Dear Editor Zhang:

Please find below our itemized responses to the reviewer's comments and a mark-up manuscript. We have addressed all the comments raised by both reviewers, and incorporated them in the revised manuscript.

Thank you very much for your consideration.

Sincerely,
Xiao Lu, Lin Zhang, et al.

Reviewer 1

Overview: The paper presents a new approach to examining the influence of wildfire smoke on ozone mixing ratios at remote/rural monitoring sites in the U.S. intermountain west. Overall the paper is well written and suitable for publication in ACP. I recommend that the authors consider the following ideas in revising the manuscript.

Response:
We thank the reviewer for the valuable comments. All of them have been implemented in the revised manuscript. Please see our itemized responses below.

1) Line 285: The sentence staring with "These underestimates" requires substantially more justification/analysis/references.

Response: We move the original Figure S4 that shows these model underestimates to the main text (Figure 3), and now state:
"These underestimates, however, are not likely due to model underestimates of wildfire ozone influences. We show in Figure 3 the relationships of TFI values with measured MDA8 ozone, MLR wildfire ozone enhancements, and MLR residuals to assess the model performance for the subset of high ozone days (MDA8 > 70 ppbv). The MLR model residuals for those high ozone days have little correlation with TFI, and most of the model underestimates occur when there are small fire impacts or fires not captured by the FLEXPART retroplumes. We suggest that these underestimates may be associated with other factors not included in the statistical model such as transport from Asia or California, from lightning emissions or stratosphere. These processes could episodically produce more than 10 ppbv ozone in summer over the US Intermountain West (Zhang et al., 2014)."

2) Line 315: There are many reasons that a model like GEOS-Chem will not adequately represent the role of fires. The standard versions of GEOS-Chem do not emit short lived VOCs, and the emission factors for NOx emissions from fires are quite variable in reality. The model also adds all the emissions within the boundary layer. The authors clearly recognize this because they use a 5km cut off for the FLEXPART analysis, and are certainly aware of recent work by Val Martin et al. (e.g. 2010) with respect to plume heights over North America. This should be discussed in depth or omitted. A reference to Zhang et al., (2014) is inadequate.

Response: We agree and add more text discussing why GEOS-Chem may not adequately represent wildfire chemistry.
We now state: "We can see that GEOS-Chem simulates up to 40 ppbv wildfire ozone enhancements for the short-distance sites, much higher than the MLR estimates (mean value of 3.96 ppbv versus 1.85 ppbv). A sensitivity simulation with a reduced wildfire NOx emission factor (from 3.0 g to 1.0 g NO per kg of dry mass burned) would decrease the GEOS-Chem mean ozone enhancement for the short-distance sites from 3.96 ppbv to 2.06 ppbv. On the other hand, for the long-distance sites, the GEOS-Chem wildfire ozone enhancements become substantially lower than MLR (0.77 ppbv versus 1.02 ppbv). We see GEOS-Chem largely overestimates wildfire ozone influences near the source regions but fails to capture continued ozone production in wildfire plumes downwind, as also pointed out by Zhang et al. (2014). It reflects the difficulties for Eulerian models such as GEOS-Chem to simulate wildfire ozone production due to, e.g., missing short-lived VOCs (Jaffe and Wigder, 2012), inadequate PAN chemistry (Alvarado et al., 2010; Fischer et al., 2014), and limiting all fire emissions in the boundary layer without considering their injection heights up to the troposphere (Val Martin et al., 2010; Sofiev et al., 2013)."

3) Why does this paper narrowly focus on the intermountain west? This region has many wildfires, but the smoke travels and the impact on ozone may be larger downwind (see Brey and Fischer, 2016). S. Brey and E.V. Fischer (2016), Smoke in the City: How often and where does smoke impact summertime ozone in the United States, Environ. Sci. Tech., DOI:10.1021/acs.est.5b05218.
Response: This study follows our previous work of Zhang et al. (2014), which focused on the Intermountain West where background ozone concentrations are high and the ozone trends are not fully understood as we described in the Introduction. It also demonstrates feasibility of our statistical approach to quantify wildfire ozone influences. We expect future work to apply the approach to other regions in the US or over the world.

We state in the Conclusion: "A recent study by Brey and Fischer (2016) investigated fire impacts on ozone at urban sites over the contiguous US, and found that fire ozone influences can be even higher at locations with high NOx emissions."

4) I have two questions with respect to Figure 7 (and the associated discussion). First, is it appropriate to use the entire range of 1989-2010 to look at the number of exceedance days. There have been trends in ozone during this time. Second, and more importantly, would it be more appropriate to view the exceedance days as a percentage of the total, rather than as a count. Yes, there will be more exceedance days as we lower (tighten) the ozone standard, all things held the same. However, do we have a way to determine if the relative importance of fires will increase?
Response: To answer the two questions: (1) Figure 7 (now Figure 9) has shown the time series of summer ozone exceedance days during 1989-2010. There is no significant trend in the exceedance days with or without wildfire impacts. And (2) we also calculate the percentage of wildfire contributed vs. total exceedance days, but find no increase in the

relative importance of fires as lowering the ozone standard.

We now state in this section "We find no statistically significant trends in the number of exceedances for both the measured ozone concentrations and ozone in the absence of wildfires during the summers 1989-2010", and "In total, wildfires contribute 28%, 31% and 32% of the days with MDA8 ozone exceeds 65, 70, and 75 ppbv, respectively, reflecting small changes in the relative importance of wildfire influences as lowering the air quality standard over this region."

5) Finally, I think all the SI materials should be moved into the main paper. There are very important figures in the SI materials, and I had to refer to them to follow the paper. Without them in the main manuscript, it would be easy to overlook the fact that the MLR really does not do a good job reproducing the highest ozone days. This is an important point in considering the value of this analysis.

Response: We now move the original Figure S3, Figure S4 (now Figure 2 and 3), and Table S1 (now Table 1) to the main text. Figure S3 and S4 explains that the MLR model underestimates of high ozone values are not associated with fire impacts. Tables S1, as also suggested by the Reviewer 2, shall be included in the main text. We think the rest can be kept as SI materials for limiting the length of the paper.

Reviewer 2:

This paper uses back trajectories from the Lagrangian particle dispersion model FLEXPART and estimated fire emissions for the years 1989-2010 to define a Fire Index for 13 CASTNet sites in the Intermountain West. This fire index and various meteorological parameters are used as predictors in a multi-linear regression (MLR) model that predicts daily MDA8 O3 at these sites. The estimated impact of the fire index terms in the model is then used to determine the influence of wildfires on the MDA8 O3, and this estimate is compared to estimated of the Eulerian chemical transport model GEOS-Chem. The authors find that wildfires enhance the summer mean MDA8 O3 by 0.3-1.5 ppbv, with episodic daily increases of 10-20 ppbv at individual sites. They find that GEOS-Chem tends to over-predict the near source formation of O3 and under-predict the downwind formation, consistent with previous Eulerian model studies. Finally, they find that the influence of wildfires is especially important on high O3 days, where 31% of the days with MDA8 O3 over 70 ppbv would not have occurred in the absence of wildfires.

This is a well-done, innovative study and a well-written manuscript. The development of the fire index and the MLR both help to understand the complex influence of fire emissions on O3 in the intermountain west and to expose errors in Eulerian models of this process. The methodology is generally sound and the results are consistent with our understanding of fire chemistry. While I have a few concerns that I would like to see addressed before publication, as detailed below, in general this is a very nice study that should be published.

Response:
We thank the reviewer for the valuable comments. All of them have been implemented in the revised manuscript. Please see our itemized responses below.

Major Concerns:
I have concerns with two of the conclusions of the paper:
1. The abstract states (P2, L32-33) that wildfires contribute 15% of the measured increasing but statistically insignificant trend in MDA8 O3, and this is also stated in the conclusions section (P26, L461-462). However, as neither trend is statistically significant, I disagree with including the 15% value as a major conclusion of the paper, where it might be erroneously quoted without proper context. Thus I recommend that the abstract and conclusion statements be removed from the paper, but the discussion in Section 4.3 remain, as the trend results are given proper context there.
Response: We agree that considering the complexity of wildfire impacts and uncertainties in the trends, 15% may not be well constrained. We now remove the statements from the abstract and conclusion, while keeping them in the discussion section.

2. P20, L357-360 states that the interannual variability in MDA8 O3 appears to be more controlled by interannual variations of the meteorological parameters, as the meteorological variables can account for "most" of the interannual variability in the MDA8 O3, even without fires. I do not think this conclusion is adequately supported by the presented evidence. The fact that the MLR for the met parameters has roughly the same interannual variability as the measurements could be just a statistical artifact of the MLR procedure, with the interannual variability incorrectly accounted for by the meteorological predictors. The conclusion would be more convincing if evidence were presented of the interannual variability of specific meteorological parameters (Temperature, RH, etc.), and if the highs and lows in the summer means of these raw variables were consistent with the highs and lows in MDA8 O3.
Response: Thanks for pointing it out. To support this conclusion, we now present such a figure in supplement (Figure S4) comparing the interannual variability of relative humidity and temperature with MDA8 ozone.
.
We also state in the text: "This is further supported by the strong interannual correlations between summer mean MDA8 ozone and meteorological parameters such as daytime mean RH and surface temperature at individual sites and for the regional averages (*r* = -0.69 for RH, r = 0.48 for temperature), as shown in Figure S4."

Minor Concerns:
P7, L122: Please add the latitude-longitude or ID number for the SalLake City site you are using.
Response: We now state here "we use hourly ozone measurements from 1990-2010 at the Salt Lake City (SLC, 40.6N, 111.9W, 1300m) urban site (data available at https://www3.epa.gov/airdata/) for comparison with the CASTNet background sites and

the previous work of Jaffe et al. (2013)."

P9, L156: 250,000 is a huge number of particles to track, and is probably overkill. Usually 500 particles per receptor (time step and location) is sufficient. How many time steps are there each day, and how many particles are released in each time step?
Response: The particle number is selected to ensure that model calculated retroplumes are statistically robust. It is in the middle of two previous studies using the FLEXPART model: 40000 in Cooper et al. (2010) and 1 million in Stohl et al. (2012).

To address this comment, we now state in the text: "For each day at a receptor site, FLEXPART was run in backward mode, with 250,000 particles released at the site location at a constant hourly rate (~10k particles per hour) during the first 24 hours. Previous studies have used the particle sizes of 40000 (Cooper et al., 2010) and 1 million (Stohl et al., 2012) represent a retroplume."

Reference:

Cooer et al., Increasing springtime ozone mixing ratios in the free troposphere over western North America, Nature, 463, 344-348, doi: 10.1038/nature08708, 2010.

Stohl et al., Xenon-133 and caesium-137 releases into the atmosphere from the Fukushima Dai-ichi nuclear power plant: determination of the source term, atmospheric dispersion, and deposition, Atmos. Chem. Phys., 12, 2313-2343, doi: 10.5194/acp-12-2313-2012, 2012.

P9, L157-158: Is this e-folding time supposed to account for the deposition of smoke along the path? How is this done – is a number on each particle decreased, or do some of the particles actually disappear during the simulation?
Response: The e-folding time of 5 days is the mean lifetime of ozone over the Intermountain West accounting for the loss due to dry deposition and chemistry, and it is applied to the mass of the particles in the FLEXPART model.

We state following the previous comment in this section: "Each particle carries a small account of mass decaying with an e-folding time of 5 days (mean lifetime of ozone in the Intermountain West due to chemical loss and dry deposition as shown in Fiore et al. (2002))."

P10, L169: My understanding is that MISR observations suggest that plumes go above the boundary layer 20-25% of the time, so "often" seems a little vague and misleading.
Response: Thanks for the correction. We now state here: "We use 5 km in the vertical because previous studies have shown that fire emissions are occasionally lifted to above the planetary boundary layer and up to 5 km above the surface (Val Martin et al., 2010; Sofiev et al., 2013)".

