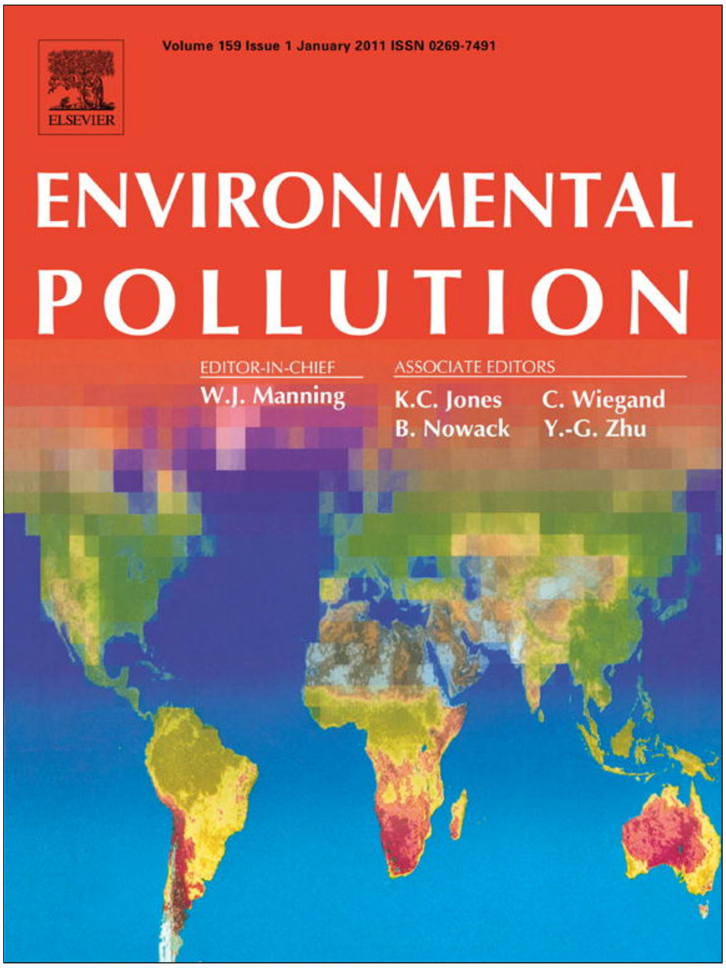

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The role of a peri-urban forest on air quality improvement in the Mexico City megalopolis

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ABSTRACT

Air quality improvement by a forested, peri-urban national park was quantified by combining the Urban Forest Effects (UFORE) and the Weather Research and Forecasting coupled with Chemistry (*WRF-Chem*) models. We estimated the ecosystem-level annual pollution removal function of the park's trees, shrub and grasses using pollution concentration data for carbon monoxide (CO), ozone (O_3), and particulate matter less than 10 microns in diameter (PM_{10}), modeled meteorological and pollution variables, and measured forest structure data. Ecosystem-level O_3 and CO removal and formation were also analyzed for a representative month. Total annual air quality improvement of the park's vegetation was approximately 0.02% for CO, 1% for O_3, and 2% for PM_{10}, of the annual concentrations for these three pollutants. Results can be used to understand the air quality regulation ecosystem services of peri-urban forests and regional dynamics of air pollution emissions from major urban areas.

1. Introduction

The central plateau region of Mexico comprises 33% of the country's population including Mexico City and the surrounding states of Morelos, Mexico, Puebla, Tlaxcala and Querétaro. This region has been designated a Megapolis (PROAIRE, 2007) or an extensive metropolitan area or a group of continuous metropolitan areas (Gottmann, 1961). Mexico City is still one of the most polluted cities in Latin America despite improving air quality trends since the 1990s (PROAIRE, 2007). This air pollution detrimentally affects human health, visibility and damages vegetation (Dockery and Pope, 1994). Regional anthropogenic emissions are largely a result of combustion from power generation, industrial operations, motor vehicle traffic and residential activities (PROAIRE, 2007).

Vegetation helps mitigate some of the negative effects of the urban environment such as mitigating storm water runoff and heat island effects (DeSanto et al., 1976; McPherson and Simpson, 1998; Xiao et al., 1998) as well as sequestering carbon (Nowak and Crane, 2002; Nowak et al., 2002). Studies in Santiago, Chile (Escobedo and Nowak, 2009) and in various cities in the United States (Dochinger, 1980; McPherson and Simpson, 1998; Nowak et al., 2002, 2006) have demonstrated that urban tree cover can also reduce atmospheric pollution such as ozone (O_3), particulate material (PM_{10}), sulfur dioxide (SO_2), carbon monoxide (CO) and nitrogen oxides. Escobedo and Chacalo (2008) have estimated air pollution removal by urban trees in Mexico City and Escobedo et al. (2008) determined that using urban forest management to improve air quality in Santiago of Chile was economically viable.

The effects of peri-urban forests in mitigating air pollution from adjacent urban areas, however, have been less studied. Alonso et al. (2011) used the CHIMERE chemistry transport model and meteorological inputs from the MM5 model, to study a peri-urban forest adjacent to Madrid Spain that functioned as a sink for O_3 and found that evergreens broadleaf trees removed more O_3 than conifers. Other studies such as those of Dominguez-Taylor et al. (2007) and Paoletti (2011) have looked at biogenic emissions and effects of ozone on urban-rural forests.

Since the role of urban vegetation in removing air pollution and subsequent air quality improvement has been well studied, further research is needed to better understand the role of peri-urban forests on air quality in adjacent, highly populated, cities in developing

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countries. Therefore, the specific objectives of this study were to use a coupled model approach to quantify the ecosystem-level removal of atmospheric pollutants and subsequent air quality effects of the peri-urban forests of the Iztaccíhuatl–Popocatépetl Zoquiapan National Park (IPZNP) in the Central Mexico Megapolis (i.e., Mexico-Puebla airshed).

2. Material and methods

2.1. Study area

The IPZNP is approximately 40,000 hectares and located directly southeast of Mexico City and west of the City of Puebla and well within the airshed of both cities. The IPZNP has the second and third highest mountain peaks in Mexico, Popocatépetl (5452 msl) and Iztaccíhuatl (5280 msl) from which the park name is derived. Major forest types include: *Abies sp*., *Abies religiosa*, *Pinus hartwegii*, mixtures of *Abies sp*. and *Pinus sp*., and other stands of conifers (Bobbink and Heil, 2003). Areas where trees have been removed as a result of agricultural activities and fire are characterized by alpine grass meadows and small shrubs at higher elevations (Bravo et al., 2002). Bobbink and Heil (2003) characterized altitudinal vegetation gradients as pine and mixed conifer at lower elevations grading into high alpine bunch grasslands at higher elevation at around 4000 m. Bobbink et al. (2003) characterized the IPZNP's climate as sub-humid, mild to cool, temperate grading into cold "alpine" climate zone at higher elevations.

2.2. Modelling approach

We calculated peri-urban forest pollution removal rates using three steps: 1) sampling the forest ecosystem structure of the IPZNP, 2) compilation of site-specific hourly pollution concentration and meteorological data and, 3) analyzing the sources and sinks of air pollutants in the study area during one month. The Weather Research and Forecasting model coupled with Chemistry (WRF-Chem) and field data were used to model the pollution and meteorological data inputs necessary for the Urban Forest Effects (UFORE) model.

