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In-situ monitoring of trace gases in a non–urban environment

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ABSTRACT

A set of commercial instruments measuring carbon monoxide (CO), ozone (O_3), sulfur dioxide (SO_2), and nitrogen oxides [nitric oxide (NO), nitrogen dioxide (NO_2), and odd nitrogens (NO_X)] was integrated and deployed in a non–urban environment. The deployment occurred between July 2, 2007 and August 7, 2007 in Richland, WA. The mixing ratios of all species were lower than in most rural–suburban environments, and strong diurnal patterns were observed. NO_2 was depleted by photochemically formed ozone during the day and replenished at night as ozone was destroyed. The highest ozone concentration during these episodes was 45 ppb. The overall average was 15 ppb with readings approaching near zero at times. This observation is low compared to average daytime summer readings of 60–80 ppb in highly populated and industrialized urban areas in the Pacific Northwest region. Back-trajectory analysis and prevailing weather conditions both indicated that much of the ozone was transported locally or was produced *in–situ*. Analysis of SO_2 as a tracer for O_3 advection further indicated lack of long–range regional transport of pollutants to Richland. We also present results of analysis of high ozone episodes and comparisons relative to other areas in the Pacific Northwest region. These results provide a useful sample data set to study the historical record of air quality in rural Eastern Washington.

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1. Introduction

Atmospheric trace gases are chemical compounds found in very low concentrations in the atmosphere; despite low concentrations, however, they can exert considerable influence on a range of environmental processes and health problems (Seinfeld, 2004). Knowledge of the interactions among these gases is crucial to understand their atmospheric concentrations and lifetimes and the environmental impacts that can be expected with modifications to their sources and sinks. Ozone (O_3), nitrogen oxides (including NO, NO_2, and NO_X), carbon monoxide (CO), and sulfur dioxide (SO_2) are not only pollutants themselves but also react with many other compounds such as volatile organic compounds (VOCs) leading to changes in atmospheric composition (Atkinson, 2000).

Accurate *in–situ* measurements are crucial to provide the foundation for investigating complex photo–oxidation processes. With population growth being a common phenomenon in many rural areas, historical records are becoming increasingly important to identify air quality trends associated with local sources relative to increases resulting from long range transport. The Tri–Cities, including Richland, Pasco, and Kennewick in the state of Washington, is one of the statistically fastest growing metropolitan areas in the country, defined as a core urban area with at least 50 000 people (USCBa, 2008). It added almost twenty percent to its population in the last six years (Cohen, 2007), indicating the importance of documenting air quality before the area becomes far more developed.

The study presented here has two purposes. From an engineering standpoint, the motivation was to integrate multiple trace gas analyzers into one system and identify issues related to this integration process. Combining basic trace gas analyzers to one system has several advantages. First, it saves space. Second, it is convenient to move or transfer these analyzers. Third, it provides integrated data acquisition and consistent time stamps for ease of data collection, display, and analysis. In addition, the Thermo Electron, Inc., trace gas analyzers used in this study were being updated from C–Series to *i*–Series. The newer *i*–Series instruments offer improved measuring capabilities, user options, and storage space. This work gives a practical solution to issues associated with acquiring data from instruments having different manufacturer configurations. For instance, compared with standard serial connections, our approach provides fast time resolution as each instrument allows. It also provides flexibility for users to set their own instrument connection scheme.

The second purpose of this study was to provide a base case of pollutant concentrations, and in particular, O_3 concentrations, in Richland, WA. Richland is a rural yet growing area in the Pacific Northwest region of the United States, which at present has ozone concentrations far less than those found in urban parts of the United States. Rural areas have historically been underrepresented when studying air pollution and a data set for Richland prior to major growth may prove very valuable in its future. Source regions associated with "high" ozone episodes were studied using the National Oceanic and Atmospheric Administration's (NOAA) HYSPLIT model to identify the back trajectories of air parcels associated with elevated pollutants. The deployment took place in summer, because photochemistry is most vigorous. As a result, ozone often peaks. This potentially can provide a good opportunity to study ozone at this rural location.

2. Materials and Methods

2.1. Instrumentation and experimental setup

Measurements of the trace gases were made using individual trace gas analyzers (Thermo Electron) for O_3, CO, SO_2, and $NO/NO_2/NO_X$. The instruments were installed in an instrument rack, and the resulting unit deployed just south of the main campus of the Pacific Northwest National Laboratory (PNNL) in Richland, WA (lat 46° 21'N, long 119° 17'W, elevation 120 m MSL) (Figure 1). Maps were made using the ESRI ArcMap software (version 9.3). The geographic information was obtained from the Washington State Department of Transportation (WSDOT, 2010). The instruments were arranged in the rack according to how data were logged in sequence. As will be described in more detail, the O_3 analyzer was used to communicate between the data logger and the rest of the instruments. Sample collection was performed between July 2 and August 7, 2007. Local standard time (Pacific Daylight Saving Time, PDT) was used in data recording. The conversion between universal time (UTC) and PDT is UTC – 7 hours = PDT.

