

Identification of chemistry-dependent artifacts on gravimetric PM fine readings at the T1 site during the MILAGRO field campaign.

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Abstract

As part of the MIRAGE (MILAGRO) study conducted 7-30 March 2006 in Mexico City and its Metropolitan Area (MCMA), fine particulate matter ($PM_{2.5}$) was collected using two Tapered Element Oscillating Microbalance (TEOM) systems, and a Partisol instrument at the T1 super-site (Tecamac, State of Mexico). Inorganic analysis was performed on filter-based (PM_1 , $PM_{2.5}$ -URG) measurements also collected at this site. Measurements from the gravimetric (TEOMs, Partisol) and URG systems were inter-compared with chemical speciation measurements using a Particle Into Liquid Sampler (PILS) and Thermal Optical methods.

Mass and chemical balances applied over the first part of the study (11-22 March) showed that a TEOM using a device (SES) that retains a fraction of semi-volatile material (SVM) for retention and reduction of particle-bound water and a fraction of semi-volatile compounds, gives readings ~30% larger than a conventional TEOM.. In the second part of the study (26-30 March), the loss of SVM during TEOM-heated filter collection (both systems) represented a significant fraction of $PM_{2.5}$ mass due to changes in particle composition. Overall, when nonvolatile nitrate dominated (i.e., when associated with crustal species and not NH_4^+) and/or sulfate dominates (SO_4^{2-}/NO_3^- molar ratio is >1), $PM_{2.5}$ mass readings are in agreement with those reported for the T1 site if TEOM is an SES device. However, when volatile nitrate dominates (i.e., NH_4NO_3) or SO_4^{2-}/NO_3^- molar ratio is <1 , a larger fraction is lost from both TEOMs (with or without the SES device). Under the latter regime, uncertainties are large and gravimetric losses may reach 30%-50%. The gravimetric PARTISOL instrument recorded lower readings under all of the aforementioned conditions with differences versus TEOMs decreasing with increasing RH. These findings call for a careful characterization of such volatilization biases to improve current PM (PM_{10} , $PM_{2.5}$) measurements/networks, especially in alkaline-rich environments that can favor such biases.

With regards to PM_1 and $PM_{2.5}$ filter-based measurements, findings are: 1) crustal-related elements are important features in the $PM_{2.5-1}$ size fraction; 2) a factor of ~2 overestimation of SO_4^{2-} concentrations is recorded on substrates during PM collection and 3) main elements of a typical urban aerosol size distribution are concentrated in the 1 μm (versus 2.5 μm) size fraction. Concentrations of measured ions suggested that anthropogenic activities (especially mobile-sources) affected PM concentrations measured at the sub-urban T1 site.

1. Introduction

Atmospheric pollution in the Mexico City basin is mainly due to high levels of ozone (O₃) and aerosols (i.e., particulate matter, PM) and has received considerable scientific attention in recent years since it impacts nearly 20 million inhabitants (Molina and Molina, 2002). Mexico, a developing country located at tropical latitudes where chemistry and atmospheric processing of pollutants are quite different than at mid-latitudes is also considered an example for studying transport of pollutants at regional (and global) scales (Fast et al., 2007). Mexico City's pollution problem, favored by its high insolation, elevation of 2.2 km above mean sea level (msl) and location in a basin surrounded by mountains, is the result of high emissions by mobile sources (~4 million of vehicles), unrestricted growth of population and a number of industries within the valley. Beginning in the 1990's, the federal and local government officially recognized a significant pollution problem in this megacity and implemented stricter regulations focused on lowering the levels of toxic gases and particles in the urban atmosphere. Although these actions have led to a reduction of measured concentrations of O₃ and PM₁₀ (particulate matter with diameters less than 10 μm) from 1992 until 2007 (e.g. Figure 2 of Stephens et al., 2008), the current number of days per year that the population is exposed to high levels of these criteria pollutants still represents a major concern (SIMAT, 2009).

Atmospheric aerosols reduce visibility, affect air quality, and adversely impact human health. Although in past years particles having diameter < 2.5 μm were regarded as "fine" and those larger as "coarse" (e.g. Seinfeld and Pandis, 1998), this distinction is more recently done between particles smaller/larger than 1.0 μm. This new definition reflects the large number of health-related studies recognizing that fine particles, and particularly submicron sizes, penetrate deep into lung, exacerbate chronic respiratory and pulmonary diseases and also induce morphological and functional alterations in human pulmonary epithelial cells (Ramgolam et al., 2009). A strong link has also been established between high fine aerosol concentrations and cardiovascular effects (Dominici et al., 2006). In this regard, the aerosol-related findings from one of the first international field campaigns in Mexico City (IMADA-AVER study; Edgerton et al., 1999) provided scientific support for the implementation of

regulations on smaller sizes of PM, as seen by the introduction in 2005 of a Mexican 24-h standard of $65 \mu\text{g m}^{-3}$ for $\text{PM}_{2.5}$. Since then, Mexico City air quality monitoring network (SIMAT) records gravimetric levels of this pollutant as well. The levels of gases and particles in Mexico City along with the scarcity of information on their chemical atmospheric processing has motivated, since the aforementioned IMADA-AVER, other international initiatives carried out more recently in the Mexico City Metropolitan Area (MCMA) during 2003 (MCMA-2003) and 2006 (MILAGRO).

Measurements of aerosol and gas-phase species were made in March 2006 as part of the MILAGRO field campaign (Molina et al., 2010). MILAGRO was composed of several collaborative field experiments (MCMA-2006; MAX-Mex, IMPEX, and MIRAGE-Mex) that involved aircraft and surface measurements and was supported by various U.S. and Mexican Institutions. The MIRAGE-Mex (Megacity Impacts on Regional and Global Environments-Mexico) component was focused on studying the chemistry and processing of pollution outflow from the Mexico City Basin through analysis of regional and large-scale measurements (C-130 aircraft). Though recent publications of MILAGRO (from the several components) have brought a wealth of information regarding chemical composition of aerosols measured within the city (at “T0” or MCMA-2006 site) (Querol et al., 2008; Aiken et al., 2009), or as they are transported from Mexico City towards the northeast site (“T1” or MIRAGE-Mex) into the regional environment (Fountoukis et al., 2009), the objectives of the present study cover different aspects of MC aerosols, specifically the effect that variations in chemical composition (under typical MC conditions) have on $\text{PM}_{2.5}$ mass recorded by using different gravimetric methods. Filter-based gravimetric methods have been the standard used by several organizations (the US Environmental Protection Agency, the World Health Organization, among others) for evaluating PM concentration levels (EPA, 1990; CEN, 2003). On the other hand, many of the urban monitoring networks in the US, Europe and Mexico City are using on-line automatic systems such as the Tapered Element Oscillating Microbalance (TEOM) due to low cost and less time-consuming operation compared to the manual filter-based gravimetric methods. The current levels of fine particulate matter in the MCMA frequently exceed international 24-h threshold values (European community: $35 \mu\text{g m}^{-3}$; US-EPA (NAAQS): $35 \mu\text{g m}^{-3}$; WHO: $25 \mu\text{g m}^{-3}$), so that it is particularly important to

