Atmospheric Pollution Research 7 (2016) 66–74

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Atmospheric Pollution Research

journal homepage: http://www.journals.elsevier.com/locate/apr

Original article

Air quality over a populated Andean region: Insights from measurements of ozone, NO, and boundary layer depths

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ARTICLE INFO

Article history:
Received 23 May 2015
Received in revised form
13 July 2015
Accepted 18 July 2015
Available online 20 October 2015

Keywords:
Quito
Air quality
Ozone
NO
Boundary layer

ABSTRACT

In this study, a hypothesis based on observations is offered to explain levels of ambient ozone in Quito, a busy urban center located at high altitude along the equatorial Andes. Supporting data includes first-time measurements of boundary layer depths in addition to ozone, NO (nitric oxide), and oxidized nitrogen observations. Mixing layer measurements were taken in June and July 2014 and in April 2015. The air quality data set is presented for the months of July through September 2014. From a total of four midday soundings launched under sunny conditions, a deep mixing layer up to 2200 magl (meters above ground level) was found only once when surface temperature was unusually high. In the other three cases, layered structures were found with the top of the mixing layer at 687 magl on average. These measurements were obtained when surface temperatures were within the usual range. Furthermore, the morning boundary layer depth was measured twice between 07:00 and 08:00. On average, a depth of 185 magl was determined. Air quality measurements for the study period show that ozone stayed below 55 ppbv while NO levels were routinely higher than 100 ppbv in the morning rush hour, and oxidized nitrogen stayed high during daytime. Observations of a generally shallow boundary layer indicate that the environment at this Andean location has the potential to accumulate pollutants. Thus, vertical dilution alone is unable to explain the observed low levels of ambient ozone. When ozone reached the highest values in the second half of September 2014, it was found that it increases with decreasing NO levels during daylight hours between 11:00 and 16:00. Therefore, air quality observations along with findings of shallow mixing layers suggest that inhibition of ozone production potentially occurs due to a NO_x-saturated chemical regime.

1. Introduction

The Metropolitan District of Quito is located at high altitude on the complex Ecuadorian Andean topography and encloses a busy urban center (2800 masl, meters above sea level) and densely populated adjacent valleys (2350–2500 masl). The population of the entire district is approximately 2.24 million inhabitants (INEC, 2010). Over the past few years, Quito has undergone fast economical growth and expansion, accompanied by critical traffic management challenges across the urban and suburban areas.

For the past ten years the city has been operating an air quality monitoring network that provides information about levels of criteria pollutants in the ambient air in order to protect public health (Secretariat of Environment, 2013). An analysis of historical hourly ozone averages from the public records between 2007 and 2012 shows that values usually remain well below the 8-h air quality standard of 100 μg m^{-3} in standard conditions (50.9 ppbv) (Cazorla, 2012). Such low ozone levels in a high altitude city with intense traffic and year round equatorial solar radiation seem counterintuitive at first. One possible explanation is that ozone production is actually high but mixing in a deep boundary layer acts to dilute pollutant concentrations in the ambient air (the effect of vertical mixing on ground level ozone has been studied in previous research, for example Holzworth, 1967; Zhang and Rao, 1999). Another possibility is that the types and abundance of emissions result in the production of species other than ozone (Roberts et al.,

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Peer review under responsibility of Turkish National Committee for Air Pollution Research and Control.

http://dx.doi.org/10.1016/j.apr.2015.07.006

1995; Sillman, 1995). Until now there have been no studies conducted in Quito to measure the boundary layer depth nor to identify the chemical production regime of ozone.

Among the most important ancillary measurements needed to place levels of ambient ozone within an appropriate chemical context is NO. As has been studied previously by several authors elsewhere, ambient NO concentrations determine whether radical chemistry leads to ozone formation or whether ozone termination chemical reactions take place (for example, Logan et al., 1981; Kleinman et al., 1997; Kleinman, 2005). In this regard, there is a substantial amount of published work (Tonnesen and Dennis, 2000; Kleinman et al., 2002; Kleinman, 2005) that explains in detail mechanisms that differentiate between NO_x-saturated versus NO_x-limited ozone production regimes (NO_x is the sum of nitric oxide and nitrogen dioxide). In NO_x-saturated environments, secondary pollutants other than ozone, such as peroxyacetyl nitrate (PAN) and nitric acid (HNO_3), form with the same precursors (Roberts et al., 1995; Sillman, 1995; Roberts, 2007; Song et al., 2011). For example, an afternoon abundance of nitric acid greater than ambient hydrogen peroxide concentrations is an indicator of a NO_x-saturated environment (Sillman, 1995).

Whether the production regime of ozone in Quito is NO_x-limited or NO_x-saturated has not been explored previously. Thus, daytime NO concentrations in the local air have not been linked to the chemical nature of ambient ozone. One consequence of not addressing this problem is that the capability of the NO_x species to shift the local regime of ozone production (NRC, 1991; Sillman, 1993) in the event of a change in emissions remains hidden. In this paper we explore a NO_x-saturated chemical regime as the underlying reason for low ozone levels in Quito.