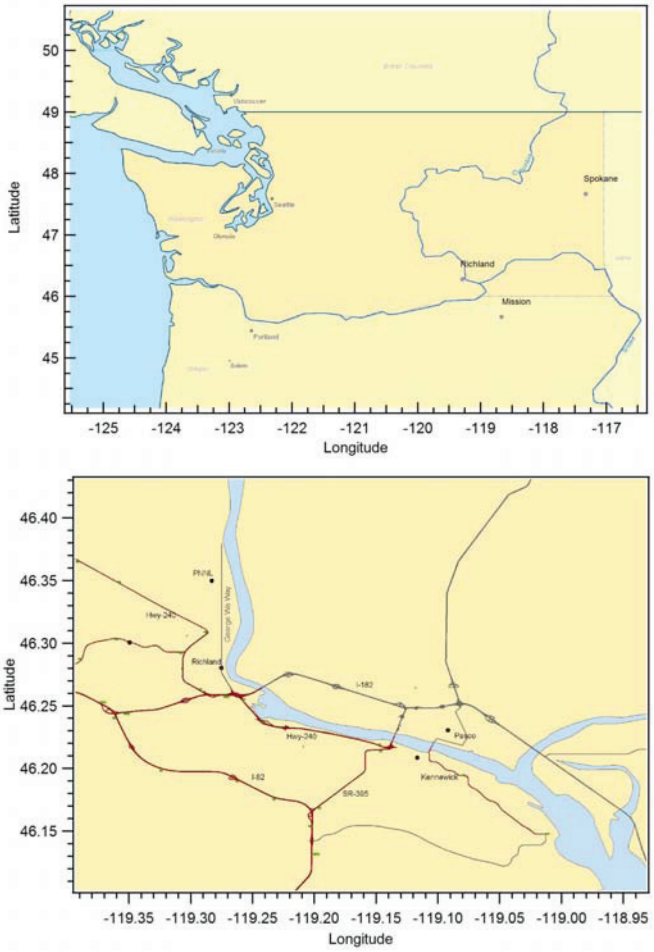

Figure 1. *Top is a map of the Pacific Northwest with selected ozone monitoring stations identified (NCDC, 2007). Bottom is a map of Washington's Tri-cities area, including the observation site at PNNL denoted by the black dot.*

All of the instruments were connected to a Campbell Scientific, Inc., (C.S.) CR23X Micrologger. The data logger communicated with a Dell Laptop for on–line display via a serial cable. The data acquisition program was written in Edlog, a programming tool within C.S.'s Logger Net (C.S., 2002), and downloaded to the data logger. The data logger was used to store selected instrument outputs and control instrument zero and span checks twice a day. Instrument readings were measured as voltages from the analog voltage outputs of the instruments and transmitted to the differential voltage analog inputs of the data logger (see the Supporting Material, SM, Figures S1 and S2). Ambient air was sampled through ¼–in Teflon sampling tubing, whose inlet was approximately four meters above the ground and passed through a sampling port in the wall. Figure 2 illustrates how air passed through Teflon filters (2 µm pore, 47 mm Zefluor, Gelman P5PJ047) before entering into the instruments' sample bulkhead. The exhaust lines from each instrument were collected into a common manifold that returned the air to the atmosphere after scrubbing the exhaust in a pack filled with activated carbon.

A Dynamic Gas Calibrator (Thermo Electron, Model 146i) was used to calibrate the instruments automatically on a regular basis using zero and standard gases (Scott Specialty Gases). The dynamic calibrator uses two mass flow controllers to regulate the flow of zero and span gas, and a Teflon mixing chamber to achieve complete mixing of the two components at the desired concentration level. High purity zero air containing less than 0.5 ppm total hydrocarbons was used, while the standard gas mixture consisted of 10.1 ppm NO, 10.1 ppm CO, and 10.0 ppm SO_2, balanced with high purity N_2. The ozone analyzer was calibrated using a primary standard ultraviolet (UV) photometric ozone calibrator (Thermo Electron, Model 49C), following the EPA transfer standards for calibration of air monitoring of analyzers for ozone (EPA, 2009).

A UV Photometric O_3 Analyzer (Thermo Electron, Model 49i) was used to measure O_3. Atmospheric SO_2 was determined with a Trace Level–Enhanced Pulsed Fluorescence SO_2 Analyzer (Thermo Electron, Model 43i). CO was determined by a Trace Level CO Analyzer (Thermo Electron, Model 48C). Nitrogen oxides (NO, NO_2, and NO_X) were measured with a Trace Level Chemiluminescence $NO–NO_2–NO_X$ analyzer (Thermo Electron, Model 42C). The ozonator used to convert NO to NO_2 requires a supply of dry air, and Drierite (Cole–Parmer) was used to remove water vapor from ambient air for this purpose. A more detailed description of the principles of operation of these instruments is reported elsewhere (Platt, 1999) and the operation principles of each analyzer are briefly summarized in Table 1.

A Precision Spectral Pyranometer (PSP) (Eppley Laboratory) was used to measure the solar radiation reaching Earth's surface. The PSP uses a thermoelectric device that produces an electric current proportional to the broadband shortwave solar radiation reaching the detector. The detector is painted black and mounted in an optical glass sphere for protection from the elements. It samples at wavelengths between 0.3 µm and 3 µm at one minute intervals. A humidity measurement probe (Vaisala, Model HMP45C) was used to measure the temperature (in degrees Celsius) and relative humidity of the sampled air. Wind speed and direction were measured by a propeller anemometer (R.M. Young, Model 05103 Wind Monitor) located about fifteen meters to the north of the trace gas sampling area. Data were collected every minute and averaged to five minutes for final reporting.

2.2. Instrumentation error

Background concentration checks using zero air were conducted to correct instrument drift. High–purity air was sent into the instruments to obtain a daily true zero. It is critical that the CO instrument be continuously purged with a low purge flow (140 cc/minute recommended) of zero air, otherwise significant drift may interfere with data quality. Purging is used to prevent interference from ambient levels of CO as air flows through the filter wheel assembly, which contains CO on one side and N_2 on the other. All analyzers underwent background corrections as often as time permitted, and the CO analyzer was continuously purged with high purity zero air while sampling was occurring.