evaluate the accuracy of the various methods. The main purposes of this work are to: 1) Inter-compare gravimetric PM_{2.5} mass measured by a number of different techniques used routinely in Mexico City for recording PM_{2.5} mass since 2005, 2) Evaluate chemistry-dependent artifacts for measuring PM_{2.5} mass via TEOM and manual filter-based methods, and, 3) validate manual PM filter-based measurements versus real-time instrumentation deployed at the T1 site.

2. Experimental

2.1 Atmospheric conditions during the study

Mexico City's elevation at 2.2 km and location at ~19°N latitude provide a temperate climate throughout the year. The T1 site, located approximately 28 km NE from the Mexico City Metropolitan Area (MCMA), experiences a similar climate. During the period of analysis (11-30 March 2006) the weather was typically dry with diurnal (06:00-18:00 hours, all values in local standard time LST) average RH and temperature (T) of approximately 36% and 19°C, respectively. Diurnal trends were similar throughout the entire period, although for the selected periods of study (11-22 and 26-30 March) there was an important difference in the RH decrease from early morning (06:00-09:00) values of about 70-80% (both periods) to RH levels in the late morning (09:00-12:00) of ~30% for the 11-22 March period, whereas only decreasing to ~50% for the 26-30 March period. This difference appears to alter the aerosol chemical composition (e.g., humidity-dependent NH₄NO₃ formation) and therefore presents an ideal case study for investigating chemistry-dependent artifacts on gravimetric PM readings. Meteorological conditions for the March field campaign were described by Fast et al. (2007). For 11-20 March winds were highly variable and mainly from the WSW, while westerlies dominated the second analysis period (26-30 March).

2.2 Sampling site and aerosol measurements description

Data reported here are from the T1 ground-based site located, at the Universidad Tecnológica de Tecamac (19.708 N latitude, 98.982 W longitude, 2.72 km above sea level). A complete description of the site is presented elsewhere (Molina et al., 2010). All measurements reported in our analyses were performed on the roof of the Georgia Institute of Technology (GIT) trailer. Inlets for aerosol measurements (all systems) were located ~9 meters above the

ground. Measurements were made 7-30 March 2006, though the present analysis focuses on two specific time periods of the study: 11-22 March and 26-30 March due to better data completeness among the different aerosol systems to be inter-compared and contrasting meteorological conditions between these two periods. Gravimetric $PM_{2.5}$ analysis were performed by comparing three systems: two TEOMs (Tapered Element Oscillating Microbalance) one operated by the GIT (TEOM-GIT) and the other by SIMAT (DF-Government, TEOM-DF), and an integrated filter-based method (a Partisol instrument) operated also by the latter. The TEOM data were hourly averages. TEOM-GIT operated with a SES (Sample Equilibration System) device (Meyer et al., 2000) at 30 °C. $PM_{2.5}$ mass was collected through a 10 μm cyclone followed by a 2.5 μm very sharp-cut cyclone (Kenny and Thorpe, 2001). It was operated at a flow rate of 16.7 liters per minute (lpm), uncertainty of 10%. The measurement principle of the instrument is described in detail elsewhere (Patashnick and Rupprecht, 1991). Recommended temperature of operation for the TEOM is 50 °C (Allen et al., 1997); however, the TEOM-DF was operated at 35 °C, to minimize semi-volatile material losses during PM collection (Castillejos et al., 2003).

Partisol (FRM-model 2000) measurements were collected for a sample collection period of 24 hours starting at 06:00 (LST) using 46.2 (2 μm pore-size) PTFE Teflon filters (Pall Life Sciences, Ann Arbor, MI). Measurements were performed at ambient temperature and RH. The inlet flow rate of the sampler was also 16.7 lpm, with an uncertainty of 10%. Filters were preserved from evaporation by storing immediately after each collection. The PTFE filters were pre- and post- weighed using a Cahn C-33 Microbalance after equilibration of 48 hours under controlled humidity ($40\% \pm 5\%$) and temperature ($20^{\circ}C \pm 2^{\circ}C$) conditions to determine particle mass concentration. The Partisol sampler has a 10 μm inlet followed by a Well Impactor Ninety-Six (WINS), which has a 2.5 μm -cutoff size in particle aerodynamic diameter. Partisol measurements are employed by the Mexico City air quality monitoring network for determining compliance with the national $PM_{2.5}$ ambient air quality standard. Due to the lack of a federal procedure the instrument was operated during the mission according to the U.S. EPA Federal Reference Method (USEPA, 1999). Quality assurance/quality control activities in field and laboratory are the same as required by the USEPA-FRM. Flow rate is keep at 16.67 lpm with a precision of 5% and a bias of 2%. For

the MILAGRO study, flow rate, ambient temperature, filter temperature and barometric pressure sensors responses were verified continuously during the mission.

For consistency tests of the gravimetric systems, we used data from a Particle-Into-Liquid Sampler (PILS) coupled with dual ion chromatographs (IC) (Metrohm, Herisau, Switzerland; Orsini et al., 2003) to quantify anions: SO_4^{2-} , NO_3^- , Cl^- and cations: NH_4^+ , Na^+ , Ca^{2+} , Mg^{2+} . Basic and acid-coated denuders immediately upstream of the PILS were employed to remove possible interference from gases (e.g., NH_3 , HNO_3 , SO_2) from the sample air stream. PILS flow rates were checked throughout the experiment and had an uncertainty of approximately 10%. Data were blank-corrected by periodically passing the ambient sample through a Teflon (Pall-Life Science, Ann Arbor, MI) filter also upstream of the PILS. The ICs were calibrated before and after the mission with NIST- certified liquid standards, and performance during the experiment was monitored by periodically running a single standard.