2.3. WRF-Chem model

The WRF-Chem model couples the Weather Research and Forecasting community model with atmospheric chemistry modules to simulate three dimensional meteorological fields and trace gases and particles (Grell et al., 2005). The WRF-Chem code used for this study is a modification of the Pacific Northwest National Laboratory's (PNNL) WRF-Chem version 3 that was originally developed for use in the Mexico City region (Fast et al., 2007, 2009). A description of the meteorological algorithms in WRF is provided by Skamarock et al. (2005). The atmospheric chemistry in gas phase was calculated using the Carbon Bond Mechanism modified by Zaveri and Peters (CBM-Z) (Zaveri and Peters, 1999) and the particulate phase was implemented with the Modal Aerosol Dynamics Model for Europe coupled with the Secondary Organic Aerosol Model (MADE/SORGAM) (Ackermann et al., 1998; Schell et al., 2001). Emissions of trace gases and particulates were obtained from the 2002 Mexico City Metropolitan Area (MCMA) inventory and the 1999 National Emissions Inventory (NEI; CAM, 2004). The inventory used for this analysis contained surface and point source emissions for 26 trace-gas and 13 particulate species.

Two modeling domains were used, the first being the outer domain encompassing the whole country of Mexico with a 12 km^2 grid spacing and another inner domain that covered the central region of Mexico with a 3 km^2 grid spacing. The month of March 2006 was selected for the study's simulations since this time period was also used by Fast et al. (2009) in an intense field campaign in the Mexico City area, including the Altzomoni monitoring station inside our study area (Fig. 1), that measured ground and airborne based measurements and developed chemical transport models to simulate prevailing pollution conditions (Molina et al., 2010). March is also a relatively precipitation free month, thus minimizing effects of wet deposition in our analyses, and as such is a representative month for the whole year in the airshed. The initial and boundary conditions were based on Fast et al. (2009) and the modified speciation used in the CBM-Z mechanism coupled with the MADE/SORGAM aerosol model. Based on these measurements, the WRF-Chem model was validated and adjusted for this study area and time period, thus facilitating validation with actual measurements (Salcedo et al., 2006; Fast et al., 2009).

2.4. UFORE model

The UFORE model has been used by Nowak and Crane (2000) to calculate the removal of CO, O_3, NO_2 and PM_{10} by urban vegetation using site-specific forest structure, average hourly pollution concentration, and mean hourly meteorological data. The UFORE model is a dry deposition and biochemical processes model that also calculates emissions of volatile organic compounds, production of CO and O_3, as well as deposition of CO, O_3 and PM_{10} to trees, shrubs and grass leaf area (Nowak et al., 2002). To our knowledge there are few studies where the UFORE model has been applied to peri-urban forested areas using weather and pollution data from peri-urban areas.

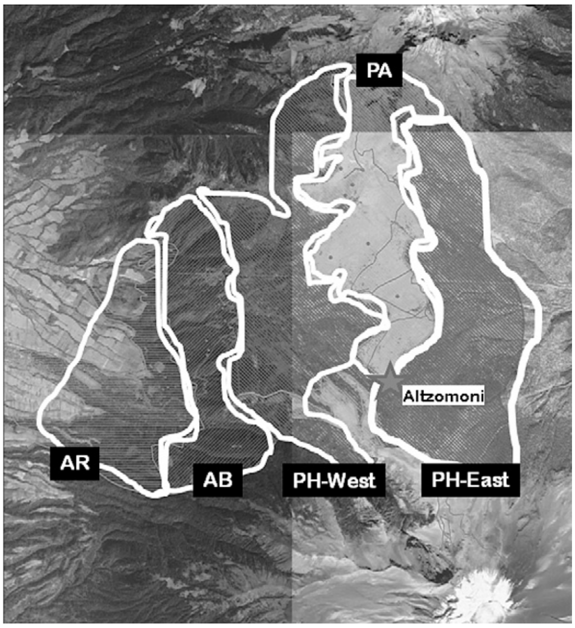

Fig. 1. The four ecosystems in the Iztaccíhuatl–Popocatépetl-Zoquiapan National Park, Mexico. Note that AR, AB, PH and PA refer to the principal ecosystems found in the study area: *Abies sp.* (AB), *Abies religiosa* (AR), *Pinus hartwegii* (PH), respectively, and high mountain meadow (PA). PH-West and PH-East indicate PH ecosystems located on the east and west slopes of the study area. Altzomoni refers to the monitoring site location where meteorological and pollution measurements were made during March, 2006.

2.5. Forest structure

The IPZNP's trees, shrubs and grasses were sampled in an area encompassing 7461 hectares on the west slope and accounted for approximately 19% of the park's total area. Seventy six, random, 0.04 ha plots were located in the study area and accessed from the park's main road. Plots were sampled to characterize forest structure on the IPZNP's four major ecosystems that are based on the Mexican *Instituto Nacional de Estadísticas Geográficas e Información* classifications for soil and vegetation types: 1) Transition between agricultural and forested zones, dominated by *Abies religiosa* (AR), 2) forest of predominately *Abies religiosa* mixed with various types of shrubs (AB), 3) forest of *Pinus hartwegii* (PH) and 4) high alpine grass meadows (PA) of primarily *Festuca sp.* and *Muhlenbergia sp.* (Fig. 1; Table 1). The centers for each plot were located and recorded using a handheld Global Positioning System with an accuracy of $\pm 0.001°$. Measured field variables on these plots (i.e., species, covers and biometrics for the trees, shrubs and grasses) were used as input data in the Urban Forest Effects (UFORE) model (Table 2). Specific field methods are outlined in Nowak et al. (2002) and Escobedo and Nowak (2009).

The UFORE model quantified plot-level forest structure (e.g., species composition, tree density, Leaf Area Index (LAI), and leaf biomass) using field data (i.e., tree and shrub cover, percent evergreen leaf composition) to calculate ecosystem-level dry deposition and VOC emissions. The LAI is the projected area of the tree crown on the ground and is calculated by UFORE using regression equations and shading coefficients for urban deciduous trees (Nowak, 1996). The model estimates conifer LAI using average shading coefficients and height-to-width ratios from the literature (Nowak et al., 2002). Shrub LAI was calculated from the biomass foliage and

Table 1
Sampled ecosystems and number of measured plots in the Iztaccíhuatl–Popocatépetl-Zoquiapan National Park, Mexico.

Ecosystem	Ecosystem area (ha)	Area sampled (ha)	Percent of ecosystem sampled	Number of plots (*n*)
Abies religiosa and agricultural ecotone	952	0.49	0.05%	13
Abies religiosa forests	1026	0.68	0.07%	18
Pinus hartwegii Forests	3927	0.68	0.04%	38
High alpine meadow	1556	0.27	0.02%	7
Total	7461	2.88	0.04%	76

Table 2
Measured tree and shrub variables of the Iztaccíhuatl–Popocatépetl-Zoquiapan National Park, Mexico. Listed variables were used as inputs in the Urban Forest Effects model.

