lower slopes and valleys.
Conger Creek	Choteau	7/16/2007	n/a	Lightning	25,150	10 Timber (litter and under-story); Fuel Model 10
Rat Creek	Wisdom	8/9/2007	n/a	Lightning	25,327	Timber with forest litter and understory vegetation. Trees are sub-alpine fir, lodgepole pine and Douglas-fir.
Pattengail Creek	Wisdom	7/13/2007	n/a	Lightning	15,297	10 Timber (litter and understory) Lodgepole pine, sub-alpine fir, heavy dead and downed, heavy bug kill.
Jocko Lakes	Seeley Lake	8/3/2007	10/1/2007	Lightning	36,338	10 Timber (litter and understory) Combination of Fuel Models 2, 8, 10. Heavy, more continuous ground fuels in older timber (fir-spruce-lodgepole) stands.

Incident	Location	Date of Origin	Containment Day	Cause	Size (acres)	Fuel involved
Rombo Mountain	Darby	7/31/2007	n/a	Lightning	27,800	Timber (litter and understory) with heavy bug-killed timber and a dense canopy.
Skyland	Kalispell	7/23/2007	n/a	Lightning	45,760	Fuel Models 1, 8, 10 and 11 (grass, litter & understory,timber & old burn)
Chippy Creek	Thompson Falls	7/31/2007	9/3/2007	Lightning	99,090	10 timber (litter and understory). Continuous timber, dead and downed lodgepole and recent logging slash.
2007 Bitterroot Fire Use Complex	Darby	7/7/2007	n/a	Lightning	19,464	Timber (litter and understory), subalpine fir, grand fir, ponderosa pine and grass/bear grass on the lower slopes on south aspects.
Black Cat	Frenchtown	8/14/2007	9/2/2007	Lightning	11,754	Timber litter and understory.
Brush Creek	Whitefish	7/26/2007	8/26/2007	Lightning	29,921	light grasses and dense saplings to old growth with heavy slash, lodgepole pine, western larch, subalpine fir and spruce.
Merlwether	Gates of the Mountain Wilderness	7/21/2007	n/a	Lightning	43,298	Timber, grass, and shrub understory. 10 Timber
Road Creek	Broadus	8/12/2007	8/14/2007	Lightning	5,700	grass/shrub
Garcaeu	Polson	7/24/2007	8/4/2007	Lightning	3,045	Timber, grass and understory
Middle Fork	Utica	6/20/2007	9/15/2007	Lightning	1,146	Hardwood Litter. Ponderosa Pine Litter
Mile Marker 124	Clinton	7/28/2007	8/8/2007	Human	6,231	Grass, open pine stand and mixed confers.
Madison Arm	West Yellowstone	6/27/2007	7/3/2007	Human	3,660	Mature lodgepole pine with scattered dense clumps and bitterbrush forest

Appendix B. Description of characteristics of high and typical ozone days

Event A1: July, 05 to July 06, 2007. Weather conditions and smoke concentrations are shown in Figure 7-1, while the trajectories of air masses arriving in Boise at 500m and 2500m and the locations of wildland fires in the Northwestern US are presented in Figure 7-2. Weather was characterized by very low surface wind speeds facilitating stagnant conditions in the Treasure Valley. This is further supported by the strong northwest-southeast orientation of air mass transport at 500m and 2500m during the last 24 hours prior to arrival in the Treasure Valley. While the impact of smoke on July 5th was negligible, wildland fires sparked by lightning at several locations northwest (Weiser), southeast (Malta) and southwest (Silver City) of the Treasure Valley had a considerable effect on July 6th, 2007. Particulate smoke concentrations were between 2-4 µg m^{-3}. Note that the use of large quantities of fireworks on July 4th, may result in increased levels of VOCs in the atmosphere. According to ACHD, pavement of the mainline of Locust Grove (east of St. Lukes) started on July 6, and was completed on July 9, 2007 (Table 3-8).

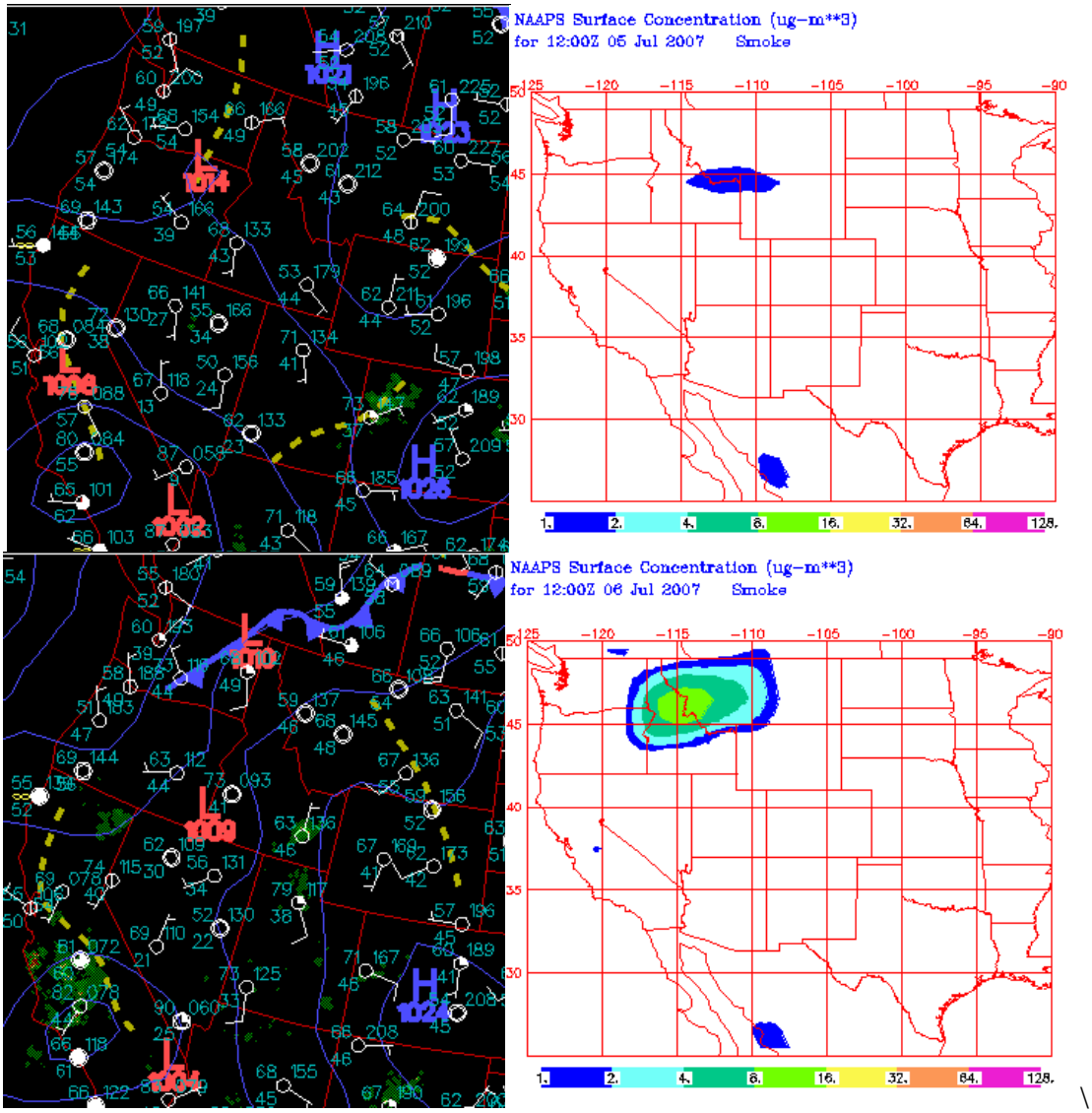
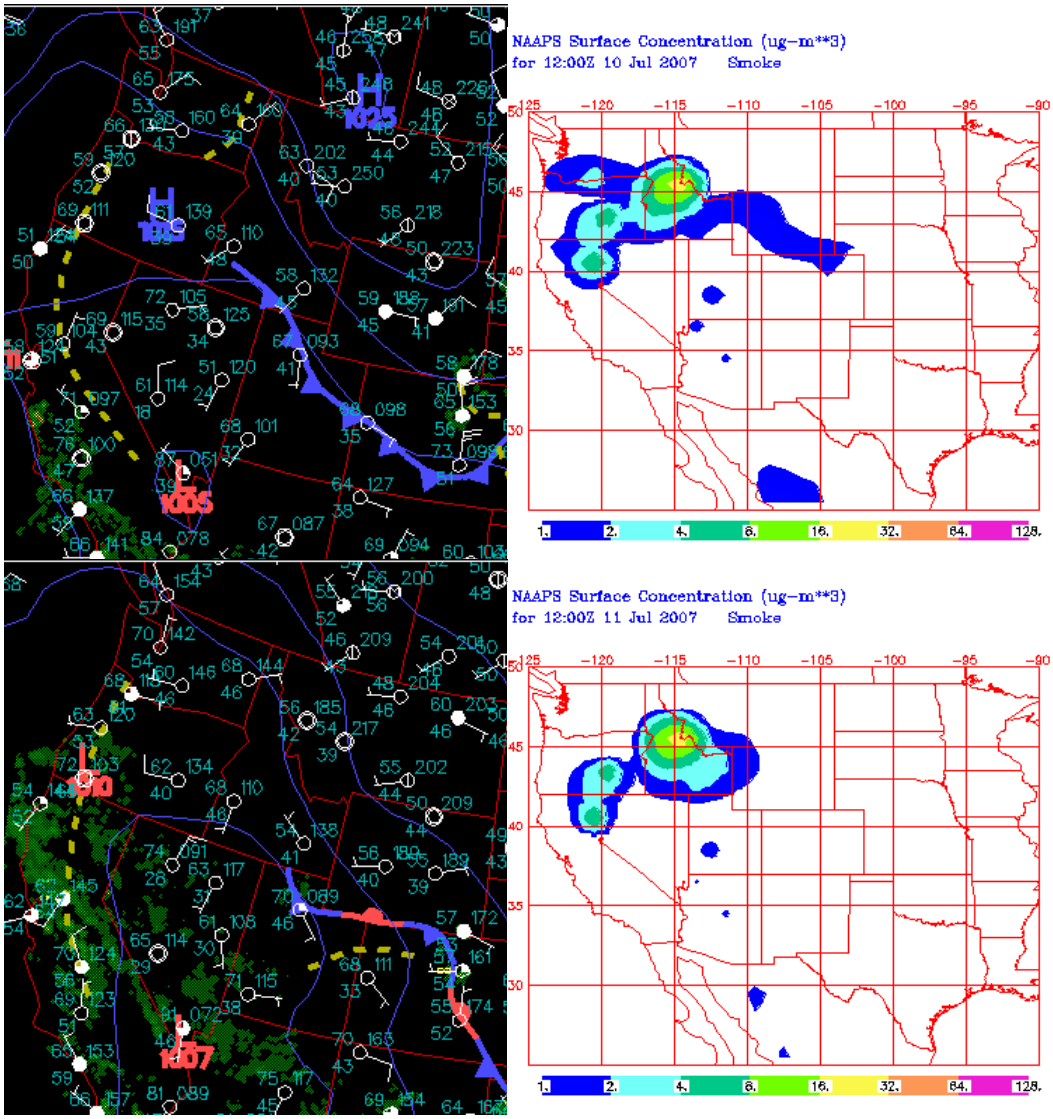


Figure 7-1 Surface weather conditions and smoke concentration (µg m^{-3}) for July 5-6, 2007

Figure 7-2 Backward trajectories at 500m (top) and 2500m (bottom) and locations of wildland fire events (red indicators) during July 5-6, 2007

Event A2: July, 10 to July 14, 2007. Weather conditions and smoke concentrations are shown in Figure 7-3, while the trajectories of air masses arriving in Boise at 500m and 2500m and the locations of wildland fires are presented in Figure 7-4. Weather was characterized by very low surface wind speeds. Trajectories at both 500m and 2500m remained over southwest Idaho and northern Nevada for 2-3 days, indicating rather stagnant regional conditions. During this period,

there were several wildland fires in Idaho, Washington, Oregon and northern Nevada, with the biggest fire at Payette National Forest (300,000 acres burned). Particulate smoke concentrations were between 2-8 μg m^{-3}. The significant input of smoke from wildland fires is further identified in GOES-11 satellite images that showed a large area of Treasure Valley covered by smoke (Figure 7-5). According to ACHD, there were maintenance operations in areas A3 (that include the St. Lukes site) and B3 (Table 3-8).



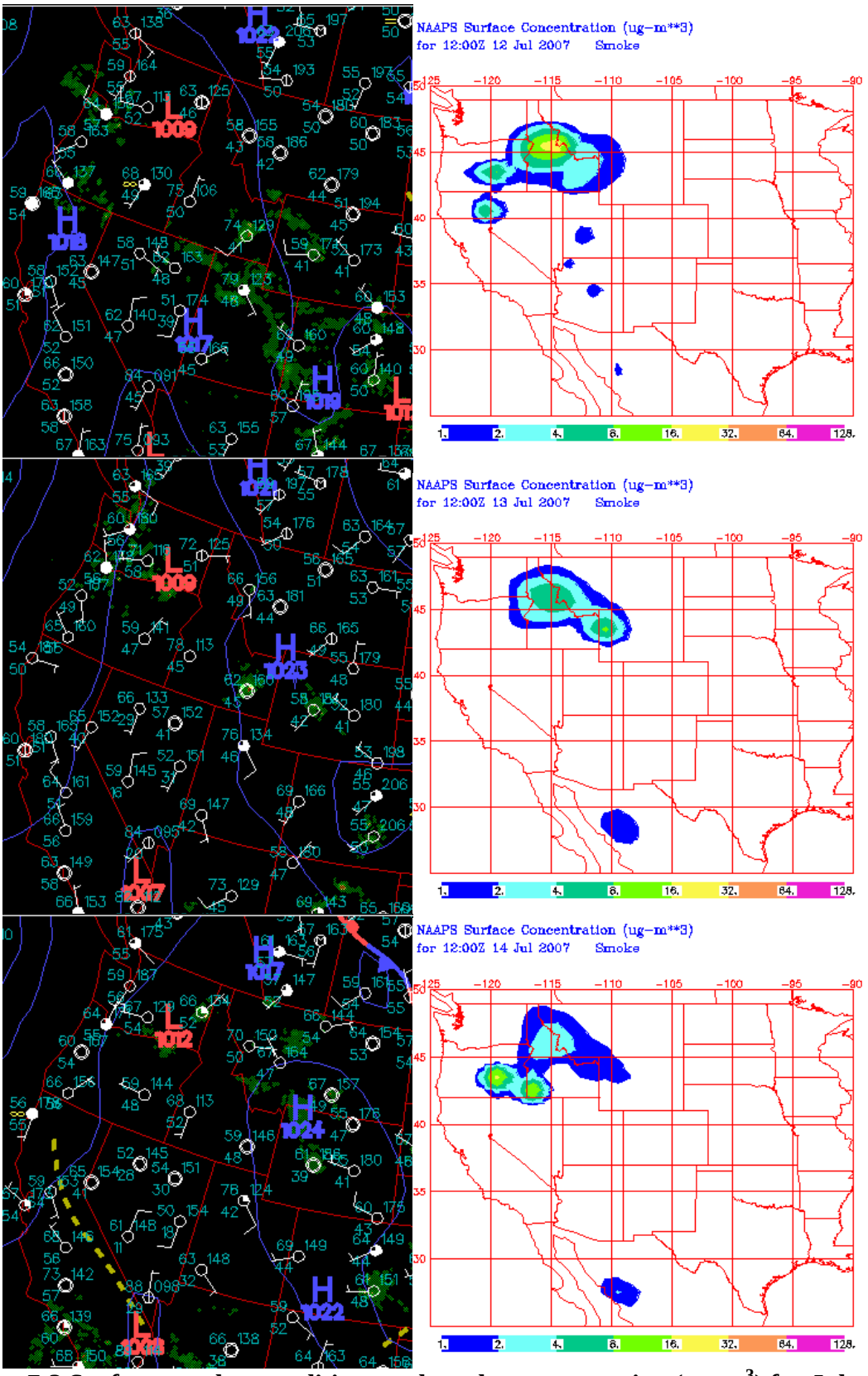


Figure 7-3 Surface weather conditions and smoke concentration (µg m^{-3}) for July 10-14, 2007