Water-soluble organic carbon was determined at 6-minute averages with a PILS coupled to a Total Organic Carbon analyzer (Sievers, Boulder CO). Possible artifacts due to interfering gases were reduced with an activated carbon denuder (Eatough et al., 1993) and a pre-programmed automated valve that shunted sample through a Teflon filter (Pall-Life Science, Ann Arbor, MI) to provide an automated blank. Subtraction of this blank accounted for possible interferences due to collection and analysis of any water-soluble organic gases and contaminants in the ultra-pure water used in this system. To complete the mass balance, hourly-averaged measurements of the carbonaceous aerosol were made with a Sunset Labs field OCEC instrument based on thermo-optical transmission. Measurements were performed at ambient temperature and RH. The OCEC instrument was operated following NIOSH method 5040 (NIOSH, 1996). Although an activated carbon denuder (Eatough et al., 1993) was placed upstream of the instrument, positive artifacts for these non-blank corrected OC data are possible (Peltier et al., 2007).

Inorganic PM analysis was also performed on filter-based measurements with two URG systems (URG, Chapel Hill, NC), one with cutoff in aerodynamic diameter at $1\ \mu\text{m}$ (PM_{10}) and the other at $2.5\ \mu\text{m}$ ($\text{PM}_{2.5}$). The sampling of PM was conducted diurnally, in 6-h periods as follows: 1st: 6:00-12:00; 2nd: 12:00-18:00 hrs. A full description of the collection of inorganic compounds (anions: SO_4^{2-} , NO_3^- , Cl^- ; cations: NH_4^+ , Na^+ , Ca^{2+} , Mg^{2+} and K^+) is presented elsewhere (Matías, 2007). Briefly, 47 mm polycarbonate filters (Millipore) were

used. Measurements were performed at ambient temperature and RH. Flow rates were checked at the beginning and end of every sampling period. Filters were preserved from evaporation by storing immediately after each collection. Once collected, the substrates were weighed before and after sampling on a microbalance accurate to 1 μg (Sartorius, Germany). Before weighing, the filters were conditioned for approximately 48 h in the weighing room at a relative humidity (RH) of $35\% \pm 5\%$ and at $\sim 20^\circ\text{C} \pm 2^\circ\text{C}$. The filters were preserved in darkness at -5°C until chemical analysis. No denuders were employed upstream of the URG-systems and positive artifacts due to interference with inorganic gases are possible.

For chemical and physical consistency tests of the URG- $\text{PM}_{2.5}$, hourly-averaged PILS (Fountoukis et al., 2009) and OCEC measurements (to obtain the sum of species) was also used as described in following section.

Details of each $\text{PM}_{2.5}$ instrumentation along with URG systems ($\text{PM}_{2.5}$, $\text{PM}_{1.0}$) are shown in Table 1.

2.3 Analytical methods and uncertainties (filter-based URG)

Aerosol inorganic components collected by the URG systems were analyzed by high performance liquid chromatography (HPLC) methods. The analytical limits of detection for all ions determined by IC were in the range of 1.1-5.0 neq ml^{-1} . Details are depicted elsewhere (Moya et al., 2004). Overall, the concentrations of all ions were sufficiently above the analytical limit of detection or within the variance of the measured blanks. The field blanks concentrations were always below the lower detection limit. Nevertheless, artifacts, such as the loss of nitrate from filter-based measurements (negatives, Chow et al., 2002), due to changes in temperature, relative humidity, and pressure across the filter, and positives, such as absorption and adsorption of material on collected PM due to the absence of denuders upstream the URG systems are possible and will be subject of discussion in following section.

3. Results and Discussion

3.1 Gravimetric systems: Physical and chemical consistency tests

Figure 1 presents the PM_{2.5} gravimetric daily average for the TEOM-GIT, TEOM-DF and Partisol-DF systems for the two selected periods (11-22 March and 26-30 March). Daily gravimetric profiles for the TEOMs systems reported here were obtained by averaging 24 1-hr values while daily PM_{2.5} mass values reported from filter-based Partisol correspond to 24-hours of uninterrupted sampling as detailed in Section 2. The figure also shows the sum of species (using Sunset OCEC and PILS ions measurements except for K⁺ from URG-2.5), which were also averaged over 24 hr and is defined as:

$$\text{Sum of species} = 1.6[\text{OC}] + [\text{EC}] + \text{sum of ions (cations + anions)}$$

where [OC] = organic carbon, [EC] = elemental carbon, and with cations and anions as detailed in section 2.

A consistency test (Chow et al., 1994) requires that the sum of species should be less since not all chemical species may be measured (e.g., insoluble mineral dust, etc.) and the 1.6 value converting OC to organic matter is a lower limit, or equal to the gravimetric mass measured over the same 24 hr period. As seen in Fig. 1, this test is met for PM_{2.5} data observed with the TEOM-GIT instrument for the period 11-22 March. For the TEOM-DF instrument, the consistency test fails for some points, although the pattern of temporal variation is generally similar to those observed with TEOM-GIT and the sum of species. Partisol-DF deserves particular attention as it significantly underestimates TEOMs values and furthermore does not follow their pattern. On the other hand, in the second period under analysis, 26-30 March, the consistency test fails for both TEOMs and Partisol, as the sum of the species exceeds the other measurements, for reasons to be discussed below.

For the first part of the study (11-22 March), PM_{2.5} average mass from TEOM-GIT is ~37 μg m⁻³ while TEOM-DF is ~27 μg m⁻³ and Partisol-DF is ~21 μg m⁻³. PM_{2.5} gravimetric daily profiles from TEOM-GIT readings are in the range of those reported by Querol et al. (2008), ~33 μg m⁻³ on average, for the entire March period at the T1 site.

