

Article

Ozone concentrations *in situ* in the Mexico City basin forests and influence of elevation

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Abstract:

The presence of photochemical pollutants in the Mexican Basin is a reality and the damage they cause to human health and vegetation is evident. Lack of data on ozone concentrations in the forests of the Mexico City Basin was the main reason to carry out this survey in three forested areas: *El Ajusco* (AJU), *Desierto de los Leones* (DDL) and *Izta-PopocatépetI* (IZP). CanOxy Plate[™] monitors were used and exposed for three-weekly periods during 14 months (November 10th, 2004 to

January 20th, 2006), in nine monitoring plots. The ozone concentrations recorded in the three forested areas were between 15.41 and 53.8 ppb. Two peaks with higher ozone concentration were identified, one in August and second one in November, 2005. The average ozone concentration for each area was 32.87 ppb for AJU, 28.34 for DDL and 28.60 ppb for IZP. The DDL and IZP ozone concentrations recorded were lower, in spite of the proximity to the emission source in the case of the first area; the reason was due to two of the monitoring plots were located leeward, it means, they were not exposed to the polluted air masses from Mexico City. For IZP, ozone concentrations were similar to the ones from the DDL, highlighting winds direction. Ozone concentrations were higher in the way that altitude increased. Exposure to the polluted air masses, wind and altitude roles were tested.

Key words: *Ajusco*, photochemical pollutant, *Desierto de los Leones*, *Izta-Popocatépetl*, passive monitoring, ozone.

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Introduction

The ozone that is present in the stratosphere provides protection to the living beings against the short-wavelength UV solar radiation in the troposphere. However, it is a photochemical pollutant as well as a greenhouse gas (Booker *et al.*, 2009). Out of the many oxidants existing in polluted atmospheres across the world, ozone (O_3) was one of the first pollutants to be identified as producing damage in agricultural crops (Ashmore, 2005). Treshow and Stewart (1973) determined the damage threshold for this chemical compound in 70 herbaceous, shrub and woody species, most of which exhibited damage at concentrations of 15 ppmh. Miller (1992) and Miller *et al.* (1963, 1992) also detected ozone-induced damages in *Pinus*

ponderosa Douglas ex. C. Lawson forests of the United States of America, particularly in sensitive taxa. Naveh *et al.* (1980) and Alonso *et al.* (2003) cite damages in *Pinus halepensis* Mill in the Mediterranean coast.

In regard to Mexico, the first reports of ozone-induced damage in forest species date back to the 1980s, when they were found in *Pinus hartwegii* Lindl. (Bauer *et al.*, 1985; Hernández-Tejeda and Bauer, 1986) and in *P. montezumae* (Hernández-Tejeda and Bauer, 1982; Hernández-Tejeda and Bauer, 1984) in the forested areas of the south and southwest of the Mexico City Basin. In subsequent studies, the ozone-induced damage was confirmed in various vegetal taxa of the Valley of Mexico (Bauer and Krupa, 1990; Bauer and Hernández-Tejeda, 2007). At the same time, an unprecedented mortality in *Abies religiosa* (Kunth) Schtldl. & Cham. was documented in the same region (Vázquez, 1987; Alvarado *et al.*, 1991, 1993; Alvarado and Hernández-Tejeda, 2002). Unfortunately, data from ozone monitors were not available during those years, but there was evidence that this pollutant was involved (Bauer and Krupa, 1990). Today, ozone is recognized as the main atmospheric pollutant in the urban and rural areas, as it affects both human health and material goods (Ashmore, 2005).

Most prominent among the ozone-induced damages to the vegetation are the disturbance of biochemical processes like photosynthesis and breathing (Guderian, 1985; Fumagalli *et al.*, 2001); of biological processes such as reproduction (Wolters and Martens, 1987; Hernández-Tejeda *et al.*, 2001; Hernández-Tejeda, 2014), as well as structural damage (cuticular degradation) (Grulke *et al.*, 2004).

