

Chemical characterization of extractable water soluble matter associated with PM₁₀ from Mexico City during 2000

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Abstract

We report the chemical composition of PM₁₀-associated water-soluble species in Mexico City during the second semester of 2000. PM₁₀ samples were collected at four ambient air quality monitoring sites in Mexico City. We determined soluble ions (chloride, nitrate, sulfate, ammonium, sodium, potassium), ionizable transition metals (Zn, Fe, Ti, Pb, Mn, V, Ni, Cr, Cu) and soluble protein. The higher PM₁₀ levels were observed in Xalostoc (45–174 $\mu\text{g m}^{-3}$) and the lowest in Pedregal (19–54 $\mu\text{g m}^{-3}$). The highest SO₂ average concentrations were observed in Tlalnepantla, NO₂ in Merced and O₃ and NO_x in Pedregal. The concentration range of soluble sulfate was 6.7–7.9 and 19–25.5 $\mu\text{g m}^{-3}$ for ammonium, and 14.8–29.19 for soluble V and 3.2–7.7 ng m⁻³ for Ni, suggesting a higher contribution of combustion sources. PM-associated soluble protein levels varied between 0.038 and 0.169 mg m⁻³, representing a readily inhalable constituent that could contribute to adverse outcomes. The higher levels for most parameters studied were observed during the cold dry season, particularly in December. A richer content of soluble metals was observed when they were expressed by mass/mass units rather than by air volume units. Significant correlations between Ni–V, Ni–SO₄⁻², V–SO₄⁻², V–SO₂, Ni–SO₂ suggest the same type of emission source. The variable soluble metal and ion concentrations were strongly influenced by the seasonal meteoroclimatic conditions and the differential contribution of emission sources. Our data support the idea that PM₁₀ mass concentration by itself does not provide a clear understanding of a local PM air pollution problem.

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1. Introduction

Epidemiological studies have provided evidence associating PM levels and adverse health effects using gravimetric analysis of regulated PM (e.g. PM₁₀ or PM_{2.5}). However, the complex mixture of compounds associated to PM₁₀ in urban areas has shown that mass

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concentration by itself does not provide a clear understanding of a local PM air pollution problem as well as its potential impact on human health (Harrison and Yin, 2000; Tsai et al., 2000). The exact chemical and physical properties associated with health effects are uncertain and their toxicity mechanisms remain unclear (Paoletti et al., 2002). Among the potential hazardous characteristics of PM₁₀ discussed are their physical properties (e.g. size, number, surface area), particle acidity (H^+ , SO_4^{2-} , NO_3^- , NH_4^+), inorganic components (salts and metal oxides), organic compounds (PAH and derivatives) biological components (allergens, endotoxins) and the co-pollutant interactions (O_3 , SO_x , NO_x , CO) (Dreher, 2000). PM₁₀ toxicity can be related to soluble components, particularly the soluble transition metal content (Suarez and Ondov, 2002; Voutsas and Samara, 2002), a crucial factor in lung inflammation probably due to their bioavailability (Dreher et al., 1997; Frampton et al., 1999). Reactive transition metals, such as V, Zn, Fe and Cu, irritate respiratory tissues by stimulating local cells to release reactive oxygen species (ROS) and inflammatory mediators, such as tumor necrosis factor alpha, nuclear factor-kappaB and interleukin-6 (Carter et al., 1997; Jimenez et al., 2000). These observations are important considering that PM include first-series transition metals present as insoluble (e.g. silicates, aluminates) or soluble salts (e.g. sulfates) (Carter et al., 1997; Ondov and Wexler, 1998), able to exchange electrons and catalyze free radical production such as: superoxide anion ($\text{O}_2^{\bullet-}$), hydroxyl radical (HO^\bullet), singlet oxygen ($^1\text{O}_2$) and hydrogen peroxide (H_2O_2). It has been well documented that Fe, along with other transition metals such as Cu and V, has the ability to generate free radicals via the Fenton reaction (Donaldson and MacNee, 2001).

Air quality in Mexico City has become a serious concern due the persistent high mass concentration of PM and ozone (O_3) levels. The physical and chemical aspects of PM from different locations of Mexico City have been well documented (Salazar et al., 1989; Aldape et al., 1991; Castellanos et al., 1991; Miranda et al., 1992; Chianelli et al., 1998; Chow et al., 2002; Mugica et al., 2002; Vega et al., 2002, 2003). The concentration has decreased, from average excesses of the PM₁₀ daily standard ($150 \mu\text{g m}^{-3}$) of 47.7% of days per year in the period of 1996–1998, to only 5% and 12% of days in 1999 and 2000, respectively. On the other hand, since 1995 annual average concentrations have exceeded the annual maximum level standard ($50 \mu\text{g m}^{-3}$). In 2000, the annual average levels fall in the range of $50\text{--}70 \mu\text{g m}^{-3}$, yet the northeast region in Mexico City has become a typical risk area since the levels reported are 2–3-fold higher than in other areas of Mexico City. Nonetheless, these studies have focused on evaluating mass concentration, elemental analysis or acid soluble species but little data is available on the occurrence of water soluble

species in PM. In this study we report the chemical composition of the water-soluble species associated to PM₁₀ in Mexico City during the second semester of 2000, with particular attention to chemical species described in the literature as potentially toxic to human health.

2. Materials and methods

2.1. Samples, reagents and filters

PM₁₀ samples were simultaneously collected at four ambient air quality monitoring sites from the Air Quality Monitoring Network—SIMAT, GDF in Mexico City. Downtown-Merced located in an area with high vehicular emissions, Northeast-Xalostoc and Northwest-Tlalnepantla, representing large and complex industrial areas with high traffic and poor vegetation, and Southwest-Pedregal, a typical low traffic residential area. A total of 122 samples were obtained from these sites during July to December of 2000 (an average of five samples per month, per site). Samples were collected on glass fiber filters with a Sierra Andersen High-Volume PM₁₀ sampling system, operated at constant flow rate ($1.13 \text{ m}^3 \text{ min}^{-1}$) and programmed to collect 24 h samples. Quality audits of flow rates were found within specifications. The PM₁₀ mass was determined by gravimetric analysis on glass fiber filters stabilized and weighed before and after sampling (45% humidity and $20 \pm 2^\circ\text{C}$ constant temperature). The air volume pulled through each filter was 1630 m^3 and the mass ranged from approximately 30.8 to 286.6 mg per filter (EPA Method IO-2.1; US-EPA, 1999). Meteorological data (wind speed and direction) and data for other gas pollutants were collected simultaneously.

2.2. Extraction of water soluble compounds

The filters were fractionated and one fraction was shaken in a 50 ml conical glass tube with 10 ml Milli-Q deionized water for 15 min in a Branson ultrasonic bath. Soluble components were separated from the insoluble by centrifugation at 2500 rpm for 10 min. The supernatant was filtered twice using nylon and hydrophilized poly(tetrafluoroethylene) membrane filters (0.45 and $0.2 \mu\text{m}$) and stored frozen (-40°C) until chemical analysis (Frampton et al., 1999; Salonen et al., 2000). Extractions of 20 mg of a well-characterized urban dust (SRM 1649a standard reference material NIST), field samples and filter blanks were handled and analyzed under the same procedure, for quality assurance.

2.3. Determination of ionizable metal concentration

Zinc, iron, nickel, vanadium, copper, manganese, chromium and lead were measured in the supernatants

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