Trace-metal concentrations in African dust: Effects of long-distance transport and implications for human health

Virginia Garrison[A], Paul Lamothe[B], Suzette Morman[B] and Geoffrey Plumlee[B]

[A]U.S. Geological Survey, St. Petersburg, FL, USA, Email ginger_garrison@usgs.gov
[B]U.S. Geological Survey, Denver, CO, USA, Email plamothe@usgs.gov, smorman@usgs.gov, gplumlee@usgs.gov

Abstract
The Sahara and Sahel lose billions of tons of eroded mineral soils annually to the Americas and Caribbean, Europe and Asia via atmospheric transport. African dust was collected from a dust source region (Mali, West Africa) and from downwind sites in the Caribbean [Trinidad-Tobago (TT) and U.S. Virgin Islands (VI)] and analysed for 32 trace-elements. Elemental composition of African dust samples was similar to that of average upper continental crust (UCC), with some enrichment or depletion of specific trace-elements. Pb enrichment was observed only in dust and dry deposition samples from the source region and was most likely from local use of leaded gasoline. Dust particles transported long-distances (VI and TT) exhibited increased enrichment of Mo and minor depletion of other elements relative to source region samples. This suggests that processes occurring during long-distance transport of dust produce enrichment/depletion of specific elements. Bioaccessibility of trace-metals in samples was tested in simulated human fluids (gastric and lung) and was found to be greater in downwind than source region samples, for some metals (e.g., As). The large surface to volume ratio of the dust particles (<2.5 µm) at downwind sites may be a factor.

Key Words
African dust, human health, trace-element enrichment, long-distance transport, metal bioaccessibility.

Introduction
The African dust system is the largest in the world, annually exporting billions of tons of eroded mineral soils to the Caribbean and Americas, Europe and Asia via atmospheric transport. Dust from Africa is a known source of nutrients and co-factors to downwind organisms and ecosystems, both terrestrial (e.g., the Amazon Basin, Swap *et al.* 1992) and marine (e.g., Jickells 1999). During long-distance transport, larger particles are removed via gravitational settling such that the air mass becomes enriched in fine particles (<2.5 µm aerodynamic diameter) as they are transported to the Caribbean and beyond. The resulting small particles are a cause for concern because fine particles are respirable and have been associated with increased incidence of cardiovascular and pulmonary disease and mortality. As part of a larger study investigating the effects of African dust air mass composition (trace elements and anthropogenic contaminants such as pesticides, polycyclic aromatic hydrocarbons, and polychlorinated biphenyls) on human health and downwind ecosystems such as coral reefs (Garrison *et al.* 2003), samples of African desert dust were collected in a dust source region and at downwind sites and analysed for trace-element concentrations and enrichment. Bioaccessibility of dust-borne metals in simulated lung and gastric fluids was also investigated.

Methods
Sites
A. Source region:
1. dust - Emetteur Kati, Mali (12.69°N, 8.02°E; 555 m elevation; 2-15 April 2008; n = 8)
2. dry deposition - Bamako, Mali (12.65 °N, 8.03 °E; 385 m; 19 Mar-15 May 2002, Apr 2003; n = 3).

B. Downwind sites:
1. SE Caribbean: Flagstaff Hill, Tobago (11.33°N, 60.54°W; 329 m; 27 May-22 June 2008; n = 5)
2. NE Caribbean: St. Croix, Virgin Islands (17.75°N, 64.59°W; 27 m; 20 Jun-24 Aug 2008; n = 5)

Field sampling
Samples of total suspended particles were collected using high-volume brushless motors (110v/12 amp or 220v/6amp) to pull 200 – 1000 m^3 air through pre-baked (600C, 8 hrs) and pre-weighed 90 mm quartz-microfiber filters (QM/A) in Teflon filter holders. Flow rates were determined using a Gilmont #6 calibrated flowmeter. Field blanks were collected during each sampling period at each site. Samples and blanks were placed in individual sealable plastic bags and frozen until analysis. Air samples at downwind sites were collected only when: the wind direction was from the east to southeast; the Navy Aerosol Analysis and

1 – 6 August 2010, Brisbane, Australia. Published on DVD.

Prediction System model indicated African dust; and when Saharan dust was observed in the atmosphere. The presence of Saharan dust was confirmed in the field by: 1) the presence of reddish-brown particles on filters; 2) high Fe content of particles; and, with further confirmation after trace-element analysis by 3) La-Sc-Th ratios within the range of African dust (Muhs *et al.* 2007).

