

NATURAL AND MAN-MADE EMISSIONS ON EXPOSURE TO AIR POLLUTION IN A MID-SIZED ANDEAN CITY: MANIZALES, COLOMBIA.

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Abstract

Public transportation and volcanic emission source dynamics were analyzed with daily variation of PM_{10} , SO_4^{2-} scavenging, vehicular distribution, and simulation of a volcanic SO_2 plume using the WRF/Chem model; in densely populated Andean city of Manizales, Colombia. Air quality of Manizales is affected by anthropogenic and natural emissions of suspended particles and SO_2 . The city is located on the western slopes of the central range of the Andes (pop 380,000; 2150 m.a.s.l.). Suspended particles have been found to be associated with increased sulfate concentrations in rain through scavenging processes. In addition, there is significant SO_2 emission from the nearby volcano that likely contributes to acid rain formation. However, there is little information for the area with respect to point and non-point source contribution of these pollutants, or the diurnal differences in source timing. In order to provide a better understanding about sources, fate and transport of particles and SO_2 , this work analyzes the effect of vehicular versus volcanic emissions, and highlights the importance of modeling aerosol exposure, sulfate and its role in particle formation, particle scavenging and acid rain formation. Two urban zones were compared to analyze effects of vehicular distribution. A DustTrak aerosol monitor was used to measure PM_{10} daily distributions in three points of the city (two at downtown and one in the central area). Higher levels of particles were observed during early morning and early evening and were associated with increased public transportation during rush hours. Higher vehicular density was associated with higher PM_{10} concentrations downtown, and higher sloped roads were associated with higher PM_{10} levels due to the increased fuel consumption requirements. Natural SO_2 emissions from the Nevado del Ruiz volcano - located 27 km southeast of the city - were analyzed using WRF/chem model. Two 24 h periods were simulated including daily SO_2 emissions from the volcano. Due to the lack of information about emission inventories in the city and the nonexistence of subroutines to model air quality in Manizales, it was necessary to modify the subroutine `emiss_v3` used for the NEI in the WRF/Chem model. Behavior of plume dispersion of SO_2 towards Manizales suggests that volcanic SO_2 is a significant source of acid rain formation in the city (mean VWM-pH levels around 4.9 units). These preliminary results suggest factors important to modeling both anthropogenic and natural emissions in the mid-sized Andean city of Manizales.

Key words: Particulate matter, SO_2 , mobile sources, volcanic emissions, plume dispersion, atmospheric modeling.

Introduction

The Identification of principal sources of atmospheric pollutants and its dynamics over urban air quality is an essential tool for developing air quality management policies, and for establishing strategies of atmospheric pollution prevention and control. One of the principal atmospheric pollutants released in urban environments is particulate matter, defined as a mixture of solid and liquid droplets and formed by elemental and organic carbon, ammonium, nitrates, sulfates, mineral dust, trace elements and water (Aldabe et al., 2011). Aerosol particles arise from natural and anthropogenic sources such as

windborne dust, sea-spray, volcanic emissions, vehicular fuel combustion, and industrial emission processes. These particles can be emitted directly into the atmosphere, or formed as secondary pollutants through chemical reactions of gaseous precursors (Seinfeld and Pandis, 2006; Kumar et al., 2010; Xu et al., 2012).

Vehicular emissions are recognized as one of the major sources of particles into the atmosphere, including those with diameter less than 10 μm (PM_{10}) and particles with diameter less than 2.5 μm ($\text{PM}_{2.5}$) – recognized as the fine fraction of PM_{10} . According to Echeverri and Maya (2008), this finer fraction, more damaging to human health, has been found to comprise the majority of PM_{10} mass fraction in principal urban areas of Colombia.

Composition and mass of particulate matter are also influenced by the levels of sulfur in fuel (Zhang et al., 2009). In mid-sized Colombian cities values of sulfur content in fuels are relatively high with 300 ppm in gasoline and 500 ppm in diesel since 2010 (Resolution 1180, 2006). As well as, one of precursors to the formation of sulfate aerosols in the atmosphere are SO_2 emissions (Calvo et al., 2012). The sulfate content of particulate aerosols has impacts in increased sulfate concentrations in rain through scavenging processes encouraging phenomenon like acid rain (González and Aristizábal, 2012).