TEOM-GIT readings, at least for conditions related to this part of the study, is likely to have less artifacts than a conventional TEOM, as it uses a device that reduces particle-bound water and permits retention of a fraction of semi-volatile mass by decreasing the heating at the inlet from 50°C to 30°C (Meyer et al., 2000). However, a negative systematic error in

TEOM-GIT data can also not be completely ruled out. The TEOM-DF and Partisol-DF gives readings ~ 30% and 40% lesser than TEOM-SES, respectively. Nevertheless, Partisol readings are different to patterns reported in literature for PM measurements in other cities in the world (e.g., Williams and Bruckmann, 2001; Allen et al., 1997), this instrumentation has been evaluated for MC conditions at three sites during the past three years (2006-2009) versus 24-hr integrated values measured by TEOM's coupled to a Filter Dynamic Measurement System (TEOM-FDMS) model 8500 (Rupprecht & Patashnick, Albany, NY). Results show a pattern of under-measurements in the range of 20-40% for the Partisol versus TEOM-FDMS system (A. Retama, SIMAT, private communication). Nevertheless the TEOM inter-compared in our study uses a different device (SES) for retention of semivolatile compounds, results in our analysis indicate that a strong volatilization is also occurring in filter-based Partisol measurements (~ 40% versus TEOM-SES) under T1 atmospheric conditions. As Partisol represents the reference method employed by the Mexico City network (SIMAT) for determining compliance with the national PM_{2.5} ambient air quality standard, this finding suggests the need for more investigation on this regard. It should be noted that filter-based gravimetric measurements (Partisol-DF) are also subject to mass losses during collection (changes in atmospheric conditions such temperature and RH), and handling of substrates (Chow, 2005) among other artifacts (negatives and positives such as absorption and adsorption of material on collected PM). Under ambient conditions of the T1 site, semi-volatile NH₄NO₃ and organic compounds are expected to be the predominant components lost (Fountoukis et al., 2009). TEOM-GIT readings (30% higher than conventional TEOM) are likely the result of operating with a device (Table 1) that reduces particle-bound water by means of a dryer and capture a fraction of semi-volatile material. Nevertheless, it does not account for a complete determination of SVM as when TEOM is equipped with both SES and FDMS devices (Favez et al., 2004).

3.2 Changes in chemical composition of PM: 26-30 March period.

a) Ion Balances

Different meteorological conditions for the 26-30 March period lead to a change in the particle composition and lower readings on PM gravimetric values. For this period, PM_{2.5} average mass from TEOM-GIT is ~23 µg m⁻³ while TEOM-DF and Partisol-DF are ~17 µg

m^{-3} . Unlike the 11-22 March period where TEOM-GIT was higher than the sum of measured chemical species masses, during this period all mass measurements were lower than the speciated sum. TEOM-GIT and TEOM-DF give ~20%-40% lower readings, respectively, than the sum of species. The range of under-readings are similar when these TEOM and Partisol data are compared with the reported value of $33 \mu\text{g m}^{-3}$ daily $\text{PM}_{2.5}$ mass measured by Querol et al. (2008) for the entire period, 01-29 March, of the field campaign at T1 using High-Volume data corrected by optical counter real-time measurements: ~30% for TEOM-SES and 50% for conventional TEOM.

To support the hypothesis that changes in chemical composition are enhancing mass volatilization on PM samples for the 26-30 March period, electroneutrality balances (diurnal averages) for the 2 selected periods of study are shown in Figure 2 (PILS data). In the first part (11-22 March), the molar ratio, i.e., $\text{NH}_4^+/\text{sum of anions}$ ($\mu\text{eq/ m}^3$) is ~0.5 (indicating a NH_4^+ deficiency environment) while for the second (26-30 March), the ratio is within 10% of unity. Moreover, for the first part of the study, concentrations of mineral dust (mainly calcium) were significantly higher, whereas in the second period dust played a more minor role and ammonium was a more dominant cation (e.g., NH_4^+ sufficiency environment). *Some important dust-elements (i.e., SiO_2) are not measured by PILS; however, data analyzed is indicative of the presence of dust-related elements.* This change in chemical composition (favoring the formation of semi-volatile compounds, e.g., NH_4NO_3) in the later period, apparently has an important effect on gravimetric measurements of PM, as shown in the present analysis.

b) Sulfate-to-Nitrate molar ratio

During the 11-22 March period when it was dry and crustal elements were more prevalent, sulfate dominated over nitrate ($\text{SO}_4^{2-}/\text{NO}_3^-$ molar ratio predominantly >1). Under these features of chemical composition in the system a TEOM coupled with an SES device capture a fraction of semi-volatiles that gives greater readings than the other two gravimetric systems studied as shown. On the other hand, during the and 26-30 March period when $\text{SO}_4^{2-}/\text{NO}_3^-$ molar ratio is less than unity and nitrate dominates in the system (associated with ammonium in the volatile form), a larger fraction is lost when measuring $\text{PM}_{2.5}$ mass and none of the

instruments analyzed here (TEOM with/without SES device or filter-based Partisol) are reliable in accounting for all gravimetric PM_{2.5} mass. Under this regime, one should expect significant losses of semi-volatile material.

Under the regime of NH₄⁺ sufficiency environment (associated with production of semivolatile NH₄NO₃), often observed within the valley of Mexico as reported in several research studies (Chow et al., 2002; Moya et al., 2004; Salcedo et al. 2006), the findings reported here should be taken into account as TEOM is routinely the method for reporting real-time PM levels within the MCMA. The recorded values of PM_{2.5} in this area represent the primary guidance for setting thresholds and design regulations at the local and federal levels as well as other restrictive actions (contingency or pre-contingency situations) for lowering concentration of pollutants. The fine PM levels (TEOM-SES data) reported here exceed, on most of the sampled days, the U.S. EPA and EC threshold value (35 µg m⁻³, short-term PM_{2.5} standard), and therefore are of concern to the extent that the T1 site is representative of the sub-urban (or urban-rural) environment of the MCMA. Nevertheless this research represents only a semi-quantitative analysis of PM_{2.5} levels routinely performed under standard methodologies; the fact that higher levels of fine particle matter are normally recorded within the urban environment of Mexico City, as well as the issue of significantly underestimated PM readings when changes of composition favor formation of semi-volatile components (occurring typically under MC conditions), both call for a more extensive investigation on this regard.

The analysis presented here also suggests that the strong variation in PM_{2.5} mass readings between the two selected periods of study is the result of changes in chemical composition of particle mass (production of semi-volatile material) and atmospheric conditions (such as changes in RH and T) that favored them. The extent of the difference between TEOMs and gravimetric Partisol readings under aforementioned conditions should be further examined as this may represent only a fraction of the divergence. Spatial and seasonal differences between these instrumentation might be assessed as the effects of air quality on public health requires reliable measurement of PM_{2.5} mass and its chemical components throughout the Metropolitan Area of Mexico City (MCMA).