Field variable	Description of measurement (units)
Trees	
Direction	Azimuth from plot center to the tree (living or dead) in compass degrees
Distance	Distance, measured parallel to ground, to tree (living or dead) from plot center (m)
Species	Botanical classification
Diameter Breast Height	Diameter of the tree taken at a height of 1.3 m above surface (cm)
Total height	Height to top (alive or dead) of tree crown (m)
Height to crown base	Height to base of live crown (m)
Crown width	Crown width is the average of two measurements: N–S (North–South) and E-W (East-West) axes (m)
Percent canopy missing	Percent of the crown volume that is **not** occupied by leaves
Dieback	Percent crown dieback in crown. This dieback does not include normal/natural branch dieback/pruning due to crown competition/shading in the lower portion of the crown.
Crown Light Exposure	Recorded on a scale of 0–5. Number of sides of the tree receiving sunlight from above. Top of tree is counted as one side. Divide the crown vertically into four equal sides. The number of sides that would receive direct light if the sun was directly above the tree are counted.
Shrubs	
Species	Botanical classification
Height	Height of the shrub mass for the species (m)
Percent Area	Of the total ground area of all shrubs on the plot, the percent of the ground area that is occupied by this species/height combination
Percent Shrub Mass Missing	Of the volume (height × ground area) of this species/height combination, the percent of the volume that is missing, i.e., not occupied by leaves
Grasses	Percent cover and height (m)

conversion factors that have been derived empirically (Nowak et al., 2002). Average LAI values by ecosystem type and genera were obtained from the literature (e.g., Scurlock et al., 2001). The methodology for calculating the LAI for grasses using measured height was estimated using methods outlined in Escobedo et al. (2008).

Statistical differences in tree LAI and leaf biomass, key forest structure parameters affecting air quality, among the four ecosystems were determined using one-way Analyses of Variance with the PROCGLM procedure in the Statistical Application Software. Tree leaf biomass data were log transformed to obtain homogeneity of variance and statistical differences in both LAI and leaf biomass among ecosystems were determined using a Tukey test.

Ecosystem-level UFORE model outputs included: 1) Dry deposition of gases and particles to the leaf surfaces of trees, shrubs and grasses, 2) Volatile organic compound emissions from woody plants and, 3) The O_3 and CO that are subsequently formed by photochemical reactions. The UFORE model was developed for urban forests; however, there is nothing that is urban-specific in its dry deposition and biogenic emission components that restricts its use in non-urban applications since several of the algorithms discussed below were developed for natural forests such as the ones in this study. For a more detailed discussion of the UFORE calculations, algorithms and assumptions see Nowak and Crane (2000), Escobedo and Chacalo (2008), and Escobedo and Nowak, (2009).

2.6. Emissions of VOCs

The net interaction of the IPZPN's vegetation with anthropogenic gases and particles that are in air masses transported to the park by local and larger scale circulation is a balance between natural Volatile Organic Compound (VOC) emissions from shrubs and trees, and the removal of gases and particles through deposition. Deposition occurs via the physical interaction of gas molecules and aerosol particles on the vegetation. The VOCs produced by the plants are a source of CO, O_3 and particles, all of which are secondary byproducts of photochemical reactions involving the isoprene, monoterpenes and other VOCs naturally emitted by woody foliage (Carter, 1994, 1998). Hence, to estimate the beneficial effects of peri-urban forests on the removal of pollutants, the rates of removal must be weighed against the rates of production of these same pollutants.

Ecosystem-level biogenic emissions estimated by UFORE include: tree and shrub VOC (e.g., isoprene, monoterpenes, and other volatile organic compound; OVOCs) emissions and estimates of subsequent O_3 formation based on field and meteorological data, tree and shrub emission factors from the literature, and estimated O_3 and CO formation based on VOC emissions. Certain physiological processes in plants, in addition to meteorological conditions (e.g., temperature and solar radiation), lead to VOCs emissions that contribute to O_3, CO and aerosol particle formation (Brasseur and Chatfield, 1991 and references therein). The VOC emissions were calculated by multiplying the biomass foliage per species calculated by UFORE, using species or genus-specific emission factors from the literature that have been standardized to 30 °C and a photosynthetically active radiation (PAR) of 1.000 μmol $m^{-2}s^{-1}$. Specific modeling algorithms are detailed in Nowak and Crane (2000). In our March 2006 analysis, we adjusted the UFORE model and included site-specific *Abies religiosa* VOC emission factors developed by Dominguez-Taylor et al. (2007). To better understand the amount of O_3 produced by VOC emissions, O_3 incremental reactivity scales (g O_3 produced/g VOC emitted) for isoprene, monoterpenes, and OVOC were used as a simplified approach (Carter, 1994, 1995, 1998).

2.7. Dry deposition of atmospheric pollutants

We calculated hourly, monthly, and annual dry deposition of O_3, SO_2, NO_2, CO and PM_{10} using estimated tree and shrub leaf area and LAI along with meteorological and atmospheric pollution concentration output data from the WRF-Chem model. The pollutant flux (F; in g m^{-2} s^{-1}) was calculated as the product of the dry deposition velocity (V_d; in m s^{-1}) and the pollutant concentration (C; in g m^{-3}):

$$F = V_d C \quad (1)$$

where deposition velocity is calculated as the inverse of the sum of the aerodynamic (R_a), quasilaminar boundary layer (R_b) and canopy (R_c) resistances (Baldocchi et al., 1987):

$$V_d = (R_a + R_b + R_c)^{-1} \quad (2)$$

The hourly meteorological data from the WRF-Chem model were used to estimate R_a and R_b.

The average hourly pollutant flux (g m^{-2} of tree, shrub, or grass canopy coverage) estimated for the major ecosystems found in the IZPZN from the UFORE model, was multiplied by ecosystem-level tree, shrub and grass cover (m^2) to estimate total hourly pollutant removal by the different ecosystems across the study area. Total tree, shrub and grass removal of O_3, NO_2, SO_2, and PM_{10} were estimated using the typical range of published in-leaf dry deposition velocities (Lovett, 1994). The boundary-layer heights in the study area were calculated using the WRF-Chem model and UFORE pollution concentration outputs (μg m^{-3}) to calculate the total amount of pollution within the study area's boundary layer. This extrapolation from ground-layer concentration to total pollution within the boundary layer assumed a well-mixed boundary layer common in daytime conditions and strong solar heating (Stull, 1988; Baumgardner et al., 2009).

3. Results and discussion

3.1. Forest structure

The IPZNP's forest structure and composition varied across the four major ecosystems found in the IPZNP as a function of topography, aspect, and elevation (Table 3). The Agriculture-AR transition zone was characterized by *Abies sp.* and *Cupressus lusitanica* trees while *Abies religiosa* tree stands were common on steeper canyons and slopes with a northern aspect. High elevation alpine meadows were dominated by *Senecio cinerariodes* shrubs. *Pinus hartweggii* predominated on the lower slopes of the volcanoes and was the ecosystem located immediately below the high alpine meadow ecosystem. *Pinus hartwegii* stands had the highest proportion of evergreen tree cover while the transition zone and *Abies sp.* stands had a similar composition of evergreen species (Table 3). The amount of evergreen cover has implications for the proportion of forest structure that will have year round air quality effects (Smith, 1990; Alonso et al., 2011).

Table 3
Characteristics of the four major ecosystems types found in the Iztaccíhuatl–Popocatépetl-Zoquiapan National Park, Mexico. Note: –, Not applicable.