Production, fate and transport of PM_{10} and other pollutants like SO_2 are important especially in Manizales because of its geography, altitude and urban development. Manizales is a city located on the western slopes of the central range of the Andes (2150 m.a.s.l.) in the Colombian department of Caldas. The urban zone (pop 380,000) is surrounded by steep slopes; as a consequence, the area available for development is limited showing relatively high urban density. Moreover, environment pollution studies in Manizales are justified due to identification of some sources of PM_{10} and SO_2 that impact the air quality of the city. One of them are vehicular emissions, in a city with high vehicular ownership in Colombia (130 vehicles per 1000 inhabitants) and the use of fuels with considerable sulfur content. Industrial activity, leading thermal processing of wastes, metal recycling and foods, also contributes to pollution in the city. As well as, 27 km southeast of the city, there is influence from an active volcano (Nevado del Ruiz), a natural source of reduced and oxidized forms of sulfur, nitrogen and particles.

Manizales is a city with unique ridge topography and climate, influenced by the Central range of the Andes. The urban zone is located along ridge topography occupying slopes with limited area for development; as a result, the city is densely populated. Manizales is unique for air pollution studies due to its tropical Andean climate with high humidity, high annual precipitation and low wind velocity. There have been studies related with air pollution in high urban plateaus and mountain valley zones (Toro et al., 2006; Zárate et al., 2007), but no studies have been published for urban areas located on a major tropical mountain slope like Manizales occupying the halfway position of the western slope of the Cordillera Central at 5° N latitude. Recent publications highlight the necessity for further studies of the sources, fate and transport of air pollutants in Manizales, incorporating the most comprehensive data into atmospheric models as a tool to understand the dynamics of air pollution (Aristizábal et al., 2011; González and Aristizábal, 2012). The aim of this work is to provide a better understanding about sources, fate and transport of suspended particles and SO_2 , analyzing the effect of vehicular versus volcanic emissions, and highlighting the importance of modeling aerosol exposure, sulfate and its role in particle formation, particle scavenging and acid rain formation.

Materials and methods

Three stations were chosen in Manizales in order to evaluate airborne PM_{10} concentrations. Two stations were located in the most densely urban downtown area (Agustinos and Liceo) and one station was located in the central area (Palogrande) (Figure 1a). Agustinos and Liceo are influenced by high surrounding traffic emissions of public transportation, however Agustinos is surrounded by sloping roads and Liceo is more characterized by flat roads. Palogrande is a residential area influenced by one of the most important avenues connecting Palogrande with downtown Manizales to the northwest. Cars

fueled with gasoline and public transportation fueled with diesel are the principal air pollution sources in all stations evaluated. A real-time PM₁₀ analyzer (DustTrak™ Aerosol Monitor model 8520) was implemented in order to determine diurnal PM₁₀ profiles and establish critical periods of pollution. The equipment was set up to analyze PM₁₀ concentrations in air each 30 seconds during 24 h. Samples were collected during September, 2010 and July, 2011.

In order to analyze natural SO₂ emissions from the Nevado del Ruiz volcano, the WRF/Chem model was evaluated. Due to the complex topographic conditions (zone influenced by the Central range of the Andes) and the use of input meteorological data from GFS model, three nested domains were defined (Figure 1b). Two 24 h periods were simulated including only daily SO₂ emissions from the volcano, at a constant rate of 9.1 kg SO₂ s⁻¹.