3.3 Inorganic filter-based PM₁ and PM_{2.5} measurements. URG-systems

a) Overall

Figure 3 presents the result of some physical and chemistry consistency tests (Chow et al., 1994) applied on data from URG-PM₁ and URG-PM_{2.5} systems. Figure 3a shows PM_{2.5} versus PM₁ gravimetric mass ($\mu\text{g m}^{-3}$) for the whole period of study (11-30 March). From this analysis, consistency of PM_{2.5} data points is ~89% (*i.e.*, either larger or equal than PM₁ or the sum of species or within outliers), and for PM₁ data is ~81% (within outliers). The rest of the points (~10% and 20% for PM_{2.5} and PM₁, respectively) are not considered for the detailed analysis of anions and cations presented in subsequent section. In a comparison of PILS versus URG measurements, readings of the latter were mainly (though not in a constant pattern) slightly higher than PILS ionic values. Comparison by chemical species showed that only in the case of URG-sulfate measurements there was a constant artifact, estimated as 2.0 times the PILS value. Figure 3b shows a comparison of SO₄²⁻ measurements by URG and PILS and Figure 3c presents the sum of ions measured by URG versus PILS data. Correction for the constant artifact of sulfate-URG was applied for constructing the figure. For validation of inorganic PM_{2.5} measurements (URG system) we considered PILS data from diurnal hours (06:00-18:00 hrs). We are more confident of PILS sulfate data for the following reasons: PILS has been compared in a number of field studies (Orsini et al., 2003, Sorooshian et al., 2006) versus several PM instrumentations and under a variety of conditions, and secondly, denuders were not set up upstream of the URG systems, as mentioned in Section 2, so that reactions of gases are possible in the substrates. This hypothesis was corroborated by analyzing NH₄⁺ as well as Ca²⁺ data (basic chemical species) recorded from the URG systems and compared versus PILS measurements. The URG readings were also slightly higher although a precise numeric factor cannot be obtained for the latter two chemical species such as in the case of SO₄²⁻. Sulfate artifacts resulting as an interaction of SO_{2(g)} with basic particles have been reported previously on glass fiber filters (Radojevic and Harrison, 1992) and on the polycarbonate substrates used in our URG-systems (Trebs et al., 2008). URG measurements for other ions (such as chloride, sodium or nitrate) were periodically higher (not all the time) though not in a constant pattern, probably due to the reaction of HNO₃ (no denuders upstream URG systems) and crustal species (such

as Na) on substrates. This was observed particularly during the second period of study when higher NO_3 concentrations were present.

b) Distribution of ions

Figure 4 and 5 show the distribution of all ions (Cations: NH_4^+ , Na^+ , Ca^{2+} , Mg^{2+} , K^+ and anions: SO_4^{2-} , NO_3^- , Cl^-) measured by URG systems stratified by size range (1, 2.5 μm) and sampling period (06:00-12:00 hours and 12:00-18:00 hours) for the 11-22 March (Figure 4) and 26-30 March (Figure 5) periods at T1. Correction for the constant artifact of sulfate-URG (~ 2 times SO_4^{2-} from PILS) was applied for constructing the figures. Important findings related to these distributions are: (1) Overall, the predominant ionic species in both size ranges are NH_4^+ , SO_4^{2-} and NO_3^- . For the 11-22 March period SO_4^{2-} exceeds NO_3^- while for the 26-30 period NO_3^- is larger. (2) These ions along with K^+ are concentrated in particles less than 1 μm (rather than 2.5 μm). (3) Sodium and dust-related elements (Ca^{2+} and Mg^{2+}) are important in the $\text{PM}_{2.5-1}$ size fraction. (4) The 26-30 March period shows substantial ammonium, which seems to favor semi-volatile NH_4NO_3 formation (as previously discussed), while the 11-22 March period is characterized by NH_4^+ deficiency (i.e. insufficient to fully neutralize SO_4^{2-} , NO_3^- , Cl^-) and these anions may be associated with non-volatile dust-crystal elements (mainly Ca^{2+} and Na^+). This is supported as well by ion balances and sulfate-to-nitrate molar ratios discussed previously in section 3.2. Although not shown, 90% of particle masses collected during the morning sampling periods were higher than in the afternoon, in agreement with findings previously reported for Mexico City (Moya et al., 2004). Major anions (SO_4^{2-} , NO_3^-) and K^+ are related to anthropogenic activities. It should be noted, however, that levels of concentration of all measured ions at T1 might be considered as moderate amounts (100-300 neq m^{-3} in our analysis), relative to those documented for downtown MC (500-1000 neq m^{-3} ; Matías, 2007) or at the University Campus (UNAM) (100-150 neq m^{-3} ; Zepeda, 2003). K/Na weight mass ratios were ~ 1 and 0.5 for PM_1 and $\text{PM}_{2.5}$, respectively. For PM_1 the observed alkali concentration is likely a result of anthropogenic emissions sources. Ratios less than 1 observed for $\text{PM}_{2.5}$ are interpreted as a combined effect of sea-salt and aerosol of anthropogenic origin (Svane et al., 2005). A possible origin of moderate-high concentrations of Na found in PM samples at T1 is the nearby dry lake of Texcoco (Edgerton et al., 1999). The influence of anthropogenic

emission sources was further supported by analysis of gas phase SO_2 measured from the GIT trailer (up to 320 ppb) and particulate SO_4^{2-} concentrations (up to 420 neq m^{-3} , PILS), particularly on the first days of holidays (e.g. March 18, 2006; not shown). The influence of the pollution plume from MCMA and dust re-suspension on PM samples at T1 has been previously reported by Querol et al. (2008) although that analysis is based on TSP- PM_{10} - $\text{PM}_{2.5}$ while ours is focused on PM_1 - $\text{PM}_{2.5}$ inorganic profiles.

4. Concluding Remarks

An inter-comparison between a conventional TEOM, a TEOM with an SES device and a Partisol sampler for the monitoring of $\text{PM}_{2.5}$ mass readings was carried out for two selected periods (11-22 March; 26-30 March) of the 2006 MILAGRO field campaign (T1 site). The analysis between the selected periods indicates that changes in chemical composition of PM led to chemistry-dependent artifacts which overall resulted in lower readings of $\text{PM}_{2.5}$ mass. When SO_4/NO_3 ratio was > 1 or nitrate mainly associated with non-volatile crustal-dust elements, as corroborated by ionic balances, lower readings may be on the order of $\sim 30\%$ for a conventional TEOM (no devices). However, when SO_4/NO_3 ratio was < 1 and nitrate dominated in the volatile form (NH_4NO_3 in our analysis), both TEOMs give significantly lower readings which may account up to 50% for a conventional TEOM. Filter-based Partisol recorded lower readings under all of the conditions of the study. As the reference method employed by the Mexico City network (SIMAT) these findings indicate that a more detailed investigation of Partisol artifacts is warranted. Finally, filter-based PM_1 and $\text{PM}_{2.5}$ inorganic analysis indicates anthropogenic origin activities more related to sub-micron sizes, while $\text{PM}_{2.5-1}$ size fraction was characterized by presence of crustal and dust-related elements during the MILAGRO study (T1 site).

