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The oxidative potential and biological effects induced by PM_{10} obtained in Mexico City and at a receptor site during the MILAGRO Campaign

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ABSTRACT

As part of a field campaign that studied the impact of Mexico City pollution plume at the local, sub-regional and regional levels, we studied transport-related changes in PM_{10} composition, oxidative potential and *in vitro* toxicological patterns (hemolysis, DNA degradation). We collected PM_{10} in Mexico City (T_0) and at a suburban-receptor site (T_1), pooled according to two observed ventilation patterns ($T_0 \rightarrow T_1$ influence and non-influence). T_0 samples contained more Cu, Zn, and carbon whereas; T_1 samples contained more of Al, Si, P, S, and K ($p < 0.05$). Only SO_4^{-2} increased in T_1 during the influence periods. Oxidative potential correlated with Cu/Zn content ($r = 0.74$; $p < 0.05$) but not with biological effects. T_1 PM_{10} induced greater hemolysis and T_0 PM_{10} induced greater DNA degradation. Influence/non-influence did not affect oxidative potential nor biological effects. Results indicate that ventilation patterns had little effect on intrinsic PM_{10} composition and toxicological potential, which suggests a significant involvement of local sources.

1. Introduction

Adverse health effects that have been linked to particulate matter (PM) in air pollution are related to the mass and size of the particulates, which are two variables that are routinely monitored in urban environments (Krewski et al., 2009). Evidence at the experimental and population levels indicates that variations in the mixture of the PM components may account for the observed heterogeneous health effects that vary according to season, location and health outcome (Bell et al., 2007, 2008; Perez et al., 2009; Zanobetti et al., 2009; Alfaro-Moreno et al., 2010; Atkinson et al., 2010; Tong et al., 2010). For example, studies in the USA have observed that significant changes in particulate matter with aerodynamic diameter $\leq$2.5 μm ($PM_{2.5}$) can cause specific hospital admissions, and cardiovascular disease admissions have been correlated to increased levels of specific $PM_{2.5}$ components, such as Br, Cr, Ni and Na^+. In addition, diabetes admissions have been correlated with increased As, organic carbon and SO_4^{-2} PM concentrations (Zanobetti et al., 2009). A recent study in London indicated that cardiovascular effects are associated with particle number concentrations, and the respiratory outcomes are associated with non-primary PM components (sodium and ammonium nitrate, sulfate, chloride and organic carbon) (Atkinson et al., 2010). Most of the existing evidence on the role of the PM composition in PM-related toxicity and deleterious health effects has been based on local and seasonal variability, and the local sources appear to play a pivotal role. The long-range transport of PM is an additional factor that is capable of affecting the PM mixtures. Studies in Spain have indicated that dust blown from the Sahara can enrich Barcelona's air pollution mix, which increases mortality risk during

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Abbreviations

DMPO	5,5-dimethyl-1-pyrroline N-oxide
EC	elemental carbon
EPR	electron paramagnetic resonance
HPLC	high-performance liquid chromatography
IMP	Instituto Mexicano del Petróleo
MCMA	Mexico City Metropolitan Area
MILAGRO	Megacities Initiative: Local And Global Research Observations
NIST	National Institute of Standards and Technology
OC	organic carbon
OP	oxidative potential
PBS	phosphate buffered saline
PM	particulate matter
$PM_{2.5}$	particulate matter with aerodynamic diameter $\leq$2.5 μm
PM_{10}	particulate matter with aerodynamic diameter $\leq$10 μm
PIXE	particle-induced X-ray emission
PCA	principal component analysis
T_0	time 0, urban location
T_1	time 1, suburban location receptor site

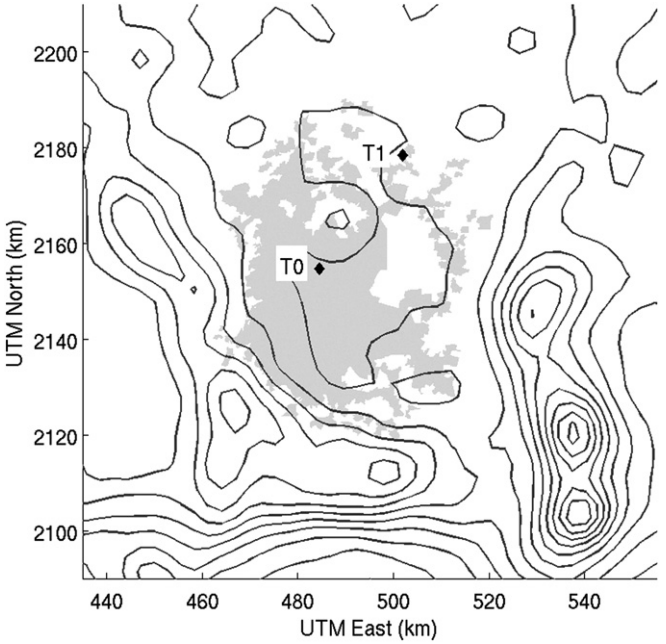

Fig. 1. The map shows the basin where the MCMA resides. The urban area is shaded, and the location of sites T_0 and T_1 are indicated. Terrain contours are every 500 m.