Figure 7-4 Backward trajectories at 500m (top) and 2500m (bottom) and locations of wildland fire events (red indicators) during July 10-14, 2007

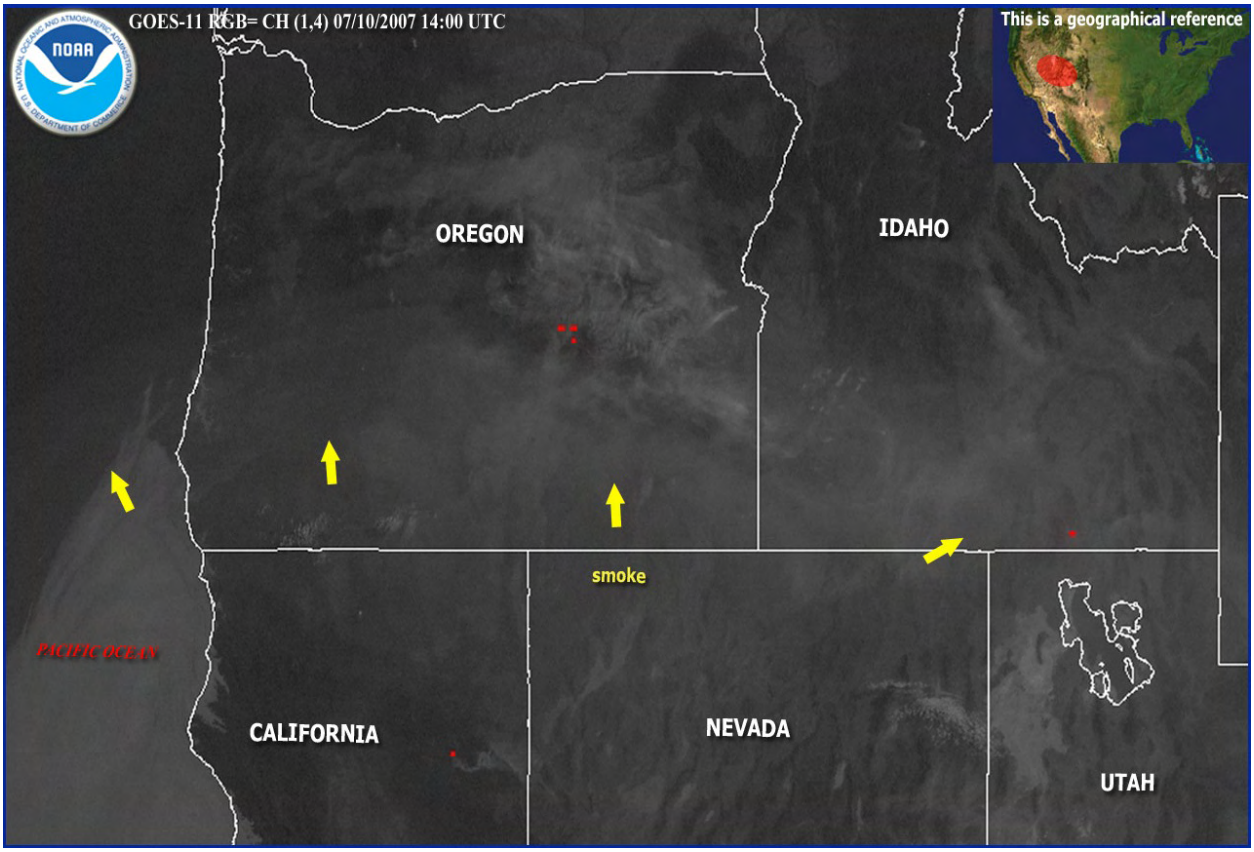


Figure 7-5 GOES-11 satellite image on July 10, 2007 at 1400 UTC (NOAA)

Event A3: July 27 to July 29, 2007. Weather conditions and smoke concentrations are shown in Figure 7-6, while the trajectories of air masses arriving in Boise at 500m and 2500m and the locations of wildland fires are presented in Figure 7-7. Weather was characterized by very low surface wind speeds. Trajectories at 500m traveled through the Columbia River Gorge and along the I-84 while air masses at 2500m originated from California. In both cases, air masses remained over southwest Idaho for 1-2 days, indicating air circulation was limited. During this period, there were several wildland fires in Idaho, Washington, Oregon and northern Nevada, while two big fires in Idaho at Payette National Forest and Twin Falls were still active. Particulate smoke concentrations were as high as 2-4 $\mu g\ m^{-3}$ on July 29, 2007. According to ACHD, there were maintenance operations in areas A3 (that include St. Lukes site) and B3 (Table 3-8) while Vista and Ustick Roads were paved.

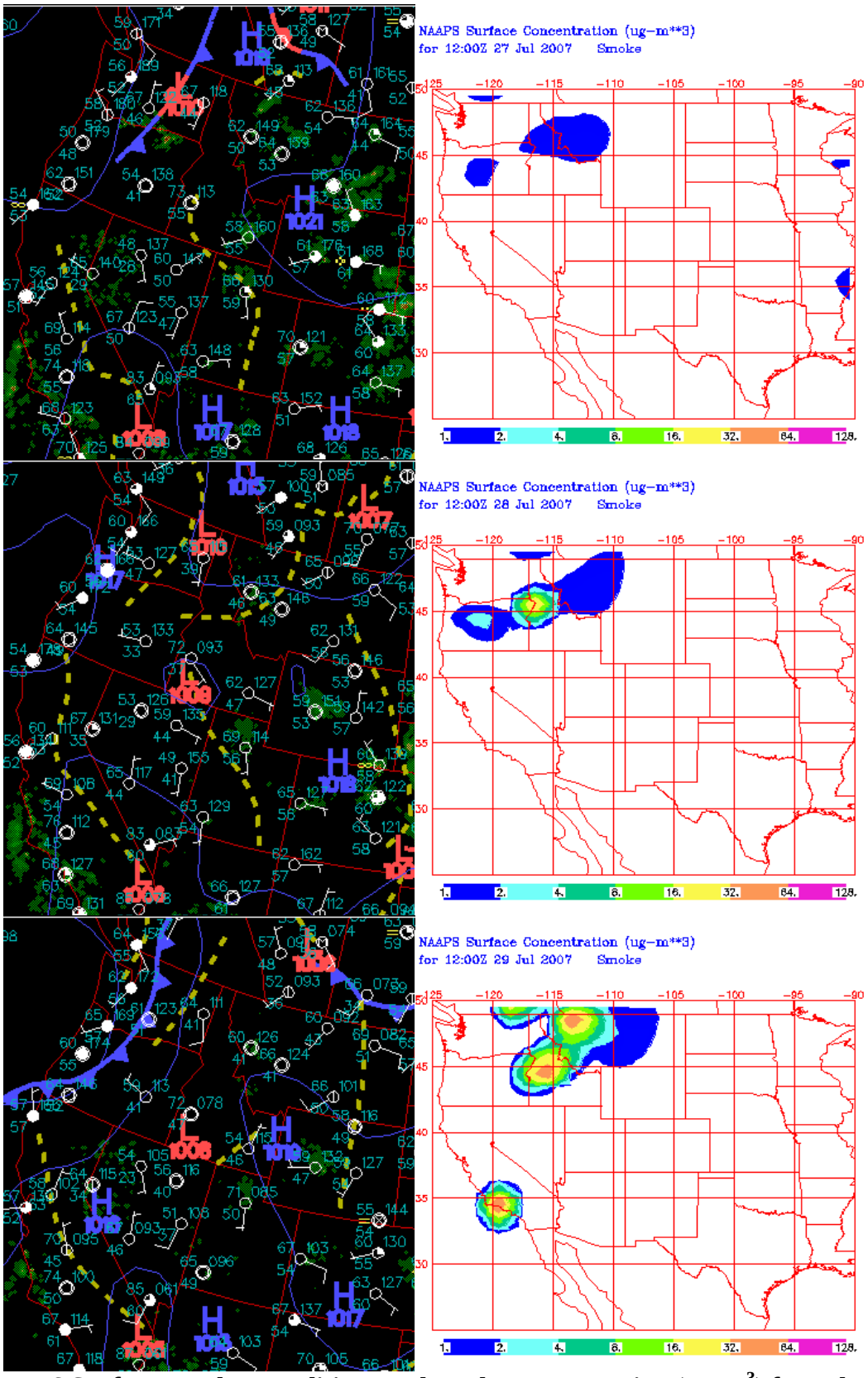


Figure 7-6 Surface weather conditions and smoke concentration (µg m^{-3}) for July 27-29, 2007

Figure 7-7 Backward trajectories at 500m (top) and 2500m (bottom) and locations of wildland fire events (red indicators) during July 27-29, 2007

Event A4: August 1, 2007. Weather conditions and smoke concentrations are shown in Figure 7-8, while the trajectories of air masses arriving in Boise at 500m and 2500m and the locations of wildland fires are presented in Figure 7-9. Weather was characterized by very low surface wind speeds. Trajectories at 500m originated from northern Oregon and passed over the Payette National Forest (still on fire) while air masses at 2500m traveled at higher speed. During this period, there were several wildland fires in Idaho, Washington, and Oregon. Particulate smoke

concentrations were as high as 16 μg m^{-3} on August 1, 2007. According to ACHD, there were maintenance operations in area B3 and pavement activities on Vista Road (Table 3-8).

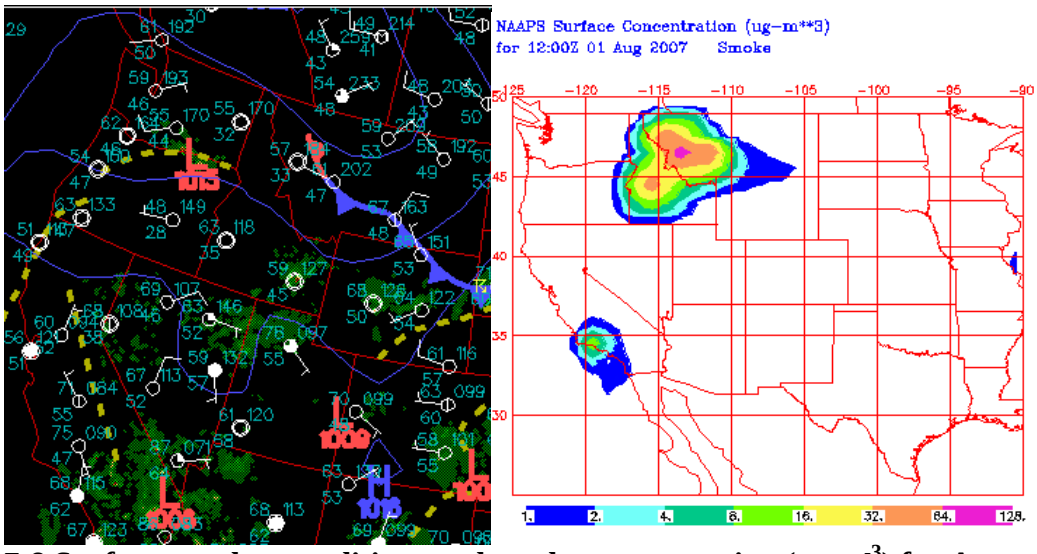


Figure 7-8 Surface weather conditions and smoke concentration (μg m^{-3}) for August 1, 2007

Figure 7-9 Backward trajectories at 500m (top) and 2500m (bottom) and locations of wildland fire events (red indicators) during August 1, 2007

Event A5: August 3, 2007. Weather conditions and smoke concentrations are shown in Figure 7-10, while the trajectories of air masses arriving in Boise at 500m and 2500m and the locations of wildland fires are presented in Figure 7-11. Weather was characterized by very low surface wind speeds. Trajectories at 500m remained over the Treasure Valley for a couple of days with variable origins, while air masses at 2500m originated mostly from southeast Oregon. During this period, there were several wildland fires in Idaho, most of them in the late stages of containment. Particulate smoke concentrations were 0-2 μg m^{-3} on August 1, 2007. GOES-11 satellite images show the presence of moderate levels of smoke over Treasure Valley, northeast Nevada, Montana and the Great Plains from fires in Idaho, Montana and British Columbia (Figure 7-12). According to ACHD, there were maintenance operations in area B3 (Table 3-8).