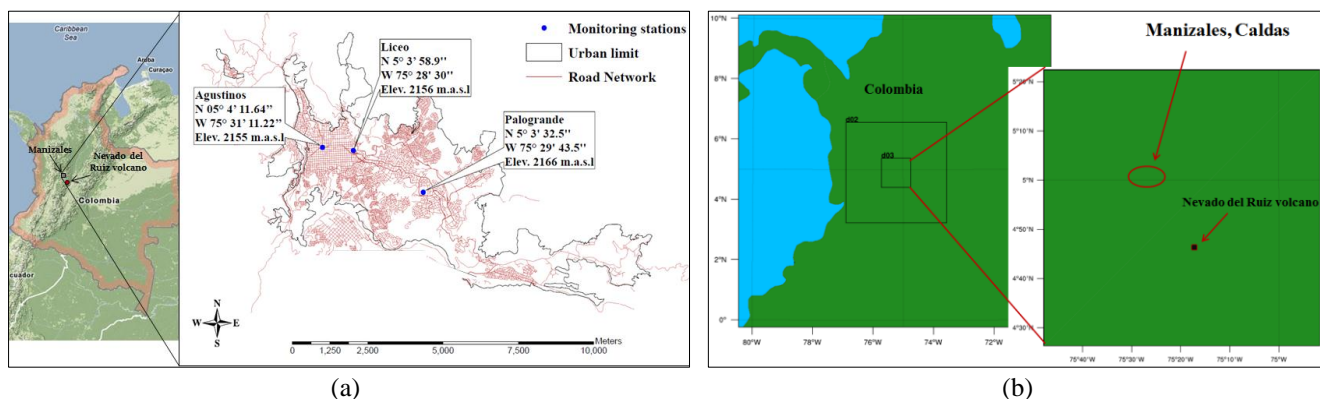
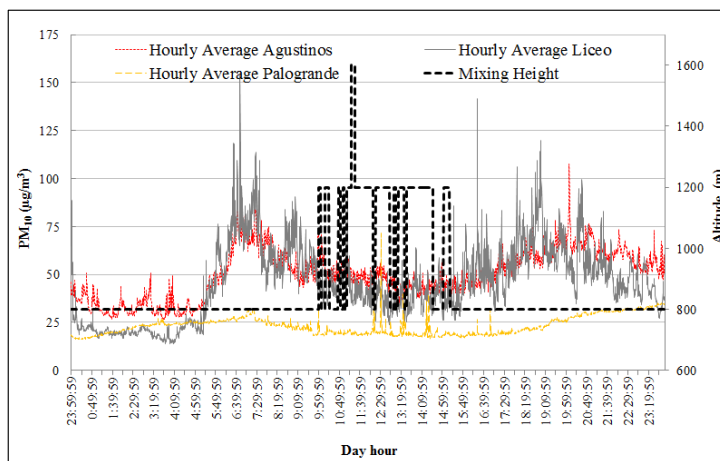


Figure 1. PM₁₀ sampling stations and simulation domains used in WRF/Chem modeling. a) Manizales map and PM₁₀ stations b) Nested domains defined for WRF/Chem simulation.

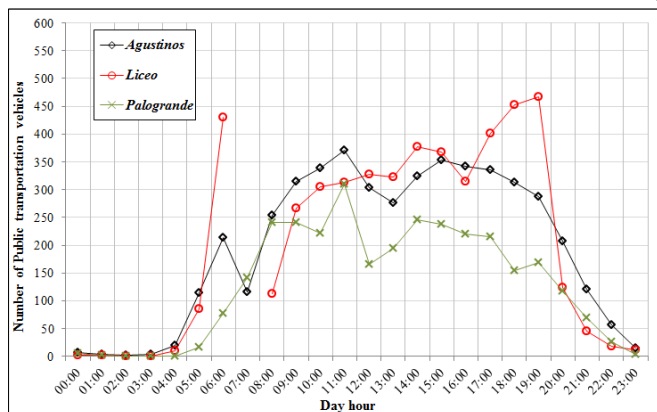
Results and discussion

Emissions from mobile sources were strongly associated with higher increments in PM₁₀ daily profile, characterized by two diurnal critical periods of PM₁₀ pollution: early morning (from 6:30 a.m. to 8:30 a.m) and early evening (5:45 p.m. to 7:45 p.m). Figure 2 shows diurnal variations of PM₁₀ concentration (Fig 2a), public transportation traffic (Fig 2b) and automobile traffic (Fig 2c) at the three stations analyzed. Higher levels of PM₁₀ were observed in the downtown area (Agustinos and Liceo) in comparison with Palogrande station; this behavior was associated with higher public transportation traffic at downtown with respect to Palogrande (Fig 2b). Mean 24 h PM₁₀ levels showed higher values at Agustinos (50 μg m⁻³), followed by Liceo (45 μg m⁻³) and lower levels at Palogrande (23 μg m⁻³). Previous studies have hypothesized that diesel and gasoline combustion are the principal sources of emissions in downtown Manizales (Aristizábal et al., 2011; González and Aristizábal, 2012). Differences in PM₁₀ levels between Agustinos and Liceo were associated with higher sloped roads around Agustinos and the subsequent increment in fuel consumption requirements.