P10, L170: It is true that 5 km and 5 days generally gave the best correlation, but the change in the fit wasn't very significant compared to 2 km (PBL height) and 5 days.

Response: We now state: "as shown in Table S1, it provides slightly better correlations with the OC aerosol concentrations than values with 2 km and 2-4 days."

P10, L175: I'd like to see an equation for variable tr(i,j) as well, that shows how the residence time for a single layer is calculated and how the layers are integrated vertically.
Response: We suggest readers refer to previous work of Stohl et al. (2003) and Seibert and Frank (2004) for the detailed calculation of residence time, which is difficult to express in 1-2 equations here.
We state in the text, "tr(i,j)) is FLEXPART calculated daily residence time as described in detail by Stohl et al. (2003) and Seibert and Frank (2004)".

Reference:
Stohl, A., et al.: A backward modeling study of intercontinental pollution transport using aircraft measurements, J. Geophys. Res., 108, doi: 10.1029/2002JD002862 , 2003.
Seibert, P., and Frank, A.: Source-receptor matrix calculation with a Lagrangian particle dispersion model in backward mode, Atmos. Chem. Phys., 4, 51–63, 2004.

P11, L189: Since Table S1 defines the variables, I think it should be moved to the main paper.
Response: We now move this Table to the main text (Table 1).

P11, L198: I understand the choice of MLR limits what you can do to look at nonlinearity, but why did you choose the square root of the index instead of, say, the square of the index?
Response: We now state: "We also include the square root of FI_s and FI_l ($SqrFI_s$ and $SqrFI_l$) as variables in the regression model to at least partly account for the non-linearity of ozone chemistry in wildfire plumes, and to narrow the distribution of FI values that are highly episodic."

P11, L202: You should briefly discuss how the model doesn't include interaction terms between the predictors, and the effect this might have on the model performance.
Response: Collinearity between predictors can affect the model performance without the interactions terms.
We state in this section "We do not include the interaction terms to simplify the MLR models. We acknowledge that including FI and meteorological parameters while neglecting their interaction terms in the MLR models inevitably leads to some degree of collinearity. A measure of it is called tolerance (calculated as percent of variance in the predictor that cannot be accounted for by the other predictors) or variance inflation factors (VIF, the inverse of tolerance), with VIF values greater than 10 suggesting a strong collinearity (Field et al., 2009). Our MLR models for all sites (Section 3) show tolerable VIF values (<5), supporting our approach described above to limit the collinearity."

P14, L236: Do you mean this is just a reanalysis of the Zhang et al. (2014) output, or did you rerun the simulations? You note later that the NOx emissions in this simulation are too high – why didn't you use the lower value here?

Response: We have run the model simulation with the standard GEOS-Chem v8-02-03 as presented in Zhang et al. (2014) and a sensitivity simulation with the reduced NOx emission factor. Both simulations are analyzed in this study, and they do not affect our conclusion.

We now state in the text: "We conduct the GEOS-Chem ozone simulations over North America for three-year (2006-2008) using the wildfire area burned of Yue et al. (2013). Zhang et al. (2014) has suggested that wildfire NOx emission factor in the standard GEOS-Chem simulation can be too high by a factor of 3. We thus also conduct a sensitivity simulation with a reduced wildfire NOx emission factor (from 3.0 g to 1.0 g NO per kg of dry mass burned following Zhang et al. (2014))."

P14, L250: I think you mean "all except for GRC" show weaker correlations, or there is an error in Table S2.
Response: Values in Table S2 (now Table S1) are correct. We now state: "We also test the correlations of OC aerosols with Fire Index calculated using trajectory residence time at lower altitudes or shorter backward time periods, and they in general show slightly weaker correlations (Table S1)."

P15, L267: Can you explain why you get poorer correlations for Salt Lake City than in the Jaffe et al. (2013) study? What does this imply for your other results?
Response: This is largely because the two studies focused on different months and periods (June-Augest 1989-2010 in our study vs. June-September 2000-2012 in Jaffe et al).
We now state in the text: "Here we also applied our MLR models to MDA8 ozone concentrations at SLC in the summers 1990-2010. We find FI and meteorological variables can explain 48% of the daily MDA8 ozone variation for summers 1990-2010 (46% if meteorological variables alone are used, and 57% if September data are also considered that explains the higher correlation reported in Jaffe et al. (2013))".

P15, L270: I think this dependence of the performance on altitude makes sense, but a scatter plot of R2 versus site altitude in the supplement would help to prove it.
Response: We now add such a figure (scatter-plot of R2 vs. site altitude) in the supplement as Figure S3, and state in the text:
"In addition, as shown in Table 2 and Figure S3 the MLR model R^2 values for higher-altitude CASTNet sites (> 2000m such as CNT, MEV, PND) are generally lower than values for lower-altitude sites (such as GLR, CHA and BBE)."

P15-16, L287-L290: Since you include the fire index as a predictor, the fact that the residuals don't correlate with TFI just shows that the MLR procedure is working as expected, right? The second clause of this sentence, that underestimates occur even in the absence of fires, seems like more convincing evidence to me.
Response: The MLR models are applied to individual daily FI values (rather than TFI) for the whole dataset, and thus the model performances for a particular subset (MDA8 >

70 ppbv) worth emphasizing.
We now state here: "We show in Figure 3 the relationships of TFI values with measured MDA8 ozone, MLR wildfire ozone enhancements, and MLR residuals to assess the model performance for the subset of high ozone days (MDA8 > 70 ppbv). The MLR model residuals for those high ozone days have little correlation with TFI, and most of the model underestimates occur when there are small fire impacts or fires not captured by the FLEXPART retroplumes."

P21, L367-L371: I didn't understand what you were trying to say here – please elaborate or rephrase?
Response: We elaborate in the text: "As we can see here, the wildfire-driven interannual variability (0.3-1.5 ppbv) is much weaker than what can be explained by meteorological parameters (49.4-53.5 ppbv for the regional averaged MLR no wildfire ozone). We suggest that some of the strong correlation between summer mean MLR total ozone concentrations and wildfire activities reflects their common relationships with meteorological parameters such as RH and temperature at the interannual scale, e.g., hot and dry summers would have higher ozone concentrations due to stronger photochemistry as well as more wildfire emissions than cold and wet summers (Figure S4)."

P21, L377: Can you please explain why you chose these percentile ranges?
Response: We now state in the text: "The three percentile ranges are used to quantify trends in the low, median, and high windows of summer MDA8 ozone concentration. They also allow us to properly calculate the corresponding mean wildfire ozone contributions to total ozone by using percentile ranges rather than a single percentile. We find similar results when using other percentile ranges (49-51th or 47-53th)."

P24, L420-422: I'd suggest cutting this sentence, as the context of the study is already established in the introduction and this statement is incomplete – Eulerian model errors are not just about resolution, but about errors in amount, location, and timing of biomass burned, error in emission speciation, errors in chemistry, numerical diffusion errors, etc.
Response: We now remove the sentence as suggested.

P25, L435: Make clear how this average R2 is calculated.
Response: We now state here: "We show that the MLR models explain 60% (estimated for the ensemble of 13 CASTNet sites) of the variability of MDA8 ozone over the US Intermountain West (16%-59% at individual sites), which is comparable with results from current Eulerian CTMs (R^2 = 0.25-0.48 as reported in recent studies)."

Typos and Wording Suggestions:
P7, L112-L113: I'd suggest making this a single list:"ozone, organic carbon (OC) aerosols, meteorological parameters, and wildfire area burned data"
Response: Changed as suggested.

P7, L115: Expand CASTNet acronym and provide a little more descriptions than just the website.
Response: "CASTNet" is fully expanded when first mentioned in Section 1. We add here: "are accessed from CASTNet, a long-term monitoring network established to assess the trends in air pollution and acid deposition due to emission regulations (http://www.epa.gov/castnet)".

P11, L189: Period should go after the parentheses, not before.
Response: Changed as suggested.

P14, L244: Figure S2, not S3.
Response: Changed as suggested.

P14, L247: Need a comma after "strong"
Response: Changed as suggested.

P16, L280: "as would be expected" delete "it"
Response: Changed as suggested.

P21, L364: Say "summer mean" to be as clear as possible.
Response: Changed as suggested.

P22, L389: Don't need comma after "Strode et al."
Response: Changed as suggested.

P23, L411-412: I suggest putting parentheses around the phrase "accounting for 22% of the summer days"
Response: Changed as suggested.

P25, L437-438: I suggest cutting everything after the R2 value - these references are already discussed in the main text and do not need to be repeated here.
Response: Changed as suggested.

P25, L442-443: I don't see much consistency at all between the MLR and GEOS-Chem predictions, so you need to make clearer what consistencies you see.
Response: We now state here: "We compare wildfire ozone enhancements estimated by the MLR models with those from the GEOS-Chem CTM for summer 2007. While some consistency is found as reflected by their moderate correlations (r=0.34-0.48, statistically significant $p < 0.05$), the two methods show rather different patterns."

P27, L474: "model in" instead of "model to"
Response: Changed as suggested.

P33, L677: Add unit '(m)' of terrain elevations to caption, as it is not on the figure color bar.

Response: Changed as suggested.

P34, L689: “those from the GEOS-Chem” instead of “those by the GEOS-Chem”
Response: Changed as suggested.

P38, Figure 6: The wildfire trend values are very hard to see – maybe plot on a secondary y axis? In addition, since the trends are generally not statistically significant perhaps this could be moved to the supplement?
Response: We now re-plot the figure with a secondary y-axis representing the wildfire contribution values. We agree that the trends are generally not significant, and have removed relevant statements from the Abstract and Conclusion, also based on another comment above. We think this analysis is valuable to keep in the discussion.

P38, L734: remove “S” from “SMLR” for consistency with the rest of the paper.
Response: Changed as suggested.

P40, L741: Need a space between “relative humidity” and “(RH)”
Response: Changed as suggested.

Figure S1, Caption, L3 and 7: “residence time” not “resident time”
Response: Changed as suggested.

Table S1, Footnotes, L37: Should say “m (PBLH, HGT)”, delete the rest.
Response: Changed as suggested.

Table S1, Footnotes, L38: change to “mean represents the average”
Response: Changed as suggested.

Table S3, Footnote c: Put the explanation for the bold text in the figure caption, not the footnote.
Response: Changed as suggested.

Wildfire influences on the variability and trend of summer surface ozone in the mountainous western United States

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Abstract. Increasing wildfire activities in the mountainous western US may present a challenge for the region to attain a recently revised ozone air quality standard in summer. Using current Eulerian chemical transport models to examine the wildfire ozone influences is difficult due to uncertainties in fire emissions, inadequate model chemistry and resolution. Here we quantify the wildfire influence on the ozone variability, trends, and number of high MDA8 (daily maximum 8-h average) ozone days over this region in summers (June, July and August) 1989-2010 using a new approach. We define a Fire Index using retroplumes (plumes of back-trajectory particles) computed by a Lagrangian dispersion model (FLEXPART), and develop statistical models based on the Fire Index and meteorological parameters to interpret MDA8 ozone concentrations measured at 13 Intermountain West surface sites. We show that the statistical models are able to capture the ozone enhancements by wildfires and give results with some features different from the GEOS-Chem Eulerian chemical transport model. Wildfires enhance the Intermountain West regional summer mean MDA8 ozone by 0.3-1.5 ppbv (daily episodic enhancements reach 10-20 ppbv at individual sites) with large interannual variability, which are strongly correlated with the total MDA8 ozone. ~~Wildfires also contribute 15% of the measured increasing but statistically insignificant trends of 0.14-0.19 ppbv year^{-1} in 1989-2010.~~ We find large fire impacts on the number of exceedance days; for the 13 CASTNet sites, 31% of the summer days with MDA8 ozone exceeding 70 ppbv would not occur in the absence of wildfires.