Ecosystem	Vegetation type	Mean cover (%)	Leaf area index (LAI)[a]	Evergreen canopy (%)	Mean grass height (m)	Tree density (Number of Trees/ha)	Leaf biomass (kg/ha)[a]	Leaf area (m^2/ha)
Agricultural Transition/	Grasses	33	0.6	100	0.3	–	–	–
A. religiosa	Shrubs	26	2.1	4	–	–	410	5335
	Trees	40	6.7a	91	–	500	4115ac	26,870
A. religiosa	Grasses	26	1.0	100	0.5	–	–	–
	Shrubs	30	1.0	13	–	–	240	2965
	Trees	59	6.3a	93	–	560	5035a	37,300
Pinus hartwegii	Grasses	46	1.9	100	0.7	–	–	–
	Shrubs	12	0.4	6	–	–	30	460
	Trees	37	3.9ab	97	–	255	1525c	14,730
High alpine meadow	Grasses	52	2.9	100	1.0	–	–	–
	Shrubs	9	0.9	12	–	–	60	805
	Trees	8	1.6b	25	–	–	95b	100
Total Area	Grasses	43	1.6	100	0.6	–	–	–
	Shrubs	16	0.9	8	–	–	115	1500
	Trees	35	4.8	93	–	295	2040	16,570

[a] Tree LAI and leaf biomass means with different letters are significantly different using one-way Analyses of Variance at $\alpha = 0.05$.

Tree and shrub cover were greater on *Abies religiosa* stands and progressively decreased with increasing elevation. Conversely, grass cover increased as tree cover decreased at higher elevation. The transition zone, with the greatest amount of visual anthropogenic disturbance (e.g., fires, forest utilization, grazing, and other activities associated with agriculture) had a lower tree density, leaf biomass and area as well as higher shrub biomass and leaf area relative to *Abies sp.* ecosystems. Anthropogenic disturbance likely reduced tree cover and opened gaps in the canopy and allowed for increased understory growth (Bobbink et al., 2003). Tree leaf biomass ($F = 12.27, P < 0.001$) and LAI ($F = 5.46, P < 0.0019$) were significantly different between the high alpine meadows and the other three forested ecosystems, while the agriculture transition zone and *Abies religiosa* stands were not statistically different at $p < 0.05$.

3.2. Pollution concentration and meteorology

Annual O_3, CO, NO_2 and PM_{10} removal were estimated using the UFORE model with inputs of pollution concentration, meteorological parameters (e.g., temperature, barometric pressure, mean wind speed and direction) and boundary layer height data obtained using the WRF-Chem model and the 3 km^2 grid thus allowing for each

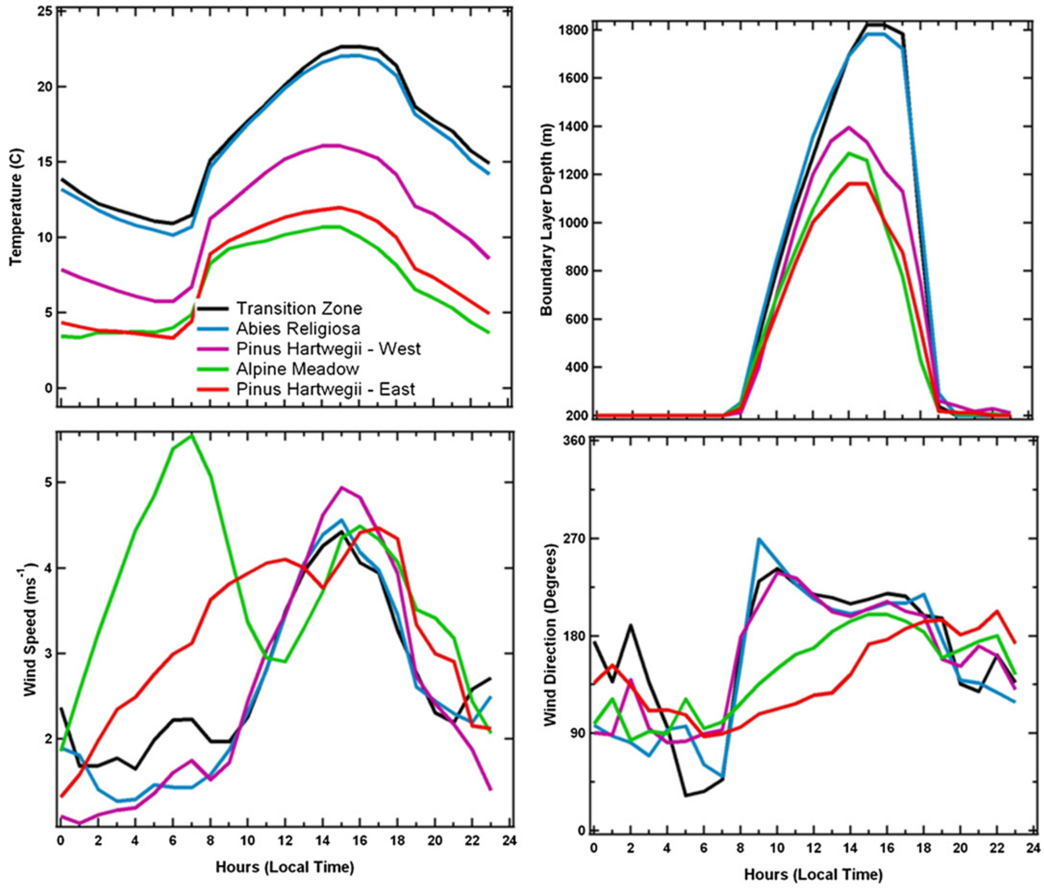

Fig. 2. Mean daily temperature, wind speed, wind direction and boundary layer heights for the month of March 2006 in the Iztaccíhuatl–Popocatépetl-Zoquiapan National Park, Mexico. Mean hourly values were used as inputs in the Urban Forest Effects model.