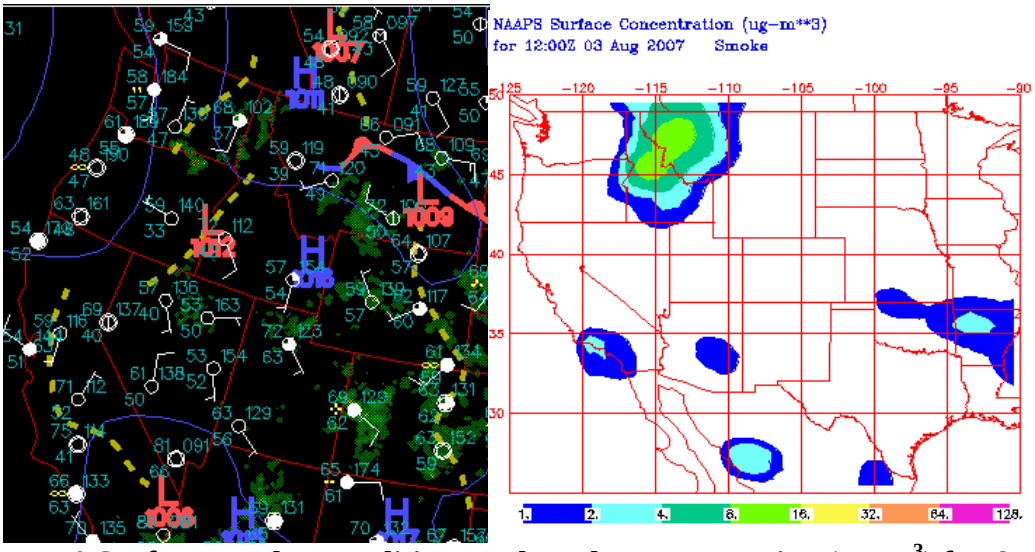


Figure 7-10 Surface weather conditions and smoke concentration (µg m^{-3}) for August 3, 2007

Figure 7-11 Backward trajectories at 500m (top) and 2500m (bottom) and locations of wildland fire events (red indicators) during August 3, 2007

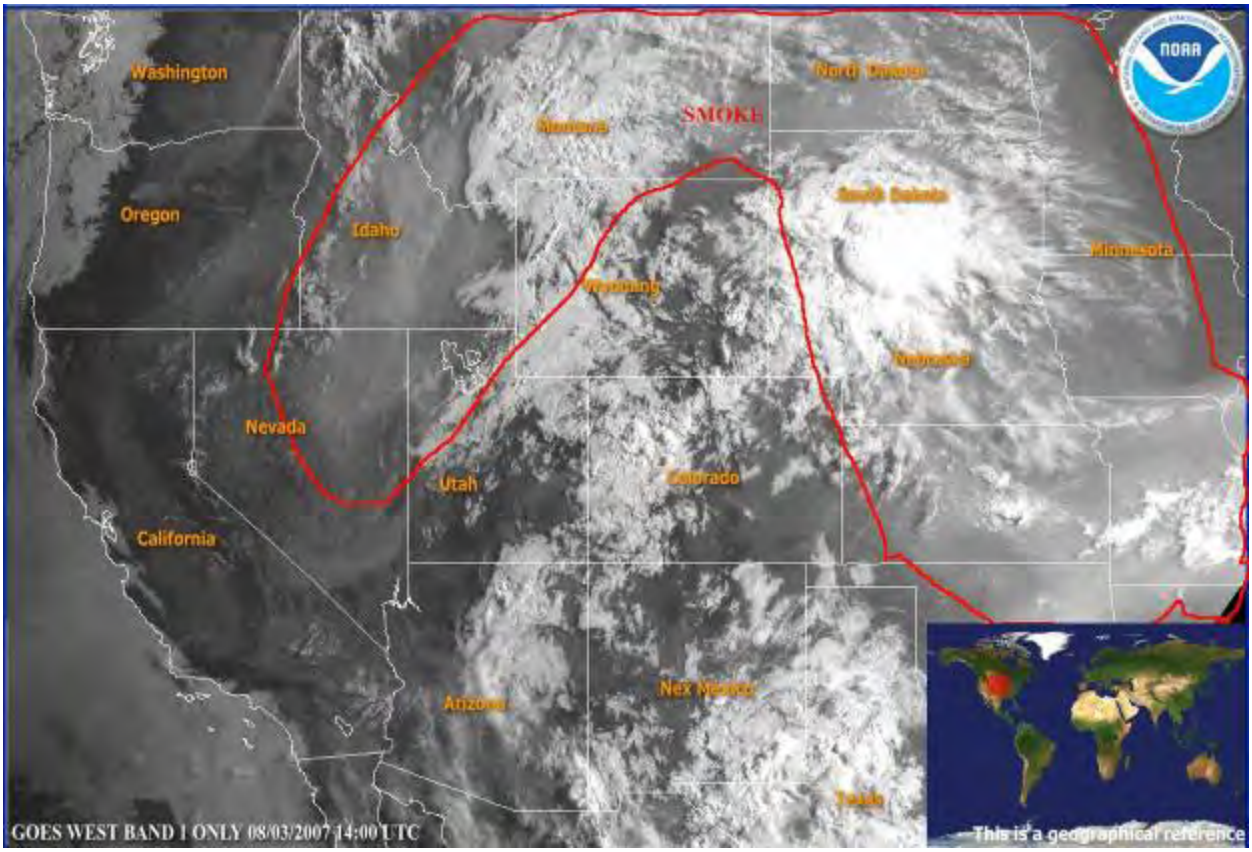


Figure 7-12 GOES-11 satellite image on August 3, 2007 at 1400 UTC (NOAA)

Event A6: August 29, 2007. Weather conditions and smoke concentrations are shown in Figure 7-13, while the trajectories of air masses arriving in Boise at 500m and 2500m and the locations of wildland fires are presented in Figure 7-14. Weather was characterized by low surface wind speeds. Trajectories at 500m and 2500m originated from the northwest and west but air masses remained in the Treasure Valley for a couple of days. During this period, there were several wildland fires in Boise National Forest in Idaho, northeast of Treasure Valley. Particulate smoke concentrations were 2-8 μg m^{-3} on August 29, 2007. According to ACHD, there were maintenance operations in area B3 (Table 3-8).

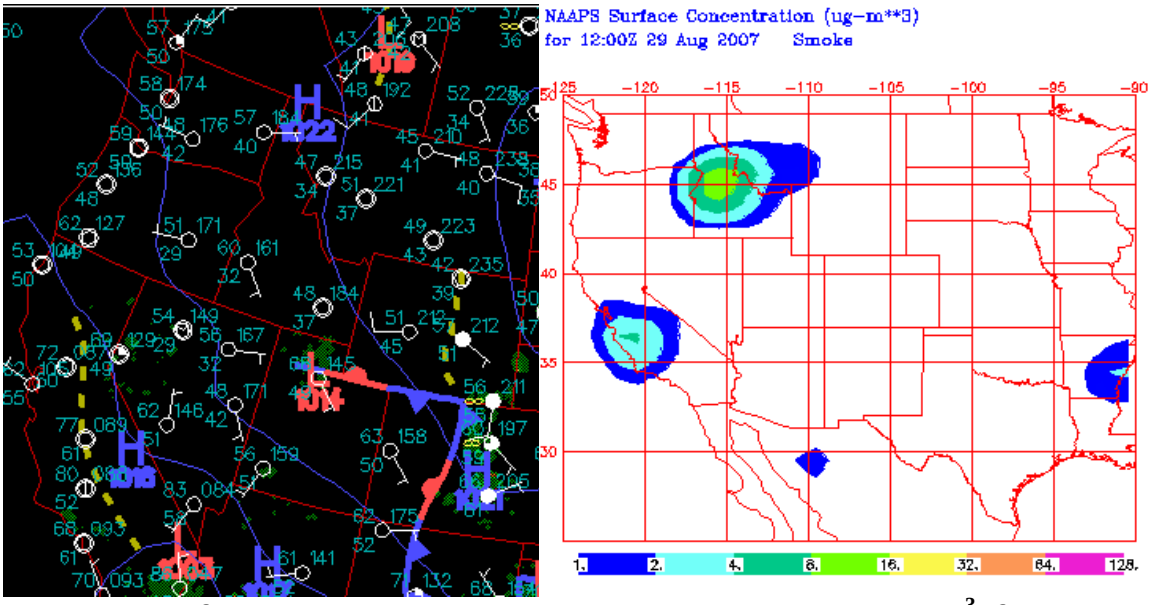


Figure 7-13 Surface weather conditions and smoke concentration (μg m^{-3}) for August 29, 2007

Figure 7-14 Backward trajectories at 500m (top) and 2500m (bottom) and locations of wildland fire events (red indicators) during August 29, 2007

Event A7: September 1, 2007. Weather conditions and smoke concentrations are shown in Figure 7-15, while the trajectories of air masses arriving in Boise at 500m and 2500m and the locations of wildland fires are presented in Figure 7-16. Weather was characterized by very low surface wind speeds. Trajectories at 500m and 2500m originated from the north and west but air masses remained in Treasure Valley for a couple of days. During this period, there were several wildland fires in Boise National Forest in Idaho, northeast of Treasure Valley. Particulate smoke concentrations were 0-2 µg m^{-3} on September 1, 2007. There were no maintenance or construction operations in Treasure Valley (Table 3-8).

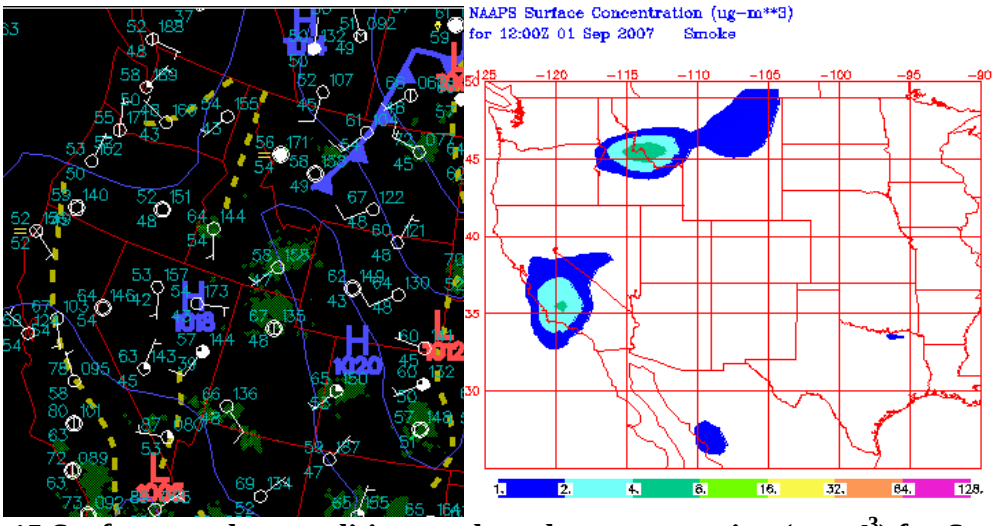


Figure 7-15 Surface weather conditions and smoke concentration (µg m^{-3}) for September 1, 2007

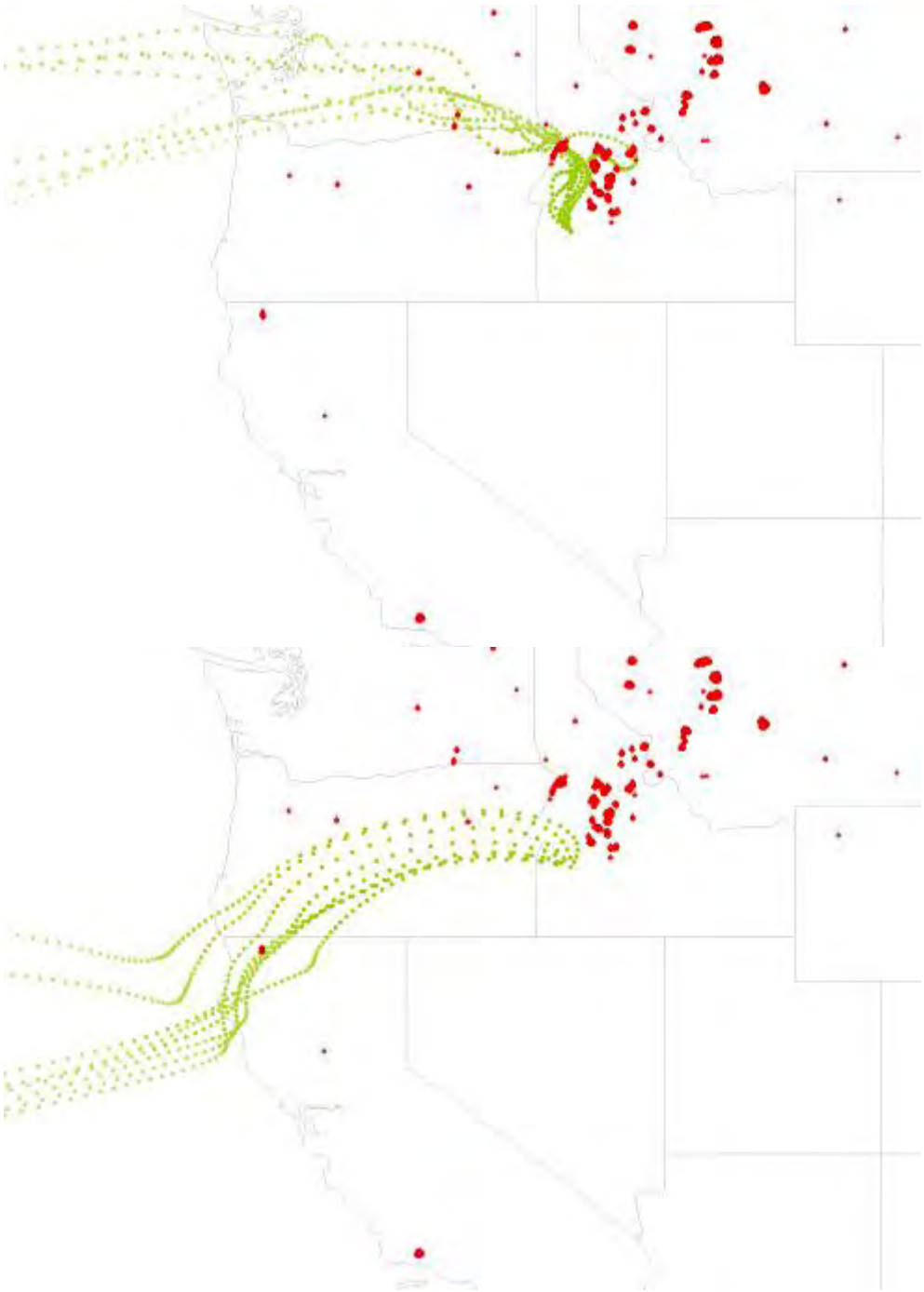


Figure 7-16 Backward trajectories at 500m (top) and 2500m (bottom) and locations of wildland fire events (red indicators) during September 1, 2007

Event A8: September 3, 2007. Weather conditions and smoke concentrations are shown in Figure 7-17, while the trajectories of air masses arriving in Boise at 500m and 2500m and the locations of wildland fires are presented in Figure 7-18. Weather was characterized by very low surface wind speeds. Trajectories at 500m originated from northwest California and remained in Treasure Valley for a couple of days. Air masses at 2500m moved faster from the Pacific Ocean

and did not intercept any active wildland fires. During this period, there were several wildland fires in Boise National Forest in Idaho, northeast of Treasure Valley (Figure 7-18). Particulate smoke concentrations were 2-4 μg m^{-3} on September 3, 2007. According to ACHD, there were no maintenance or construction operations in Treasure Valley (Table 3-8).