1 Introduction

Ozone is a secondary air pollutant that exerts negative effects on human health and vegetation, and is also a short-lived greenhouse gas with a positive radiative forcing of 0.40 (0.20 to 0.60) W m^{-2} (Shindell et al., 2013; Stevenson et al., 2013; Stocker et al., 2013; Cooper et al., 2014; Monks et al., 2015). Tropospheric ozone is generated through sunlight driven chemical oxidation of CO, CH_4, and other non-methane volatile organic compounds (NMVOCs) in the presence of nitrogen oxides (NO_x=NO+NO_2). It can also be transported from the stratosphere. In October 2015, the US Environmental Protection Agency (EPA) lowered the National Ambient Air Quality Standard (NAAQS) for ozone, defined as the annual fourth-highest daily maximum 8-h average (MDA8) concentration averaged over three years, from 75 ppbv to 70 ppbv (US EPA, 2015). Attaining this lower ozone air quality standard places new challenges for the US states (Cooper et al., 2015).

Ozone over the mountainous western US (US Intermountain West), extending between the Sierra Nevada/Cascades to the west and the Rocky Mountains in the east, has recently drawn an increasing attention (Cooper et al., 2015; Lin et al., 2015a). Unlike in the eastern US, where NO_x emission controls have led to ozone declines, surface ozone concentrations in the Intermountain West have been increasing in the 1990-2010 period most likely caused by rising background ozone (Jaffe et al., 2007;

Cooper et al., 2012; Lin et al., 2015a), although recent research suggests that these trends flatten out or even reverse in the later decade (2000-2010) (Cooper et al., 2014; Simon et al., 2015; Strode et al., 2015). The North American background ozone, defined by the US EPA as the surface ozone concentration that would be present over the US in the absence of anthropogenic emissions from North America (US EPA, 2006), is particularly high in the Intermountain West due to high elevation, arid landscape, and frequent large-scale air subsidence (Fiore et al., 2002; McDonald-Buller et al., 2011; Zhang et al., 2011; Emery et al., 2012; Dolwick et al, 2015). The background ozone includes ozone contributed by anthropogenic emissions outside North America, e.g., over Asia and Europe (Zhang et al., 2009; Cooper et al., 2010; Lin et al., 2012a), as well as natural sources such as lightning (Mueller et al., 2011; Zhang et al., 2014), wildfires (Jaffe et al., 2008, 2013; Mueller et al., 2011; Zhang et al., 2014), and stratospheric influxes (Lin et al., 2012b, 2015b; Zhang et al., 2014). A number of studies have shown that model simulations considering rising Asian emissions and global methane can only explain part of the observed increasing ozone trends in the western US (Fiore et al., 2009; Koumoutsaris et al., 2012; Parrish et al., 2014).

Wildfires are potentially important sources of background ozone, as they emit large amounts of NO_x, CO, and NMVOCs particularly in summer under hot and dry weather conditions conducive to ozone formation. There is evidence that the frequency and intensity of wildfires in the western US have been

increasing from 1970s to 2005 driven by increasing temperatures and earlier snowmelt (Westerling et al., 2006). The number of high-ozone days is shown to have a strong interannual correlation with wildfire burned area over this region (Jaffe et al., 2008; Jaffe and Wigder 2012). However, quantifying ozone production in wildfire plumes is complicated by various uncertainties including those in wildfire emissions, chemical reactions, and variations in meteorology such as changes in temperature (Jaffe and Wigder ~~et al.,~~ 2012). Fire emissions of ozone precursors vary significantly among different ecosystem types, biomass nitrogen loads, and combustion efficiency (Andreae et al., 2001; Akagi et al., 2011). Ozone chemistry in fire plumes shows strong non-linearity with observations of ozone over CO enhancements ($\Delta O_3/\Delta CO$) in fire plumes ranging from -0.1 to 0.9 ppbv $ppbv^{-1}$ depending on plume ages, aerosol effects, and mixing with urban emissions (Real et al., 2007; Jaffe and Wigder ~~et al.,~~ 2012; Singh et al., 2012; Parrington et al., 2013; Baylon et al., 2014). Previous studies also suggested that rapid conversion of NO_x to peroxyacetyl nitrate (PAN) would limit ozone production near the fires (especially at low temperatures), but decomposition of PAN could lead to additional ozone production further downwind of the fires (Alvarado et al., 2010; Jaffe et al., ~~2012,~~ 2013).

A standard approach to quantify the influence of a particular source on ozone concentrations is provided by chemical transport models (CTMs) using the differences between model simulations with and without this source. This Eulerian approach has been applied in numerous studies to examine ozone

from different sources based on global and regional CTMs (Pfister et al., 2007; Alvarado et al., 2010; Grell et al., 2011; Jiang et al., 2012; Zhang et al., 2014). However, application of this approach to assess wildfire ozone influences in the US Intermountain West is particularly challenging due to uncertainties in wildfire emissions and model chemistry as well as limited model resolution (Zhang et al., 2014). Our current understanding of wildfire influences on the variability and long-term trends of surface ozone is rather limited (Jaffe and Wigder~~et al.,~~ 2012; Fiore et al., 2014).

In this study, we propose a new approach to estimate the influence of wildfires on surface ozone concentrations in the US Intermountain West. We define a Fire Index using the retroplumes (plumes of back-trajectory particles) calculated by a Lagrangian particle dispersion model (FLEXPART) combined with a daily high-resolution wildfire area burned dataset. We then develop multiple linear regression (MLR) models to estimate surface ozone concentration as a function of the Fire Index and other meteorological parameters, which allow us to separate the influences of wildfires and meteorology. We apply this approach to interpret surface ozone concentrations measured at CASTNet (the Clean Air Status and Trends Network) sites in the US Intermountain West during the summers (June, July and August) 1989-2010, and to quantify wildfire influences on the ozone interannual variability, trends, and exceedance days (MDA8 ozone>70 ppbv) over this region. The Lagrangian-based wildfire ozone influences are also compared with those estimated by a Eulerian model (GEOS-Chem) to evaluate the

consistency and difference between the two.

2 Materials and Methods

2.1 Data description

We use measurements of ozone, ~~and~~ organic carbon (OC) aerosols, meteorological parameters, and~~as well as~~ wildfire area burned data at daily temporal resolution. Hourly measurements of ozone as well as meteorological parameters including surface temperature, wind speed, relative humidity (RH), and solar radiation are accessed from CASTNet, a long-term monitoring network established to assess the trends in air pollution and acid deposition due to emission regulations (http://www.epa.gov/castnet). We focus on measurements at 13 CASTNet sites in the US Intermountain West for 1989-2010 (Figure 1 and Table 2). Most CASTNet sites have ozone measurements for the 22-year period except for Mesa Verde National Park (NP) (MEV), Great Basin NP (GRB), Canyonlands NP (CAN), and Big Bend NP (BBE) (since 1995), and Petrified Forest (PET) (since 2003). The Yellowstone NP (YEL) site experienced monitor relocation in 1996, and we access the 1989-1995 measurements at the earlier YEL site from the National Park Service (NPS) following Jaffe et al. (2007) and Cooper et al. (2012).

In addition, we use hourly ozone measurements from 1990-2010 at the Salt Lake City (SLC, 40.6N, 111.9W, 1300m) urban site (data available at https://www3.epa.gov/airdata/) for comparison with the

CASTNet background sites and the previous work of Jaffe et al. (2013). Measurements of OC aerosol are from collocated sites of the Interagency Monitoring of Protected Visual Environments (IMPROVE, http://vista.cira.colostate.edu/improve/). OC aerosol concentrations are 24-hour averages measured every 3 days.

We also use the daily wildfire area burned data over North America for 1989-2010 developed by Yue et al. (2013) that has a 0.5°×0.5° horizontal resolution. This inventory is constructed using the inter-agency fire reports from the national Fire and Aviation Management Web application system (FAMWEB, https://fam.nwcg.gov/fam-web/), and applied with a daily scaling factor for the duration of each fire event based on local meteorological variables (Yue et al., 2013). The total areas burned in the Intermountain West range from 90,000 to 2,000,000 hectares (ha) in the summers 1989-2010 with a large spatial and interannual variability. This wildfire area burned inventory has been used in Zhang et al. (2014) and was able to capture the episodic enhancements of OC aerosol concentrations measured in the Intermountain West for the summers 2006-2008.

2.2 Fire Index calculation with the FLEXPART model

Jaffe et al. (2008) previously identified the impacts of wildfires on ozone at a measurement site using values of monthly wildfire area burned or carbon burned within a certain region around the site (e.g.,

10°×10° or 5°×5°). This fire indicator generally ignores the variable influence of transport of fire plumes to the site. For instance, a fire downwind of the measurement site, even one burning in the immediate vicinity, would not influence the site. Here we propose a new fire indicator using 5-day retroplumes simulated by the FLEXPART Lagrangian particle dispersion model and the daily wildfire area burned inventory mentioned above. A retroplume consists of a large number of back trajectory particles that are released from a particular receptor location (Cooper et al., 2005). We use FLEXPART version 8.02, which is first described by Stohl et al. (2005) and has been applied to examine transport of ozone (Cooper et al., 2010) and radionuclides across the Pacific Ocean (Stohl et al., 2012). FLEXPART simulates the long-range and mesoscale transport, diffusion, dry and wet deposition of gases or particles (Stohl et al., 2005). It is driven by the National Center for Environmental Prediction (NCEP) Climate Forecast System Reanalysis (CFSR) data with 1-hour temporal resolution, 0.5°×0.5° horizontal resolution, and 37 vertical levels extending from the surface to 1 hPa.

For each day at a receptor site, FLEXPART was run in backward mode, with 250,000 particles released at the site location at a constant hourly rate (~10k particles per hour) during the first 24 hours. Previous studies have used the particle sizes of 40000 (Cooper et al., 2010) and 1 million (Stohl et al., 2012) represent a retroplume. ~~The particles are set to have~~Each particle carries a small amount of mass decaying with an e-folding time of 5 days (mean lifetime of ozone in the Intermountain West due to

chemical loss and dry deposition as shown in Fiore et al. (2002)., ~~and~~ Tt~~t~~rajectories of these particles are calculated backwards for 5 days (120 hours), together tracing the retroplume of the air arriving at the site. The model outputs are in the same 0.5°×0.5° horizontal resolution as the wildfire area burned data, and are hourly residence times of the particles in each grid cell. The residence time provides a quantitative measure of the sensitivity of the simulated mixing ratio at the site location to emission input (Stohl et al., 2003; Seibert and Frank, 2004; Cooper et al., 2010). In total, we have computed over 28000 FLEXPART retroplumes for the 13 Intermountain West CASTNet sites and SLC site for the summers 1989-2010.

We then define a Fire Index (FI) as the product of daily FLEXPART residence time integrated from the surface to 5 km and daily wildfire area burned, in unit of s•ha. We use 5 km in the vertical because previous studies have shown that fire emissions are occasionally~~often~~ lifted to above the planetary boundary layer up to 5 km above the surface (Val Martin et al., 2010; Sofiev et al., 2013), and~~,~~ as shown in Table S1~~2~~, it provides slightly better ~~best~~ correlations with the OC aerosol concentrations than values with 2 km and 2-4 days. The sum of Fire Index over the 5-day period is defined as Total Fire Index (TFI). The formulas are given as:

$$\mathrm{FI}\,(n) = \sum_i \sum_j \mathrm{E}_{\mathrm{fire}(i,j,n)} \times \mathrm{t}_{r(i,j,n)} \quad (1)$$

$$\mathrm{TFI} = \sum_{n=1}^{5} \mathrm{FI}(n) \quad (2)$$

Here $E_{fire(i,j,n)}$ is the wildfire area burned in the model grid cell *i* (longitude) and *j* (latitude) on day *n*, $t_{r(i,j)}$ is FLEXPART calculated daily residence time as described in detail by Stohl et al. (2003) and Seibert and Frank (2004), and *n* defines the backward day in the 5-day period. Figure S1 shows an example of Fire Index for the site CAN on July 14, 2006. In this case, the particles are released on July 14 (day *n*=1) in the FLEXPART model, and daily residence time is calculated backwards for 5 days (July 10-14). FI(5) then represents the product of residence time on July 10 and wildfire areas burned on that day. TFI as the sum of FI(1)-FI(5) estimates the total impact of wildfires during the 5 days for that site and day.