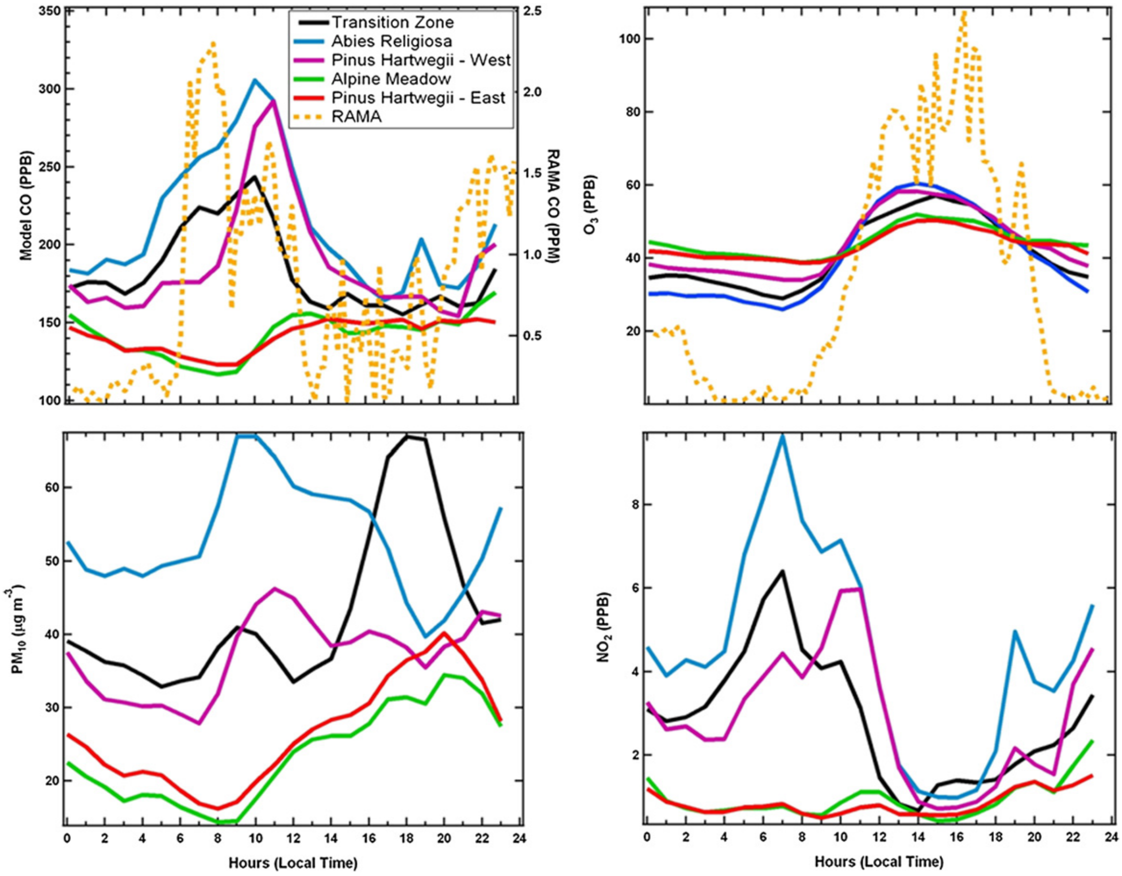

Fig. 3. Mean PM_{10}, CO, O_3 and NO_2 concentrations during March, 2006 in the Iztaccíhuatl–Popocatépetl-Zoquiapan National Park, Mexico. Mean hourly values were used as inputs to the Urban Forest Effects model. Note: RAMA is the *Red Automática de Monitoreo Atmosférico* or Mexico City's air pollution monitoring network.

ecosystem to contain at least one model grid point. Figs. 2 and 3 show average diurnal trends in meteorological and pollutant parameters for each of the four ecosystems. To analyze pollution dynamics between the city of Puebla and the IPZNP, model simulations were also made for a modeled PH ecosystem located on the east slope of the park (PH-East).

Fig. 2 illustrates the large variation in the meteorological conditions of the four ecosystems, and additionally east slope PH forests, of the IPZNP. This and local topography affected tree-shrub VOCs emissions which were sensitive to temperatures that varied from 4 to 10 °C within the PA and PH-East ecosystems (Fig. 2) and between 10 and 23 °C at the AB and AR ecosystems (Fig. 2). Likewise, pollution deposition velocities were sensitive to wind velocity and the total amount of pollution removed per hour depends on boundary layer height (Wesley and Hicks, 2000). In our study, both parameters were very different depending on ecosystem type and location, in terms of both absolute magnitude and diurnal trends.

The diurnal concentrations of CO, O_3, PM_{10} and NO_2 varied substantially (Fig. 3) depending on the location and were similar to trends observed for the meteorological parameters in Fig. 2. Fig. 3 also displays the average daily concentrations for CO and O_3 as measured in Mexico City at one of the air pollution monitoring sites (RAMA) closest to the IPZNP. Note that CO concentrations from the monitoring site were displayed on a different scale than those from the simulations. Maximum concentrations in Mexico City of about 2 ppm occur at 0800 local standard time (LST), whereas the maxima in the IPZNP ranged from 150 to 300 ppb and occurred later in the day depending on the distance and elevation from the emissions source.

Fig. 3 also shows that the AR and AB ecosystems experience the highest concentrations of CO, NO_2 and PM_{10} due to their close proximity to Mexico City. Ozone concentrations are similar at all locations and do not appear to be sensitive to distance from the city. The trends in CO, NO_2 and PM_{10} are different due to the complex interactions among meteorology, photochemistry and primary emissions. The Agricultural transition/*A. religiosa* ecosystems has lower levels of CO than the AB and AR ecosystems, despite this ecosystem being closest to Mexico City where higher concentrations-emissions are likely. Further research is needed to pinpoint the source of these differences; however, as will be discussed in a later section, the oxidation of VOCs leads to the production of CO. That is, more CO is produced by these ecosystems since the AB and AR ecosystems have greater leaf biomass. Average concentrations varied except for O_3 and NO_2, and the peak values

Table 4
Average and maximum (in parentheses) daily simulated concentrations of atmospheric pollutants within the ecosystems of the Iztaccíhuatl–Popocatépetl-Zoquiapan National Park, Mexico. AB = *Abies sp.*; AR = *Abies religiosa*; PH = *Pinus hartwegii*; PA = high alpine meadow. Note: PH-West and PH-East indicate PH ecosystems found on the west and east slopes of the park, respectively.

Ecosystem	Carbon monoxide (ppb)	Nitrogen dioxode (ppb)	Ozone (ppb)	Particulate Matter less than 10 microns ($\mu g/m^3$)	Sulfur dioxide (ppb)
AR	183 (549)	3 (17)	41 (72)	43 (183)	4 (21)
AB	213(837)	4 (33)	40 (88)	53 (210)	17 (152)
PA	142 (374)	1 (12)	44 (77)	23 (82)	147 (867)
PH-West	141 (313)	1 (5)	43 (72)	26 (91)	198 (1098)
PH-East	188 (1055)	3 (33)	44 (96)	37 (129)	60 (422)

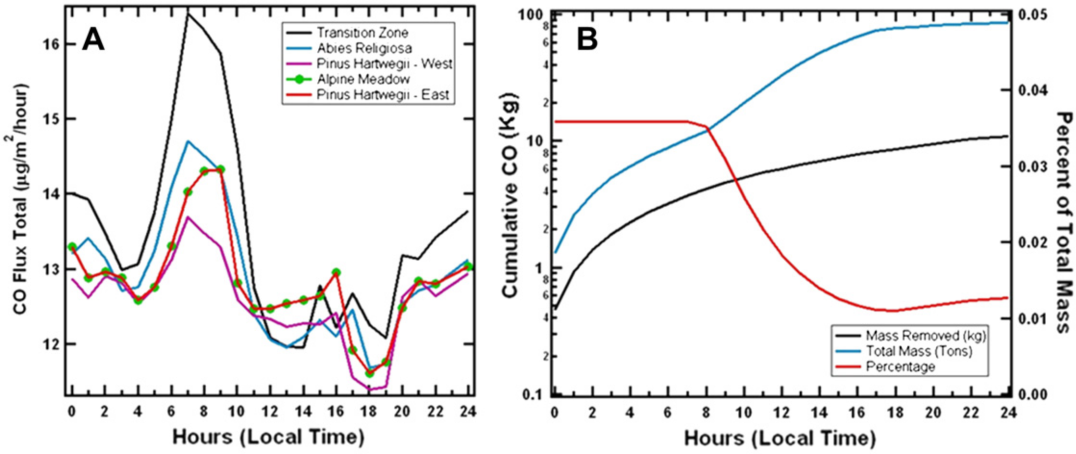

Fig. 4. (A) Mean hourly total flux, (B) cumulative removed and percent total mass removed of carbon monoxide in five ecosystems in the Iztaccíhuatl–Popocatépetl-Zoquiapan National Park, Mexico.

