Summary of Findings from the Uintah Basin Ozone Study: Preliminary Update from 2013 Field Study[1]

BACKGROUND

The Uintah Basin is a rural area of northeastern Utah where the majority of the state's oil and gas production occurs. Ozone concentrations in excess of the current national air quality standard have been measured in the Basin during the winter. These high ozone levels are only observed in the Basin during winter inversion periods when the ground is covered by snow; ozone levels outside of these periods have remained below the air quality standard and conditions resulting in exceedances of the standard do not occur every year.

In the first quarter of 2012, a multi-phased study (the Uintah Basin Ozone Study, UBOS) was begun to identify the emissions sources and the unique photochemical processes that cause elevated winter ozone concentrations, and to identify the most effective strategies to reduce winter ozone. UBOS 2012 included measurements of ozone and ozone precursor concentrations and meteorological conditions throughout the Basin. Meteorological conditions during UBOS 2012 were not conducive to ozone formation due to a lack of snow cover; no exceedances of the 8-hour average 75 parts per billion (ppb) National Ambient Air Quality Standard (NAAQS) were observed during UBOS 2012. Key findings from UBOS 2012 are described in a summary report (http://www.deq.utah.gov/locations/uintahbasin/2012study.htm).

UBOS 2013 took place between January and March 2013. In contrast to UBOS 2012, conditions during UBOS 2013 were favorable to ozone formation and numerous exceedances of the NAAQS were observed.

Presented here is an update to the interim findings from UBOS 2012 to reflect the considerable additional information obtained during UBOS 2013. These findings are drawn from preliminary analyses of data and results and will be updated in the coming months. A final report for UBOS 2013 is currently under preparation and planned for completion by December 2013. Additional analysis and results will also be included in peer-reviewed papers to be published by participating researchers.

[1] Prepared by researchers and air quality managers at Utah State University, University of Utah, National Oceanic and Atmospheric Administration, ENVIRON, University of Colorado, Utah Department of Environmental Quality and EPA.

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PRELIMINARY FINDINGS

Key findings from UBOS 2013 are summarized below:

I. Air Quality

a. Maximum 8-hour average ozone concentrations measured at Ouray, which typically has the highest readings in the Basin, reached 142 ppb during the December 2012 – March 2013 winter study, exceeding the EPA 8-hour standard (75 ppb) by 89%. Exceedances of the standard (i.e., a daily maximum 8-hour average in excess of 75 ppb) occurred at 17 of the 20 monitoring sites operating during the study. Monitors in the major Basin population centers exceeded the standard on a total of 22 days at Vernal and 29 days at Roosevelt during 2013 with all of the exceedances occurring between January 9th and March 6th. Note that the occurrence of an exceedance does not by itself constitute a *violation* of the EPA standard; a violation only occurs when the annual fourth highest daily maximum 8-hour average, when averaged over three consecutive years, is greater than 75 ppb. Exceedances occurred in the Basin during seven separate multi-day ozone episodes which were separated by periods of lower ozone levels coinciding with the passage of storm systems. These observations are in sharp contrast to conditions during the 2011-2012 winter study, when daytime 8-hour average ozone levels did not exceed 63 ppb.

b. Individual ozone episodes ranged from 3 to nearly 15 days in length, with ozone concentrations generally increasing from one day to the next during each episode, indicating a lack of ventilation.

c. Daytime ozone concentrations at locations close to but outside of the Uintah Basin, at the time of high surface ozone events inside the basin, ranged from 40 to 60 ppb. Ozone concentrations measured inside the Basin above the temperature inversion during these periods were also in the 40 to 60 ppb range. These facts, combined with observations of winds around the Basin, confirms that high surface ozone concentrations within the basin are not influenced to

any significant extent by transport of ozone or precursors from outside of the Basin.

