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Inhalable desert dust, urban emissions, and potentially biotoxic metals in urban Saharan–Sahelian air

V.H. Garrison [a,*], M.S. Majewski [b], L. Konde [c], R.E. Wolf [d], R.D. Otto [e], Y. Tsuneoka [f]

[a] US Geological Survey, 600 4th Street South, St. Petersburg, FL 33701, USA
[b] US Geological Survey, 6000 J St., Sacramento, CA 95819-6129, USA
[c] US Embassy, Bamako, Mali
[d] US Geological Survey, Denver Federal Center, Lakewood, CO 80225-0046, USA
[e] US Department of State, Office of Medical Services, 2401 E. Street NW, Washington, DC 20522-0101, USA
[f] Embassy of Japan in Sri Lanka, No. 20 Gregory's Road, Colombo 7, Sri Lanka

HIGHLIGHTS

- $PM_{2.5}$ and PM_{10} exceeded air quality limits 58–98% of days sampled in Bamako, Mali.
- PM_{10} contains potentially biotoxic and bioactive metals and metalloids.
- PM_{10} is predominately from crustal material; anthropogenic emissions are secondary.
- Inhalable particulate levels may threaten human health in urban West Africa.

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ABSTRACT

Saharan dust incursions and particulates emitted from human activities degrade air quality throughout West Africa, especially in the rapidly expanding urban centers in the region. Particulate matter (PM) that can be inhaled is strongly associated with increased incidence of and mortality from cardiovascular and respiratory diseases and cancer. Air samples collected in the capital of a Saharan–Sahelian country (Bamako, Mali) between September 2012 and July 2013 were found to contain inhalable PM concentrations that exceeded World Health Organization (WHO) and US Environmental Protection Agency (USEPA) $PM_{2.5}$ and PM_{10} 24-h limits 58 – 98% of days and European Union (EU) PM_{10} 24-h limit 98% of days. Mean concentrations were 1.2-to-4.5 fold greater than existing limits. Inhalable PM was enriched in transition metals, known to produce reactive oxygen species and initiate the inflammatory response, and other potentially bioactive and biotoxic metals/metalloids. Eroded mineral dust composed the bulk of inhalable PM, whereas most enriched metals/metalloids were likely emitted from oil combustion, biomass burning, refuse incineration, vehicle traffic, and mining activities. Human exposure to inhalable PM and associated metals/metalloids over 24-h was estimated. The findings indicate that inhalable PM in the Sahara–Sahel region may present a threat to human health, especially in urban areas with greater inhalable PM and transition metal exposure.

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1. Introduction

The World Health Organization (WHO) declared air pollution "the world's largest single environmental health risk" and estimated that exposure to outdoor inhalable particulate matter (PM) caused 3–4 million premature deaths in 2012, with more than 80% of those in cities and rural areas in low- and middle-income countries (WHO, 2014). Over the past 20 years, evidence from a rapidly growing body of literature has shown that inhalable PM has an adverse effect on human health over a time frame of hours to years (review by Brook et al., 2010), most notably increased mortality from heart attack and stroke and increased respiratory diseases and cancers of the lung and urinary tract (WHO, 2014). Particles <10 micrometers (μm) aerodynamic diameter (PM_{10}) can be inhaled into the lungs and particles <2.5-μm aerodynamic diameter ($PM_{2.5}$) reach more deeply into the lungs where gas exchange occurs (alveolar spaces). Most recent epidemiological studies quantify increased risk of morbidity (disease incidence) or mortality from heart disease, stroke, respiratory disease, and/or all causes

* Corresponding author at: 600 4th Street South, St. Petersburg, FL 33701, USA. Tel.: +1 408 329 2841; fax: +1 727 502 8032.
E-mail addresses: ginger_garrison@usgs.gov (V.H. Garrison), majewski@usgs.gov (M.S. Majewski), lacikonde.lk@gmail.com (L. Konde), rwolf@usgs.gov (R.E. Wolf), ottord@state.gov (R.D. Otto), yutaka.tsuneoka@mofa.go.jp (Y. Tsuneoka).