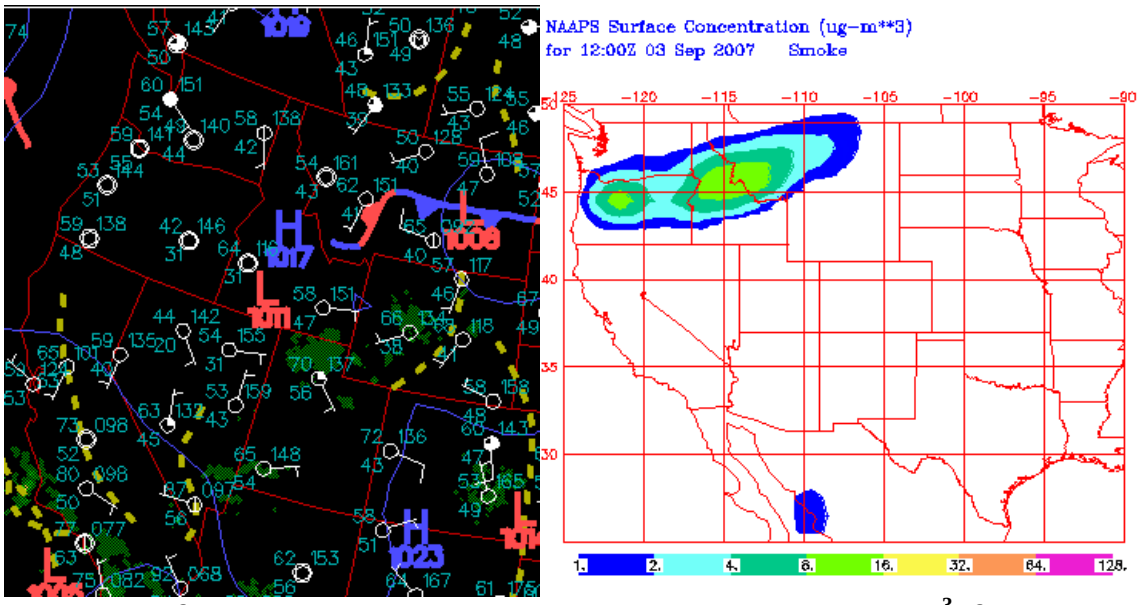


Figure 7-17 Surface weather conditions and smoke concentration (μg m^{-3}) for September 3, 2007

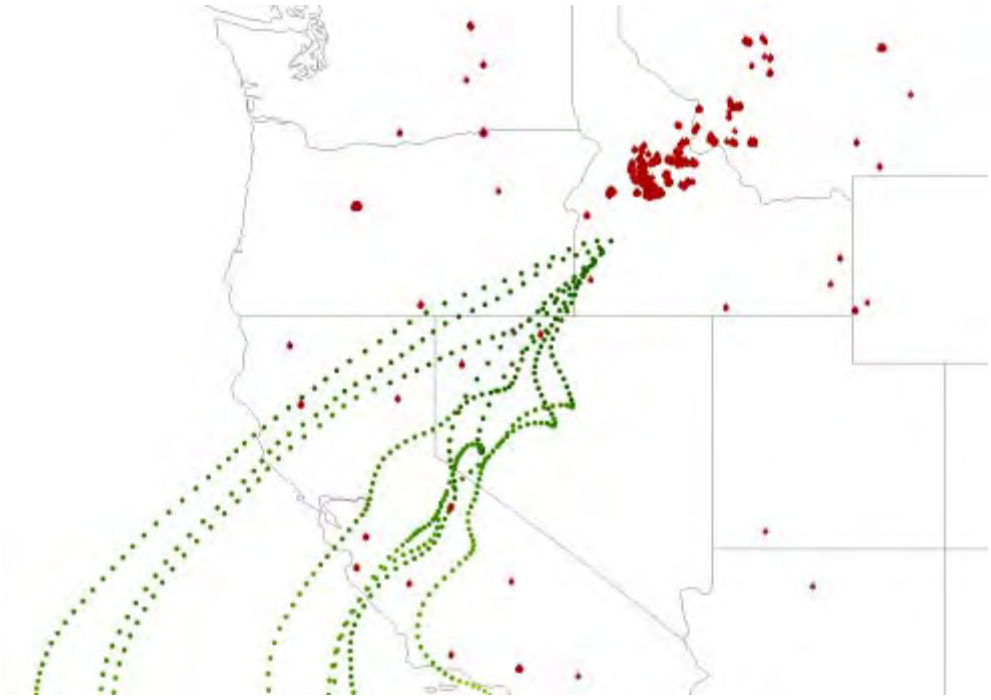


Figure 7-18 Backward trajectories at 500m (top) and 2500m (bottom) and locations of wildland fire events (red indicators) during September 3, 2007

Event A9: September 13, 2007. Weather conditions and smoke concentrations are shown in Figure 7-19, while the trajectories of air masses arriving in Boise at 500m and 2500m and the locations of wildland fires are presented in Figure 7-20. Weather was characterized by very low surface wind speeds. Trajectories at 500m originated from northeast Oregon and remained in Treasure Valley for a couple of days, while trajectories at 2500m came over northern California and intercepted the Moonlight Fire that was burning for ten days (fully controlled on 9/15/2007). During this period, there were several wildland fires in central Idaho, northeast of Treasure Valley). Particulate smoke concentrations were 4-8 $\mu g\ m^{-3}$. There were no maintenance or construction operations in Treasure Valley (Table 3-8).

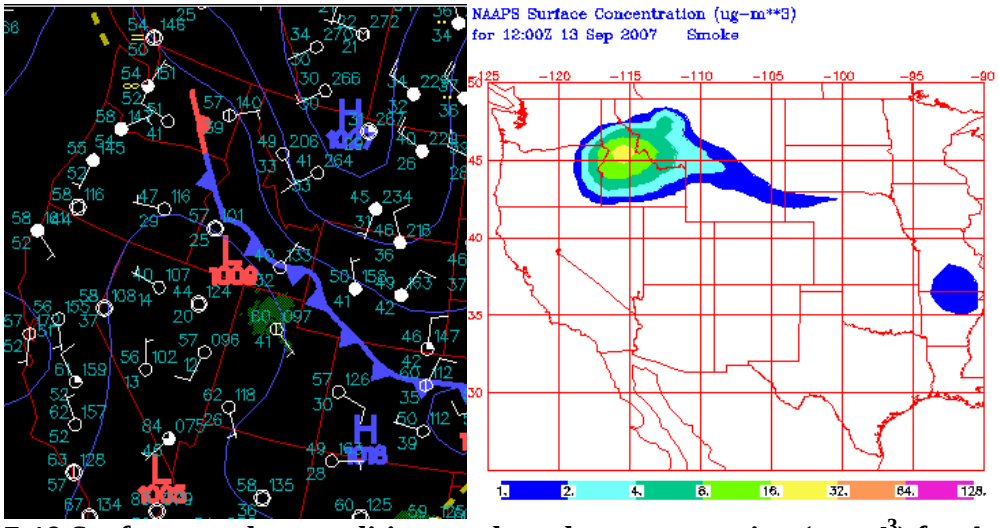


Figure 7-19 Surface weather conditions and smoke concentration (µg m^{-3}) for August 29, 2007

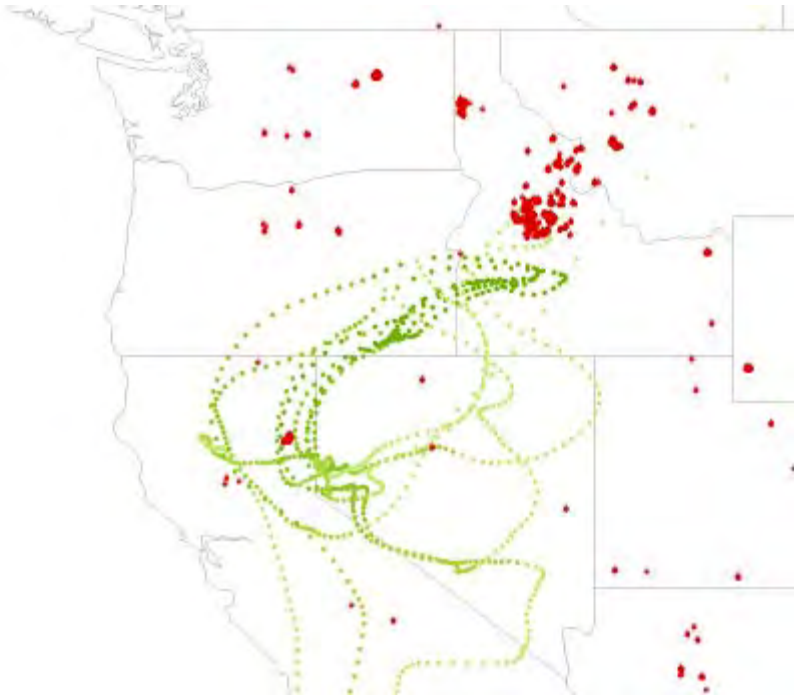
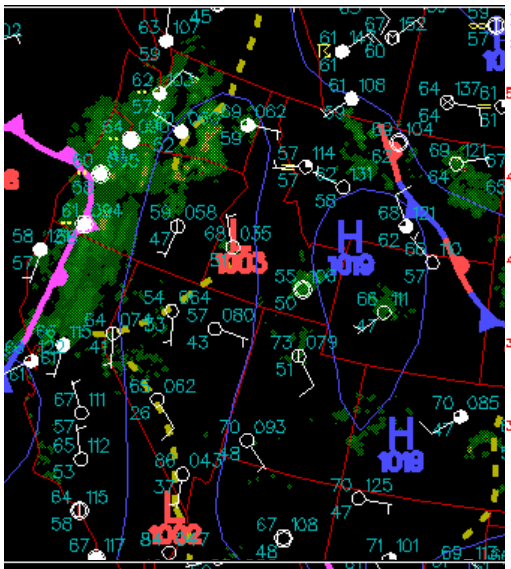
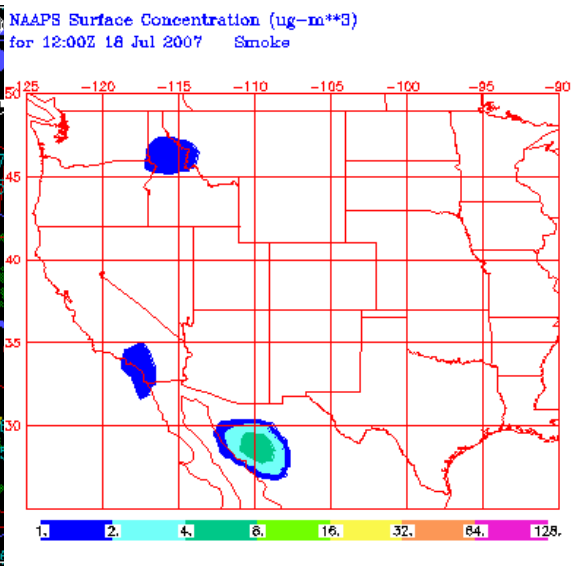
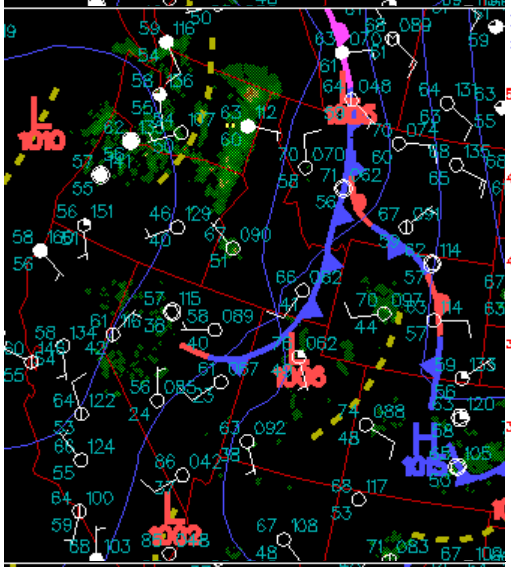


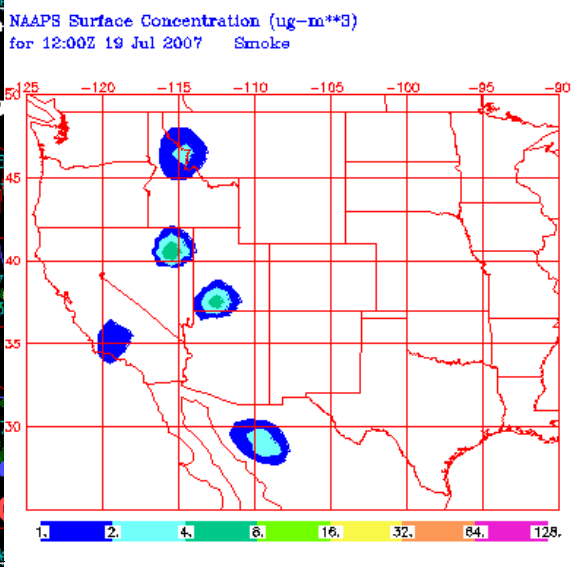
Figure 7-20 Backward trajectories at 500m (top) and 2500m (bottom) and locations of wildland fire events (red indicators) during September 13, 2007

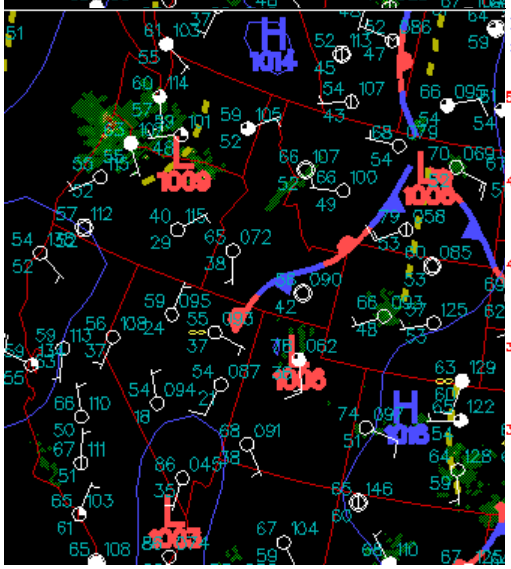
Event B1: July 18 to July 21, 2007. Weather conditions and smoke concentrations are shown in Figure 7-21, while the trajectories of air masses arriving in Boise at 500m and 2500m and the locations of wildland fires are presented in Figure 7-22. Weather was characterized by low surface wind speeds. Trajectories at 500m and 2500m originated from the southwest and remain in the Treasure Valley for a couple of days. During this period, there were several wildland fires in southern Idaho and northern Nevada). Particulate smoke concentrations did not appear to be a factor on July 18 and 19, 2007, but a major plume was observed on July 20 and 21, 2007, probably caused by wildland fires in Boise NF. The significant contributions of wildland fire smoke was further supported by a GOES-11 satellite image that showed widespread smoke in northern Nevada, southern Idaho, including Treasure Valley and northeast Utah. According to ACHD, there were maintenance activities on A3 and B3 sectors and paving operations on the mainline of Locust Grove (Table 3-8).