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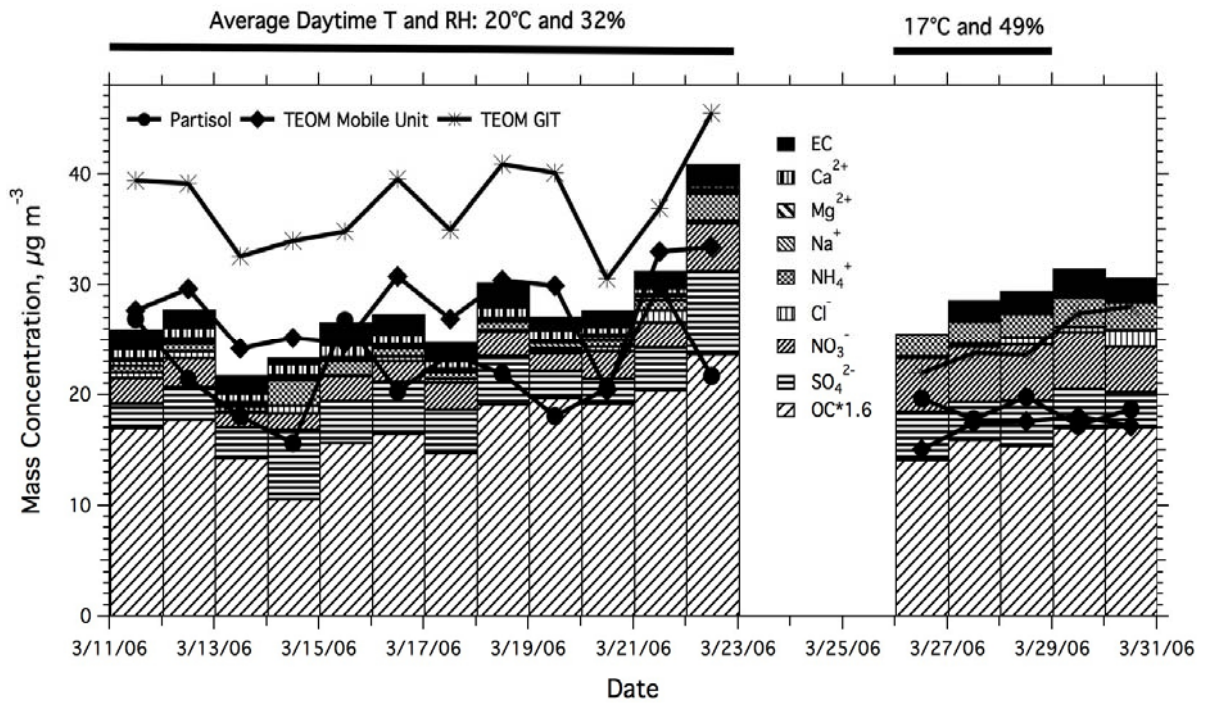


Figure 1. $\text{PM}_{2.5}$ gravimetric profile for TEOMs and Partisol systems along with the sum of species (ions-PILS plus OCEC) for the 11-22 and 26-30 March periods.

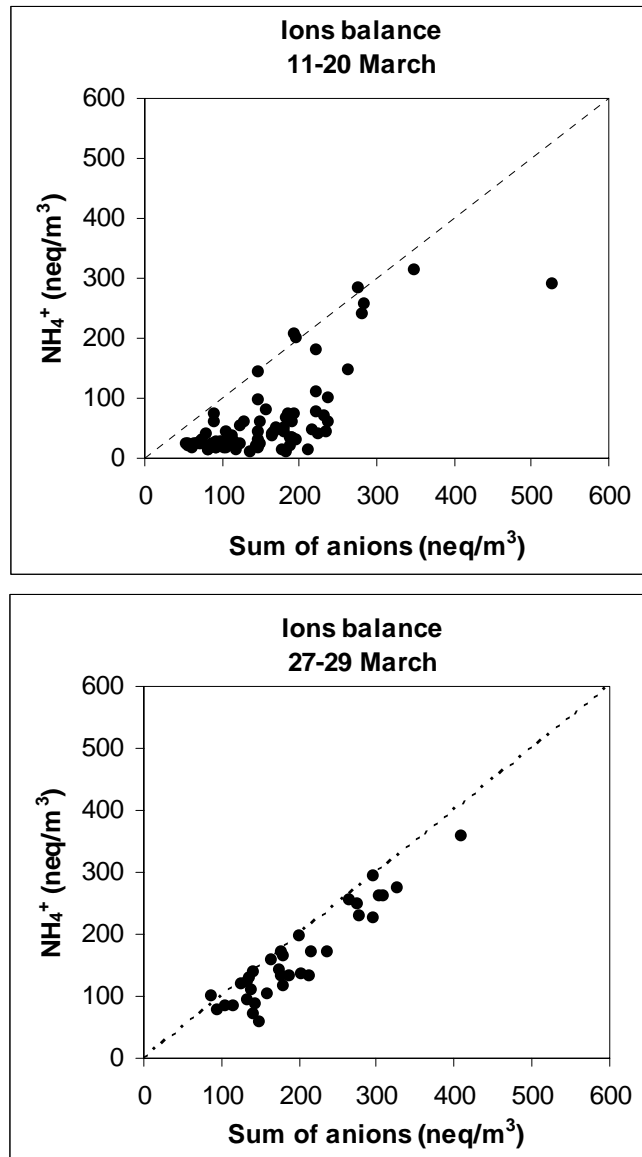


Figure 2. PM_{2.5} electroneutrality balances for 11-20 and 26-30 March periods (NH₄⁺ deficiency and sufficiency conditions, respectively). PILS data.