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with increases in ambient PM_{10}, $PM_{2.5}$, or other PM fractions such as ultrafine particulates (UFP, <0.1 μm). A recent study of 11 groups in 5 European countries estimated a 13% increased risk of heart attack with a 5 microgram per cubic meter (μg/m^3) increase in $PM_{2.5}$ and 12% increased risk with a 10 μg/m^3 increase in PM_{10} (Cesaroni et al., 2014). These increases were found to be valid at PM concentrations below current European Union (EU) mean annual limits and target levels (Cesaroni et al., 2014). Estimates vary among studies due in part to differences in PM chemical composition, particle size/shape, meteorological conditions, and experimental design.

Epidemiological studies and laboratory investigations of toxicity and physiological pathways have been conducted almost exclusively in Europe, the US, and to a lesser extent China, with only a few studies conducted in the Sahara–Sahel region of Africa, an area with some of the highest PM concentrations in the world (de Longueville et al., 2010, 2013 and Ginoux et al., 2001). The Sahara–Sahel is the largest source of atmospheric PM in the world. An estimated 300–800 million metric tonnes of Saharan dust (SD) are eroded from the surface each year, mobilized into the atmosphere (d'Almeida et al., 1986; Kaufman et al., 2005; Marticorena et al., 1997 and Ridley et al., 2012), and transported within Africa, to the Americas, Europe, the Gulf of Guinea, and to a lesser extent, Asia (Washington et al., 2003 and Resch et al., 2007). Airborne PM is predominately mineral dust (Formenti et al., 2008). Particles of biogenic origin also are present — diatoms from the Bodélé Depression (Bristow et al., 2009), microorganisms (Kellogg et al., 2004) and associated endotoxins (Sandström and Forsberg, 2008), pollen (Cariñanos et al., 2004), insects (Ritchie and Pedgley, 1989), and particulates from burned biomass (from cooking fuel, land-clearing, and agricultural waste disposal) (Formenti et al., 2008 and Ruellan et al., 1999). Saharan–Sahelian urban areas have undergone rapid expansion in the past few decades, with resulting increases in emissions of PM and persistent organic contaminants such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls, and pesticides (Garrison et al., 2014) from urban/industrial activities such as fossil-fuel combustion (vehicles, power plants, industrial machinery), traffic, refuse incineration, manufacturing, oil recovery and refining, and mining (Csavina et al., 2012; Dieme et al., 2012; Koçak et al., 2011; Petzold et al., 2011 and Rodríguez et al., 2011).

Total suspended particulate (TSP) concentrations in the Sahara–Sahel are high, 13,735 μg/m^3 at a rural site in central Mali during an intense SD incursion (Gillies et al., 1996). Clearly, people in the Sahara–Sahel are exposed to exceptionally high concentrations of PM. But what concentrations of PM are people exposed to over time, how frequently are they exposed, what is the composition of PM, and what are the health implications (de Longueville et al., 2010, 2013)? Few investigations have quantified PM, much less inhalable PM, in the Sahara–Sahel for more than weeks at most (e.g., Weinstein et al., 2010), and none have done so in urban areas. The African Monsoon Multidisciplinary Analysis international program monitored PM_{10} mass and particle concentrations over 3 years at three rural sites along a Niger - Mali - Senegal transect and reported median daily mass concentrations of 75.3–87.2 μg/m^3 (Marticorena et al., 2010).

Investigations now focus on physical properties, chemical composition, origins (crustal or anthropogenic) of PM_{10} and subfractions ($PM_{2.5}$, UFP) and how they differentially affect biotoxicity, bioactivity, and ultimately, human morbidity and mortality. To date, few studies have investigated inhalable PM composition at urban sites in the Sahara–Sahel that are exposed to both mineral dust and anthropogenic PM. Those investigations, although informative, were either short in duration (Weinstein et al., 2010) or focused on toxicity of a few PM_{10} and $PM_{2.5}$ samples (Dieme et al., 2012 and Val et al., 2013).