A large amount of evidences, generally from studies of seedlings, indicate that ozone may impact the growth of forest trees (Kolb *et al.*, 1997). Few researches have been documented under field conditions, and among the main damages cited are defoliation (Zierl, 2002; Paoletti, 2006; Ferreti *et al.*, 2007a, 2007b) and decreased radial growth (Peterson *et al.*, 1991; Somers *et al.*, 1998). Other studies indicate effects on the development of the foliage of temperate forest trees, e.g. leaf chlorosis, premature fall of the needles, followed by a premature senescence

process which leads to the partial or total death of individuals in large vast forest areas (Miller *et al.*, 1994; Grulke and Lee 1997; Skelly *et al.*, 1997; Somers *et al.*, 1998; Krupa, 1999; Hernández-Tejeda, 2014).

In the United States of America huge ozone-induced losses of crops were estimated (US EPA, 1996). Unfortunately, the losses of woody species are unknown (Chappelka and Samuelson, 1998).

In most of the cited studies, the effects of pollutants, particularly ozone, are qualitative (London, 1985). Traditionally, ozone concentrations are measured using automated methods, and although these are highly accurate, these devices are expensive and require to be put in a special place where they can be protected against vandalism and against the climate conditions. Furthermore, a permanent source of electric energy must be available to ensure their proper functioning.

This evidenced the need to have a practical system to quantify the ozone in remote areas, especially in the microclimate that prevails within the canopy. This system uses passive monitors that are small –and therefore unconspicuous–, have a low-cost, and, most importantly, do not require a continuous power supply (Krupa and Nosal, 2001). All this allows a high spatial resolution and renders them very adequate for studying the air pollution and afford the possibility of covering large surface areas. Because of these attributes, the passive monitors have become an attractive option for estimating the ozone concentrations in forested areas (Cox and Malcolm, 1999). Nevertheless, there are also disadvantages, including their limited temporal resolution; therefore, one-month or longer exposures are not recommended (Ferreti *et al.*, 2007); although the detection boundaries are reliable, they are approximate, and the laboratory analyses take a long time.

One of these low-cost monitors is known as Can Oxy PlateTM (Cox and Malcolm, 1999). The use of this technology makes it possible to quantify the tropospheric ozone in forest areas, in order to obtain real, reliable information about *in situ* ozone concentrations.

It should be noted that the symptoms developed by the presence of ozone in the vegetation is useful to determine the current status, the changes and the tendencies toward leaf damage, and the optimal development and growth of the vegetal species (Stolte, 1996).

In Mexico, passive monitoring of ozone in forest areas, although very recent, is very scarce (González *et al.*, 2010; Hernández-Tejeda, 2014). The information registered with this type of monitors in certain forests of the Basin has not been formally published; in order to fill this void, we decided to publish this paper containing data collected approximately ten years ago.

The purpose of this study, which is based on the hypothesis that air pollution with ozone is responsible for the decline of fire-pine forests in the Mexico City Basin (Alvarado-Rosales *et al.*, 1991, 1993; Alvarado-Rosales and Hernández-Tejeda, 2002; Alvarado and Saavedra, 2007), was to determine the *in situ* tropospheric ozone concentrations in sacred fir (*Abies religiosa* (Kunth) Schltdl. & Cham.) and pine (*Pinus* sp.) forests in three forested areas of the Mexico City basin: *Desierto de los Leones, Ajusco* and *Izta-Popocatépetl*, as well as the altitude, the distance, and the exposure of the study areas to the source of emission of the ozone precursors.

Materials and Methods

Study areas

Physiographically, the Mexico City Basin is the southern portion of the Mexican High Plateau, located at an altitude of 2 250 to 2 400 masl; it is surrounded by mountain chains of the Neovolcanic Axis reaching heights of up to 5 465 meters above the Plateau, and has an elliptical shape that measures 125 km from north to south, and 90 km from west to east, and a surface area of 8 050 km². The Basin consists of Mexico City (1 503 km²) and the southern regions of the state of *Hidalgo*, the southwest of *Tlaxcala*, and the northeast of the State of Mexico (Gio-Argáez *et al.*, 1989). It contains one of the largest urban complexes, where air pollution issues

have worsened in the last few years. Within this stretch, three forested areas were selected for the purpose of monitoring ozone concentrations: the *Desierto de los Leones* Cultural and Recreational Park, *Ajusco*, and the *Izta-Popocatépetl* Park (Figure 1).



Source: Modified by Marín *et al.*, 2002.

Figure 1. Location of the forested areas where *in situ* ozone concentrations were monitored.