Knowledge of boundary layer depths are also critical for understanding the accumulation and dispersion of pollutants such as ozone (Russell et al., 1974; Holzworth, 1967). In Quito, the inhomogeneity of the Andean terrain adds further difficulty to resolving the ozone budget, since complex topography has an impact on the evolution of air mass circulations and mixing depths (Whiteman, 1982; Whiteman et al., 2000). A complete absence of upper-air observations in the Quito region has limited substantially the capability to propose mechanisms that explain levels of atmospheric pollutants. As already mentioned, a possible explanation for low levels of ozone could be dilution in a large mixing volume. However, high altitude lowers surface temperatures, in spite of the equatorial latitude. Surface temperature in turn influences the maximum depth that the mixing layer reaches during daytime (Holzworth, 1964). Environments with a potential for developing shallow mixing layers are likely to accumulate atmospheric pollutants. If this is the case in Quito, low ozone levels would be indicative of a chemical regime that inhibits ozone formation.

The lack of specific information about factors that affect pollution locally has an impact on environmental modelling. For example, air quality models need appropriate boundary layer parameterization and inputs of a substantial number of atmospheric species in order to perform runs that are founded in reality (for example, Anjaneyulu et al., 2012). For these reasons, in the current case a realistic model run that would give insight into regimes of photochemical production of ozone is still out of reach. Hence, from an atmospheric modeling perspective, there is a real need to develop deep comprehension of physical and chemical mechanisms in order to narrow down and even refine model schemes in a way that they are applicable to Quito's particular pollution conditions.

This study was carried out to contribute to a better understanding of processes that influence the formation and accumulation of pollutants in Quito's air. The investigation was performed in Cumbayá, a populated valley within the Metropolitan District. In this paper, first-time measurements of morning and afternoon mixing depths are shown in detail. Furthermore, the effect of surface temperature on the development of a fully mixed afternoon boundary layer is explored in light of ground station measurements. A topographic cross-section over the launching site is also presented to illustrate the need to further study boundary layer processes in this Andean region. Moreover, measured ambient ozone is interpreted for the first time according to measured mixing depths and detected high levels of NO. Finally, future experimentation and modelling is discussed to prove the proposed hypothesis and to improve comprehension of local mechanisms for production of secondary pollutants.

2. Materials and methods

2.1. Experimental observations

The study was conducted at Universidad San Francisco de Quito's Atmospheric Measurement Station, EMA (Spanish acronym). USFQ's main campus is located in Cumbayá, a valley to the east of the main urban center within Quito's Metropolitan District. EMA was built over a year ago on the roof of the Science and Engineering building at 11.5 magl. The facility coordinates are 0°11′47″ S, 78°26′6″ W, and altitude is 2391 masl. A topographic map with the location of the monitoring station relative to the city is shown in Fig. 1.

Baseline physical meteorology observations (temperature, relative humidity, direct solar radiation, precipitation, wind speed and wind direction) are continuously measured at EMA. A detailed description of meteorological instrumentation, EMA operations and evaluation of initial measurements is documented elsewhere (Cazorla and Tamayo, 2014).

EMA also has instrumentation to monitor in real-time ambient ozone and NO levels. Ambient ozone is measured continuously with a Thermo 49i uv-photometer. Data is acquired at a rate of 1 Hz. During the study period, data from the 49i sensor was compared several times for several hours with DMT ozonesonde surface measurements, as a method to ensure data quality.

A Teledyne NO_x chemiluminescence analyzer model T200 is used to monitor ambient NO. For this study, instrument calibration was performed with a Teledyne T700 dilution system and a standard NO mixture. The T200 instrument uses a molybdenum catalytic converter heated to 315 °C. According to the manufacturer, due to the internal sampling design, a substantial amount of NO_y is lost before gas conversion to NO in such a way that the instrument yields NO_2 readings (NOy is reactive nitrogen). However, actual levels of NO_y present at the EMA site and lost in the instrument have not been measured. Due to the high temperature of the catalytic converter in addition to the unknown NO_y losses, at present it is misleading to present the T200 measurement as NO_2. Therefore, in this study measurements other than NO from the T200 sensor are reported as oxidized nitrogen species and are only used as an indicator of levels of such compounds in the ambient air.

During June and July 2014, a total of five pairs of iMet radio sondes coupled with DMT ozonesondes were launched from the EMA facility. Sonde preparation, balloon launching and radio communications protocols as well as data retrieval methods were performed according to the US National Oceanic and Atmospheric Administration (NOAA) procedures. The first two launches at EMA were done with the collaboration of scientists from NOAA. Material preparation and adaptation of protocols to EMA's particular conditions were done locally months ahead of the first launch. Radio and ozonesonde surface measurements were compared and validated with EMA ground observations. The launching schedule was