To better understand the quantities of inhalable PM and potentially biotoxic and bioactive elements to which people in the region's urban areas are exposed, this pilot study was undertaken in Bamako (BKO), capital of the Republic of Mali. The objectives were to: (a) quantify the daily concentrations of ambient inhalable PM ($PM_{2.5}$ and PM_{10}) throughout a year; (b) quantify the concentrations of potentially biotoxic and bioactive elements in PM_{10}; and (c) estimate the quantities of $PM_{2.5}$, PM_{10}, and PM_{10}-associated trace elements that a person could inhale over time to provide real-world concentrations of inhalable PM and potentially biotoxic and bioactive metals/metalloids for laboratory studies.

2. Methods

2.1. Study site

Outdoor air samples were collected within the US Embassy Bamako compound [12° 37.7′ N, 8° 01.2′ W; 325 meters (m) elevation], 3 kilometers (km) southwest of the BKO city center (Fig. 1). Site selection was based on distance from structures, security of equipment and personnel, and logistical requirements. BKO, a rapidly expanding urban area of more than 2 million residents, is located in the Niger River Valley in the Sahel region of northwest Africa. The region is impacted by SD air mass incursions, which are more frequent and more intense during the dust season (November–May). Many roads are unpaved. Vehicle use, especially two-stroke motorbikes, has increased dramatically in the past 15 years. Diesel-powered buses and trucks are the primary long-distance modes of transport, and generally are not well-maintained. Traffic congestion, to the point of gridlock, is commonplace. No refineries, steel, chemical, or other heavy industries operate in the area. Pesticide repackaging, plastic-bag manufacturing, leather tanning, and fabric dyeing are the largest industries, and the majority of businesses are small-to-cottage in size. Beginning in 2008, lead (Pb) additives were banned from petrol, although a small stock continued to be sold in small quantities.

2.2. Sampling

Ambient air was sampled for total suspended particulates (TSP) and two size fractions that have been shown to adversely impact human health: $PM_{2.5}$ and PM_{10}. Samples were collected for approximately 24 hours (h) (mean sampling time = 24.3 h) daily from 13 to 28 September 2012 and thereafter, Monday through Friday (1 October 2012–9 July 2013). A total of 133 $PM_{2.5}$, 132 PM_{10}, and 56 TSP samples were collected for gravimetric analysis. Only PM_{10} samples were analyzed for elemental composition. $PM_{2.5}$ and PM_{10} fractions were collected using low-volume [5 liter per minute (L/min)] battery-operated samplers (AirMetrics, MiniVol), fitted with a $PM_{2.5}$ or PM_{10} cut-off orifice. A diaphragm pump (Barnant, Air Cadet Model 400–1902; 5 L/min, 230 volts) was used to collect TSP samples. Ongoing problems with the electrical supply and diaphragm pump limited the number of TSP samples collected. $PM_{2.5}$ was collected on polytetrafluoroethylene filters [46.2 millimeter (mm) polypropylene ring; 47 mm; Whatman 7592-104]. PM_{10} and TSP were collected on quartz-fiber filters [QFF; Millipore #AQFA4700; 47 mm, 500 μm thickness; compliant with US Environmental Protection Agency (USEPA) PM_{10} ambient air-monitoring method (CFR, 1999)] that had been preconditioned at 600 °C for 8 h. All filter media were held in MiniVol filter-holder assemblies fitted with louvered inlets to protect from environmental contamination and rain. Filters were located 2 m above ground level (approximately human-head-height) and approximately 30 m apart. Samplers were checked daily for leaks and zero flow, and flow rate was adjusted to 5.0 L/min using a calibration orifice calibrated against a primary standard traceable to the National Institute of Standards and Technology (NIST). Flow rates were recorded upon deployment and retrieval of each sample. All filters were stored in 47-mm polyethylene petri dishes, away from direct light, in a desiccator, weighed [22–24 °C, 31–35% relative humidity (RH)] pre- and post-sampling on an ultra-microbalance (equipped with static ionizer), and transported in petri dishes sealed in plastic bags. Laboratory-field blanks for both media were collected monthly and handled identically to samples.