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Air quality assessment in a highly industrialized area of Mexico: Concentrations and sources of volatile organic compounds

Elizabeth Vega, Gabriela Sánchez-Reyna *, Virginia Mora-Perdomo, Gustavo Sosa Iglesias, José Luis Arriaga, Teresa Limón-Sánchez, Sergio Escalona-Segura, Eugenio Gonzalez-Avalos

Instituto Mexicano del Petróleo, Eje Central Lázaro Cardenas 152, Col. San Bartolo Atepehuacan, Distrito Federal C.P. 07730, Mexico

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ABSTRACT

Parallel to the economical benefits brought by the oil industry in Mexico, there have been some negative environmental effects due to emission of pollutants to the atmosphere. Salamanca, a city located inside one of the most important industrial corridors of the country, has been frequently affected by elevated concentrations of sulfur dioxide and particle matter. However, little is known about volatile organic compounds (VOCs), which in this study are analyzed along with criteria pollutants and meteorological parameters during February–March 2003 at urban, suburban and rural sites. Although sulfur dioxide average levels were ~0.017 ppm, a high concentration event (~0.600 ppm), attributable to emissions from the oil refinery and the thermoelectric power plant, was observed at the urban site at night time. The VOCs concentration varied from 170 ± 50 ppbC (rural) to 699 ± 212 (urban) and were constituted by 40% alkanes, 13% aromatics, 11% olefins and 11% of halogenated. The most abundant species were propane (167 ± 40 ppbC), *n*-butane (91 ± 23 ppbC), toluene (51 ± 10 ppbC) and *i*-pentane (44 ± 7 ppbC), that are related to combustion processes. Freon-114, methyl bromide and 1,2-dichloroethane which are likely emitted by application of pesticides, soil fumigation and fabrication of chemicals, showed high concentrations (48 ± 10, 50 ± 10 and 32 ± 6 ppbC respectively) in the rural sites, highlighting the importance of control measurements implementation for these species, as they represent a potential hazard for public health. Moreover, these halocarbons showed similar ratios regardless the monitoring site, suggesting same source. Modeling results indicated that meteorological conditions generally transport air masses to the northeast rural areas where the highest concentrations of ozone were calculated.

1. Introduction

Over the last century, the oil industry has emerged as the primary energy source [1]. Currently, the life style of human societies depends on energy (electricity generation, natural gas, crude oil and its refined products, coal, etc.); without it, societies as we know them would collapse. Even though the oil industry has made important contributions to the global economy, usually this has been accompanied with negative environmental impacts from a variety of activities such as oil drilling, refinery, oil spillage, gas and flaring. Moreover, deterioration of the environment may not be circumscribed to the local scale, it can reach regional and global extent due to the emission of precursors of secondary pollutants and chemical species that contribute enhancing global warming and stratospheric ozone depletion [2–4]. Public health may also be affected if emissions contain toxic or carcinogenic species [5]. In recent years concern over public health and environmental protection has become a critical issue, this means that a growing amount of investment and effort is dedicated to reconcile the environment and development of countries.

The economy of Mexico strongly depends on oil industry; in 2005 the primary distillation capacity (1540 MBD) ranked the country on the top 15 worldwide and 4 in Latin America. The crude is processed in 6 oil refineries which mainly produce gasoline, diesel, jet fuel, coal, asphalt, and lubricants. The third most important refinery is the Ing. Antonio M. Amor, which processes 197 MBD [6]. The refinery and a variety of industries constitute one of the most important industrial corridors of Mexico, known as the Bajío Industrial Corridor (BIC) located in the State of Guanajuato, in the central area of the country (Fig. 1). The BIC has nearly 465 industries, from medium to large size, including Chemical, Power Generation, Food Processing, Textile and Metal-mechanic [7].

The Salamanca city, with 250,000 inhabitants, is located at 20°34′09″N latitude and 101°11′51″W longitude, at 1720 m above mean sea level [8]. The Salamanca municipality encompasses a total area of 774 km^2. The agriculture is now the second most important economical activity, with a designated area of about 80% of the municipality. The impact of agriculture on the environment is important, especially for the use of fertilizers, pesticides,

* Corresponding author. Tel.: +52 55 91757558.
E-mail address: gsanchez@imp.mx (G. Sánchez-Reyna).

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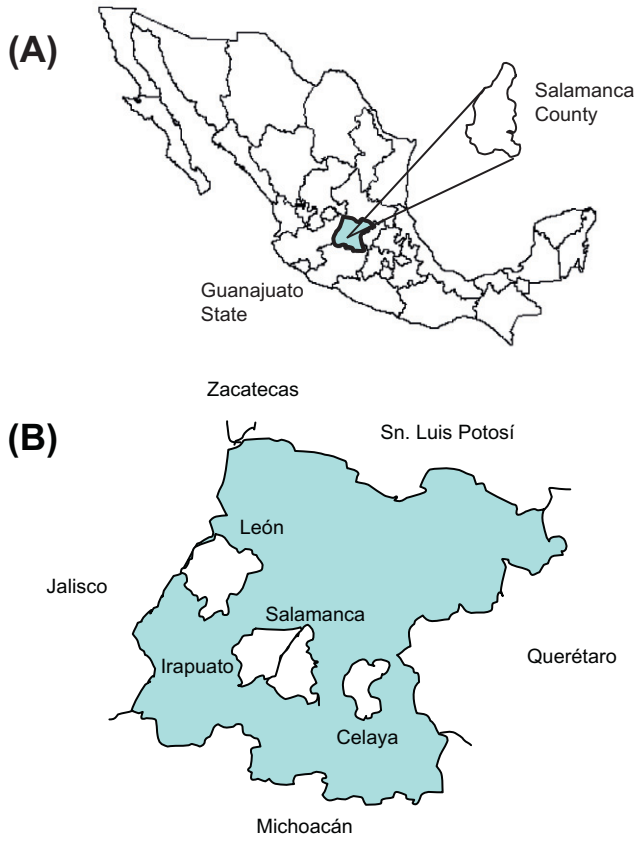

Fig. 1. Geographical location of: (A) Salamanca County and (B) The Bajío Industrial Corridor.

deforestation in the uplands and post-harvesting burning. The biggest impact to the atmosphere is represented by the post-harvesting burning, due to the emission of large amounts of ozone precursors and particulate matter [8].