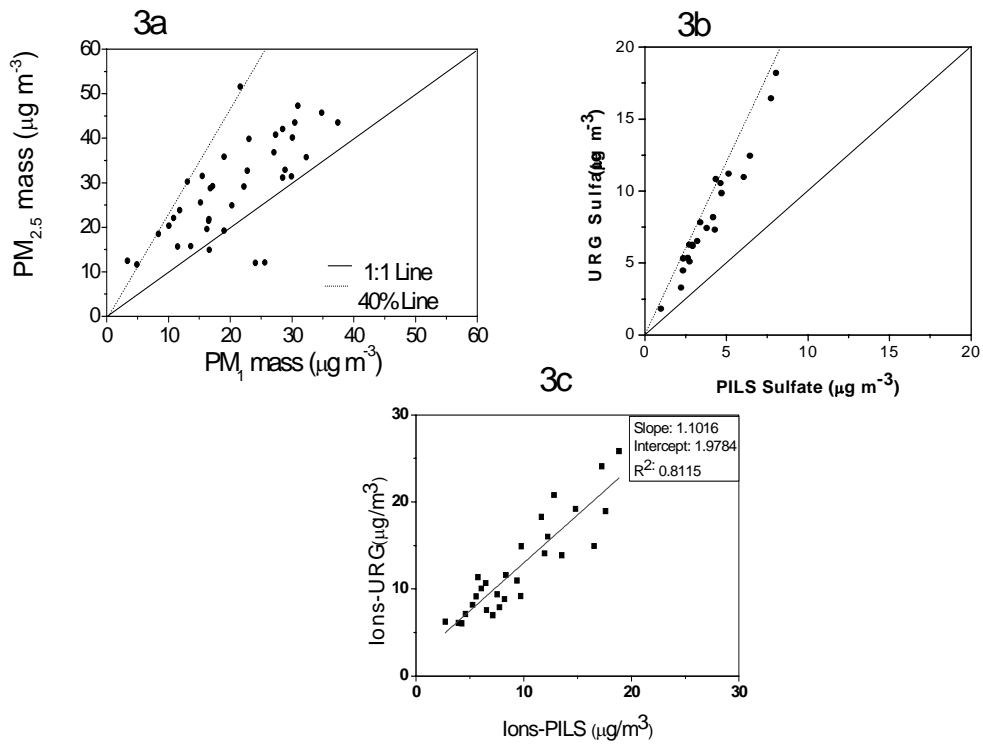


Figure 3. (a) URG- $PM_{2.5}$ versus PM_1 gravimetric mass. (b) Filter-based (URG) versus Pils sulfate measurements for the whole period of study (March 11-30). (c) Sum of species URG- $PM_{2.5}$ versus sum of species-Pils for the whole period of study (March 11-30).

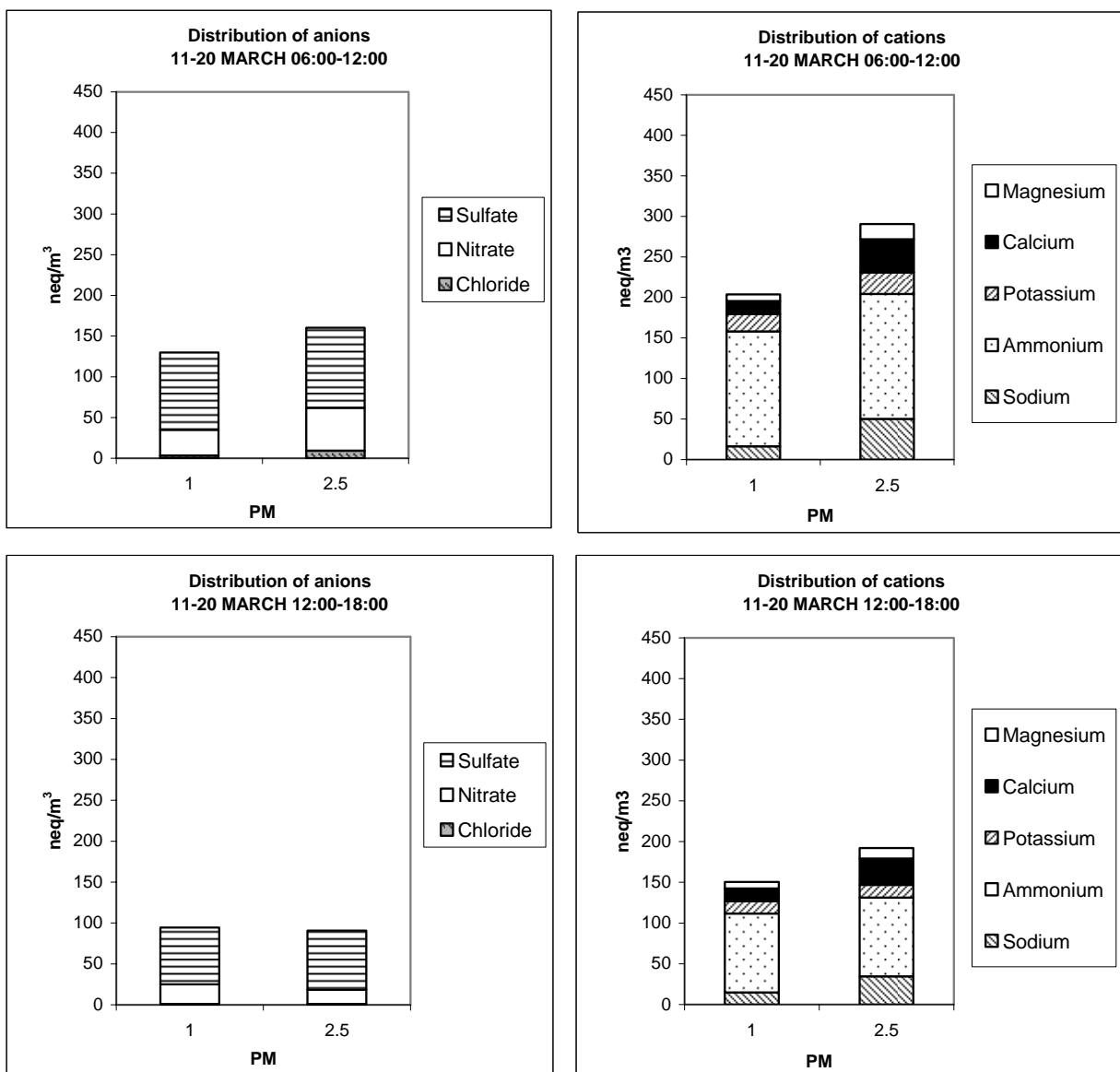


Figure 4. Distribution of URG-ions for the 11-22 March period. Sulfate was “corrected” as discussed in section 3.3.

