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Persistent organic contaminants in Saharan dust air masses in West Africa, Cape Verde and the eastern Caribbean

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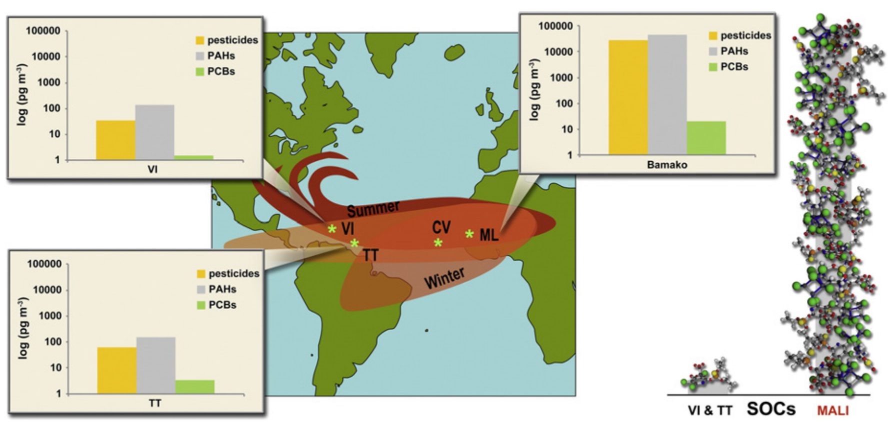
HIGHLIGHTS

- Saharan dust storms transport pesticides, PAHs and PCBs to the eastern Caribbean.
- SOC concentrations 1–3 orders of magnitude greater in Mali than eastern Caribbean
- SOC atmospheric concentrations were well below existing occupational guidelines.
- All dust storm samples contained mixtures of pesticides, PAHs and PCBs.
- Estimated PM_{10} and $PM_{2.5}$ concentrations frequently exceeded USEPA and WHO limits.

GRAPHICAL ABSTRACT



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ABSTRACT

Anthropogenic semivolatile organic compounds (SOCs) that persist in the environment, bioaccumulate, are toxic at low concentrations, and undergo long-range atmospheric transport (LRT) were identified and quantified in the atmosphere of a Saharan dust source region (Mali) and during Saharan dust incursions at downwind sites in the eastern Caribbean (U.S. Virgin Islands, Trinidad and Tobago) and Cape Verde. More organochlorine and organophosphate pesticides (OCPPs), polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyl (PCB) congeners were detected in the Saharan dust region than at downwind sites. Seven of the 13 OCPPs detected occurred at all sites: chlordanes, chlorpyrifos, dacthal, dieldrin, endosulfans, hexachlorobenzene (HCB), and trifluralin. Total SOCs ranged from 1.9–126 ng/m^3 (mean = 25 ± 34) at source and 0.05–0.71 ng/m^3 (mean = 0.24 ± 0.18) at downwind sites during dust conditions. Most SOC concentrations were 1–3 orders of magnitude higher in source than downwind sites. A Saharan source was confirmed for sampled air masses at downwind sites based on dust particle elemental composition and rare earth ratios, atmospheric back trajectory models, and field observations. SOC concentrations were considerably below existing occupational and/or regulatory limits; however, few regulatory limits exist for these persistent organic compounds. Long-term effects of chronic exposure

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to low concentrations of SOCs are unknown, as are possible additive or synergistic effects of mixtures of SOCs, biologically active trace metals, and mineral dust particles transported together in Saharan dust air masses.

1. Introduction

Long-range atmospheric transport (LRT) of semivolatile organic compounds (SOCs) is one of the primary pathways by which persistent organic contaminants such as organochlorine and organophosphorous pesticides (OCPPs), polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs) are distributed globally (e.g., Peterle, 1969; Risebrough et al., 1968, 1976). The Saharan dust system, largest in the world (Washington et al., 2003), annually exports an estimated billion tons of mineral dust from the Sahara–Sahel region of northwest Africa (e.g., d'Almeida, 1986; Ridley et al., 2012) thousands of kilometers west to the Caribbean and Americas, north to Europe, and east to Asia, periodically crossing to North America (Creamean et al., 2013; Hsu et al., 2012; McKendry et al., 2007). This global atmospheric transport system predominately carries eroded mineral soils but biogenic materials such as pollen (Cariñanos et al., 2004), microorganisms (e.g., Griffin et al., 2001; Kellogg et al., 2004), particles from fossil fuel and biomass burning in the Sahel (Formenti et al., 2008; Hand et al., 2010; Kandler et al., 2011), and insects such as African desert locusts (Ritchie and Pedgley, 1989) are periodically transported thousands of kilometers from the dust source area.

The highly heterogeneous Saharan dust air masses (see Reid et al., 2003 for detailed discussion) vary considerably in size, duration, and trajectory (Knippertz et al., 2009, 2011; Rajot et al., 2008). Quantities of dust transported and frequency of episodes vary in response to surface composition (Chiapello et al., 1997), regional meteorology (e.g., Engelstaedter and Washington, 2007), location and movement of the Intertropical Convergence Zone and North Atlantic Oscillation (Sunnu et al., 2008), and subsidence, advection and convective mixing of large-scale air masses (Reid et al., 2003). Aerosol composition, concentrations, and sizes vary spatially and temporally within a single dust episode and among episodes (e.g., Reid et al., 2003) and are a function of geologic (e.g., Ben-Ami et al., 2012; Moreno et al., 2006; Nalli et al., 2005; Prospero et al., 2002) and geographic origins (Moreno et al., 2006), meteorological conditions, human activities (e.g., agriculture, land disturbance, transportation, urbanization, and industry) (e.g., Kandler et al., 2011; Talbot et al., 1986; Tegen and Fung, 1995), and atmospheric residence time.