Ajusco (AJU). This forest stands 38 km south of downtown Mexico City and reaches its highest altitude, 3 930 m, at *Pico del Águila*, covering a surface area of 920 hectares. The climate depends on its latitude (19°12′30″ N) and on the altitude of the group of peaks on which it is located; locally, it also depends on the presence of other high peaks, such as *Sierra de las Cruces*. The dominant climates are Cw,

temperate with summer rains; Cf, temperate with rains throughout the year in the higher regions, and Et (tundra climate, prevalent in the highest areas (3 000 m), with a mean annual precipitation above 1 200 mm and a mean temperature of 13 °C) (White *et al.*, 1990; Reyes, 1981).

Desierto de los Leones (DDL). This park is located 25 km southwest of Mexico City, between the coordinates 19°20′18″ and 19°15′40″ N, and 99°17′45″ and 99°20′00″ W, and it covers a surface area of 1 529 ha (Conanp-Semarnat, 2006). Its altitude ranges between 2 700 and 3 700 m. The prevalent climate is cold, humid temperate, with summer rains. The mean annual temperature ranges between 7 and 15 °C degrees (Alvarado *et al.*, 1991), and the mean annual precipitation is 1 200 m (Cibrián, 1989). As an effect of the exposure to sun rays, the period with the highest temperatures is April through June (Melo, 1978).

Parque Izta-Popocatépetl (IZP). This area is located on the Neovolcanic Axis, 70 km southeast of Mexico City, between the coordinates 18°59'00" - 19°16'25" N and 98°34'54"- 98°42'08" W, and has a surface area of 25 679 ha (UACH-Semarnat, 1999). Its altitude ranges between 2 600 and 3 600 m up to *Paso de Cortés*, but it includes some much higher points (>5000). The climate of the area belongs to two types: a) very cold, with summer rains and a mean annual temperature below -2 °C, and b) semi-cold subhumid, with a mean annual temperature of 5 to 12 °C and, during the coldest month, of 3 to 18 °C. The mean annual precipitation is 928 mm, and the area covers several municipalities in the states of *Puebla, Estado de México* and *Morelos* (Melo, 1977).

Passive monitoring

Ozone concentrations were measured at three sites located at different altitudes above the sea level during a 14-month period, from November 10, 2004, to January 20, 2006, in the three selected forested areas (DDL, AJU and IZP). The passive ozone monitors used were CanOxy Plate[™] (Cox and Malcolm,

1999). In each area, three permanent monitoring sites were established at different altitudes (high, medium and low), with various exposures to winds coming from Mexico City (Table 1).

	•	•		
Forested area	Monitoring site and	Altitude	Exposure to	
Forested area	acronym	(m)	Mexico City	
	El Jacalito (EJ)	2927	Windward	
Ajusco(AJU)	km. 19 (K19)	3143	Windward	
	Valle del Tezontle (VT)	3432	Windward	
	El Pantano (EP)	3060	Leeward	
Desierto de los Leones(DDL)	Presa Oyameles (PO)	3265	Leeward	
	Cruz de Coloxtitla (CC)	3590	Windward	
	La Plantación (LP)	2888	Windward	
Izta-Popocatépetl(IZP)	La Curva (LC)	3356	Leeward	
	Paso de Cortés (PC)	3685	Windward	

Table 1. Forested area, location, altitude and exposure of the nine ozone

 monitoring sites in the Mexico City Basin.

Each monitor (one per site) was placed at a height of 2 m within the canopy and was replaced every three weeks. In order to avoid biases due to the natural oxidation (not ascribable to ozone) of the reagent used in the monitors, completely sealed control passive monitors were exposed. The values obtained from the monitors exposed in field were then adjusted according to the values registered by the sealed monitors.

A total of 252 monitors were exposed in the course of the study. All the monitors collected in field were transported and stored in hermetically sealed plastic bags, each containing activated charcoal in a small mesh bag. The passive monitors,

whether exposed or used as controls, were analyzed at the laboratory of Dr. Roger M. Cox, MD, in Fredericton, New Brunswick, Canada.