d. Days with high ozone in the Basin coincide with elevated levels of methane, volatile organic compounds (VOC) and nitrogen oxides (NO_x). Alkane hydrocarbons constitute the main fraction of identified VOC. VOC and NO_x are the primary chemical precursors of ozone. A review of all emissions sources within the Basin (based on WRAP Phase III and UDAQ triennial inventories) indicates that activities associated with oil and gas exploration and production are the predominant sources of ozone precursors.
e. VOC concentrations in the Basin are extremely high during ozone episodes due to large amounts of VOC emissions and limited ventilation under a strong temperature inversion. Average VOC levels at Horsepool in 2013 were 1,684 ppbC (based on C2 – C7 non-methane hydrocarbons) as compared to 232 ppbC in 2012 when inversions were not present and there was more mixing.
f. Vertical profiles show that the polluted air mass associated with ozone episodes is confined to a shallow boundary layer that varies in height from 70 – 400 m (230 – 1,300 ft) above ground level.
g. The Bonanza power plant plume does not appear to contribute any significant amount of nitrogen oxides or other contaminants to the polluted boundary layer during ozone episodes; the thermally buoyant Bonanza plume rises upwards from the 183 m (600 ft) stack and penetrates through the temperature inversion layer. As a result, emissions from the Bonanza plant are effectively isolated from the boundary layer in which the high ozone concentrations occur.

II. Meteorology

a. Observations made during the 2013 winter study confirmed that high winter ozone in the Uintah basin only occurs when the ground is covered with snow and weather conditions promote the formation of a strong temperature inversion which traps a layer of cold, stable air (a “cold pool”) within the basin. In the absence of any snow cover, warming of the earth’s surface by the sun causes too much convective mixing for a cold pool to form.
b. Chemical reactions resulting in ozone formation are driven by the illumination of the atmosphere from direct, reflected and scattered ultraviolet solar radiation. Reflection of light from the snow surface significantly increases the total flux of ultraviolet radiation and thus the rate of ozone formation.
c. Ozone episodes in the Basin are characterized by complex, diurnally varying patterns of light winds which have the potential to produce gradual but significant intra-basin transport of ozone and precursors. Factors driving winds within the polluted boundary layer include differential daytime heating

producing upslope flows (which can be modified by variations in snow cover), nighttime drainage flows resulting in convergence along the river valleys at the lowest Basin elevations, and spatial perturbations of the depth of the cold pool air mass by winds blowing over the mountains surrounding the Basin. These forcing factors appear to produce oscillations or an east-west "sloshing" of air within the basin that further contributes to intra-basin mixing. These processes result in transport of ozone and ozone precursors from one part of the Basin to another but are not strong enough to mechanically breakdown the temperature inversion.

d. Initial attempts at modeling meteorological conditions during episodes indicate that obtaining accurate results with current modeling techniques will be very challenging. Additional data collection and model development and testing will be required to produce a good working model suitable for evaluating alternative regulatory strategies.

III. Chemistry

a. Unique features of the chemical reactions involved in ozone production were observed during the 2013 winter ozone episodes which make these episodes very different from summer ozone episodes in urban areas. Nitrous acid (HONO) and formaldehyde rather than ozone photolysis were found to be the biggest contributor to the pool of chemical radicals responsible for ozone formation. However, the contribution of HONO to the radical pool is uncertain at this time due to potential chemical interferences with the HONO measurements performed during the 2013 study. This in turn results in a significant amount of uncertainty in modeling the chemistry of ozone formation.

b. Uncertainties remain regarding the likely impact of nitrogen oxides (NO_x) and, to a lesser extent, volatile organic compound (VOC) emission controls on ozone levels:

    i. Analysis of data from 2012 (when elevated ozone did not occur) suggests that ozone formation was VOC limited, i.e., VOC reductions would produce ozone reductions whereas marginal NO_x reductions may result in increases in ozone due to a lack of sufficient radicals to process the available NO_x. Further analysis of conditions during 2013 is needed to determine if this was also true during the 2013 episodes or if instead the radical pool was sufficiently increased to the point where NO_x controls start to become an effective ozone reduction strategy.

    ii. The effectiveness of NO_x controls will also be impacted by the extent to which unreactive NO_z species (including HNO_3 and organic nitrates) are being recycled back into reactive NO_x by heterogeneous chemistry in

snow and on particulates. Details of these potential heterogeneous reactions are not yet understood well enough to be included in photochemical models needed for evaluation of control strategies.

iii. Measurements made during 2013 suggest that VOC reactions in the snow may contribute to ozone chemistry within the layer of air just above the snow surface (the mixed layer). The potential implications of this finding on the efficacy of VOC and NO_x controls are not yet known and further study is needed.

iv. Oxidation of aromatic VOCs (including toluene and xylene) is an important source of radicals. Thus, VOC control measures focused on sources of these species will be particularly effective. There do not appear to be large sources of other highly reactive VOCs (alkenes) in the Basin as alkene concentrations were very low relative to alkanes and aromatics.