2.3 Multiple linear regression model

We build multiple linear regression (MLR) models of summer ozone concentrations for the 13 CASTNet sites and SLC site using Fire Index and meteorological parameters as predictors. This method has been previously used to identify the meteorological factors determining concentrations of particulate matter or ozone (Camalier et al, 2007; Tai et al., 2010, 2012; Jaffe et al., 2013). Here we use the metric of daily maximum 8-hour average (MDA8) ozone concentration, as it is the regulatory form of the NAAQS. A total of 28 meteorological parameters are considered in the MLR models including those measured at surface and from NCEP data (Table 1 and Table 2~~S1~~). Some of these meteorological variables, such as surface temperature, relative humidity, and upper level winds, have been shown

before to be correlated with surface ozone in the western US (Jacob et al., 2009; Rasmussen et al., 2012; Jaffe et al., 2013).

Wildfire ozone enhancements are sensitive to plume ages. As summarized in Jaffe et al. (2012), $\Delta O_3/\Delta CO$ values in wildfire plumes show distinct differences for plume ages of 1-2 days (average 0.018 ppbv/ppbv) versus 3-5 days (average 0.15 ppbv/ppbv). Thus instead of using TFI, we separate it to FI_s (FI(1)+FI(2)) and FI_l (FI(3)+FI(4)+FI(5)) in the MLR models. We also include the square root of FI_s and FI_l ($SqrFI_s$ and $SqrFI_l$) as variables in the regression model to at least partly account for the non-linearity of ozone chemistry in wildfire plumes, and to narrow the distribution of FI values that are highly episodic. We do not use the natural logarithm form of FI in MLR, because many of the FI values are zero that would cause invalid values in the regression.

The MLR models can be described as:

$$y = \alpha_1 \times \mathrm{FI}_s + \alpha_2 \times \mathrm{FI}_l + \beta_1 \times \mathrm{SqrFI}_s + \beta_2 \times \mathrm{SqrFI}_l + \sum_{p=1}^{\mathrm{m}} \gamma_p \times \mathrm{met}_p + c \quad (3)$$

Here y is MDA8 ozone concentration, α, β, γ are the regression coefficients, met denotes the m meteorological parameters included, and c is the constant term. We then estimate ozone enhancements from wildfires and we refer it as MLR wildfire ozone, following:

$$y_{\mathrm{fire}} = \alpha_1 \times \mathrm{FI}_s + \alpha_2 \times \mathrm{FI}_l + \beta_1 \times \mathrm{SqrFI}_s + \beta_2 \times \mathrm{SqrFI}_l \quad (4)$$

The remaining components define the contribution from other variables such as meteorology and other sources:

$$y_{\text{nofire}} = \sum_{p=1}^{m} \gamma_p \times \text{met}_p + c \quad (5)$$

To further account for the nonlinear ozone response to wildfire emissions, we divide the ozone records for each site into three subsets based on their TFI values: subset with TFI=0; subsets with the lower 50% and upper 50% TFI values (with TFI=0 excluded). In this way we are able to quantify potentially different ozone drivers under high vs. low wildfire conditions. The MLR models as described above are applied to each subset.

Prior to performing the regression, we calculate correlations among ozone and all predictors and remove those factors that show weak correlation with ozone but strong dependence on other predictors. To minimize the collinearity in the MLR model, we also apply the stepwise regression method, i.e., for each step the model selects the most powerful and significant ($p<0.05$) predictor explaining the residual, and removes predictors with insignificant influence ($p > 0.1$) (Field et al., 2009). We do not include the interaction terms to simplify the MLR models. We acknowledge that including FI and meteorological parameters while neglecting their interaction terms in the MLR models inevitably leads to some degree of collinearity. A measure of it is called tolerance (calculated as percent of variance in the predictor that cannot be accounted for by the other predictors) or variance inflation factors (VIF, the inverse of

tolerance), with VIF values greater than 10 suggesting a strong collinearity (Field et al., 2009). Our MLR models for all sites (Section 3) show tolerable VIF values (<5), supporting our approach described above to limit the collinearity.

2.4 The GEOS-Chem model simulations

We further conduct GEOS-Chem model simulations to estimate wildfire ozone enhancements, and to compare with those from the Lagrangian and statistical approach as described above. The GEOS-Chem chemical transport model is driven by the GEOS-5 assimilated meteorological fields from the NASA Global Modeling and Assimilation Office (GMAO) (http://www.geos-chem.org; v8-02-03) (Bey et al., 2001). We use a nested version of GEOS-Chem that has 1/2°×2/3° horizontal resolution over North America and adjacent oceans (140°W-40°W, 10°N-70°N) and 2°×2.5° over the rest of the world. We conduct the GEOS-Chem ozone simulations over North America for three-year (2006-2008) using the wildfire area burned of Yue et al. (2013). Zhang et al. (2014) has suggested that wildfire NOx emission factor in the standard GEOS-Chem simulation can be too high by a factor of 3. We thus also conduct a sensitivity simulation with a reduced wildfire NO_x emission factor (from 3.0 g to 1.0 g NO per kg of dry mass burned following Zhang et al. (2014)). ~~We reproduce the simulations in Zhang et al. (2014) that also used the wildfire area burned of Yue et al. (2013) for three-year (2006-2008) ozone simulations over North America.~~ Wildfire ozone enhancements are computed as differences between the simulation

with all emissions turned on and a sensitivity simulation with only wildfire emissions turned off.

3. Model evaluation

We first evaluate our Lagrangian-based Fire Index using its correlation to OC aerosol concentrations, as previous studies have shown that wildfires are an important source of OC aerosols in the US Intermountain West in summer (Park et al., 2007; Spraklen et al., 2007). As shown in Figure S23 and Table S12, the TFI values at each CASTNet site are positively correlated with OC aerosol concentrations measured at collocated IMPROVE sites (r=0.19-0.44). While the TFI vs. OC correlations are not very strong, reflecting both uncertainties in the FLEXPART retroplumes and influence from other OC aerosol sources, the correlations are better ($p < 0.01$) than those with areas burned within 10°×10° regions. We also test the correlations of OC aerosols with Fire Index calculated using trajectory residence time at lower altitudes or shorter backward time periods, and they in general show slightly weaker correlations (Table S12).

Table 21 summarizes the predictors included in the MLR models and their performance for each CASTNet site with more details given in Table S23. The MLR models explain 16%-59% of the variability in MDA8 ozone concentration among these sites. Figure 2 shows the comparison of measured and MLR predicted ozone concentrations for the ensemble of 13 CASTNet sites. The MLR

models generally reproduce the ozone measurements (R^2=0.60~~, Figure S3~~). These coefficients of determination (R^2) are comparable with, or even better than results simulated by Eulerian CTMs (e.g., R^2 = 0.43 in Zhang et al. (2014), R^2 = 0.25 in Emery et al. (2012), R^2 = 0.48 in Strode et al. (2015)) that have limited ability to reproduce the measured ozone variability in the Intermountain West probably due to the coarse model resolution and complex topography. However, they are lower than results from Jaffe et al. (2013) or Camalier et al. (2007) that applied the regression models on ozone concentrations at US urban and low-altitude sites.

Jaffe et al. (2013) analyzed the surface ozone concentrations measured at the SLC urban site in the western US during June-September 2000-2012, and showed that a MLR model using meteorological variables as predictors could explain 60% of the MDA8 ozone variation. Here we also applied our MLR models to MDA8 ozone concentrations at SLC in the summers 1990-2010. We find FI and meteorological variables can explain 48% of the daily MDA8 ozone variation for summers 1990-2010 (46% if meteorological variables alone are used, and 57% if September data are also considered that explains the higher correlation reported in Jaffe et al. (2013)), which is a higher value than at most of the CASTNet sites. In addition, as shown in Table 2~~1~~ and Figure S3 the MLR model R^2 values for higher-altitude CASTNet sites (> 2000m such as CNT, MEV, PND) are generally lower than values for lower-altitude sites (such as GLR, CHA and BBE). It appears that the MLR model performs better for

US urban and low-altitude sites than for the CASTNet high-altitude background sites. This is likely because ozone at the high-altitude CASTNet sites is more affected by regional transport from both anthropogenic and natural sources such as lightning and stratospheric ozone, and less controlled by local meteorology relative to ozone at urban or low-altitude sites.

We find that at the CASTNet sites daytime mean RH is generally the most important predictor. In the low-NO_x background environment, HO_x serves as a strong sink for ozone driving the correlation with water vapor concentrations (hence RH) (Doherty et al. 2013; Pusede et al., 2015). Fire impacts (FI_s and FI_l) are included for different sites, as ~~it~~ would be expected by their different travel times from the frequent burning areas to the receptor sites. SqrFI often shows a higher explanatory power than FI, reflecting nonlinear ozone production from wildfire emissions.

We also acknowledge that the MLR models underestimate high ozone values especially when measured MDA8 ozone exceeds 70 ppbv (Figure ~~2~~S3). These underestimates, however, are not likely due to model underestimates of wildfire ozone influences., ~~and may be associated with other factors not included in the statistical model such as transport from Asia or California or from lightning emissions.~~ We show in Figure 3 the relationships of TFI values with measured MDA8 ozone, MLR wildfire ozone enhancements, and MLR residuals to assess the model performance for the subset of high ozone days

(MDA8 > 70 ppbv). ~~As demonstrated in Figure S4, t~~The MLR model residuals for those high ozone days ~~(MDA8 > 70 ppbv)~~ have little correlation with TFI, and most of the model underestimates occur when there are small fire impacts or fires not captured by the FLEXPART retroplumes. We suggest these underestimates may be associated with other factors not included in the statistical model such as transport from Asia or California, from lightning emissions or stratosphere. These processes could episodically produce more than 10 ppbv ozone in summer over the US Intermountain West (Zhang et al., 2014).

4 Results

4.1 Consistency and difference with the Eulerian model

It is of particular value to evaluate the MLR wildfire ozone enhancements with those from the Eulerian approach. We show in Figure ~~4~~2 such a comparison with the wildfire ozone enhancements estimated by the GEOS-Chem model in the summer 2007 when there are large wildfire emissions in Idaho. We can see that the GEOS-Chem model simulates a sharp gradient of wildfire influences with ozone enhancements greater than 20 ppbv over the Idaho and Montana burning areas, which decrease rapidly downwind to 0.5-3 ppbv.