Analysis of the spatial and seasonal variation in the concentration of ozone

The data registered for ozone concentrations using passive monitors during 14 months were analyzed with the statistic package SAS (version 9.4), using the variance analysis of repeated measures (Moser *et al.*, 1990; Gumpertz and Brownie, 1993), i.e., by taking measurements on different dates at the same sites, taking into account the locality (L) and the altitude (E), according to the model proposed by Hernández-Tejeda (2014):

$$Y_{ijkl} = \mu + L_i + E_{j(i)} + a_{k(ij)} + F_l + (F^*L)_{li} + F^*E(L)_{li(j)} + \beta_{ijkl}$$

Where:

 Y_{ijkl} = Value observed on the I^{th} date in the k^{th} repetition on the j^{th} elevation of the i^{th} locality

 $\mu + L_i + E_{j(i)} + a_{k(ij)}$ = Represent the effects between locations, with

 μ = Mean ozone concentration

 L_i = Effect of the *i*th locality

 $E_{j(i)}$ = Effect of the j^{th} elevation within the i^{th} locality

 $a_{k(ij)}$ = Error associated with the k^{th} repetition on the j^{th} elevation within the i^{th} locality

 $F_{l} + (F^{*}L)_{li} + F^{*} E(L)_{li(j)} + \beta_{ijkl}$ = Represent the effects within the subjects (localities) associated with ozone concentration, with

 F_{l} = Effect of the I^{th} monitoring date;

 $(F^*L)_{li}$ = Effect of the interaction between the I^{th} monitoring date and the i^{th} locality $F^* E(L)_{li(j)}$ = Effect of the interaction between the I^{th} monitoring date and the j^{th} altitude within the i^{th} locality

 β_{ijkl} = Sampling error associated with each monitoring date

The decision was made to use this statistical model because of the need to determine whether or not there were differences in ozone concentrations registered in and between the three studied localities. The model contemplates the monitoring dates and the altitudes where the passive monitoring of ozone was carried out.

The minimum and maximum ozone concentrations during the study period were estimated. Using the mean concentrations, the forested area and the period with the highest concentrations through 14 months of assessments were determined. Using the SASTM (Statistical Analysis System) statistic software, version 9.4, the total, maximum, minimum and mean ozone concentrations and other descriptive statistics were estimated for the 21 monitoring dates in the three forested areas, in order to determine whether or not there were significant differences between them. Furthermore, according to their exposure to winds coming from Mexico City, the mean ozone concentrations for each of the nine monitoring sites were compared. Finally, in order to know the role of the altitude and distance from the source of emission of the ozone precursors, the ozone concentrations of the nine monitoring sites were compared.



Results and Discussion

Ozone concentrations during the study period

The presence of ozone; the maximum, minimum and mean ozone concentrations (ppb), and other statistics for the period between November, 2004, and January, 2006, was registered on all monitoring dates, with minimum and maximum values ranging between 15.41 and 53.8 ppb, respectively (Table 2). On the other hand, the mean ozone concentrations ranged between 21.05 and 40.36 ppb.

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Date	n	Mean	S.E. ¹	VC ²	Minimim	Maximum
Nov 10, 04	9	30.14	2.0	19.89	21.66	39.52
Dec 03, 04	8	24.11	2.02	23.70	17.85	34.56
Dec 20, 04	8	22.37	1.30	16.44	15.41	26.40
Jan 11, 05	9	30.67	1.27	12.40	24.72	37.32
Feb 03, 05	8	25.82	1.65	18.05	17.55	33.96
Feb 22, 05	9	21.05	1.12	15.91	15.87	28.01
Mar 15, 05	9	24.89	0.85	10.27	21.74	29.84
Apr 07, 05	9	32.89	1.71	15.61	24.65	40.29
Apr 27, 05	9	33.78	1.24	10.97	26.70	38.61
May 17, 05	7	35.44	20.9	15.60	27.77	41.42
Jun 07, 05	7	28.45	1.91	17.81	21.07	35.09
Jun 27, 05	9	27.03	2.18	24.24	20.83	36.32
Jul 19, 05	8	28.88	2.20	21.55	22.73	36.86
Aug 11, 05	8	29.48	4.35	41.76	15.95	47.62
Sep 01, 05	7	30.26	5.96	52.16	16.17	53.80

Table 2. Main descriptive statistics of ozone concentrations (ppb) registered on different monitoring dates (November 10, 2004–January 20, 2006)

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Sep 20, 05	9	26.96	2.11	23.44	16.62	33.49		
Oct 11, 05	8	39.27	2.08	14.96	32.89	47.38		
Nov 15, 05	9	40.36	3.69	27.41	18.23	53.80		
Dec 07, 05	9	29.10	1.26	13.01	22.81	34.26		
Dec 28, 05	9	26.55	1.31	14.83	22.65	32.81		
Jan 20, 06	9	39.54	1.86	14.08	29.92	47.32		

¹S.E. = Standard error; VC^2 = Variation coefficient.