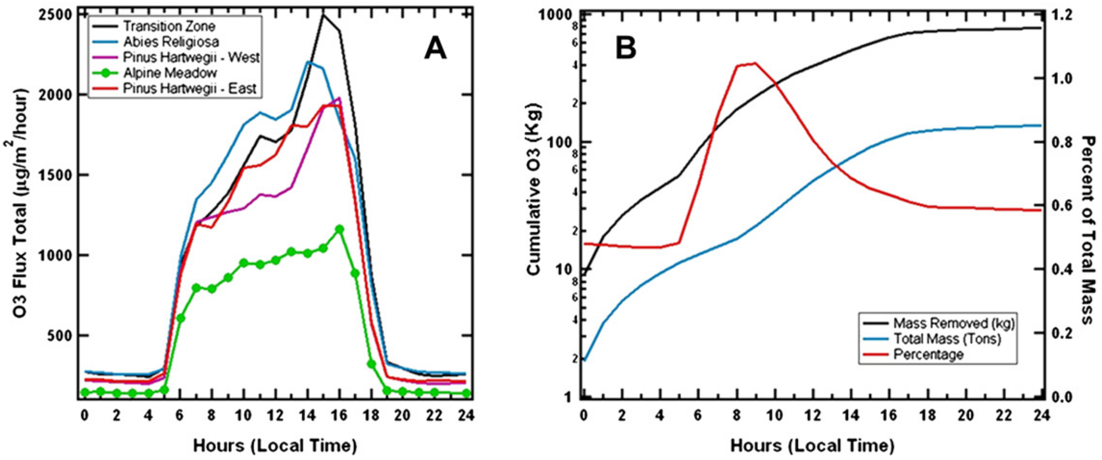

Fig. 5. Mean hourly total (A) and cumulative ozone fluxes (B) in the five major ecosystems of the Iztaccíhuatl–Popocatépetl-Zoquiapan National Park, Mexico during March 2006.

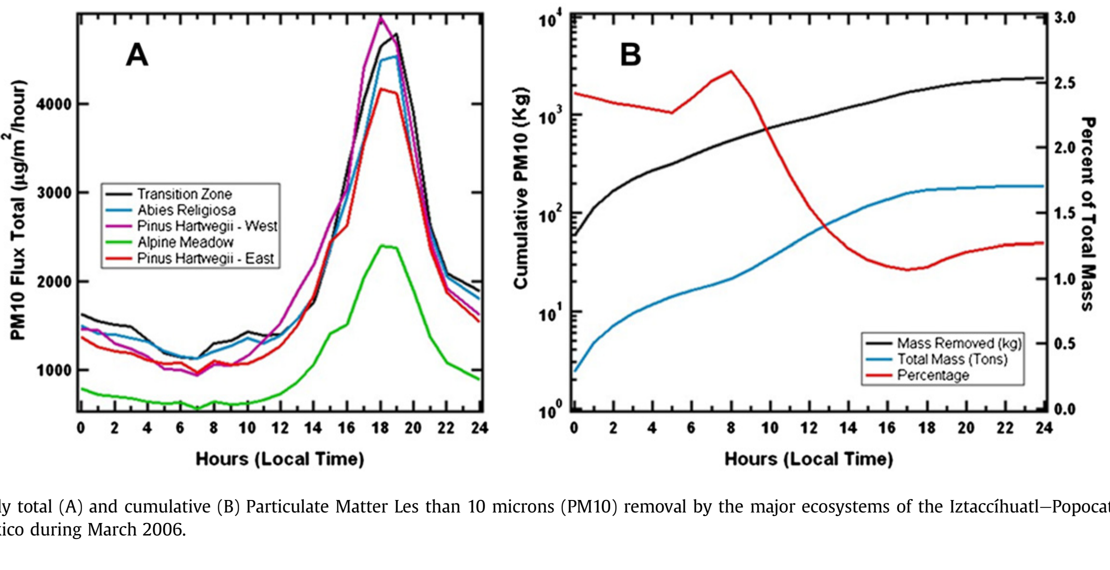

Fig. 6. Mean hourly total (A) and cumulative (B) Particulate Matter Les than 10 microns (PM10) removal by the major ecosystems of the Iztaccíhuatl–Popocatépetl-Zoquiapan National Park, Mexico during March 2006.

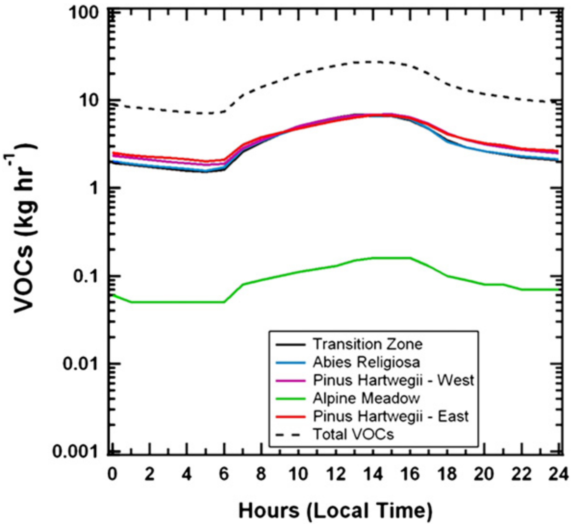

Fig. 7. Mean hourly Volatile Organic Compound emissions (VOCs) by the major ecosystems of the Iztaccíhuatl–Popocatépetl-Zoquiapan National Park, Mexico during March 2006.

indicated even larger variations (Table 4). Average CO, PM_{10} and SO_2 values varied by 51%, 100% and 5000%, respectively. The large variation in SO_2 was likely related to emissions from the nearby active Popocatepetl Volcano. Variations in the PM_{10} were due to differences in wind speed at the different locations or smoke effects from nearby vegetation fires (Bravo et al., 2002).

The WRF-Chem model output was validated at an acceptable level by comparing simulations with measurements from Altzomoni (Fast et al., 2009) and differences were less than 20% for meteorological variables and less than 30% for the pollutants. Because of our use of March as the analysis period – and that we only had output data for this same month – we tested to what extent March was representative of seasonal and annual pollution dynamics in the IPZNP by analyzing annual and seasonal average maximum concentrations of CO, O_3 and PM_{10} at an air quality monitoring station in Mexico City. We determined average and standard deviations for maximum pollutant concentrations in Mexico City for March 2006 and compared them to those for the whole year, the dry season (January–April and November–December) and the wet season (June–October). We found that indeed average values in March for the three analyzed pollutants, in particular ozone, in Mexico City were well within one standard deviation of those for the whole year. Thus, it is tenable that March can be used to characterize annual and seasonal pollution dynamics in our study area.

Table 5
Daily estimated Volatile Organic Compound (VOCs) emission from the major ecosystems of the Iztaccíhuatl–Popocatépetl-Zoquiapan National Park, Mexico in March, 2006.