Sahara-influenced events (Perez et al., 2008). Similar concerns exist in Asia where continental desert dust mixed with anthropogenic and biological pollutants can reach the eastern regions (Chen et al., 2010; Hashizume et al., 2010). More research is required on this emerging topic to improve the understanding on the impact of imported pollutants on the local pollution, such as concentration or composition, and their influence to health risks in these regions.

In this study, we explored the effects of transported pollutants by studying the toxicity patterns of particulate matter with aerodynamic diameter $\leq$10 μm (PM_{10}) samples that were collected at an urban-emitting site (T_0) and at a suburban-receptor site (T_1) (Fig. 1). Sampling occurred as part of a multidisciplinary, multicenter, international study that was designed to assess the impact of the air pollution plume from the Mexico City Metropolitan Area (MCMA) at the local, sub-regional and regional levels (MILAGRO Campaign) (Molina et al., 2010). Samples from sites T_0 and T_1 served to compare PM composition, PM oxidative potential, and *in vitro* biological effects (DNA and cell membrane disruption) by separating the measurement days into two categories based on dominant ventilation patterns (see Section 2.1) (de Foy et al., 2009; de Foy et al., 2008).

2. Materials and methods

2.1. PM sampling

Twenty-four hour PM_{10} samples were obtained daily during March 2006 at two sites as part of the MILAGRO Campaign (Molina et al., 2010). The urban site (T_0) was located at the Instituto Mexicano del Petróleo (IMP), and the suburban site (T_1) was located at the Universidad Tecnológica de Tecámac in the State of Mexico, which is located 30 km NW of site T_0 (Fig. 1). High-volume samplers (Tisch TE6070V, Roswell, GA, USA) with nitrocellulose membranes (Sartorius 11302-131, Goettingen, Germany) were used for the collection of the PM. The PM was mechanically recovered from the membranes according to previously published methods. Toxicological evaluation was conducted with aliquots of the pooled samples in three separate experiments, and each run was performed in triplicate. Aliquots were routinely autoclaved to limit the participation of viable microorganisms in the samples (Alfaro-Moreno et al., 2009).

Some of the samples were analyzed on a daily basis, and other samples were pooled into two categories labeled "influence" and "non-influence" days. The influence periods included March 8–13 and March 18–21. The non-influence periods included March 1–7, March 14–17, and March 22–30. The classification was based on a cluster analysis of the surface wind patterns during the field campaign (de Foy et al., 2008). Everyday there were similar drainage flows into the basin at night. The main difference between the days in terms of air quality impact was the wind pattern in the early afternoon. On the non-influence days, there was a predominance of clusters with transport from the north and northeast (clusters 4 and 6 in Fig. 11 of de Foy et al., 2008). On these days, the urban plume was transported to the south and did not impact T_1. On the influence days, there was more transport from the east and southeast in the early afternoon (cluster 5), and from the south and southwest in the later afternoon (clusters 7 and 8) which transports the urban plume northwards past T_1.

Overall the influence days were more homogeneous comprising stronger southwesterly winds that drove the surface winds over the basin and caused a north–south convergence zone. This convergence zone corresponded to a region of higher pollutant loadings that moved toward the northeast as the plume was vented in the late afternoon. In contrast, the non-influence days were more heterogeneous comprising three different patterns: a strong southward flow throughout the basin, Cold Surge events with northwesterly winds that were associated with strong southward surface transport and a weak northerly wind component with rain in the southern part of the basin (de Foy et al., 2008; de Foy et al., 2009).

Particle transport analysis was performed for the urban plume (de Foy et al., 2009) using WRF-FLEXPART. This shows that during the influence days there was a more continuous impact of the urban plume at T_1, whereas during the non-influence days the impact at T_1 was sporadic. It should be noted however that the separation during the two categories is not clear-cut. This is because the wind transport in the Mexico City basin is very complex with strong diurnal variations everyday that exceed the magnitude of the synoptic-scale variations from day to day.

Eulerian aerosol simulations were performed for the MILAGRO field campaign with an analysis of source contribution fractions at T_0 and T_1 (Fast et al., 2009; Hodzic et al., 2010). These suggest an important contribution to primary organic aerosols from anthropogenic sources and a lesser contribution from biomass burning. In addition, time series of elemental carbon concentrations at T_0 and T_1 further show that T_0 has higher impacts from local sources whereas T_1 has lower baseline levels and a bigger fraction during the day possibly from urban plume impacts.

2.2. Elemental analysis by particle-induced X-ray emission (PIXE)

One milligram of PM_{10} was ground with an agate mortar and placed on 3.5-μm thick Mylar substrates. The samples were analyzed with PIXE using a 2.2 MeV proton beam, which was produced by a 9SDH-2 Pelletron accelerator (National Electrostatics Corporation, Middleton, WI, USA), to identify and quantify the trace elements.

X-rays were detected with a LEGe detector (Canberra Industries, Meriden, CT, USA) at a resolution of 150 eV–5.9 keV (Miranda et al., 2000). A 12-μm thick Mylar window separated the vacuum chamber from the X-ray detector. The proton beam was 5 mm in diameter and had an energy level of 2.2 MeV with a beam current of