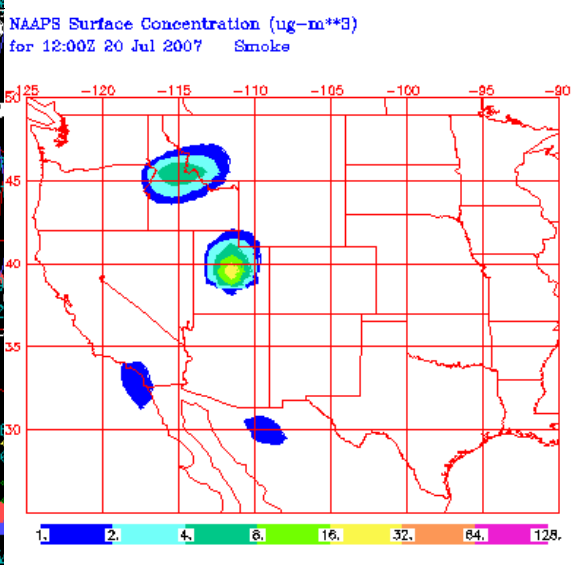



NAAPS Surface Concentration (ug-m**3)
for 12:00Z 18 Jul 2007 Smoke
-125 -120 -115 -110 -105 -100 -95 -90
50 45 40 35 30
1. 2. 4. 8. 16. 32. 64. 128.




NAAPS Surface Concentration (ug-m**3)
for 12:00Z 19 Jul 2007 Smoke
-125 -120 -115 -110 -105 -100 -95 -90
50 45 40 35 30
1. 2. 4. 8. 16. 32. 64. 128.




NAAPS Surface Concentration (ug-m**3)
for 12:00Z 20 Jul 2007 Smoke
-125 -120 -115 -110 -105 -100 -95 -90
50 45 40 35 30
1. 2. 4. 8. 16. 32. 64. 128.

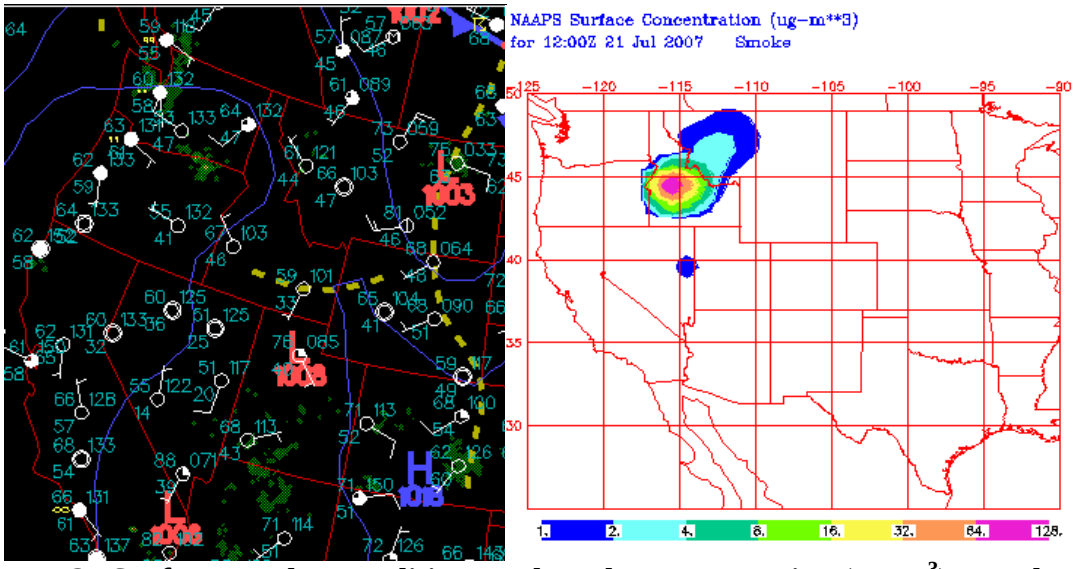
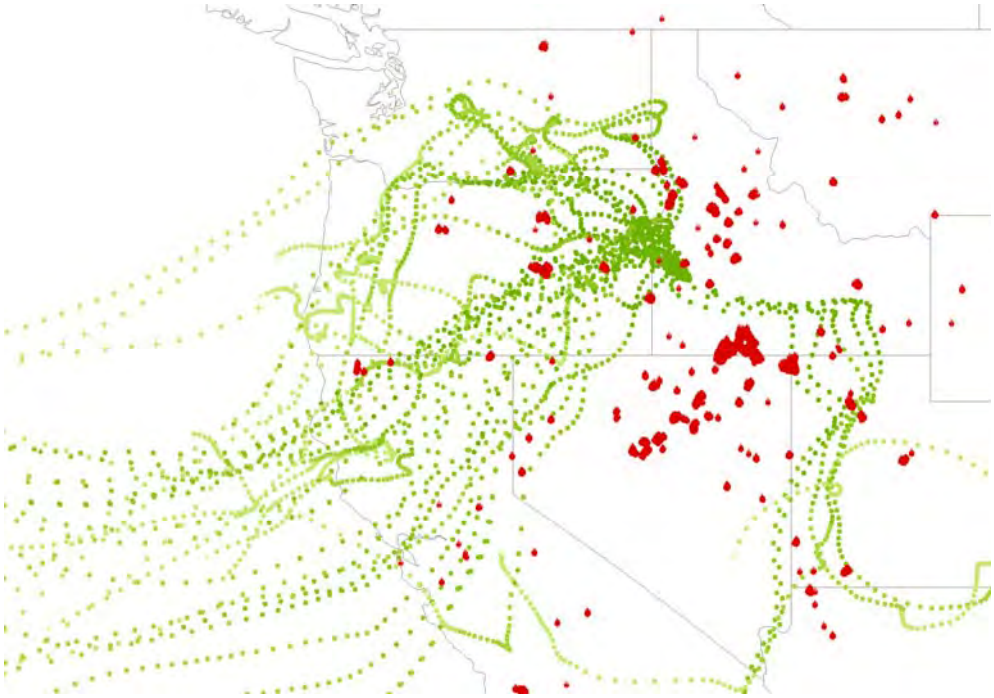


Figure 7-21 Surface weather conditions and smoke concentration (μg m^{-3}) on July 18-21, 2007



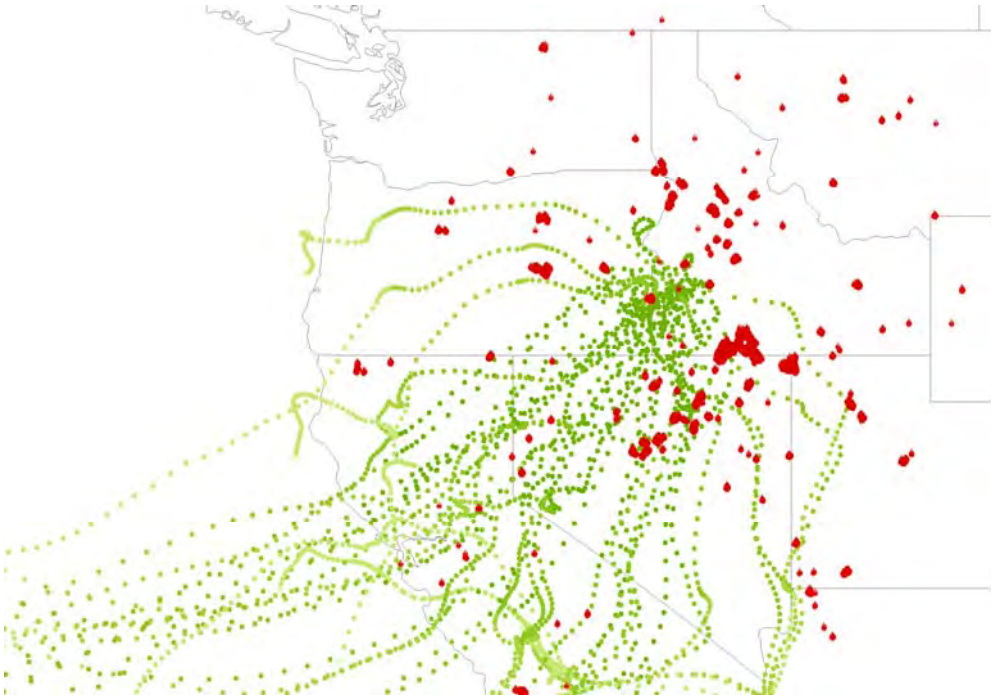


Figure 7-22 Backward trajectories at 500m (top) and 2500m (bottom) and locations of wildland fire events (red indicators)during July 18-21, 2007

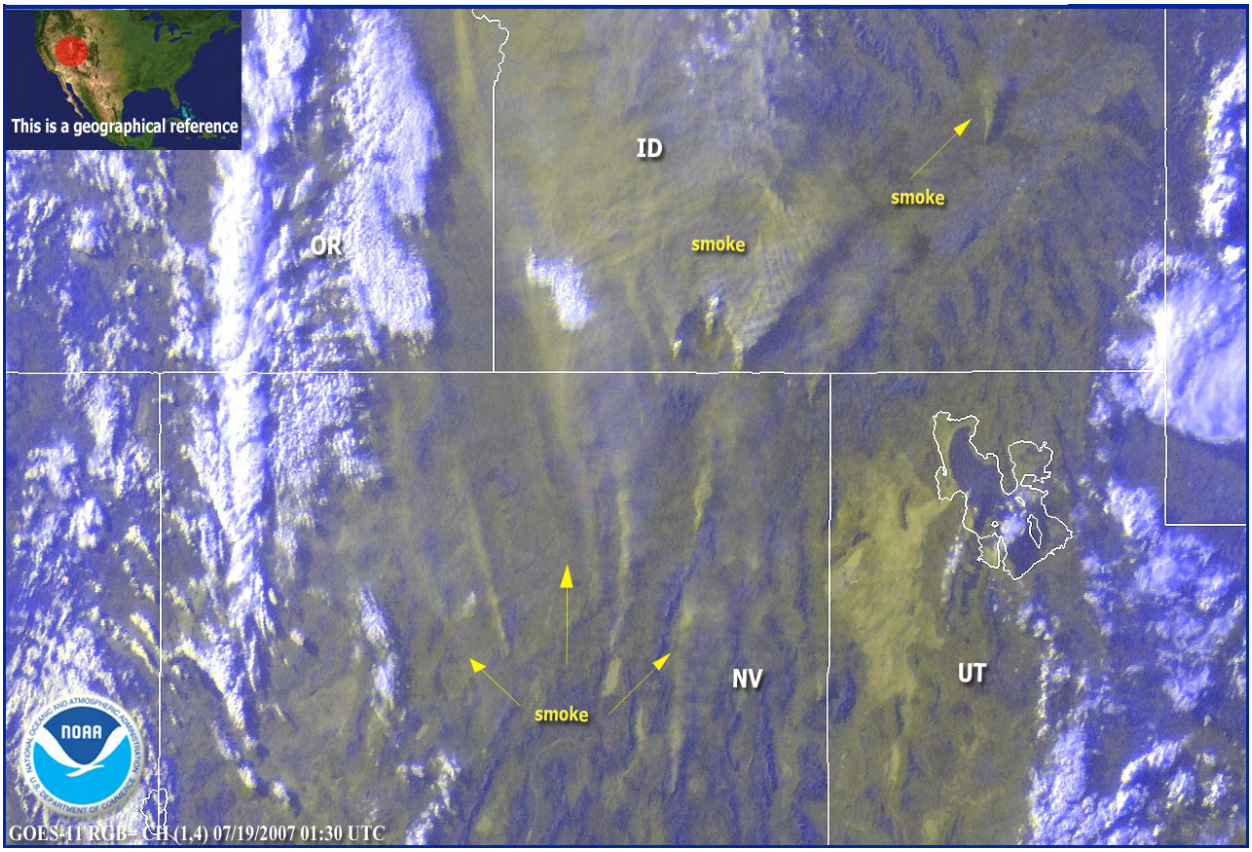
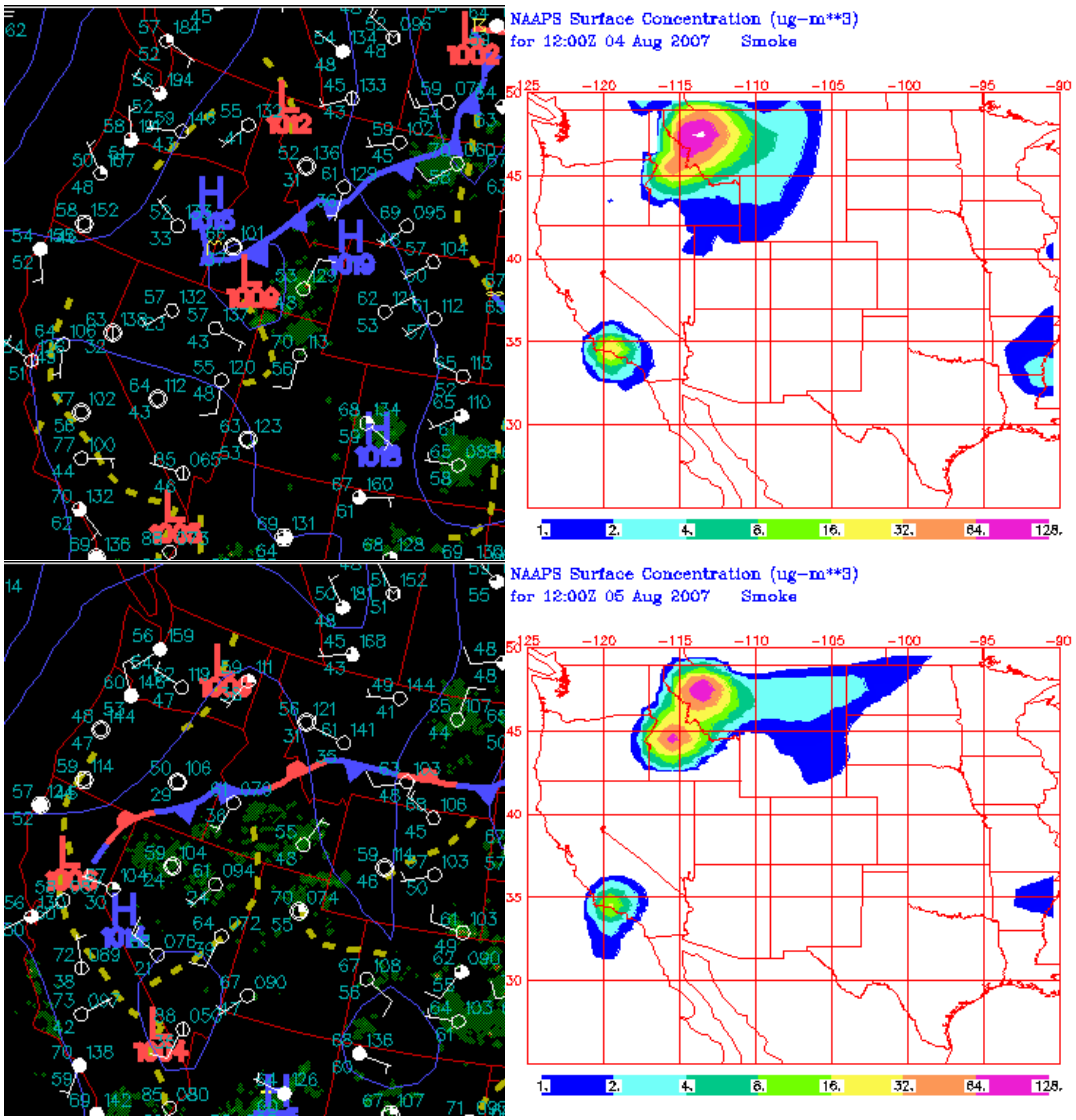


Figure 7-23 GOES-11 satellite image on July 19, 2007 at 01:30 UTC (NOAA)

Event B2: August 4 to August 8, 2007. Weather conditions and smoke concentrations are shown in Figure 7-24, while the trajectories of air masses arriving in Boise at 500m and 2500m and the locations of wildland fires in Northwest are presented in Figure 7-25. Weather was characterized by very low surface wind speeds. Trajectories at 500m and 2500m originated from west and southwest and remain in Treasure Valley. During this period, there were several wildland fires in central Idaho and northwest Montana. Contributions of particulate smoke concentrations were significant (up to 64 μg m^{-3}). There were maintenance activities on A3 and B3 sectors on August 5-7, 2007 (Table 3-8).