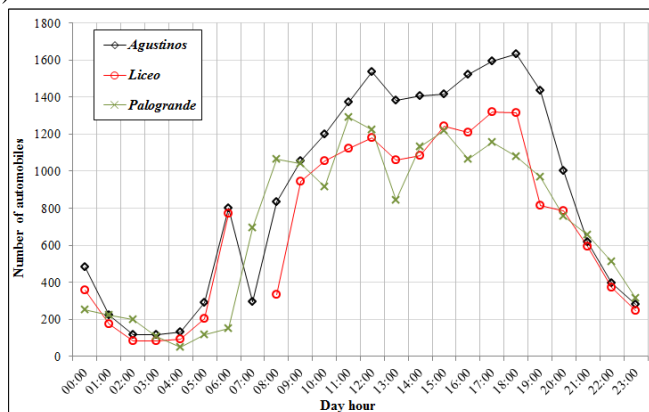
Levels of PM₁₀ showed a reduction during midday peak traffic hours. This is because the relatively high mixing height (MH) during midday rush hour (reaching 1200 m and 1600 m), in comparison with 900 m obtained for the other periods of the day (Fig 2a). Height values were calculated using the simplified methodology of Spadaro (1991) cited by Turtós et al. (2006), which uses the atmospheric stability classes and wind velocity to define an approximated value of MH.



(a)



(b)



(c)

Figure 2. PM_{10} and vehicular diurnal profiles at downtown (Agustinos and Liceo) and central area (Palogrande) of Manizales city. a) PM_{10} diurnal variation. b) Diurnal variation of public transportation and similar heavy duty vehicles (not trucks). c) Diurnal variation of automobiles.

Suspended particles have been found to be associated with increased sulfate concentrations in rain through scavenging processes, and are defined as one of the precursors to the formation of acid rain phenomenon in Manizales (González and Aristizábal, 2012). A Previous study reported that molar concentration of sulfate in PM_{10} (mean $28.5 \mu\text{mol m}^{-3}$) was three times higher than the next most concentrated ion nitrate, suggesting predominance of SO_2 emissions coming from three principal sources (González and Aristizábal, 2012): vehicular emissions due to Colombian fuels with important sulfur content, industrial emissions at southeast of the city, and sulfur gas emissions from a nearby active volcano. According to Calvo et al. (2012), SO_2 is one of the main contributors to the formation of sulfate aerosols in the atmosphere, which helps to explain the predominance of sulfate in PM_{10} of Manizales. These SO_2 sources have been proposed as the principal causes of acid rain formation in this humid tropical mountain city – with mean VWM-pH levels of 4.9 units (González and Aristizábal, 2012). However, little has been established regarding to understand the dynamics of these emissions in the formation of acid rain and the following effects in air quality of Manizales.

The plume dispersion of SO_2 was analyzed using WRF/Chem model, taking into account the significant contribution of SO_2 emission from the nearby volcano, Nevado del Ruiz (located 27 km southeast of the city). Figures 3 and 4 show the dispersion of SO_2 emissions from Nevado del Ruiz volcano, modeled for two 24 h periods: October 15, 2010 (Fig. 3) and December 14, 2010 (Fig. 4). Due to the lack of information about emission inventories in the city and the nonexistence of subroutines to model air quality in Manizales, it was necessary to modify the subroutine emiss_v3 used for the NEI in the WRF/Chem model, including a constant rate of emission equivalent to $9.1 \text{ kg } SO_2 \text{ s}^{-1}$ ($786.2 \text{ ton day}^{-1}$). Results obtained for the two periods showed a general behavior of plume dispersion of SO_2 towards Manizales, suggesting that volcanic SO_2 is

a significant source of acid rain formation in the city, and plays an important role in atmospheric chemistry processes around Manizales environment. These preliminary results highlight the importance of modeling air quality in Manizales and surrounding areas, as a tool to understand atmospheric chemistry dynamics, aerosol exposure, sulfate and its role in particle formation, particle scavenging and acid rain formation.