Two maximum concentration peaks were observed at *Ajusco*: one in August (47.64 ppb) and the other in November, 2005 (50.28 ppb). However, the values registered in the two other forested areas were also significant on dates close to these (Figure 2).



Figure 2. Mean ozone concentrations registered on the different monitoring dates for the three forested areas (November 2004–January 2006).

The ozone concentrations registered between October-November, 2005, and January, 2006, turned out to be significantly higher than the rest (p<0.0001) (Figure 3).



(Different letters indicate significant differences, with p < 0.0001).

Figure 3. Mean ozone concentrations and standard error associated to the various monitoring dates (November 10, 2004–January 20, 2006).

In situ ozone levels agree with the records indicating high levels of this pollutant for the *Ajusco* and *Desierto de los Leones* regions, especially during winter, when precipitation events are less frequent (Miller *et al.*, 1992), and during the dry season when the air temperature is high and the solar radiation is more intense, as is the case in the capital city of the country (November–April) (Schreffler and Evans, 1982; Jáuregui, 1993b). Jáuregui (1971) points out that the oxidant atmosphere prevails in Mexico City during the months when exposure to the sun rays is abundant, whereas during the rainy season (May–October) the ratio of reducing agents to oxidants increases.

Mean ozone concentrations per forested area and influence of the exposure

The mean ozone concentration of the three forested areas was above 28 ppb (Table 3).

Forested area	n	Mean	S.E ¹ .	Minimum	Maximum	-
AJU	56	32.87a	8.56	19.46	53.80	
DDL	62	28.34b	9.00	15.41	53.80	
IZP	59	28.60b	6.13	16.17	41.42	

Table 3. Main descriptive statistics of ozone concentrations in ppb registered in thethree forested areas of the Mexico City Basin.

AJU = Ajusco; DDL = Desierto de los Leones; IZP = Izta-Popocatépetl; ¹S.E. = Standard error

Statistically, the concentrations registered at AJU were higher (p<0.0001) than those of the other two localities. In the same area, Hernández-Tejeda (2014) registered a higher value (49 ppb), with the same type of monitors, from July, 1997, to November, 1998. There is the possibility that the improvement of the gasolines, along with certain actions by the Government of Mexico City in favor of the environment, may have reduced the ozone concentrations in this locality. However, the symptoms exhibited by pine trees in the area, specifically *Pinus hartwegii*, is one more evidence that the registered ozone levels are the main cause of leaf damage.

Although the concentrations registered at DDL were lower than at *Ajusco*, studies like the one carried out by González *et al.* (2010) support the hypothesis that the decline of the sacred fir is largely due to the chronic ozone concentrations. Unfortunately, this is the only study performed at *Desierto de los Leones* with passive monitors, which were exchanged every two or three weeks at 31 monitoring sites during the period between August 2001 and January 2003; the authors cite a mean concentration of 18 ppb. In the present study, the means for the three forested areas of the Mexico City Basin ranged between 20 and 40 ppb; these concentrations are slightly higher than those documented by González *et al.* (2010). The concentrations at DDL were not as high as those of AJU mainly because of the

exposure of two of the three monitoring sites (*El Pantano* and *Presa Oyameles*),

both of which were located leeward (Figure 4), *i.e.* they did not receive the polluted winds blowing from Mexico City directly. However, Miller *et al.* (1994) registered average ozone concentrations of 16 to 88 ppb per hour between May, 1990, and April 1991, at DDL, using automated electronic means.

As for IZP, no previous publications are available.