To evaluate the MLR wildfire ozone enhancements, we separate the 13 CASTNet sites into three groups

based on their distances to the major burning area in Idaho. As shown in Figure 4~~2~~, the MLR and GEOS-Chem estimated wildfire ozone enhancements for all three groups are moderately correlated (r=0.34-0.48, statistically significant $p < 0.05$), reflecting some consistency between the two approaches. There are also considerable differences. We can see that GEOS-Chem simulates up to 40 ppbv wildfire ozone enhancements for the short-distance sites, much higher than the MLR estimates (mean value of 3.96 ppbv versus 1.85 ppbv). ~~Zhang et al. (2014) has shown that wildfire NO_x emission factor in this GEOS-Chem simulation is too high by a factor of 3.~~ A sensitivity simulation with a reduced wildfire NO_x emission factor (from 3.0 g to 1.0 g NO per kg of dry mass burned) would decrease the GEOS-Chem mean ozone enhancement for the short-distance sites from 3.96 ppbv to 2.06 ppbv. On the other hand, for the long-distance sites, the GEOS-Chem wildfire ozone enhancements become substantially lower than MLR (0.77 ppbv versus 1.02 ppbv). ~~As pointed out by Zhang et al. (2014), GEOS-Chem largely overestimates wildfire ozone influences near the source regions but fails to capture continued ozone production in wildfire plumes downwind likely due to the coarse resolution and inadequate PAN chemistry.~~ We see GEOS-Chem largely overestimates wildfire ozone influences near the source regions but fails to capture continued ozone production in wildfire plumes downwind, as also pointed out by Zhang et al. (2014). It reflects the difficulties for Eulerian models such as GEOS-Chem to simulate wildfire ozone production due to, e.g., missing short-lived VOCs (Jaffe and Wigder, 2012), inadequate PAN chemistry (Alvarado et al., 2010; Fischer et al., 2014), and limiting all fire emissions in

the boundary layer without considering their injection heights up to the troposphere (Val Martin et al., 2010; Sofiev et al., 2013). The lower GEOS-Chem wildfire ozone estimates at those long-distance sites may be also attributed to the model difficulty in simulating ozone production from small-scale fires nearby. The MLR approach appears to show a more reasonable pattern.

4.2 Contribution of wildfires to the MDA8 ozone concentration

We use the MLR models to diagnose the influences of wildfires and other meteorological parameters on MDA8 ozone concentrations at the Intermountain West CASTNet sites. Figure 5~~3~~ shows the scatter-plots of observed MDA8 ozone and MLR predicted ozone at four selected sites located in different regions (GLR, ROM, GRB, and CHA). Also shown are the boxplots of MLR wildfire ozone enhancements and MLR no wildfire ozone as defined by Equation (4) and (5), respectively. The MLR models generally reproduce the measurements except for high ozone values as we have discussed above. For all the CASTNet sites, the MLR no wildfire ozone explains most of the measured MDA8 variability (R^2=0.10-0.58) compared to MLR wildfire ozone enhancements (R^2=0.02-0.12). However, wildfire ozone enhancements increase as measured MDA8 ozone concentrations increase, reflecting higher wildfire impacts on the high-ozone events. We can see in a few cases wildfire ozone enhancements reach 10-20 ppbv, causing measured MDA8 ozone to approach the ozone quality standard of 70 ppbv.

Another test to separate wildfire ozone influences from meteorological impacts follows Jaffe et al. (2008) who showed ozone concentrations in high-fire years were distinctly greater than those in low-fire years at the same temperature ranges. Here we extend their approach to other meteorological parameters and to the whole 22-year records. Figure 64 shows the relationships between MDA8 ozone concentrations and meteorological parameters (daytime temperature, wind speed, RH, and solar radiation flux) measured at a Chiricahua National Monument, Arizona (CHA). We compare measured MDA8 ozone concentrations with high versus low wildfire impacts (upper 33% versus lower 33% of the TFI values). Meteorological variations have some impacts on both wildfire activities and MDA8 ozone levels. High wildfire events are prone to occur with high temperature and solar radiation, low RH and wind speed, as indicated by the number of upper 33% versus lower 33% TFI occurrences in each increment of meteorological parameters. Ozone concentrations generally increase with increasing temperature and decreasing RH. We can also see significant differences ($p < 0.05$) in the MDA8 ozone concentrations between the upper and lower TFI values for most of the meteorological increments. For instance, in the 26-28°C temperature bin, the mean MDA8 ozone for the upper 33% TFI is about 8 ppbv higher than that for the lower 33% TFI. This confirms impacts of wildfires on ozone that are independent from meteorological variables.

4.3 Wildfire influences on the ozone interannual variability and trend

Application of the MLR models to the summers 1989-2010 ozone measurements allows us to quantify wildfire influences on the long-term ozone variability and trend. We show in Figure 7~~5~~ time series of summer mean measured and MLR predicted MDA8 ozone concentration for the Intermountain West regional average, as well as for three individual sites (GLR, YEL, and GRC) in the 22 years (1989-2010). The MLR models show good agreements with measurements with correlation coefficients of 0.85 for the regional average and 0.52-0.92 for individual sites, but underestimate the measured interannual variability. Figure 7~~5~~ also shows the summer mean MLR with and without the wildfire ozone, along with the difference between the two. The interannual variability of surface ozone over the region appears to be more controlled by the interannual variations of meteorological parameters, and hence the climate variability, as we can see that even without wildfire influences, the remaining meteorological parameters used in the MLR models still predict most of the interannual variability (MLR no wildfire ozone vs. MLR ozone r = 0.87-0.99 among individual sites). This is further supported by the strong interannual correlations between summer mean MDA8 ozone and meteorological parameters such as daytime mean RH and surface temperature at individual sites and for the regional averages (r = -0.69 for RH, r = 0.48 for temperature), as shown in Figure S4.

Wildfires contribute 0.3-1.5 ppbv to the summer mean surface MDA8 ozone averaged over the Intermountain West CASTNet sites. In the high-fire activity years such as 2003 and 2007, the summer

mean wildfire ozone enhancements can reach 3.5 ppbv at the individual sites, e.g., MEV. The interannual variability of wildfire ozone enhancements is strongly correlated with that of the MLR total ozone (r = 0.89 for the regional averages and 0.48-0.87 for individual sites). As we can see here, the wildfire-driven interannual variability (0.3-1.5 ppbv) is much weaker than what can be explained by meteorological parameters (49.4-53.5 ppbv for the regional averaged MLR no wildfire ozone). We ~~thus~~ suggest that some of the strong correlation between summer mean surface ozone concentrations and wildfire activities reflects their common relationships with meteorological parameters such as RH and temperature at the interannual scale, e.g., hot and dry summers would have higher ozone concentrations due to stronger photochemistry as well as more wildfire emissions than cold and wet summers (Figure S4). However we should acknowledge that ozone production in wildfires varies significantly (Jaffe ~~et al.~~and Wigder~~,~~ 2012), and the statistical models we use here can still underestimate the interannual variations of wildfire influences. Better resolving the causes of variations in wildfire ozone production will help us understand the source for interannual variations in ozone.

We further calculate the linear trends of surface ozone in the summers 1989-2010. Figure 8~~6~~ summarizes the results at three percentile ranges: 93-97th, 48-52th, 3-7th percentiles at the Intermountain West CASTNet sites. The three percentile ranges are used to quantify trends in the low, median, and high windows of summer MDA8 ozone concentration. They also allow us to properly calculate the

corresponding mean wildfire ozone contributions to total ozone by using percentile ranges rather than a single percentile. We find similar results when using other percentile ranges (49-51th or 47-53th). We also show the separated trends for the earlier (1989-1999) and later (2000-2010) periods following Strode et al. (2015) who suggested different trends in surface ozone for the two periods. Regional averaged summer MDA8 ozone concentrations in the Intermountain West show increasing but statistically insignificant trends of 0.14±0.21 (p=0.22), 0.19±0.21 (p=0.08), and 0.18±0.20 (p=0.09) ppbv year^{-1} at the 93-97th, 48-52th, and 3-7th percentiles, respectively, in 1989-2010. Statistically significant ($p<0.05$) increasing trends are found at the YEL (0.42±0.30 ppbv year^{-1}) and ROM (0.43±0.39 ppbv year^{-1}) sites at the median percentiles. These increasing trends primarily occurred in the earlier period (1989-1999), while nearly all sites show decreasing ozone trends during 2000-2010. Strode et al. (2015) attributed the earlier increasing trends to meteorological variations and the later decreasing trends to domestic emission controls. Our results are consistent with previous studies of Cooper et al. (2012) and Strode et al., (2015) who analyzed the ozone trends using the same CASTNet measurements but using the metric of daytime ozone concentration.

Also shown in Figure 8~~6~~ are the corresponding ozone trends contributed by wildfires as estimated by the MLR models. A distinct feature is that the trends of wildfire ozone enhancements are relatively small but generally in the same directions as the observed ozone trends. This feature can also result

from meteorological variations that modulate surface ozone concentrations and wildfires in similar directions. Most of the sites show increasing wildfire ozone in the first 11 years (1989-1999), and switch to decreases in the next 11 years (2000-2010), but only a few of them are statistically significant. Wildfire ozone enhancements averaged over the Intermountain West CASTNet sites increase at rates of 0.02 ± 0.05 ppbv year^{-1} ($p=0.48$), 0.02 ± 0.05 ppbv year^{-1} ($p=0.38$), and 0.03 ± 0.03 ppbv year^{-1} ($p<0.05$) at the 93-97th, 48-52th, and 3-7th percentile ranges, respectively, in the summers 1989-2010. These values account for about 15% of the observed ozone trends at the same CASTNet sites, representing small but important ozone influences from wildfires.

4.4 Wildfire influences on ozone exceedance days

As the ozone air quality standard becomes stricter, it is important to quantify the number of ozone exceedances caused partly by uncontrollable sources, such as wildfires. We show in Figure 9~~7~~ the mean number of days with measured MDA8 ozone concentrations exceeding 75 ppbv, 70ppbv, and 65 ppbv averaged over the 13 Intermountain West CASTNet sites in the summers 1989-2010. Also shown is the corresponding number of exceedances that would be present in the absence of wildfires (estimated as measured ozone minus the MLR wildfire ozone). We find no statistically significant trends in the number of exceedances for both the measured ozone concentrations and ozone in the absence of wildfires during the summers 1989-2010.

In the years with poor air quality conditions such as 2002 and 2003, there were more than 20 days when MDA8 ozone exceeds 65 ppbv (accounting for 22% of the summer days), and about 8 days with MDA8 exceeding 70 ppbv, the current ozone air quality standard. However, if there were no wildfire emissions, the frequency of ozone exceedance days would significantly decrease. For the total exceedance days at the 13 sites in this period, the number with MDA8 above 65 ppbv (above 70 ppbv) would decrease by 28% to 1509 days (by 31% to 474 days). This reduction is particularly important in high fire years such as 2002-2003 and 2005-2007 when one third to half of the exceedances would not occur without the fires. In total, wildfires contribute 28%, 31% and 32% of the days with MDA8 ozone exceeds 65, 70, and 75 ppbv, respectively, reflecting small changes in the relative importance of wildfire influences as lowering the air quality standard over this region.

5 Conclusions

~~Simulating the complexity in wildfires emission and chemistry requires running Eulerian models at very fine resolution (Jiang et al., 2012; Jaffe et al., 2013; Zhang et al., 2014), which presents challenges for assessing long-term wildfire ozone enhancement using those models.~~ In this study, we have applied a new approach based on a Lagrangian particle dispersion model (FLEXPART) and statistical models to quantify the wildfire influences on the ozone daily and interannual variability, trends, and exceedance

days over the US Intermountain West in the summers 1989-2010. The recent implementation of a more stringent ozone standard (70 ppbv) in the United States also motivates the need to better understand contributions and variations of natural ozone sources such as wildfires.

We introduce a Fire Index (FI), a measure of wildfires' impact at a receptor site, by using 5-day FLEXPART retroplumes (plumes of back-trajectory particles) combined with a daily high-resolution wildfire area burned dataset in the Western US. The FI values are computed for each ozone measurement day in the summers 1989-2010 for the ensemble of 13 CASTNet sites and an urban site (SLC) over the US Intermountain West. We then develop statistical MLR models that estimate MDA8 ozone concentrations at each site as a function of FI and various meteorological variables. We show that the MLR models explain 60% (estimated for the ensemble of 13 CASTNet sites) of the variability of MDA8 ozone over the US Intermountain West (16%-59% at individual sites), which is comparable with results from current Eulerian CTMs (R^2 = 0.25-0.48 ~~as reported in recent studies) (Zhang et al., 2011; 2014; Emery et al., 2012; Strode et al., 2015))~~.