Laboratory and data analysis
Samples and field blanks were analyzed for 32 elements using inductively coupled-plasma mass spectrometry (Briggs and Meier 2002), instrumental neutron activation analysis and/or graphite-furnace atomic-absorption spectrometry. Because sampler enclosures were made of aluminium sheeting, Al concentrations in samples were not reliable. Trace-element enrichment factors were determined by normalizing sample concentrations to average Upper Continental Crust (UCC) values of Wedepohl (1995). Downwind sample (TT and VI) concentrations were also compared to local (TT and VI) soils as a check for local contamination.

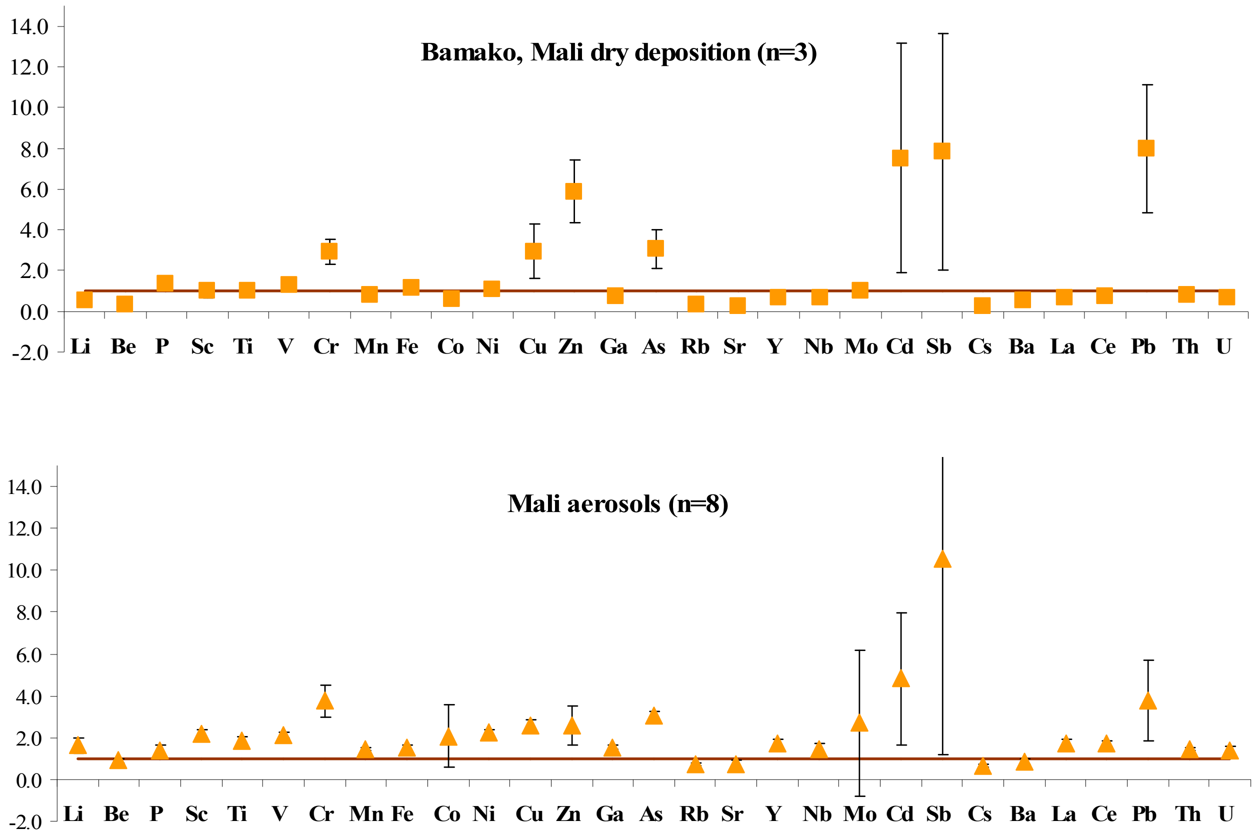

Figure 1. Enrichment of trace-metals in African dust and dry deposition samples from the dust source region relative to average upper continental crust composition (orange line; Wedepohl 1995). Enrichment factor shown on y-axis; error bars represent one standard deviation.