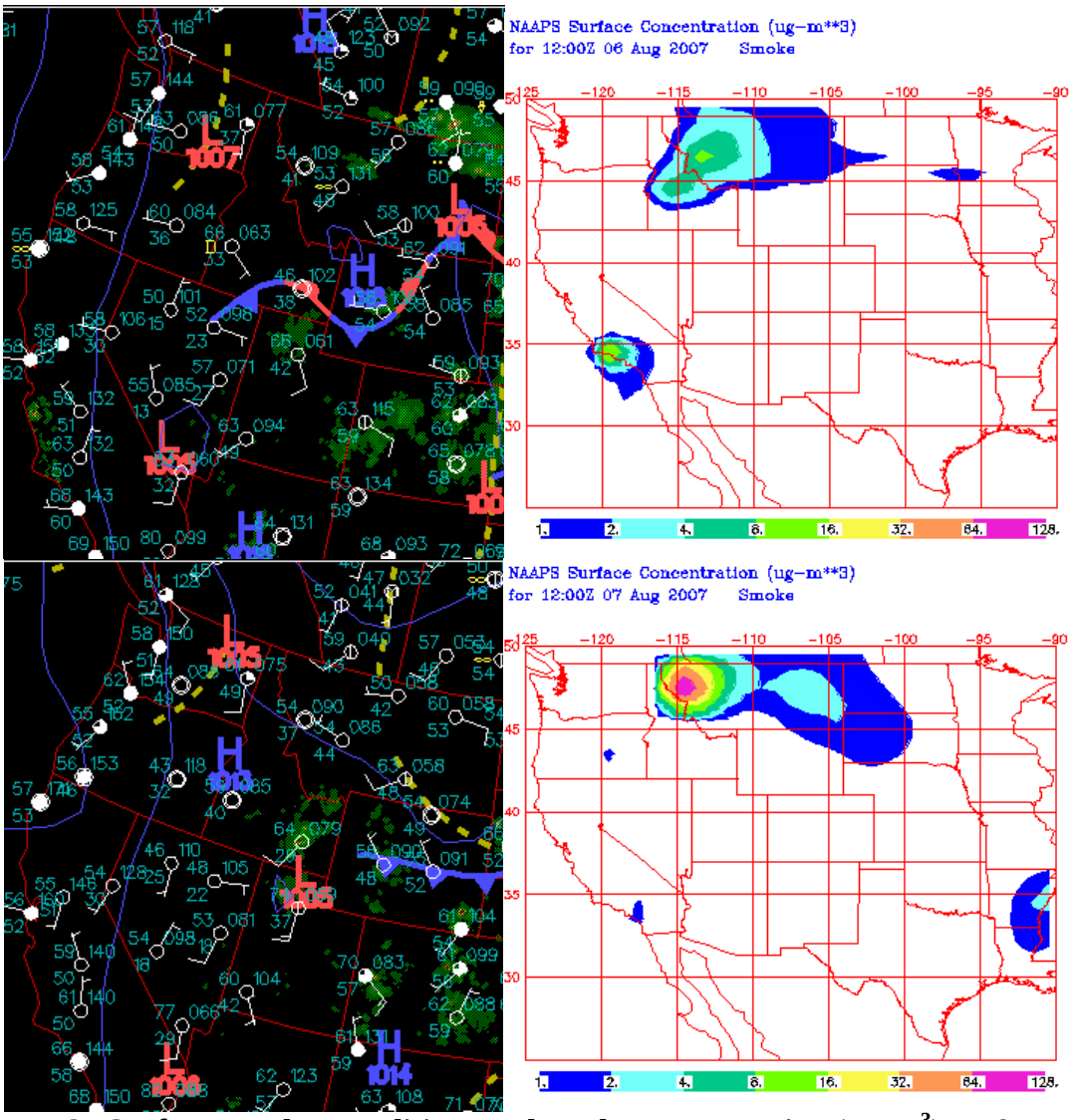


Figure 7-24 Surface weather conditions and smoke concentration (µg m^{-3}) on August 4-7, 2007

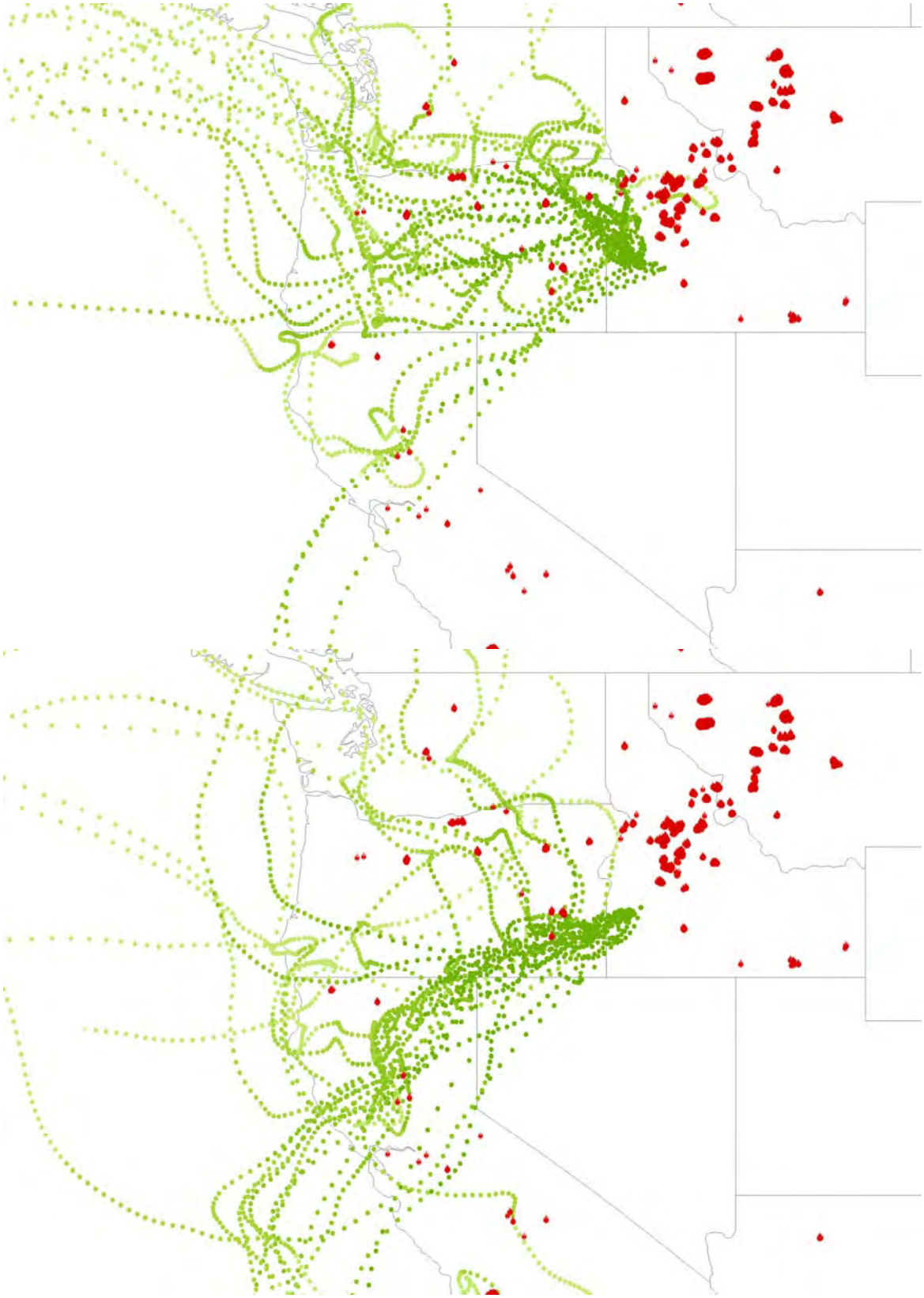


Figure 7-25 Backward trajectories at 500m (top) and 2500m (bottom) and locations of wildland fire events (red indicators)during August 4-7 2007

Event B3: August 10, 2007. Weather conditions and smoke concentrations are shown in Figure 7-26, while the trajectories of air masses arriving in Boise at 500m and 2500m and the locations of wildland fires are presented in Figure 7-27. Weather was characterized by very low surface wind speeds. Trajectories at 500m and 2500m originated from Oregon and intercepted fires in Oregon. Particulate smoke concentrations were 0-2 µg m^{-3}. There were no maintenance or construction operations in Treasure Valley (Table 3-8).

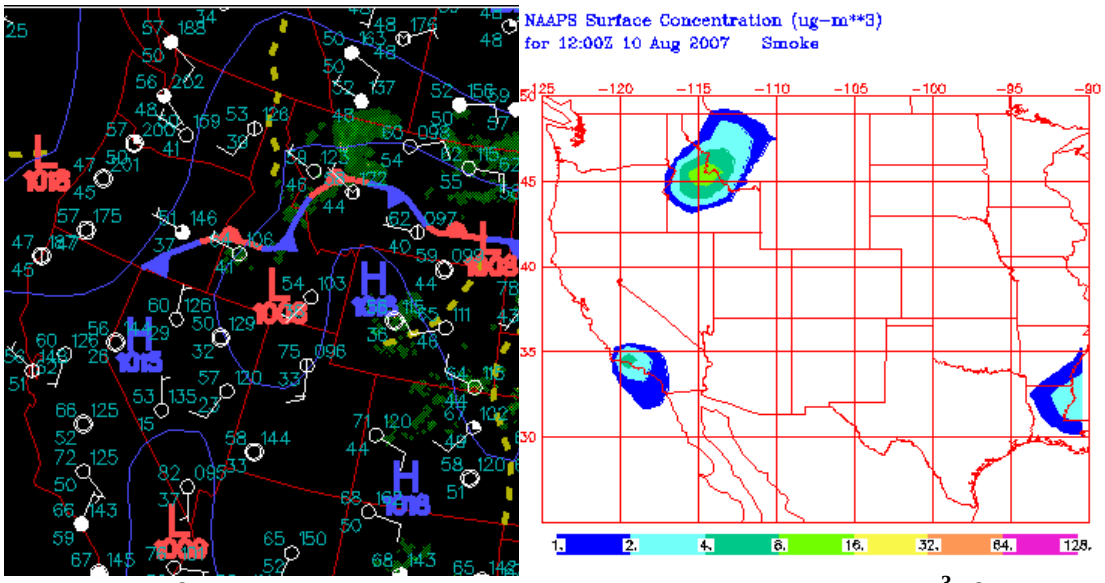
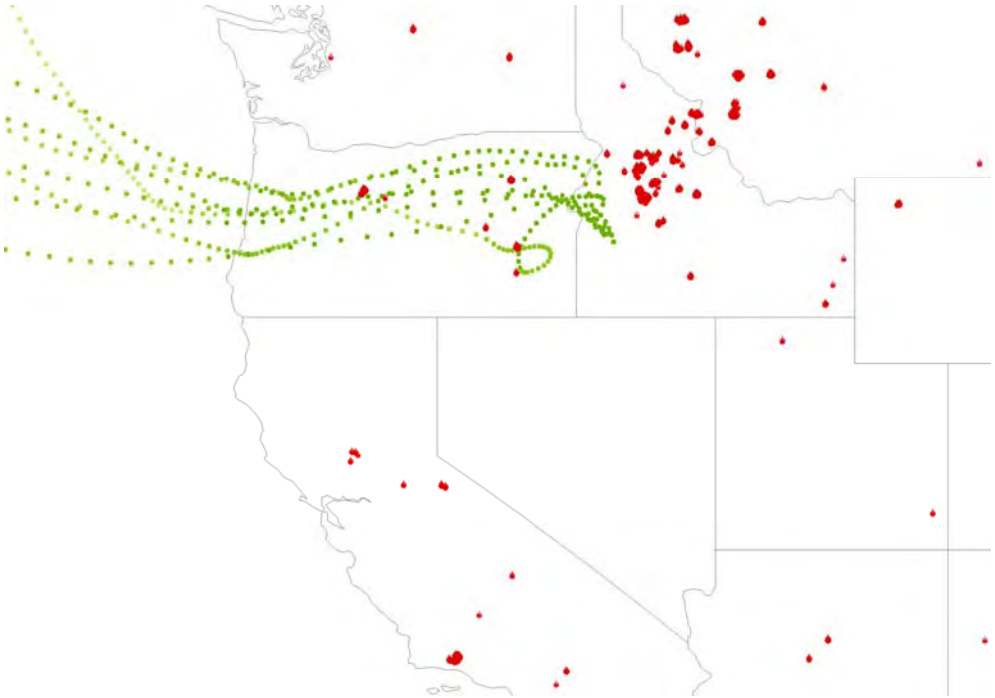


Figure 7-26 Surface weather conditions and smoke concentration (µg m^{-3}) for August 10, 2007