The MLR models allow us to diagnose the MDA8 ozone enhancements from wildfires as well as ozone controlled by meteorological variables. We compare wildfire ozone enhancements estimated by the MLR models with those from the GEOS-Chem CTM for summer 2007. While some consistency is

found as reflected by their moderate correlations (r=0.34-0.48, statistically significant $p < 0.05$), the two methods show rather different patterns. The MLR method appears to better capture wildfire ozone influences at larger distances downwind of the fires or ozone produced from small-scale fires. We find that wildfire ozone enhancements estimated by the MLR models occasionally reach 10-20 ppbv at the Intermountain West CASTNet sites, and they tend to increase as measured ozone concentrations increase, reflecting higher wildfire impacts on the high-ozone days. Meteorological variations also show distinct impacts on both wildfire activities and MDA8 ozone concentrations. High wildfire events and high ozone days are often associated with high temperatures and strong solar radiation, and low RH and wind speed.

We find wildfires increase the summer mean MDA8 ozone concentrations by 0.3-1.5 ppbv averaged over the Intermountain West CASTNet sites during 1989-2010. While the interannual variability of summer mean wildfire ozone enhancements is strongly correlated with that of the MLR total ozone, the wildfire-driven interannual variability is much weaker than the ozone variability that can be explained by meteorological parameters. We suggest that the strong interannual correlation between summer mean ozone concentrations and wildfire activities can be partly driven by their common relationships with meteorological parameters such as RH and temperature. These common relationships may also be responsible for the synchronous trends of summer mean surface MDA8 ozone concentrations and

wildfire ozone enhancements for either the 1989-2010 period or two separated 11-year periods (1989-1999 vs. 2000-2010). ~~Wildfires contribute about 15% to the observed ozone trends at the Intermountain West CASTNet sites.~~

Wildfires thus present an important source affecting surface ozone air quality in the US Intermountain West. Despite small enhancements when averaged seasonally or regionally, they have notable impact on the occurrence of ozone exceedances, reflecting the small-scale and episodic nature of wildfire emissions. We show that about one third of the summer days (1989-2010) with MDA8 ozone exceeding 70 ppbv would not occur in the absence of wildfires. A recent study by Brey and Fischer (2016) investigated fire impacts on ozone at urban sites over the contiguous US, and found that fire ozone influences can be even higher at locations with high NO_x emissions. While we have shown that our Lagrangian and statistical approach provides a quantitative estimate of ozone enhancements from wildfires, and can be applied to analyze long-term ozone records, there are still considerable uncertainties in this approach from both the FLEXPART calculation and the MLR models as discussed in the text. The approach also does not consider the complexity in fire emissions and cannot probe into the physical and chemical processes in the fire plumes. To address this issue would require more detailed fire plume measurements and finer-scale modeling approaches, such as imbedding a plume-in-grid model into ~~to~~ CTMs.

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4 Figures and 2~~3~~ Tables are included in the supplement related to this article.

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Figures and Tables

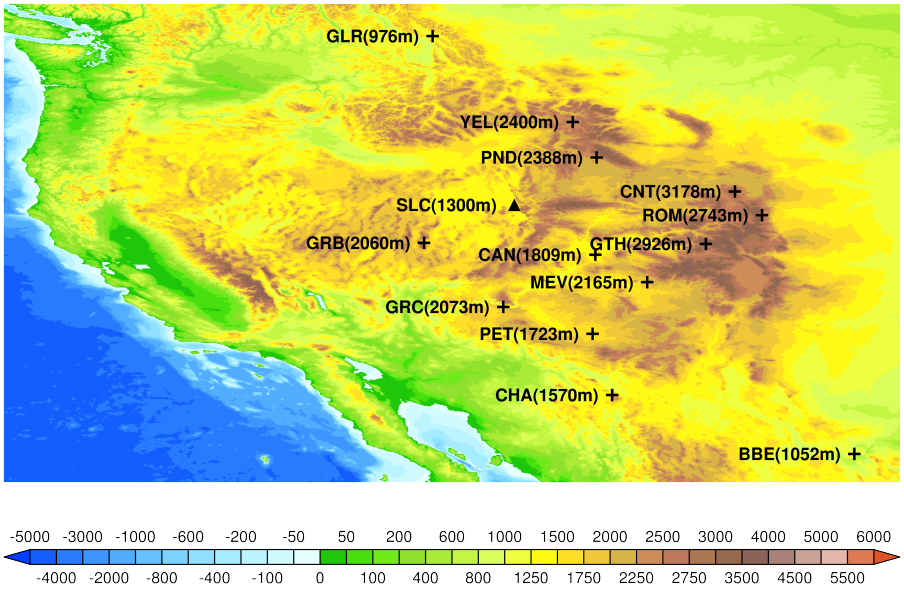

Figure 1. 13 CASTNet ozone monitoring sites (Table 2~~1~~, black pluses) in the US Intermountain West used in this study. Also shown is SLC (Salt Lake City, Utah) urban site (filled triangle). Altitudes of the sites are also labeled. The underlying figure shows terrain elevations (m) of the western US.

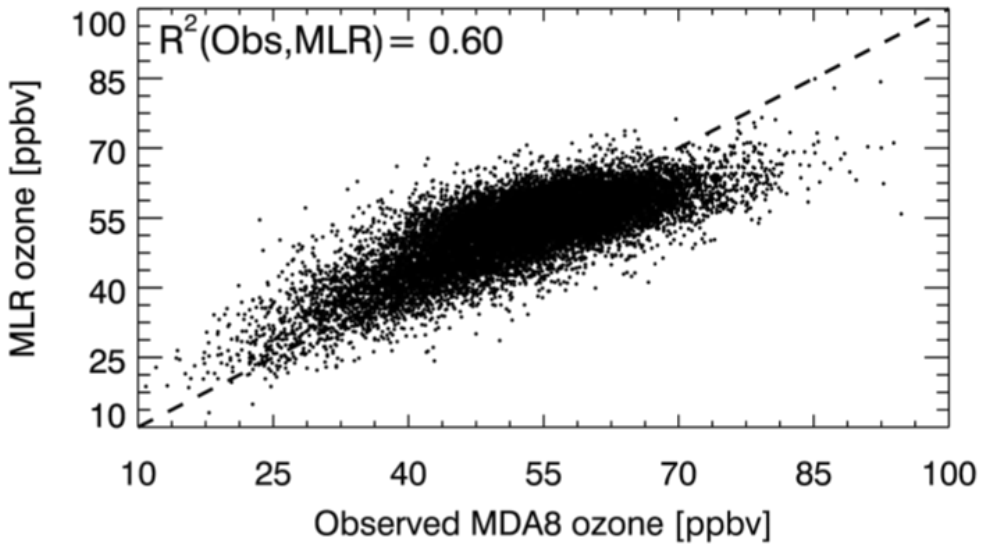

Figure 2. Comparison of the measured versus MLR predicted MDA8 ozone concentrations in the summers 1989-2010 for the ensemble of 13 Intermountain West CASTNet sites. The 1:1 line (dashed line) and the squared correlation are shown in the inset.

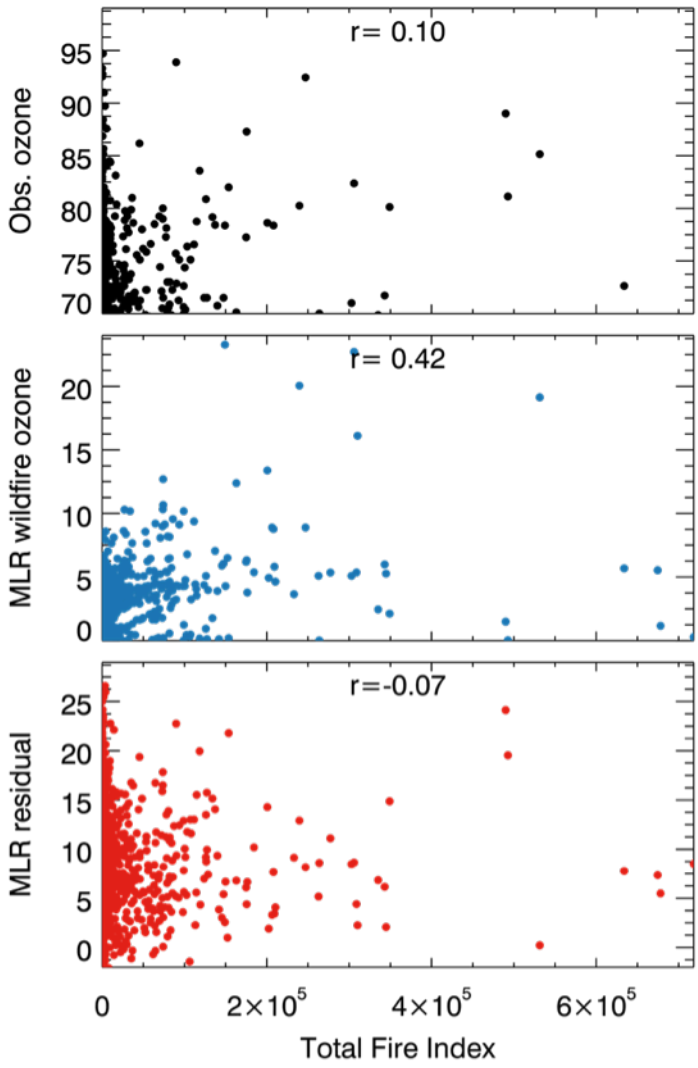

Figure 3. Evaluation of the MLR model low biases (MLR residuals) when measured MDA8 ozone concentration exceeds 70 ppbv as indicated in Figure 2. Scatter-plots of Total Fire Index (TFI) versus measured MDA8 ozone (top panel), MLR wildfire ozone enhancements (middle panel), and MLR residuals (bottom panel) are shown. The correlation coefficients are also shown inset.

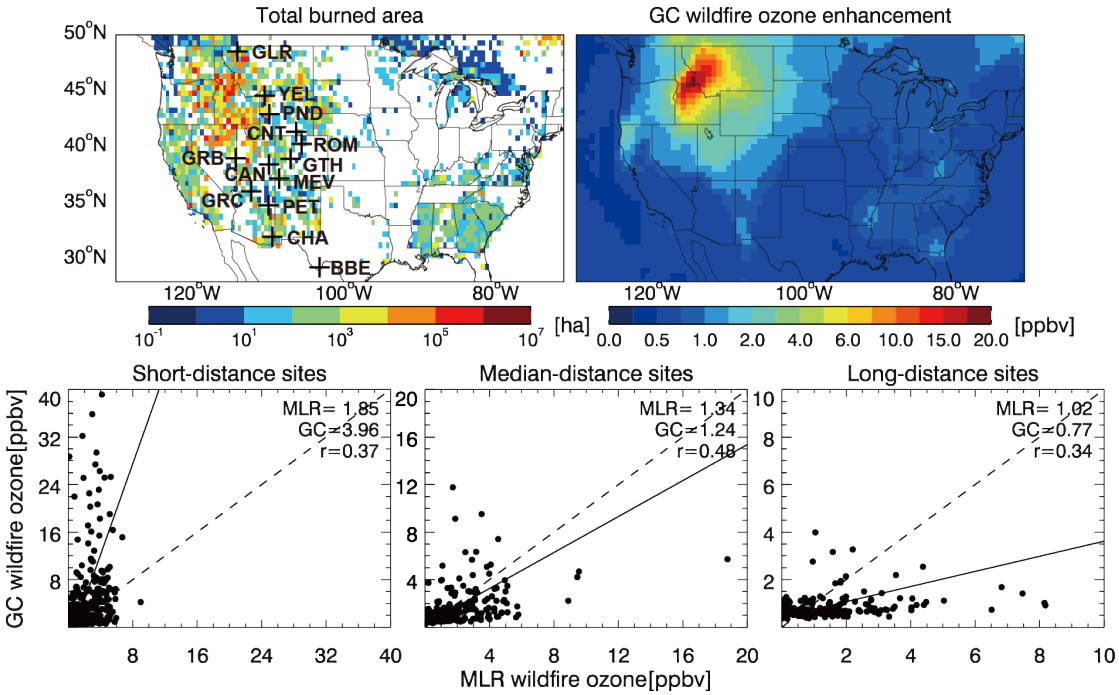

Figure 42. Wildfire ozone enhancements over the Intermountain West US in summer 2007. Top panels show the total burned area (upper-left panel) and seasonal mean wildfire ozone enhancements computed by the GEOS-Chem simulation (upper-right panel). Wildfire ozone enhancements computed by the MLR models are compared with those fromby the GEOS-Chem simulation. The comparisons are separated by their distances to the location with the maximum fire emission in Idaho: short-distance sites (bottom-left; GLR, YEL, PND, and GRB), median-distance sites (bottom-middle; CNT, ROM, GTH, CAN, MEV, and GRC), and long-distance sites (bottom-right; PET, CHA, and BBE). Mean wildfire ozone enhancements, correlation coefficients (r), reduced-major-axis regression lines (solid) and 1:1 lines (dashed) are shown inset.