Results

Concentrations of 32 elements analyzed in dust samples collected from the dust source region (Mali) and from downwind sites (TT and VI) in the Caribbean were generally found to be similar to average UCC composition (i.e., enrichment factor close to 1) but some elements exhibited evidence of depletion or enrichment (Figures 1 and 2). These findings are in general agreement with other studies (e.g., Schütz and Rahn 1982; Castillo *et al.* 2008; Trapp *et al.* 2008). Only source region dust and dry deposition samples were found to be enriched in Pb, with local/regional use of leaded fuel the most likely source. The enrichment of Cd and Zn in dry deposition samples from the Niger River Valley in Bamako, Mali (Figure 1) was similar to that reported in dust aerosol samples collected in Barbados (Trapp *et al.* 2008) and considerably lower than values associated with pollution sources such as tire dust (Ozaki *et al.* 2004; Bermili *et al.* 2006). Sb enrichment was most pronounced in Mali samples but within reported values for desert dust (Schütz and Rahn 1982). Dust particles transported long-distances (VI and TT samples) showed greater enrichment of Mo and minor depletion of other trace-elements (Li, Ti, La, Ce, Th, U) relative to source region aerosols (Figures 1 and 2). The enrichment/depletion patterns in Tobago and VI samples (Figure 2) were most likely the result of chemical and physical processes during long distance transport, the distance transported, and the resulting fine particle size of dust at downwind sites. Mo enrichment has been reported to be greatest in the finest particle fraction (0.3-1.5 µm; Castillo *et al.* 2008). Bioaccessibility of dust trace-elements in simulated human fluids (gastric and lung) was found to be greater in downwind than source region samples, for a few elements (e.g., As; Morman *et al.* 2009). Total As concentrations in fluids showed > 40% bioaccessibility in most samples (Morman *et al.* 2009). The relatively small size of particles (high surface area to volume ratio) at downwind sites may be a factor in increased bioaccessibility.