Atmospheric SOCs have been well-characterized in some regions but there is a paucity of information for the Sahara/Sahel and the eastern Caribbean. Recently established large-scale air monitoring networks using passive samplers in Africa, Europe and the Americas (e.g., Jaward et al., 2004c; Klánová et al., 2009; Pozo et al., 2004, 2006; Wong et al., 2009) provide valuable information on seasonal presence of gas-phase SOCs and, over time, trends will be identified. However, quantitative data on atmospheric concentrations of banned and current-use OCPPs, PAHs, and PCBs in source and remote regions are critical to accurately quantify exposure, and ultimately, assess risks to ecosystems, humans, and other organisms. Although transport of eroded mineral dust from West Africa to the Caribbean and the Americas has been well-studied (e.g., Delany et al., 1967; Prospero and Nees, 1977; Prospero et al., 1970, 1981), little is known of transport of other components such as SOCs. Pioneering work in the mid- to late 1960s in Barbados (Prospero and Seba, 1972; Risebrough et al., 1968; Seba and Prospero, 1971) detected organochlorine pesticides [dieldrin and dichlorodiphenyltrichloroethane (DDT) and degradates] associated with Saharan dust particles in the atmosphere but did not consider the gas-phase. Later work in Barbados sampled both gas and particle-associated phases, finding DDT and dieldrin levels 10–100 fold higher than previously reported values for particles (Bidleman et al., 1981) yet an order of magnitude less than in the Arabian and Red Seas and Persian Gulf (Bidleman and Leonard, 1982) and Gulf of Mexico (Giam et al., 1980). Subsequent to those studies, a number of pesticides widely used in the 1960s have been banned in much of the world because of their persistence in the environment and ability to bioaccumulate, biomagnify, and be toxic to humans and other organisms at low concentrations. Although use of some compounds has been banned for over three decades, some occur globally in the atmosphere today.

Pesticides were introduced in West Africa over the past several decades to control agriculture pests and disease vectors [e.g., mosquitoes (malaria, leishmaniasis), sand flies (onchocerciasis), and tsetse flies (trypanosomiasis)]. Use has increased substantially, particularly on export crops such as cotton and rice (van der Valk and Diara, 2000). Volatilization during and following application and during pesticide production and repackaging are primary sources of OCPPs to the atmosphere in the dust source region. Other potential sources are fine agricultural soils with sorbed OCPPs and contaminated desert soils. The Niger River of Mali and Niger is a prime example. Nutrients in flood-deposited sediments and proximity to water make river floodplains preferred sites to grow crops from garden plots to industrial-scale agriculture. Some OCPPs applied to crops sorb to fine floodplain soils which in turn can be lifted into the atmosphere by strong winds during the dry season, entrained in a high altitude transport system such as the Saharan Air Layer (SAL), and transported long distances. Sandy soils on the edge of the Sahara have been contaminated with DDT and dieldrin that leaked from containers staged to combat desert locust outbreaks.

Surface particles in both landscapes are prone to erosion, mobilization and LRT. Wind speed, gustiness (Engelstaedter and Washington, 2007), particle characteristics (size, shape, and composition), and regional meteorology drive the quantities of particles lifted from the surface, altitudes reached, and distances advected from the source area (e.g., Gillies et al., 1996; Reid et al., 2003). In the classical Saharan dust transport model, easterly trade winds move the SAL westward off the African coast, larger particles fall via gravitational settling to the lower altitudes of the SAL (and eventually the surface), and the dust air mass becomes enriched in finer particles with time. Generally, the smaller the particle (and higher the wind speed), the longer it can remain aloft and the farther it can be transported, such that nearly half of Saharan dust particles are <2.5 μm aerodynamic diameter ($PM_{2.5}$) when the SAL reaches the Caribbean (Li-Jones and Prospero, 1998) (Table S.1).

During the past two decades, plastics production, urbanization, and a rapid increase in motor vehicles (particularly older diesel vehicles and two-stroke gasoline engines) have resulted in an increased use of PCBs in electrical equipment and production of PAHs from fossil fuel combustion. Biomass burning in the countries bordering the Gulf of Guinea produces PAHs and black carbon that mix with Saharan dust air masses and undergo LRT to South America and to a lesser extent, the Caribbean (Rajot et al., 2008). In addition, ubiquitous small, open-flame fires throughout West Africa traditionally burned biomass for cooking fuel and to produce ash for fertilizing crops. Today, plastic bags, discarded household goods of synthetic materials, and tires are burned along with biomass (Garrison et al., 2003). PAHs and, potentially, chlorinated dioxins and furans from low temperature combustion, can rise into the atmosphere and be advected in dust air masses across oceans to distant continents.

As part of a larger investigation into the effects of Saharan dust incursions on ecosystems and human health, this study was initiated to (1) identify and quantify atmospheric anthropogenic SOC concentrations and (2) confirm the origin of air masses sampled at downwind sites off the coast of West Africa, and in the north- and southeastern Caribbean.