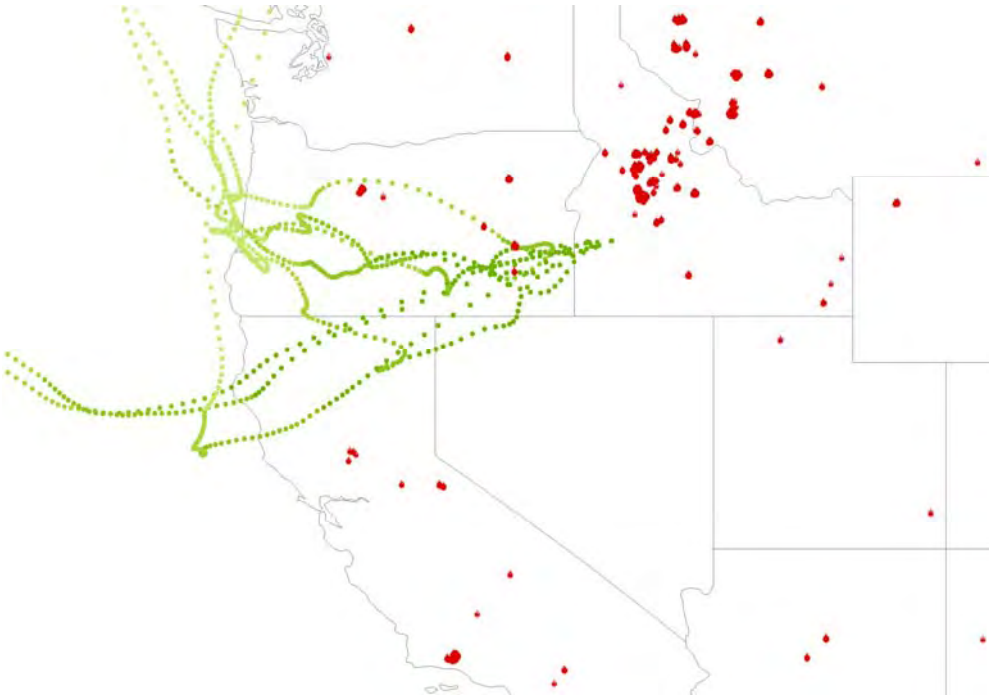


Figure 7-27 Backward trajectories at 500m (top) and 2500m (bottom) and locations of wildland fire events (red indicators)during August 10, 2007

Event B4: August 13, 2007. Weather conditions and smoke concentrations are shown in Figure 7-28, while the trajectories of air masses arriving in Boise at 500m and 2500m and the locations of wildland fires are presented in Figure 7-29. Weather was characterized by very low surface wind speeds. Trajectories at 500m and 2500m originated from Oregon and northern California. There were no wildland fires on the pathway of air masses arriving in Boise on August 13, 2007; however, there were several fires northeast of Treasure Valley triggering elevated particulate smoke concentrations (as high as 128 μg m^{-3}) in Idaho and Montana. The dispersion of the smoke plume towards the northeast was observed by GOES-11 satellite images (Figure 7-30) There were maintenance operations in sector B3 (Table 3-8).

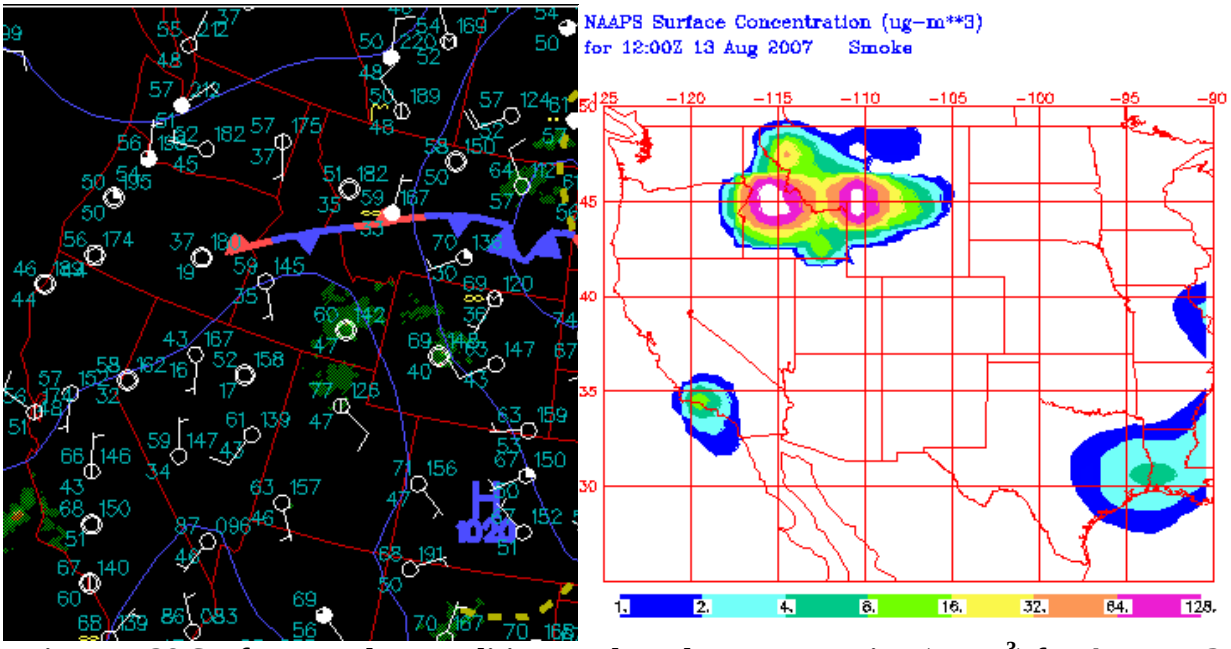
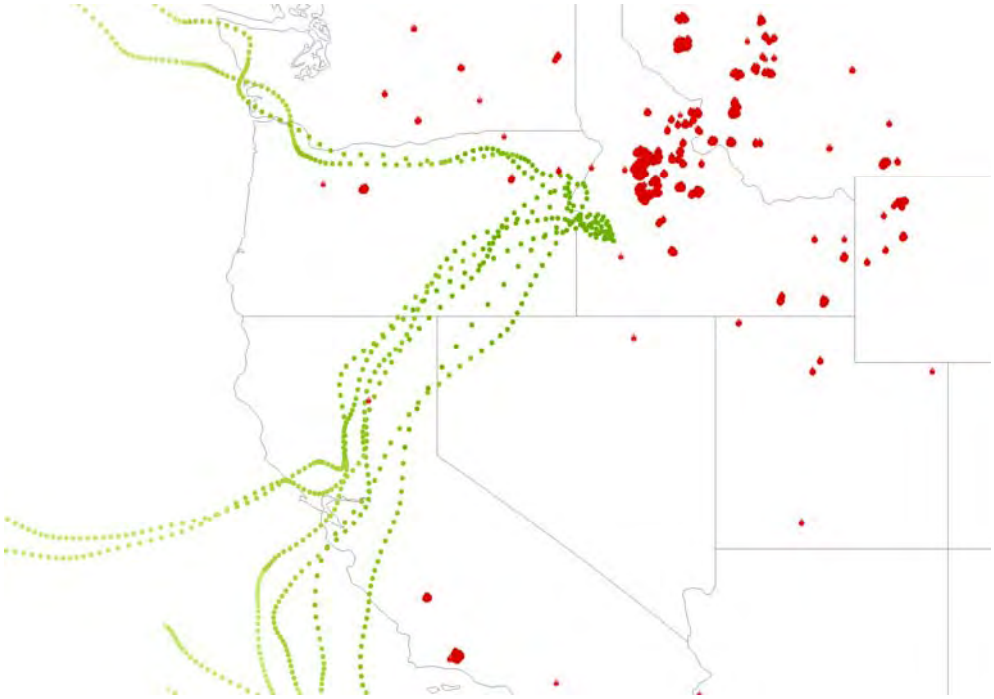


Figure 7-28 Surface weather conditions and smoke concentration (μg m^{-3}) for August 13, 2007



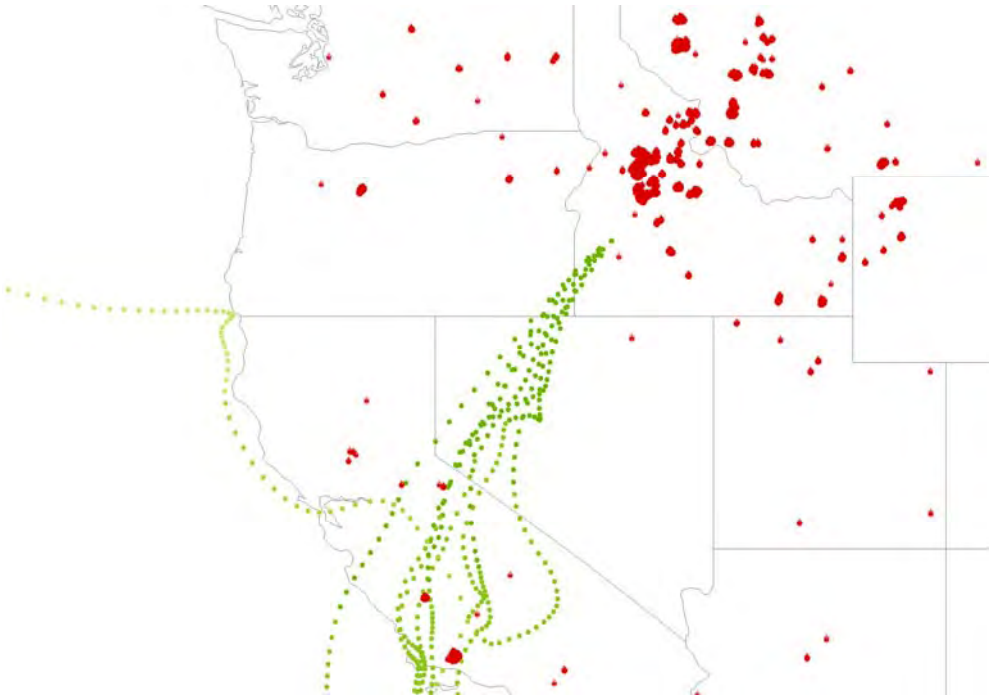


Figure 7-29 Backward trajectories at 500m (top) and 2500m (bottom) and locations of wildland fire events (red indicators) during August 13, 2007

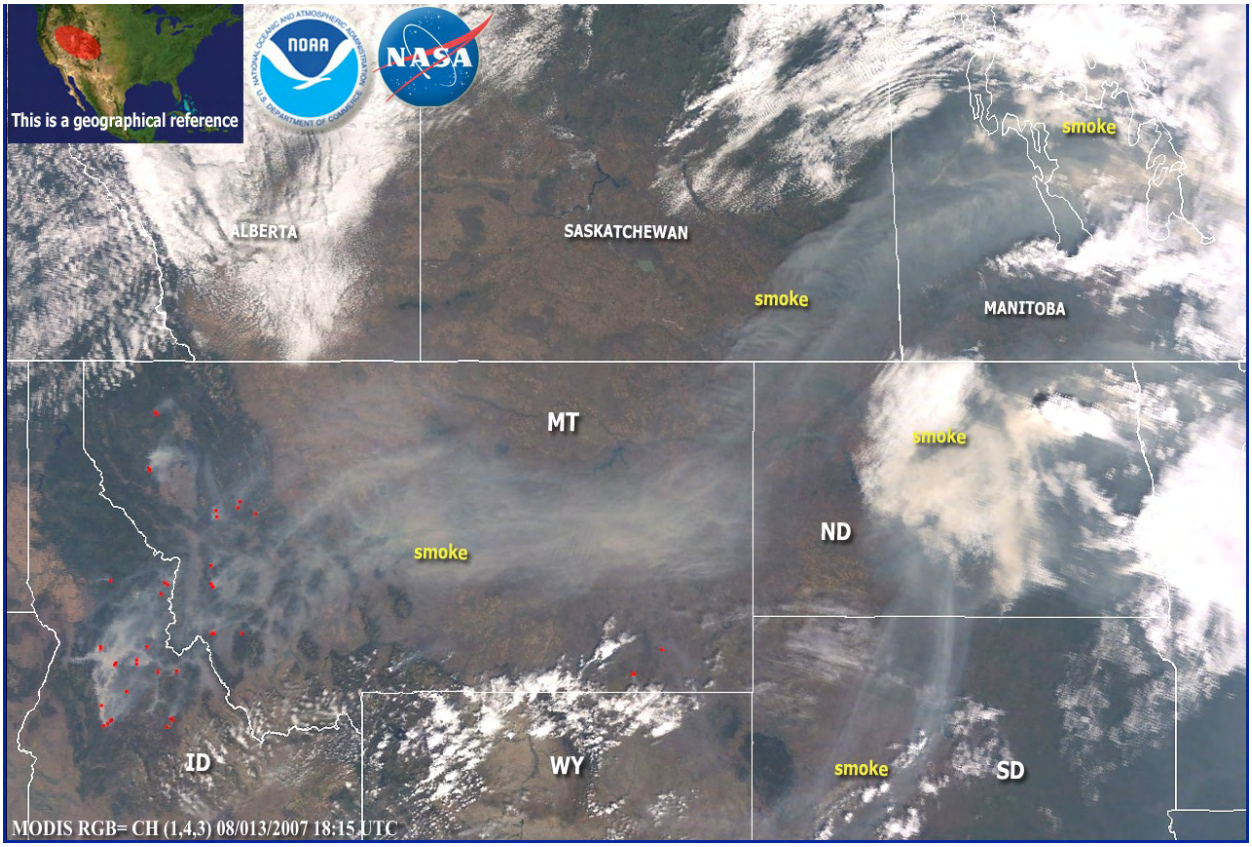


Figure 7-30 GOES-11 satellite image on August 13, 2007 at 01:30 UTC (NOAA)

Event B5: August 22, 2007. Weather conditions and smoke concentrations are shown in Figure 7-31, while the trajectories of air masses arriving in Boise at 500m and 2500m and the locations of wildland fires are presented in Figure 7-32. Weather was characterized by low surface wind speeds. Trajectories at 500m and 2500m originated from the Pacific Ocean and Oregon and there were no wildland fires in Oregon or near the Treasure Valley. This is further supported by the absence of particulate smoke. There were maintenance operations in sector B3 (Table 3-8).