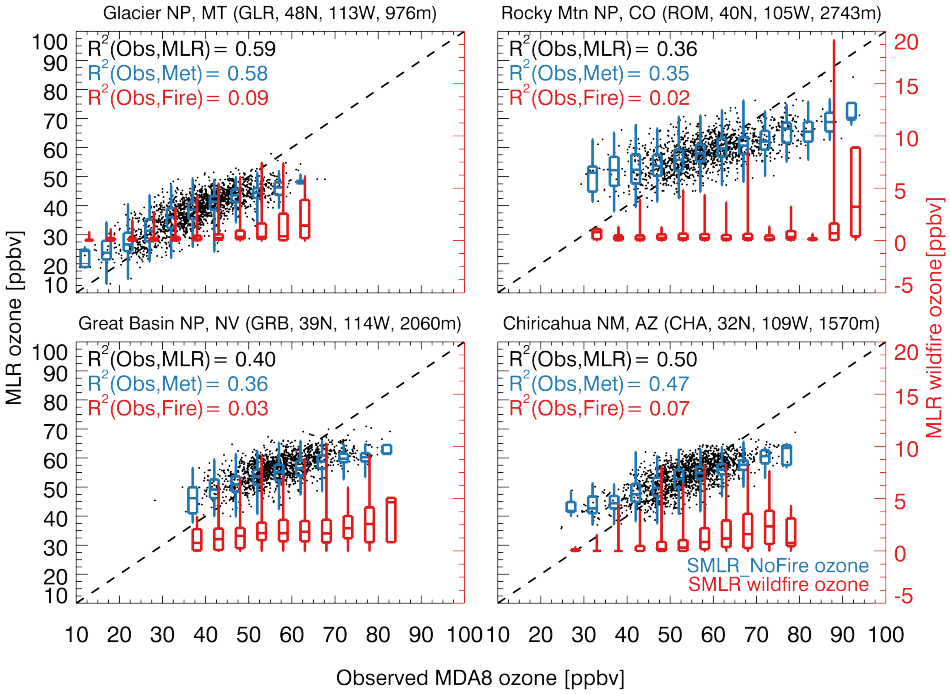

Figure 5~~3~~. Scatter-plots of observed versus MLR predicted MDA8 ozone concentrations at 4 selected CASTNet sites for the summers 1989-2010. Also shown are the box-and-whisker plots (minimum, 25th, 50th, 75th percentile, and maximum) of ozone without wildfire influences (blue) and wildfire ozone enhancements (red) for 5-ppbv bins of observed ozone concentrations; both are computed by the ~~S~~MLR model as described in the text. The 1:1 line (dashed line) and the coefficient of determination (R^2) are shown inset.

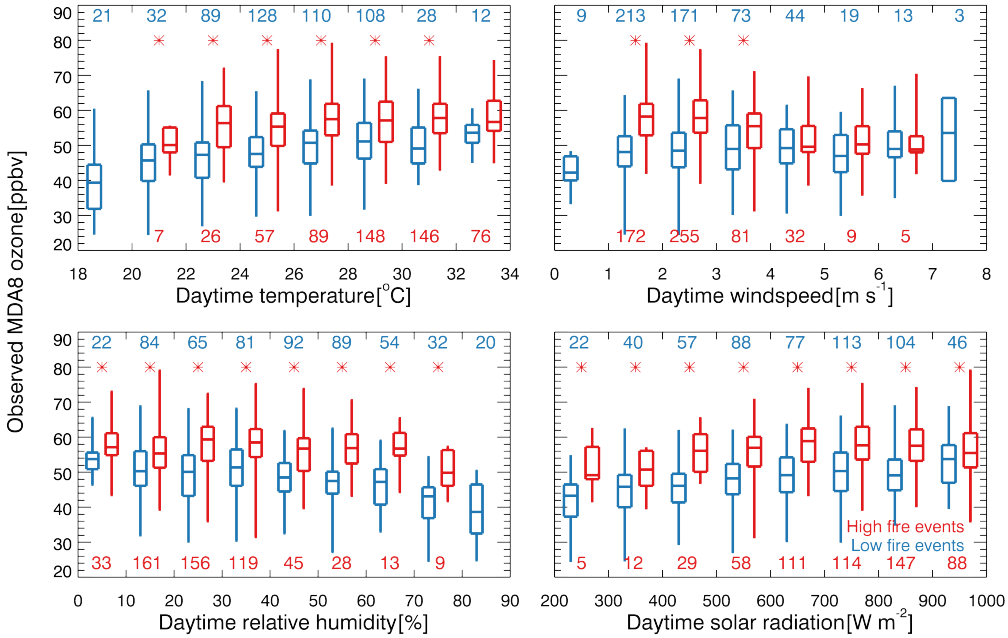

Figure 64. Box-and-whisker plots (minimum, 25th, 50th, 75th percentile, and maximum) of observed MDA8 ozone concentrations for bins of observed daytime meteorological parameters at CHA site: temperature (upper-left), wind speed (upper-right), relative humidity (bottom-left), and solar radiation flux (bottom-right). MDA8 ozone concentrations are divided by high (TFI at top 33%, red) and low (TFI at lower 33%, blue) fire events with the number of occurrences in each bin shown inset. Significant difference ($p < 0.05$) is marked by asterisks.

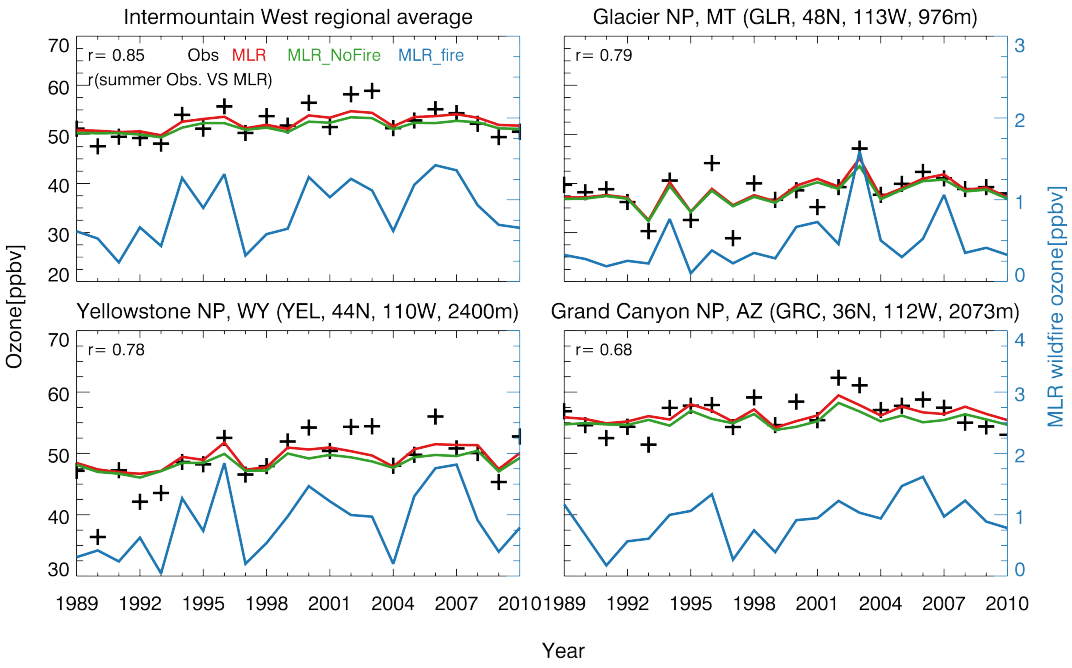

Figure 7~~5~~. Time series of summer mean MDA8 ozone concentrations for the regional averages of 8 CASTNet sites with complete 22-year measurements as well as 3 individual sites. Measurements (black pluses) are compared to the ~~S~~MLR model results (red line). Also shown are the summer mean ~~S~~MLR no wildfire ozone (green line) and ~~S~~MLR wildfire ozone (blue line, right axis). The correlations between measured and ~~S~~MLR summer means are shown inset.