According to the 2000 BIC Emissions Inventory, the emissions of particles (PM_{10}), sulfur dioxide (SO_2), carbon monoxide (CO), nitrogen oxides (NO_X) and hydrocarbons (HC) were 71,443, 112,480, 1,650,772, 142,183 and 260,296 tons per year, respectively. It is estimated that PM_{10} are released to the atmosphere mainly by commercial and service activities, SO_2 and NO_X by electricity generation, and CO and hydrocarbons by vehicle exhaust. Salamanca contributes with 18% of PM_{10}, 92% of SO_2, 8% of CO and HC and 14% of NO_X of the total BIC emissions. Thus, Salamanca is by far the major generator of SO_2 emissions in the region; while other cities release ozone precursors [8].

Parallel to the economical development of the BIC, there have been some adverse environmental impacts which have brought the attention of government agencies, civil and private associations. As a result, since 2000 a Monitoring Network in Salamanca routinely measures CO, SO_2, NO_2, O_3, and PM_{10}. According to local environmental authorities, the SO_2 air quality standard, AQS, (0.13 ppm in a 24 h average, no more than once per year) was exceeded 13%, 24% and 22% of days in 2000, 2001 and 2002 respectively in downtown Salamanca, mainly during winter. The exceedences of other gaseous pollutants is less frequent, for instance, NO_2 and CO have been practically below their AQS (0.21 ppm, 1 h average, and 11 ppm in 8 h average respectively) [8].

Although total mass of criteria pollutants is routinely measured, little is known in this highly industrialized region about the gaseous and particle contaminants that are not included in the local monitoring network, such as the volatile organic compounds (VOCs). The negative effects of VOCs on the environment and public health are well documented. From the environmental point of view, some VOCs (i.e. olefins and aromatics which are mainly anthropogenic) are reactive species that break out the natural equilibrium of generation–destruction of tropospheric ozone, thus the concentrations of this compound and other photochemically-produced pollutants are frequently high in the urban environment. Besides, the reactive organic gases can partition into the aerosol phase generating secondary organic aerosols. Other important group of VOCs is constituted by the halogenated species, which are originated almost exclusively from anthropogenic emissions due to its usage as an industrial solvent and degreaser. Some of these compounds have been the focus of intensive research, such as the chlorofluorocarbons due to their participation in the stratospheric ozone depletion. In addition, many of the halogenated species represent a potential hazard to human health due to the toxic and/or carcinogenic effect [9–15].

The public opinion on air quality deterioration in Salamanca, encouraged PEMEX (National Oil Company) to support an extensive 2-week monitoring field study with the aim of augmenting the knowledge of sources, transport and fate of air pollutants in the region, therefore effective control measurements of atmospheric pollution can be designed. The main findings of such campaign are presented in this work, particularly the chemical characterization, distribution and origin of VOCs, as well as the meteorological parameters that influence the dilution and transport of pollutants. The later was also estimated by applying a 3 D air quality model.

2. Field campaign

As an outcome of a collaborative effort, the Instituto Mexicano del Petroleo (IMP), the Instituto de Ecología de Guanajuato, the Instituto de Investigaciones Científicas at the Universidad de Guanajuato, the Centro de Ciencias de la Atmósfera at the Universidad Nacional Autónoma de México, the Patronato de Salamanca, and the Ing. Antonio M. Amor Oil Refinery, with the PEMEX sponsorship, carried out a field monitoring campaign, from February 21 to March 9 2003. The main objectives were to chemically characterize the air pollution in the urban area of Salamanca in both the particle and gas phases, and to assess the potential impact of pollutants in the regional scale. The interested reader can consult Vega et al. [16] for the particulate matter results found in this region.

The first week of measurements was focused on the characterization of urban air quality; while the second week was designed to evaluate the regional impact of urban emissions. The monitoring sites of the urban domain (10×10 km) and of the regional domain (80×80 km) are shown in Fig. 2A and B. Table 1 shows site location, description, sampling period and measurements performed.

Three automated samplers (VOCCS-ANDERSEN and AVOCS-ANDERSEN models) with a Viton diaphragm pump were used to collect VOCs (defined in this work as hydrocarbons from C_2 to C_{12}) in canisters over 12 h period (0600–1800 and 1800–0600 local time) in the urban sites and 24 h period in the rural/boundary sites. A total of 80 canisters were analyzed in the Laboratory by cryogenic pre-concentration/high-resolution GC technique, similar to the TO-14A protocol [17].

Water Sep-Pak DNPH-Silica cartridges were used to trap carbonyl species. Twelve samples were taken during the first week of the campaign at Cruz Roja (CR) urban site from 0600 to 0900 and from 1200 to 1500. The derivatives were eluted and analyzed by HPLC with UV photodiode array detector according to the TO-11A protocol [18]. Criteria pollutants were measured using a