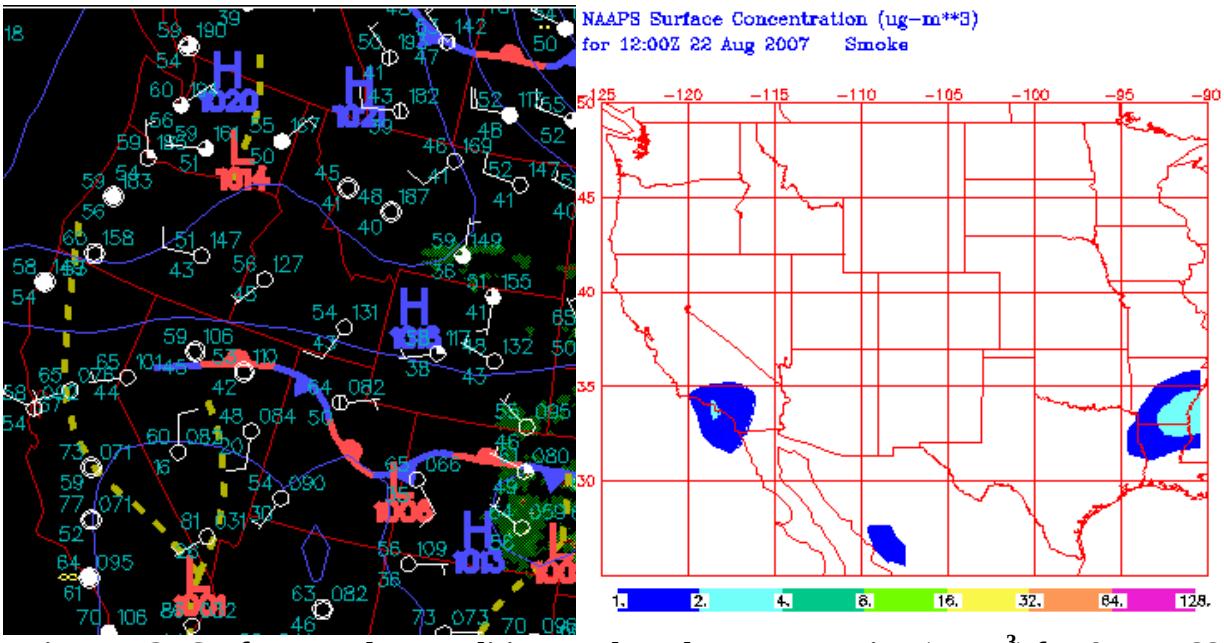
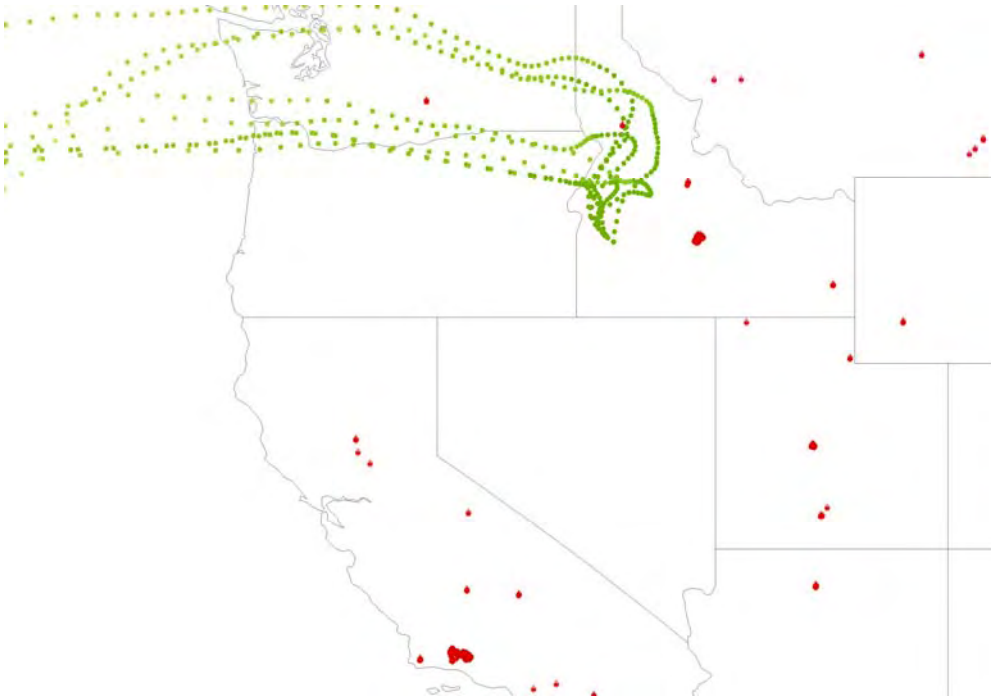


Figure 7-31 Surface weather conditions and smoke concentration (µg m^{-3}) for August 22, 2007



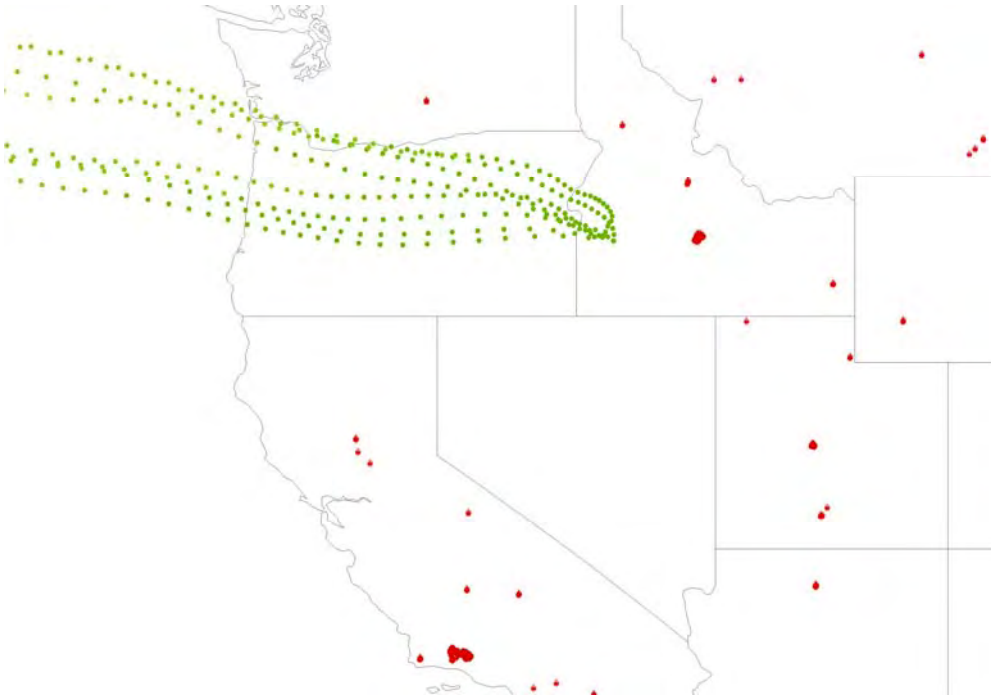
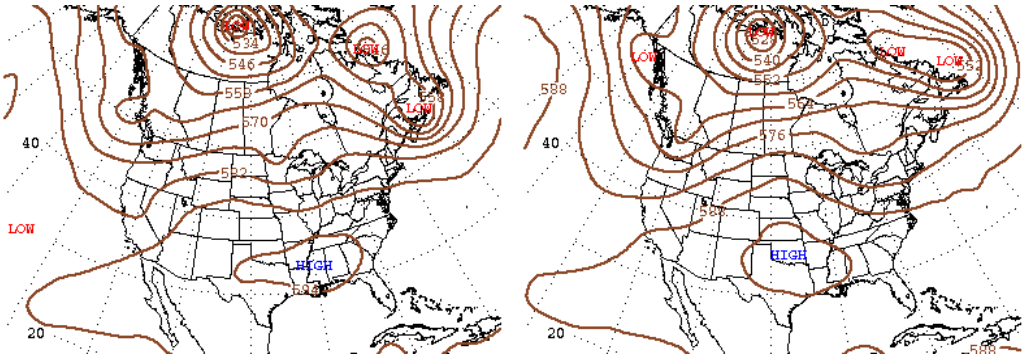


Figure 7-32 Backward trajectories at 500m (top) and 2500m (bottom) and locations of wildland fire events (red indicators) on August 22, 2007

Appendix C. Applicability of tethered-balloon measurements

The vertical profiles obtained from the tethered balloon should be useful in understanding the valley flow behavior during high ozone days. While the balloon measurements were not taken during particularly high ozone periods, the conditions were similar to several higher ozone episodes earlier in the summer. Synoptic maps for balloon measurements on the mornings of August 9-10 (top left and top right) and August 14-15 (bottom left and bottom right) are shown in Figure 7-33. Synoptic maps for the highest ozone days on the mornings of July 14 and 27 (top left and top right) and July 28 and August 1 (bottom left and bottom right) are presented in Figure 7-34



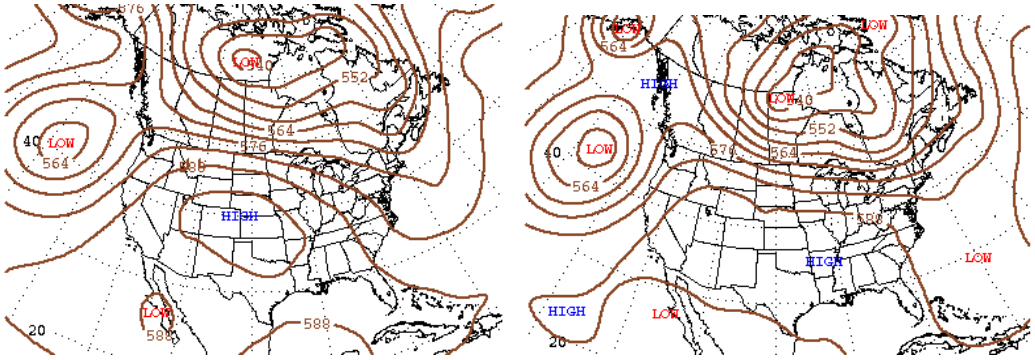


Figure 7-33 Synoptic maps for August 9-10, 2007 (top panels) and August 14-15, 2007 (Bottom panels)

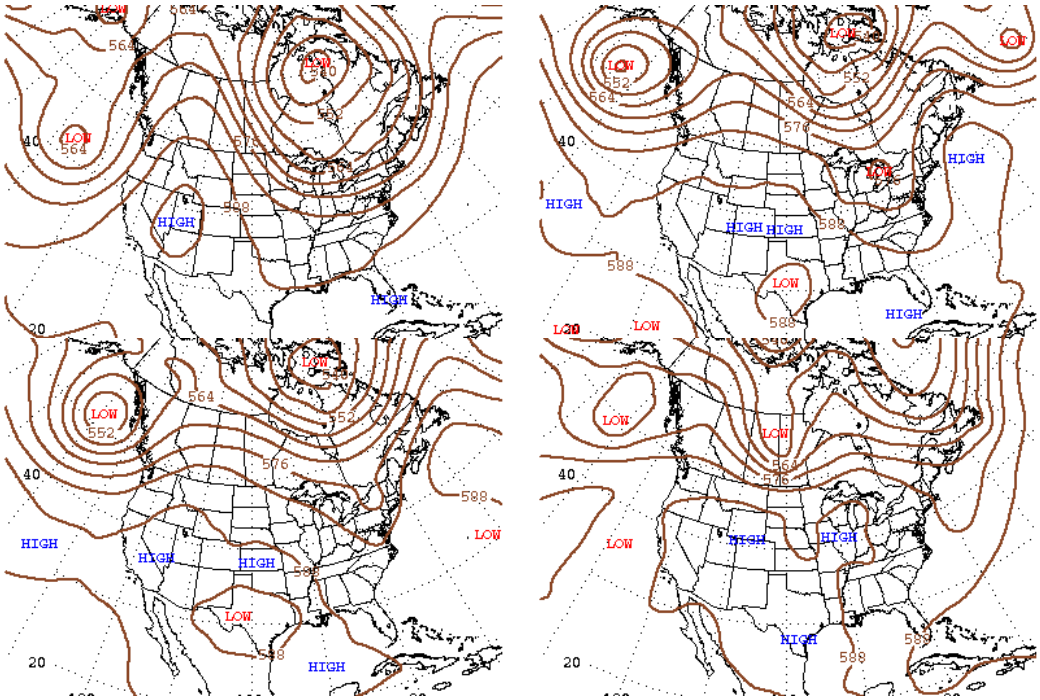


Figure 7-34 Synoptic maps for July 14 and July 27, 2007 (top panels) and July 28 and August 1, 2007 (Bottom panels)

In all the high ozone episodes, there is a strong upper level ridge over the study area and a well defined low off the coast of British Columbia with either southwest or westerly flow aloft over the Treasure Valley. Comparing these synoptic maps and looking for patterns, the August 14-15 measurement days fit this description well but the August 9-10 days do not fit as well.

Figure 7-35 shows the HYSPLIT backtrajectories during the balloon measurement days (left map) compared to those during the highest ozone days (right map) at 3000 meter AGL. The 3000 meter height was chosen to lessen the impacts from surface roughness and enhance the steering flow above the terrain. The high ozone day map includes the episodes from 7/14, 7/27, 7/28 and 8/1. From this figure, the air masses are predominantly from the southwest and are fairly slow moving with the exception of a few during the balloon measurements. However, during the highest ozone days of the summer, trajectories were much more chaotic and showed

recognizable signs of stagnant air masses, particularly during the July 27th episode. This is to be expected since this these types of patterns are characterized by long residence times in one area and when combined with smoke, they can lead to high ground level pollutants.

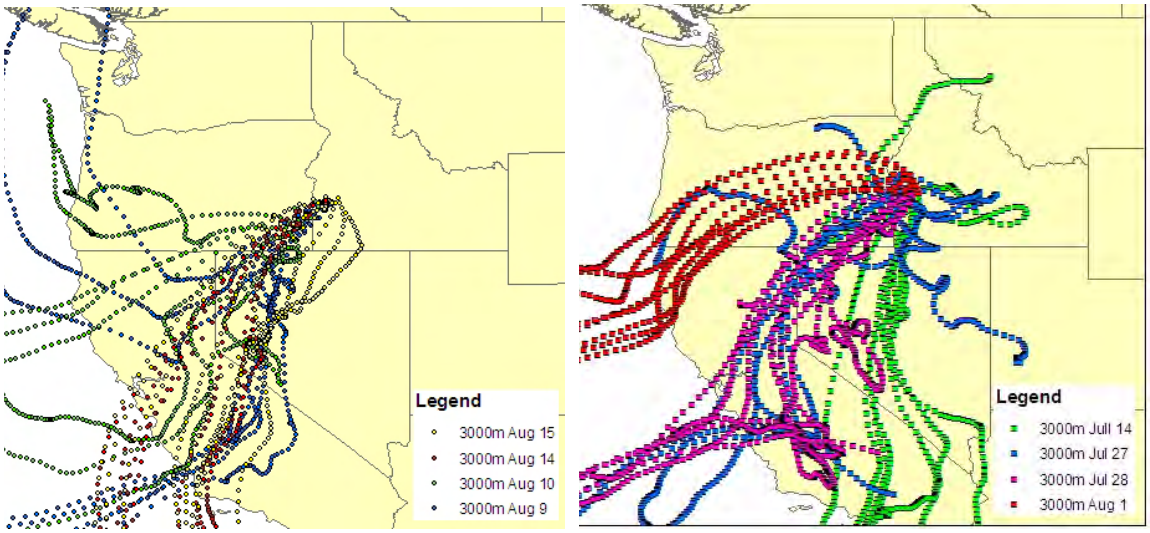


Figure 7-35 Air mass backward trajectories during the tethered-balloon measurements period (left panel) and on July 27-49 high ozone event (A3)

Even with these differences, the balloon measurements will remain a useful database for evaluating photochemical model predictions very near to the surface.