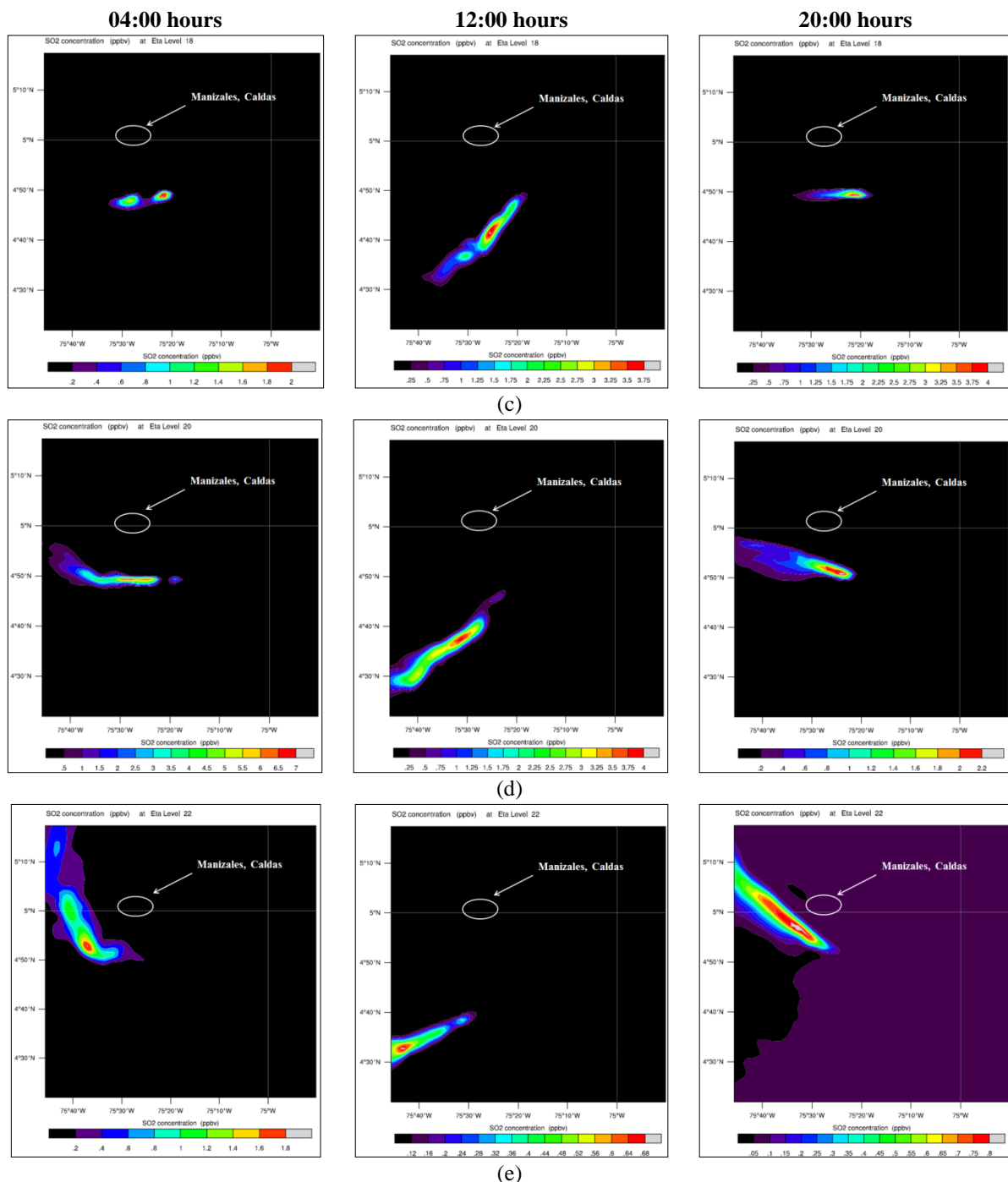


Figure 3. Plume dispersion of SO₂ (ppbv) from Nevado del Ruiz volcano during October 15, 2010. Variation for different vertical coordinates (Eta): (a) Eta 18. (b) Eta 20. (c) Eta 22.