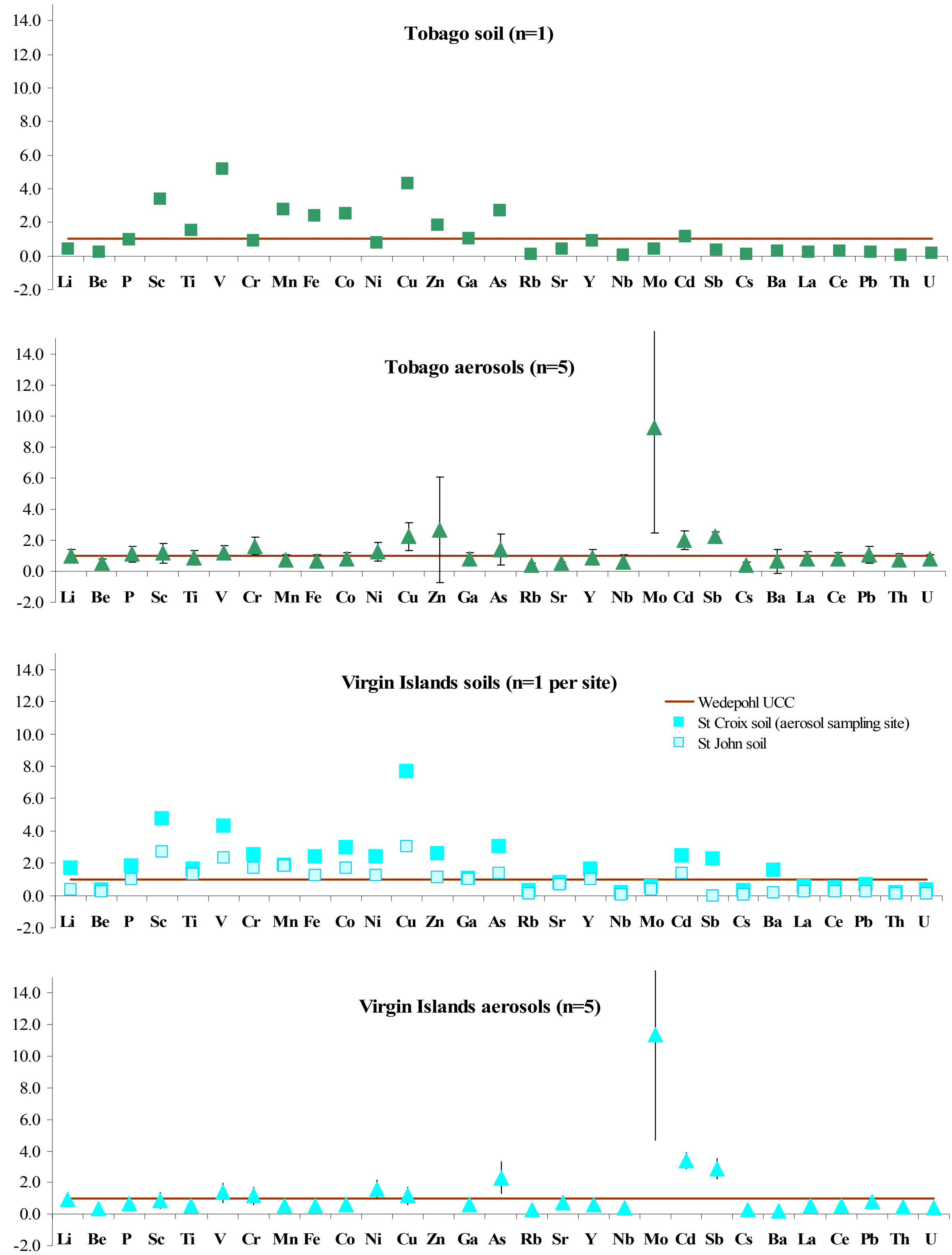

Figure 2. Enrichment of trace-metals in African dust and in soils at downwind sites to average upper continental crust composition (orange line; Wedepohl 1995). Enrichment factor shown on y-axis; error bars represent one standard deviation.

Conclusion

Trace-element concentrations in African dust collected from the source region (Mali) and from downwind sites in the Caribbean were similar to UCC composition. Minor enrichment/depletion of some trace elements was found but concentrations did not exceed those known to be toxic to humans and other animals. Dust and dry deposition samples from the dust source region were enriched in Pb, most likely due to use of leaded gasoline in the region during the sampling periods. Enrichment/depletion of trace elements in dust from downwind sites was most likely a function of chemical and physical processes during long-distance transport and distance transported. Of greatest concern are the possible effects of African dust-associated trace-elements that act as cofactors (e.g., Fe, Zn) or are known xenobiotics (As and Pb) on human health as well as microbial communities, organisms, and ecosystem processes at dust source and downwind locations. Investigation of bioaccessibility and biomobility of African dust–associated xenobiotics such as As should be the first priority.

References

Bermili W, Allen AG, Bary F, Harrison RM (2006) Trace metal concentrations and water solubility in size-fractionated atmospheric particles and influence of road traffic. *Environmental Science and Technology* **40**, 1144–1153.

Briggs PH, Meier AL (2002) The determination of 42 elements in geological materials by ICP-MS. In 'Analytical Methods for Chemical Analysis of Geologic and Other Materials, USGS Open file report 02-223'. (Ed. JE Taggert) Chapter I. (U.S. Geological Survey, Denver, Colorado, USA).

Castillo S, Moreno T, Querol X, Alastuey A, Cuevas E, Herrmann L, Mounkaila M, Gibbons W (2008) Trace element variation in size-fractionated African desert dusts. *Journal of Arid Environments* **72**, 1034–1045.

Garrison VH, Shinn EA, Foreman WT, Griffin DW, Holmes CW, Kellogg CA, Majewski MS, Richardson LL, Ritchie KB, Smith GW (2003) African and Asian dust: from desert soils to coral reefs. *Bioscience* **53**, 469-479.

Jickells T D (1999) The inputs of dust derived elements to the Sargasso Sea: a synthesis. *Marine Chemistry* **68,** 5–14.

Morman SA, Garrison VH, Plumlee GA, Lowers HA, Bunnell JE (2009) Assessing concentration and bioaccessibility of potentially toxic elements in African dust. In 'Proceedings of the Geological Society of America, Portland, Oregon, USA'.

Muhs DR, Budahn JR, Prospero JM, Carey SN (2007) Geochemical evidence for African dust inputs to soils of western Atlantic islands: Barbados, the Bahamas, and Florida. *Journal of Geophysical Research* **112**, doi:10.1029/2005JF000445, 2007.

Ozaki H, Watanabe I, Kuno K (2004) Investigation of the heavy metal sources in relation to automobiles. *Water, Air, & Soil Pollution* **157**, 203–222.

Schütz L, Rahn KA (1982) Trace-element concentrations in erodible soils. *Atmospheric Environment* **16,** 171–176.

Swap R, Garstang M, Greco S, Talbot R, Kallberg P (1992) Saharan dust in the Amazon basin. *Tellus* **44**, 133–149.

Trapp MJ, Millero FJ, Prospero JM (2008) Temporal variability of the elemental composition of African dust measured in trade wind aerosols at Barbados and Miami. *Marine Chemistry* doi:10.1016/j.marchem.2008.10.004

Wedepohl KH (1995) The composition of the continental crust. *Geochimica et Cosmochimica Acta* **59**, 1217–1232.