Ecosystems	Isoprene (kg)	Mono-terpenes (kg)	Other VOCs (kg)	Total VOCs (kg)	VOCs/Area (kg/Ha)
Agricultural/*A.religiosa*	21	15	49	85	0.09
A. religiosa Forest	14	16	56	86	0.08
P. hartwegii-West Forest	49	7	38	94	0.05
P. hartwegii-East Forest	49	7	38	94	0.05
High alpine meadow	1	0	1	1	<0.001

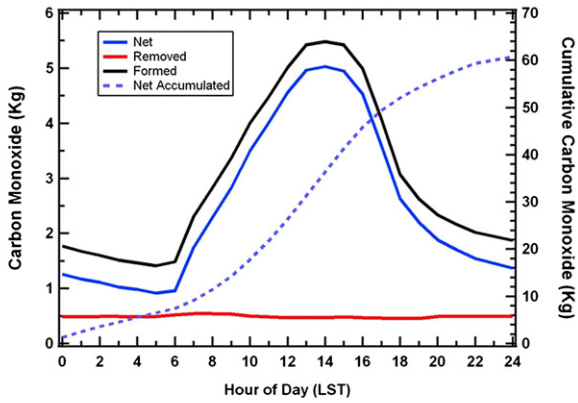

Fig. 8. Mean hourly carbon monoxide formation, removal and imbalance between local source and sinks in the Iztaccíhuatl–Popocatépetl-Zoquiapan National Park, Mexico during March, 2006. Note: LST, Local Standard Time.

3.3. Pollution emissions and removal functions

Figs. 4–6, show the total pollution removed by shrubs and trees, during each hour of the day by each of the five ecosystems (including west and east slope PH) during the month of March, 2006. The right graph in each figure displays the cumulative concentrations for the fluxes, column mass, and the fraction of pollutant removed from the total columnar mass. Cumulative concentrations (kg m^2 $hour^{-1}$) represent the pollutants removed from the atmosphere by all tree, shrub and grass surface leaf area in all the ecosystems for a typical day during the modeling period and is considered the cumulative mass or the concentration of pollutant in a volume of air defined by the product of the surface area and the height of the boundary layer over each region (Fig. 2). Hourly total pollution flux can then be used to estimate ecosystem-level annual pollution removal. The pollutant mass was estimated by taking the concentration predicted for the specific pollutant (μg m^{-3}) at the tree canopy level and multiplying by this volume, assuming a well-mixed boundary layer. The fraction of mass removed by deposition (scale on the right axis of Figs. 4–6) shows the percentage of the pollutant being removed during the modeling period.

There was a contrast in the amount of CO removed per ecosystem, particularly in the morning during peak CO emissions that originated from nearby urban areas (Fig. 4). The region closest to Mexico City, the transition zone, has the largest fluxes per unit area. The alpine

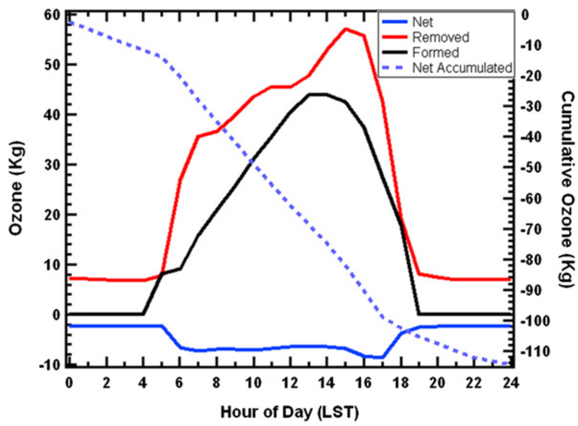

Fig. 9. Mean hourly ozone formation and removal and the imbalance between local source and sinks in the Iztaccíhuatl–Popocatépetl-Zoquiapan National Park, Mexico during March, 2006. Note: LST, Local Standard Time.

Table 6
Mass (kg) per km^2 of ozone (O_3) and carbon monoxide (CO) formed, removed and the net balance (formed-removed) effects of the Iztaccíhuatl–Popocatépetl-Zoquiapan National Park, Mexico.

Ecosystem	O_3 formed	O_3 removed	O_3 Net	CO formed	CO removed	CO Net
Agricultural/ *A. religiosa*	27.9	24.3	5.6	4.5	0.5	+4.0
Forest *A. religiosa*	11.5	19.5	−8.0	1.9	0.3	+1.6
Forest *P. hartwegii*	9.4	16.4	−7.0	1.9	0.3	+1.6
High alpine meadow	0.7	11.2	−10.5	2.0	0.4	+1.6

meadow and PH-East regions have virtually the same fluxes and might be due to their close proximity to the other large urban area in the airshed- the city of Puebla – located on the eastern slope of the IPNZP. When taking into consideration all the ecosystems and the removal of CO throughout the day, approximately 10 kg of CO are removed daily, or 3.7 metric tons annually. This represents approximately 0.015% of the total CO that is being transported annually across the IPNZP. The most efficient period for removing CO appears to be in the morning, when the CO levels are relatively low and no new CO is being produced locally, or sunrise after which the photochemical production of VOCs begins.

Ozone removal trends were similar to CO; Ag-Forest ecotone and alpine meadows removed less O_3 than areas with greater forest cover and density (Fig. 5a). Fig. 5b shows that substantially more O_3 is removed than CO, or approximately 100 kg per day (37 metric tons annually) representing 0.74% of the total mass of O_3 passing daily in the study area. Peak removal efficiency does not occur when there are peak O_3 concentrations, but just prior to a rapid increase in simulated O_3 concentrations. We surmise that the decrease in efficiency occurs when the O_3 begins to be produced due to photochemical reactions with the locally emitted VOCs as temperature increases during the day (Guenther, 1997).

Relative pollution removal was greatest for PM_{10} (Fig. 6a) and maximum removal occurred around 1800 local standard time (LST). This seems contrary to the trends in the primary emissions reflected for CO (Fig. 3), but dry deposition of particles is sensitive to the average horizontal wind -the dominant removal process- that increases during the afternoon hours (Fig. 2; Baumgardner et al., 2009). The daily, accumulated mass of PM_{10} removed in the study area was 300 kg (100 metric tons annually), or 1.6% of the ambient PM_{10} (Fig. 6b). Hence, in terms of absolute amount of pollutant and percentage of total column concentration removed, PM_{10} was the pollutant that appears to be removed most efficiently in the IPZNP.

Emissions of VOCs were oxidized by the ambient hydroxyl radical OH to produce CO and O_3 and were emitted primarily during the daylight hours, despite the background concentration of approximately 1 kg per hour per hectare at night and in the morning over all forested ecosystems as opposed to alpine meadows which emitted less VOCs (Fig. 7). The other forested ecosystems emitted approximately the same amount of VOCs. Table 3 shows that tree leaf biomass and LAI in the alpine meadows – both influential model parameters- are statistically lower than the other forested ecosystems. In addition, the emissions of VOCs increase with temperature (Pederson et al., 1995) and since the transition zone is lower in elevation and it is always about 5° warmer relative to other regions. In terms of the absolute (total Kg) and standardized (Kg per hectare) emissions the PH ecosystem emitted the largest quantity of VOCs in comparison to the other ecosystems (Table 5).

Carbon monoxide formation versus removal illustrates the imbalance between local sources and sinks (Fig. 8). More CO was produced than removed by deposition resulting in a net 60 kg per day being added to the CO that is already passing through the study area from external sources. Ozone formation versus removal shows substantially more O_3 being removed by the IPZNP's biomass than is formed through the conversion of local VOCs (Winer et al., 1983). The net balance between O_3 formation and removal is a negative 115 kg per day, i.e., almost twice as much O_3 is removed by the forest as CO is formed (Fig. 9). Table 6 summarizes the total production, removal and net CO and O_3 within the IPZNP. Alonso et al. (2011) found that evergreen, broadleaf trees removed more O_3 than conifers, whereas we found lower elevation ecosystem more apt at O_3 removal.