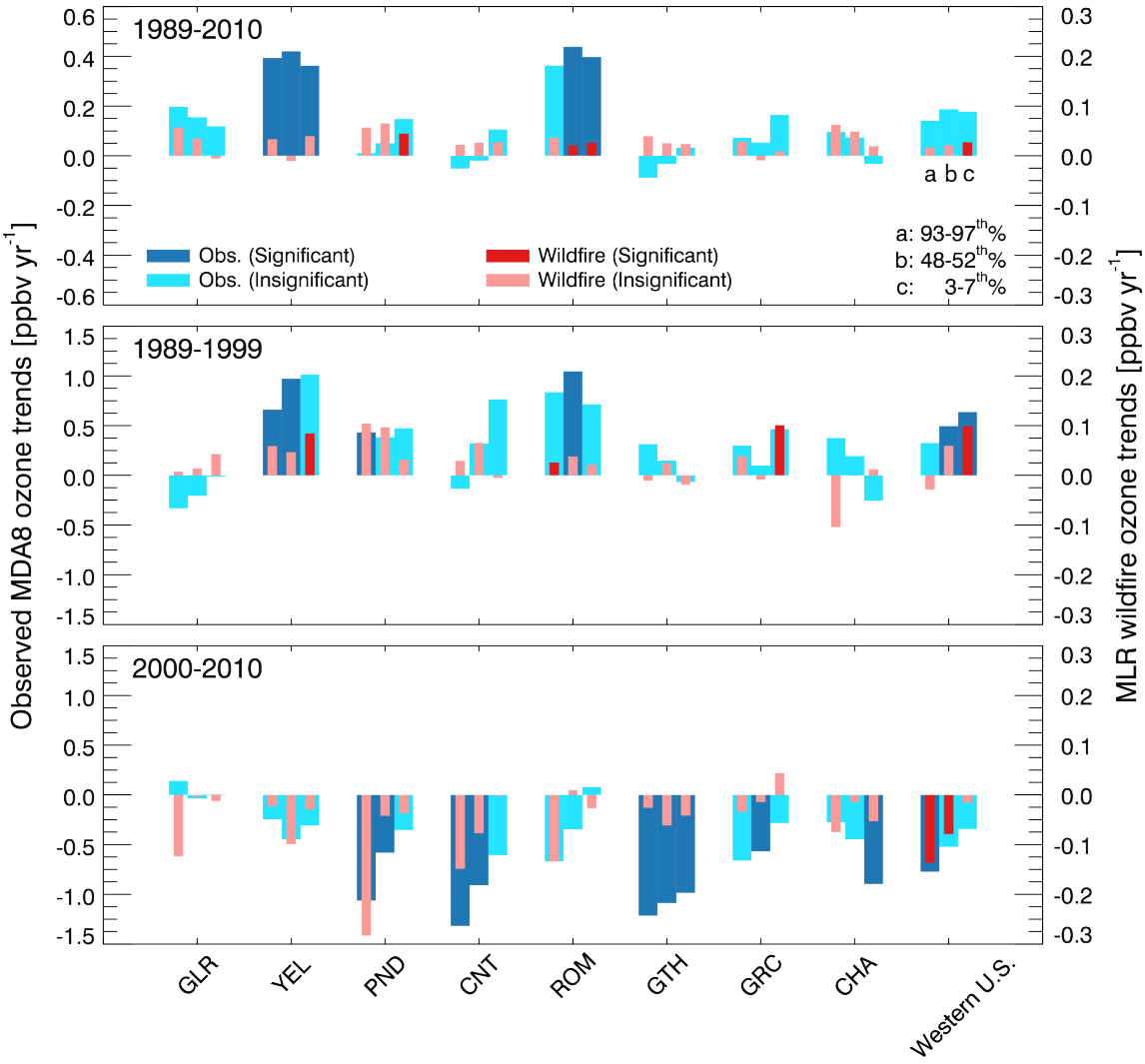

Figure 8~~6~~. Linear trends of summer mean MDA8 ozone concentrations (blue bars, left axis) for 1989-2010 (top panel), 1989-1999 (middle panel) and 2000-2010 (bottom panel) at 8 CASTNet sites and for the Intermountain West regional averages for the (a) 93th-97th, (b) 48th-52th and (c) 3-7th percentile ranges. Also shown are the trends contributed by wildfire ozone enhancements (red bars, right axis) as computed by the ~~S~~MLR models. Statistically significant trends ($p < 0.05$) are emphasized in dark color.

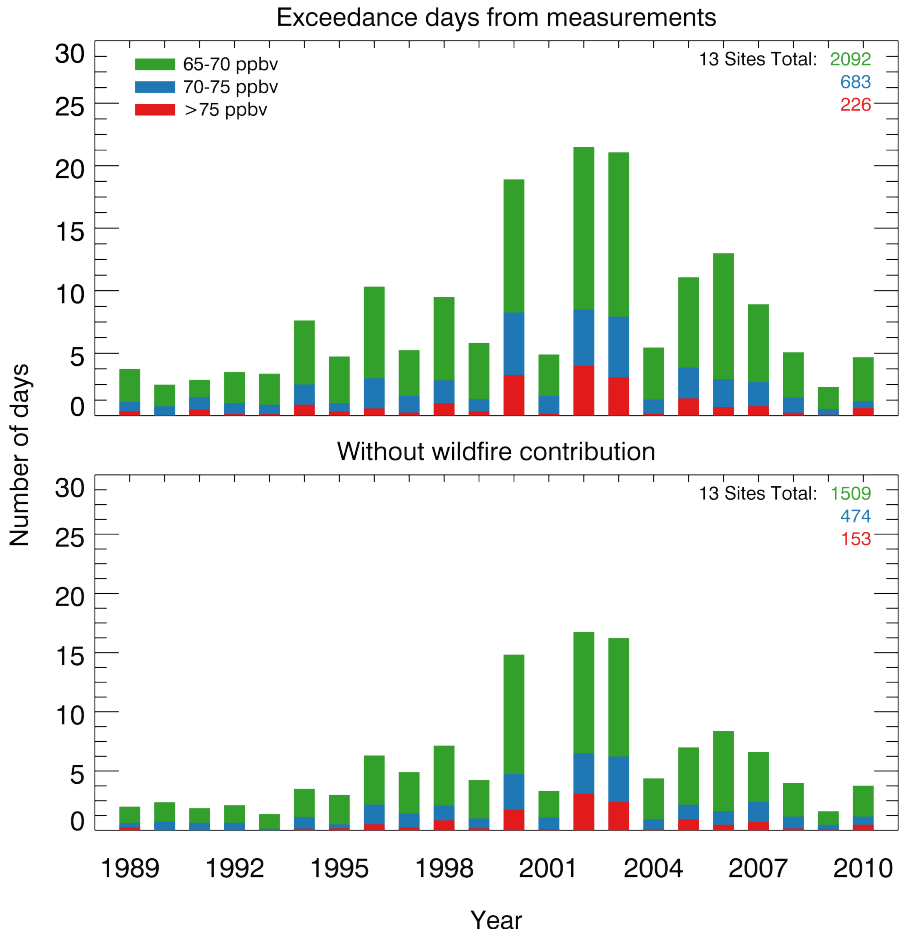

Figure 9~~7~~. Mean number of days with MDA8 ozone concentrations exceeding the thresholds of 65, 70 and 75 ppbv averaged over the 13 CASTNet sites in the Intermountain West for the summers 1989-2010. The top panel shows the exceedances computed from the measurements, and the bottom panel shows results that would be presented in the absence of wildfires (measurements minus the ~~S~~MLR estimated wildfire ozone enhancements).

Table 1. Variables used in the MLR models.

Variable	Predictors used in MLR model [a]	Data source
FI_s, FI_l	Fire Index for short/long period	FLEXPART 5-day backward trajectories and 0.5°×0.5° wildfire areas burned
$SqrFI_s$ $SqrFI_l$	Square root of Fire Index	
Tsurf	Daytime mean[b] surface temperature	CASTNet surface monitoring sites in the U.S. Intermountain West (http://www.epa.gov/castnet), for 13 CASTNet sites only
WSPsurf	Daytime mean wind speed	
RH	Daytime mean relative humidity	
SRAD	Daytime mean solar radiation	
Tmax	Daily maximum temperature	NOAA, National Climatic Data Center: Climate Data Online (http://www.ncdc.noaa.gov/cdo-web/), for Salt Lake City urban site only
AWND	Daily average daily wind speed	
PBLH	Gridded daily maximum planetary boundary height	NCEP Climate Forecast System Reanalysis (http://rda.ucar.edu/datasets/ds093.0/)
PRCP	Gridded daily precipitation	Climate Prediction Center of the National Weather Service (ftp://ftp.cpc.ncep.noaa.gov/precip/CPC_UNI_PRCP/GAUGE_CONUS/V1.0/)
U	Gridded daily mean 850, 700, 500 hPa zonal wind	NCEP/NCAR Reanalysis dataset (http://www.esrl.noaa.gov/psd/data/timeseries/daily/)
V	Gridded daily mean 850, 700, 500 hPa meridional wind	
WSP	Gridded daily mean 850, 700, 500 hPa horizontal wind	
Ome	Gridded daily mean 850, 700, 500 hPa vertical velocity	
SH	Gridded daily mean 850, 700, 500 hPa specific humidity	
HGT	Gridded daily mean 850, 700, 500 hPa geopotential heights	
T	Gridded daily mean 850, 700, 500 hPa temperature	
dT	Gridded daily mean temperature at 1000mb minus that at 850 hPa	

[a]Units are °C (Tsurf, T, dT, Tmax), m s^{-1} (WSPsurf, WSP, U, V, AWND), % (RH), W m^{-2} (SRAD), m (PBLH, HGT), $kg \cdot kg^{-1}$ (SH), 0.1 mm (PRCP) , and pa s^{-1} (Ome).

[b]Daytime mean represents the average for 10:00-17:00 local time.

Table 2. Multiple linear regression (MLR) models for summer MDA8 ozone at 13 Intermountain West CASTNet sites[a]

Sites[b]	R^2 (N)	Variables included in the MLR model[c]
Glacier NP, MT (GLR, 48N, 113W, 976m)	0.59 (1809)	RH, WSPsurf, SRAD, U, V, Ome, SH, HGT, T, dT, SH, $SqrFI_l$, $SqrFI_s$,
Yellowstone NP, WY (YEL, 44N, 110W, 2400m)	0.35 (1611)	RH, WSPsurf, Tsurf, SRAD, U, V,WSP, OME, HGT, T, dT, SH, $SqrFI_l$, $SqrFI_s$, FI_l,
Pinedale, WY (PND, 42N, 109W, 2388m)	0.28 (1888)	RH, WSPsurf, Tsurf, SRAD, U, V, WSP, Ome, HGT, T, SH, $SqrFI_l$, $SqrFI_s$, FI_s,
Centennial, WY (CNT, 41N, 106W, 3178m)	0.19 (1925)	RH, U, WSP, HGT, T, SH, $SqrFI_l$, $SqrFI_s$, FI_s,
Rocky Mtn NP, CO (ROM, 40N, 105W, 2743m)	0.36 (1367)	RH, WSPsurf, Tsurf, SRAD, PRCP, U, Ome, T, SH, FI_s, $SqrFI_l$, $SqrFI_s$,
Gothic, CO (GTH, 38N, 106W, 2926m)	0.29 (1906)	RH, WSPsurf, U, V, WSP, Ome, HGT, T, dT, SH, $SqrFI_l$, FI_l,
Mesa Verde NP, CO (MEV, 37N, 108W, 2165m)	0.23 (1321)	RH, WSPsurf, Tsurf, SRAD, U, V, T, dT, $SqrFI_l$, $SqrFI_s$,
Great Basin NP, NV (GRB, 39N, 114W, 2060m)	0.40 (1360)	WSPsurf, Tsurf, SRAD, U, WSP,Ome, SH, Ome, HGT, SH, $SqrFI_l$, $SqrFI_s$, FI_s,
Canyonlands NP, UT (CAN, 38N, 109W, 1809m)	0.16 (1379)	RH, WSPsurf, Tsurf, V, Ome, T, FI_l, $SqrFI_l$, $SqrFI_s$,
Grand Canyon NP, AZ (GRC, 36N, 112W, 2073m)	0.34 (1912)	RH, WSPsurf, SRAD, PRCP, U, V, WSP, Ome, HGT, T, SH, $SqrFI_l$, FI_l,
Petrified Forest, AZ (PET, 34N, 109W, 1723m)	0.43 (654)	RH, SRAD, V, WSP, Ome, HGT, T, dT, SH, $SqrFI_l$
Chiricahua NM, AZ (CHA, 32N, 109W, 1570m)	0.50 (1754)	RH, SRAD, PBLH, U, V, WSP, HGT, T, dT, SH, $SqrFI_l$, FI_l,
Big Bend NP, TX (BBE, 29N, 103W, 1052m)	0.46 (1196)	RH, WSPsurf, SRAD, U, V, WSP, HGT, T, $SqrFI_l$, $SqrFI_s$, FI_l, FI_s

[a] Coefficients of determination (R^2), sample numbers (N), and variables included in the MLR models.

[b] NP = National Park, NM = National Monument, MT = Montana, WY = Wyoming, CO = Colorado, NV= Nevada, UT = Utah, AZ = Arizona, TX = Texas.

[c] Fire Index (FI_l, FI_s), square root of FI ($SqrFI_l$, $SqrFI_s$), and meteorological parameters including (1) surface measurements: daytime (10:00-17:00 local time) mean temperature (Tsurf), wind speed (WSPsurf), relative humidity (RH), and solar radiation flux (SRAD); (2) gridded daily precipitation (PRCP); (3) NCEP data at 850/700/500 hPa pressure levels: daily maximum planetary boundary layer height (PBLH), daily mean zonal wind speed (U), meridional wind speed (V), horizontal wind speed (WSP), temperature(T), geopotential height (HGT), vertical velocity (Ome), specific humidity (SH), and temperature at 1000hPa minus that at 850 hPa (dT). Please refer to Table S1 and S3 for details on the parameters and MLR models.