Influence of the altitude and distance from the source of emission

Mean ozone concentrations above 24 ppb were registered at all monitoring sites. Table 4 shows the main statistics by site. When comparing the values of the nine monitoring sites, an influence of the altitude gradient was observed, since the ozone concentrations increased in direct proportion to the altitude. This behavior was evident in the three sites located at the highest altitude in the forested areas, where at least two of the monitoring sites located at the lowest altitude (*El Pantano* and *La Plantación*) had significantly lower concentrations than those located at higher altitudes (*Cruz de Coloxtitla* and *Valle del Tezontle*) (Figure 4). This variable has been shown to be decisive for a larger production of tropospheric ozone, for, according to Miller *et al.*, (1994) and Jáuregui (1993b), at a higher altitude there is more ultraviolet light available in the atmosphere, which causes the molecules to increase their photochemical reactivity (actinic flow) through absorption.

It should be noted that the levels of ozone measured at the monitoring sites of IZP were similar to those of DDL, despite the large distance between it and Mexico City (70 km). The climatic characteristics and the presence of numerous sources of emission have a strong influence on the formation and transportation of O₃, and air masses with the highest levels of photochemical oxidants are usually found leeward to the original source of emission (Corona and Calva, 1989; Treshow and Anderson, 1989; Bauer and Hernández-Tejeda, 1986). It has also been evidenced that ozone can be transported to hundreds of miles from the areas where the original precursors are (Miller *et al.*, 1994; US EPA, 1984).

Table 4. Main descriptive statistics of the mean ozone concentrations registered in the nine monitoring sites located at different altitudes in the Mexico City Basin (November 10, 2004–January 20, 2006).

Forested	Monitoring sites	Altitude	ltitude n (m)	Mean	S.E. ¹	V.C. ²	Minimum	Maximum
area	(Name of the location)	(m)						
	Valle del Tezontle	3432	18	35.30	1.73	20.77	24.72	51.66
JU	km. 19	3143	20	32.10	2.03	28.33	20.99	51.66
	El Jacalito	2927	18	31.31	2.13	28.86	19.46	53.80
DDL	Cruz de Coloxtitla	3590	21	35.65	2.01	27.87	15.41	53.80
	Presa Oyameles	3265	20	25.10	1.51	26.82	15.95	40.51
	El Pantano	3060	21	24.11	1.26	24.03	15.87	39.98
IZP	Paso de Cortés	3685	19	30.14	1.44	20.81	20.21	41.42
	La Curva	3356	20	27.06	1.32	21.75	16.17	35.47
	La Plantación	2888	20	28.67	1.38	21.50	19.92	39.92

AJU = Ajusco; DDL = Desierto de los Leones; IZP = Izta-Popocatépetl; ¹S.E = Standard error; ²V.C. = Variation coefficient.



Different letters indicate significant differences, with p<0.0001.

Figure 4. Statistical analysis of the mean ozone concentrations (±standard error) registered at the nine monitoring sites located at different altitudes in the Mexico City Basin.

According to the results obtained, it is evident that the altitude and the pattern of dominant winds circulating from the north-northeast to the south-southwest in the Mexico City Basin (Jáuregui *et al.*, 1981; Jáuregui, 1993a; Miller *et al.*, 1994; Bravo and Díaz, 1996; Raga *et al.*, 1999; Bravo *et al.*, 2001; Jáuregui, 2002), play a crucial role in the concentration and increase of ozone levels in the studied area (Jáuregui *et al.*, 1981; Jáuregui, 1993a; Miller *et al.*, 1994; Bravo and Díaz, 1996; Raga *et al.*, 2001; Jáuregui, 2002).

Conclusions

The ozone concentrations registered in the three forested areas included in the present study ranged between 15.41 and 53.8 ppb, with two high-concentration periods: August and November, 2005.

The highest concentrations were registered at *Ajusco*, and the lowest, at *Izta-Popocatépetl* and *Desierto de los Leones*.

Although *Izta-Popocatépetl* is far from Mexico City, the ozone concentrations there were similar to those found at *Desierto de los Leones*; this proves the importance of the direction of the wind for the transport of the ozone precursors.

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Conflict of interests

The authors declare no conflict of interests

Contribution by author

Dionicio Alvarado-Rosales: review of literature, field work and data analysis; Luz de Lourdes Saavedra-Romero: review of literature, field work and data analysis; Tomás Hernández-Tejeda: field work and data analysis; Roger W. Cox: quantification of ozone concentrations at the laboratory; John. W. Malcolm: quantification of ozone concentrations at the laboratory.