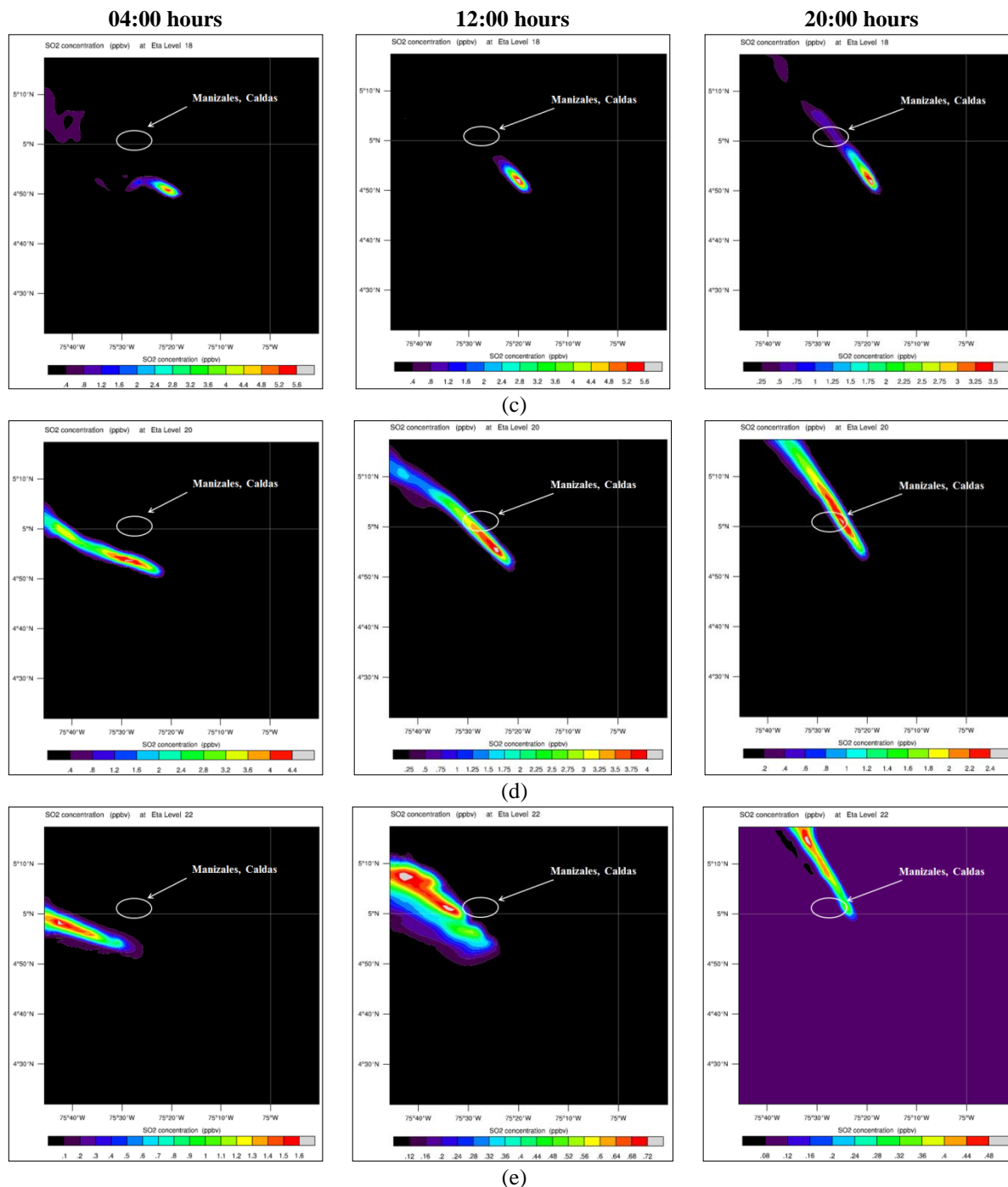


Figure 4. Plume dispersion of SO₂ (ppbv) from Nevado del Ruiz volcano during December 14, 2010. Variation for different vertical coordinates (Eta): (a) Eta 18. (b) Eta 20. (c) Eta 22.

Conclusion

Emissions from mobile sources, mainly derived from public transportation, were highly associated with PM₁₀ levels and its diurnal profiles in the densely populated mid-sized city of Manizales. The contribution of diesel and gasoline combustion emissions to the air quality in the city showed higher levels of PM₁₀ pollution in the downtown area, where vehicular traffic increased with respect to central area of Manizales. As well as, the analysis of SO₂ emissions from the nearby active volcano, through the application of WRF/Chem model, revealed that volcanic SO₂ is a significant source of acid rain formation in the city and has an important role in atmospheric chemistry processes around Manizales. These preliminary

results suggest factors important to modeling both anthropogenic and natural emissions in the mid-sized Andean city of Manizales.

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