IV. Emissions

a. Some important progress has been made on developing emission inventories for the Basin but the available data remain incomplete. Several groups, including the Utah Division of Air Quality, EPA Region VIII, and Federal Land Managers (through the Utah Air Resource Management Strategy project and the "3-States" and "West Jump" air quality modeling studies) are currently working on inventories for the Basin. Progress would be enhanced by more formal coordination of effort between these groups and the energy producers.

b. Field measurements of emissions from produced water ponds were conducted during the winter of 2012-2013 which showed that, while wintertime pond emissions comprise a small part of total VOC emissions in the Uintah Basin, VOC emitted from produced water ponds tend to be enriched in reactive VOC.

c. Field measurements made by the NOAA mobile laboratory during UBOS 2012 are being further analyzed to extract additional information about emission characteristics of sources sampled.

d. Obtaining sufficient emissions data for the Basin is made difficult in part due to a mixture of private, federal, state and Indian surface and mineral rights ownership which results in complex regulatory jurisdictions and inconsistent reporting requirements.

e. Inventory data specific to the winter ozone season are needed as emissions from some types of sources (such as evaporation ponds and methanol use) have large seasonal variations.

f. Additional information is needed on methanol use and composition, especially the degree of contamination with formaldehyde, which is a highly reactive volatile organic compound (VOC) that accelerates the formation of ozone.
g. Important components of the inventory that need to be more carefully quantified include emissions of VOCs from oil, condensate and produced water storage tanks, as well as fugitive emissions from leaking components and other sources and from venting, blowdowns and other intermittent events.

V. Recommendations for Future Analyses

a. Additional field data collection and analysis are needed to improve our understanding of several key features of the winter episodes to the point where meteorological and photochemical models suitable for analyzing alternative regulatory scenarios can be developed. Two areas of particular importance were identified:
    i. The highest priority studies would focus on improved, more robust measurements of HONO concentrations and related species, their vertical distribution and temporal variations. The response of ozone to changes in VOC and NO_x emissions is highly sensitive to HONO, so a clear understanding of HONO formation and removal mechanisms is critical.
    ii. Development of a comprehensive and accurate winter emission inventory for the Basin suitable for modeling applications (i.e., including sufficient speciation of chemical compounds and spatial and temporal detail) remains a critical requirement. There is a need to prioritize and coordinate efforts among the various groups that are currently developing inventories. In addition, work on "top-down" evaluation of inventories using available air quality observations is needed.
b. Several other data collection and analysis needs were identified by the UBOS research team; these will be detailed in the UBOS 2013 synthesis report.

VI. Implications for Control Strategies

a. Ozone levels in excess of the EPA 8-hour standard are only observed during winter inversion periods; ozone levels on the majority of days during the year are below the EPA standard and exceedances of the standard do not occur every year. This suggests that episodic or seasonal controls may be a useful component of an overall air quality management strategy for the Basin.
b. Emission reductions at the Bonanza power plant are unlikely to have any effect on winter ozone episodes.
c. Reductions in emissions of VOC will be beneficial, especially reductions in highly reactive VOC species, such as formaldehyde and aromatic VOC, that are sources

of radicals. Glycol dehydrators and produced water are two important sources of aromatic VOC.

d. Ozone response to NO_x reductions is less certain. NO_x control strategies will tend to be less effective if unreactive NO_z is converted to reactive NO_x by heterogeneous chemistry on snow or particulates, e.g., the conversion of HNO3 to HONO in snow.
e. Reducing formaldehyde would be an effective way to reduce ozone but it is not clear at this time which sources of formaldehyde (direct emissions from fuel combustion and use of methanol contaminated with formaldehyde or secondary formation of formaldehyde from VOC precursors) are most important.
f. Uncertainty in HONO sources and source strength (direct emissions or secondary formation from nitrogen precursors via several potential reaction pathways) makes it difficult to predict how responsive ozone will be to reductions in VOC and NO_x emissions.