Results show that the amount of air pollution removal is influenced by the IPZNP's ecosystems in addition to the meteorological and pollution concentration characteristics. Our findings indicate that the transition zone removed more pollutants on a per hectare basis than any other ecosystem on the IPZNP (Table 7). While variations in temperature, wind speed and boundary layer depth might not be substantially different between the transition and the AR ecosystems, pollution concentrations tended to be higher in the AR ecosystem. The AR ecosystem had more contiguous and abundant tree canopy cover and tree leaf biomass and area were greater than the transition zone. However, shrub leaf biomass and area were 71% and 80% larger, respectively, in the transition zone than the AR ecosystem due to the presence of open gaps in the tree canopy (Table 4). These gaps allowed for increased sunlight in the understory which allowed trees and shrubs to develop more abundant leaf areas per unit area (see LAI values at Table 3). Vegetation pollution removal rates of the higher elevation ecosystems progressively decreased due to lower pollution concentrations and meteorological conditions that also resulted in lower vegetation densities and cover (Bobbink et al., 2003; Paoletti, 2011).

Overall, our findings indicate that our approach can be used to better assess the air quality regulation ecosystem services of peri-urban forests and explore the dynamics between VOC emissions and the removal of pollutants that are potentially harmful to humans in urban areas and vegetation on these same ecosystems. Results show that the IPZNP produced more CO than was removed (60 kg per day); however the park's peri-urban forests removed more O_3 than they indirectly emitted (net −110 kg per day). In

Table 7
Estimated tree and shrub mean pollution removal rates per hectare (kg/ha/year) as estimated by the Urban Forest Effects and WRF-CHEM models in the Iztaccíhuatl–Popocatépetl-Zoquiapan National Park, Mexico. (T = Trees, S=Shrubs, PM_{10} = Particulate matter less than 10 microns).

Ecosystem	Pollution removal (kg/ha/year)										Total removal (kg/ha/year)		% of total removal	
	Carbon monoxide		Nitrogen dioxide		Ozone		PM_{10}		Sulfur dioxide					
	T	S	T	S	T	S	T	S	T	S	T	S	T	S
Agricultural/*A.religiosa*	0.3	0.1	0.7	0.2	29.6	5.8	101.3	14.3	2.7	0.5	134.6	20.9	87	13
A. religiosa Forest	0.2	0.1	0.7	0.2	19.7	6.4	71.3	14.5	2.3	0.7	94.3	21.9	81	19
P.hartwegii-West Forest	0.2	0.1	0.3	0.05	15.7	1.7	59.5	6.6	1.4	0.2	77.1	8.6	90	10
P.hartwegii-East Forest	0.2	0.1	0.3	0.04	14.9	1.6	66.0	7.3	1.0	0.1	82.3	9.2	90	10
High alpine meadow	0.04	0.04	0.04	0.04	1.9	1.7	5.7	5.4	0.2	0.2	7.9	7.4	52	48

addition, more than 100 metric tons of PM_{10}, produced by the Central Mexico Megapolis, were removed annually in the study area or approximately 2% of annual anthropogenic emissions. Thus the IPZNP is a both source of CO and a sink for O_3 (Figs. 8 and 9).

4. Conclusion

Studies like ours can be used to quantify the effect of conserved peri-urban ecosystems in mitigating air pollution in cities. Removing O_3 generally has a positive effect with respect to human health as evidenced by Sartor et al. (1995) who analyzed ozone levels and daily mortality in Belgium and found a relationship between ozone, high temperatures, and the number of daily deaths. Also, increased deaths in elderly people occurred at 0.034 ppm of O_3 for a 24-h time period (Hoek et al., 1997). Furthermore, Escobedo and Chacalo (2008) discuss the economic health benefits from air pollution removal by Mexico City's urban trees. Hence, for those populations within the Mexican Megapolis, removal of even a small fraction of the O_3 produced in these regions by the IPZNP's peri-urban forests is beneficial. That said, the complexity of the chemical processes that produce secondary atmospheric contaminants introduces a large degree of uncertainty such the results reported here must be interpreted cautiously.

Results can also be used to understand the emissions of volatile organic compounds from trees and shrubs in peri-urban ecosystems and subsequent ozone and carbon monoxide formation due to oxidation and photochemical reactions. Ozone, although not as strong of a greenhouse gas as CO_2, is still considered an important contributor to climate change particularly in large urban areas (Guenther, 1997). Although the average reduction compared to the anthropogenic sources is only about 1%, this makes for an important contribution towards the mitigation of climate change. Carbon monoxide is a very weak greenhouse gas compared with O_3 (IPCC, 2007) so the net increase in CO should not directly contribute to regional warming. On the other hand, CO has an indirect effect on climate change because it removes OH which subsequently leads to enhancements of methane (CH_4) and O_3.

It is important to note that the UFORE model does not take into account the production of new particles via gas to particle conversions or secondary particle production due to the production of VOCs by the vegetation (Kulmala et al., 2001; Nowak et al., 2002). It is unlikely that new particle formation is important since this requires that the vapor pressure of the VOCs is high and that there is not significant surface area of pre-existing particles onto which the VOC gases will condense (Kulmala et al., 2001; Dunn et al., 2004). Our coupled model simulations show that there are large mass concentrations of PM_{10} which indicates a significant surface area onto which some of the VOC emissions will diffuse. As a result, the UFORE model is likely overestimating the CO and O_3 that is produced by photo-oxidation of the VOCs since some fraction of the estimated VOCs are being removed by PM_{10} (Kulmala et al., 2001). However, UFORE model results show a large fraction of PM_{10}, or approximately 2% of the total column mass, is being removed in the study area. This has implications related to human health and to the direct and indirect effect of aerosol particles on climate. As with ozone, particles have a deleterious effect on human health (Dockery and Pope, 1994). Removal of some fraction of these particles by peri-urban ecosystems will have a positive influence on Mexico City's populations (Molina et al., 2007).

Another important, yet difficult to quantify aspect of removing anthropogenically produced aerosol particles is the impact on the development of clouds and precipitation. Although the debate is still open with respect to whether anthropogenic aerosols will increase or decrease precipitation (Rosenfeld et al., 2008) the weight of evidence seems to lean towards the decrease in precipitation being caused by seeding clouds with high concentrations of anthropogenic particles. A great deal more research is needed in the region of the Mexico City Megapolis to determine if indeed the increase in anthropogenic pollution has brought about a decrease in precipitation; however, it is unlikely that removing excess particle mass will have any negative impact on human or ecosystem health or climate.

In conclusion, in addition to promoting the regulation, habitat and provisioning ecosystem services and benefits of conserving the IPZPNP's ecosystems, our modeling approach is also useful for better understanding the cost-effectiveness and tradeoffs associated with implementing management objectives such as reforestation and wildfire restoration projects. Although trees remove more pollutants and sequester more carbon dioxide than shrubs or grasses per unit leaf area, forested ecosystems emitted more VOCs than alpine meadows due to differences in species composition, leaf biomass and LAI. Increased deposition of phytotoxic pollutants such as ozone could also imply detrimental damage to specific tree species and stands such as those of *Abies religiosa*. Finally, greater forest densities could also result in increased wildfire severity, altered wildlife habitat and hydrology, and reduction in recreation opportunities for humans. Therefore management objectives that optimize specific ecosystem service objectives should consider the *ecosystem disservices* and other long-term social and economic objectives as well. Modeling approaches such as ours can be useful towards understanding these tradeoffs.

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