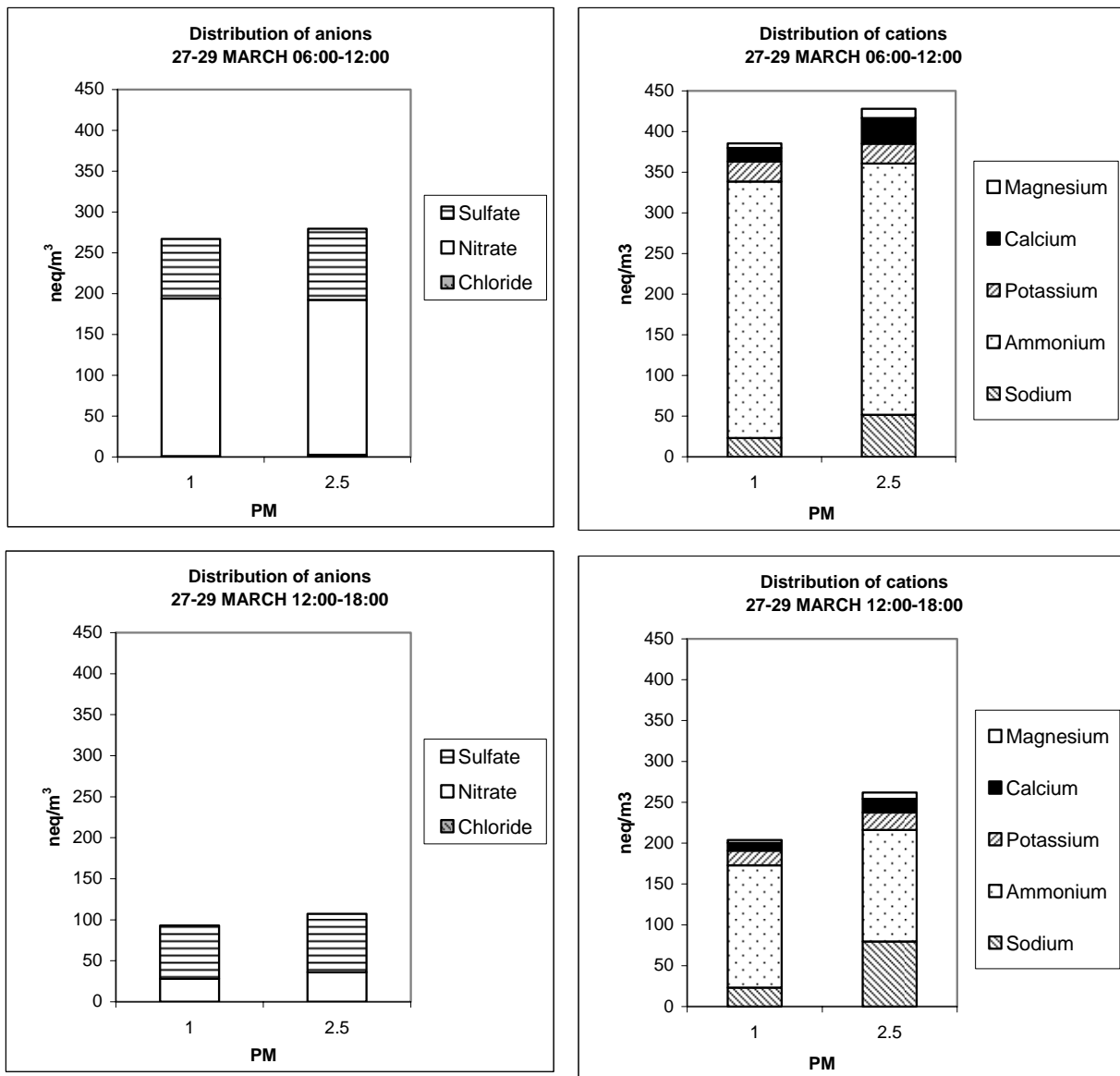


Figure 5. Distribution of URG-ions for the 26-30 March period. Sulfate was “corrected” as discussed in section 3.3.

Instrument	Operating principle	Variable	Sample duration	Model number/ manufacturer	Operating conditions	Features	Other features
TEOM-GIT ¹	Gravimetric (PM2.5), automated	Mass	Hourly-averaged	TEOM-1400a Patashnick & Rupprecht, Albany, N.Y.	T= 30°C VF ⁴ = 16.7 lpm	EPA-equivalent method	SES ² device
TEOM-DF ³	Gravimetric (PM2.5), automated	Mass	Hourly-averaged	TEOM-1400a Patashnick & Rupprecht, Albany, N.Y.	T= 35°C VF ⁴ =16.7 lpm	EPA-equivalent method	No devices
Partisol-DF ³	Gravimetric (PM2.5), Filter-based (PTFE Teflon)	Mass	24-hour averaged	FRM-2000 Patashnick & Rupprecht, Albany, N.Y.	T= ambient VF ⁴ = 16.7 lpm	EPA-referenced method	None
URG-PM(2.5)	(PM2.5), Filter-based (PC ⁵)	Inorganic anions/cations	Every 6-hours (diurnally)	Chapell Hill, NC	T= ambient VF ⁴ = 16.7 lpm	n/a	None
URG-PM(1.0)	(PM1.0), Filter-based (PC ⁵)	Inorganic anions/cations	Every 6-hours (diurnally)	Chapell Hill, NC	T= ambient VF ⁴ = 16.7 lpm	n/a	None
PILS - GIT ¹	(PM2.5), automated	Inorganic anions/cations	Hourly-averaged	GIT	T=ambient ⁶ VF ⁴ = 16.7 lpm	n/a	Denuders upstream
OCEC instrument	(PM2.5), automated	OC/EC	Hourly-averaged	Sunset Labs Field	T=ambient ⁶ VF ⁴ = 8 lpm	n/a	Denuders upstream

Notes: 1) GIT= Georgia Institute of Technology; 2) Sample Equilibration System; 3) DF= Mexico City Air Quality Monitoring Network; 4) Volumetric Flow (ambient); 5) Polycarbonate filter; 6) Sampling is also done at ambient T, but there may be changes in sample T due to differences in indoor/outdoor T, given that the sample line and instruments were in a climate controlled sampling trailer.

Table 1. Features of the PM instruments deployed at the T1 site.