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


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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 PM10 and PM2.5 concentrations frequently exceeded USEPA and WHO limits.

GRAPHICAL ABSTRACT

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: chlordane, chlorpyrifos, dacthal, dieldrin, endosulfans, hexachlorobenzene (HCB), and trifluralin. Total SOCs ranged from 1.9–126 ng/m³ (mean = 25 ± 34) at source and 0.05–0.71 ng/m³ (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
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 event 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 dichlorophenyldichloroethane (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 (Gian 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 (PM2.5) 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.
2. Materials and methods

2.1. Sites

Air was sampled between December 2001 and August 2008 (Table S.2) from (1) a Saharan dust source-region: an urban site in the Niger River valley in Bamako, Republic of Mali (BKO) and a rural area on an escarpment above the Niger River near Kati, Mali (KATI) and (2) locations downwind of Saharan dust regions: offshore of West Africa [Sal Island, Republic of Cape Verde (CV)] and in the southeastern [Galera Point, Trinidad (TRIN) and Flagstaff Hill, Tobago (TOB)] and northeastern Caribbean [East End, St. Croix, U.S. Virgin Islands (VI)] (Fig. 1). The initial source-region sampling site was moved in 2004 from the Niger River valley (BKO) to the top of the escarpment 8.6 km to the north (KATI) to minimize urban contamination and for more reliable power. Downwind sampling site locations were carefully selected to minimize contamination from local sources. Downwind site samples were collected from the windward coasts/points of the islands and only when the wind was blowing from the east, off the ocean (see Supplementary material). Availability of sufficient and reliable electricity and security for equipment and personnel were constraining factors in site selection at all locations. Despite multiple attempts, samples from the source-region and downwind sites were not temporally related due to extreme logistical constraints. Garrison et al. (2011) provides detailed methodology.

2.2. Sampling

A total of 49 samples were collected (Table S.2) from the six sites for SOC, trace metal, and particle gravimetric analysis. Sampling methods are described in detail elsewhere (Garrison et al., 2011). Briefly, ambient air was sampled for SOCs and metals in total suspended particles (TSP) and for SOCs in the gas phase using high volume blowers motors. Particle-associated and gas-phase SOCs were collected on a pre-conditioned glass fiber filter (GFF) followed by two pre-cleaned polyurethane foam plugs (PUF) housed in Teflon cartridges. Particles for metal analysis were collected on a pre-conditioned quartz fiber filter (QFF) in a nylon and Teflon filter holder. Sampling duration (24–96 h) and volume (209–822 m³) for SOCs, 231–711 m³ for metals) varied as a result of atmospheric dust concentrations and filter loading, reliable and sufficient electricity, and weather (rain, storms). Field blanks were taken for each type of analysis during each sampling period at each site and handled identically to samples. All samples were stored frozen (−4 °C) until analysis.

2.3. SOC laboratory analysis

Sixty-four targeted historical and current-use OCPs, six PAHs, and six PCB congeners (101, 118, 138, 153, 183, and 187) were measured in the particle and gas-phase components of the air samples. Descriptions of analytical methods used and lists of SOCs analyzed at each laboratory are detailed elsewhere (Garrison et al., 2011).

2.4. Elemental analysis

Total particles 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 spectrophotometry.

2.5. Data processing

SOC and metal analytical data were field-laboratory blank corrected. Some OCP data were pooled prior to data analysis: trans-chlordane, cis- and trans-nonachlor as “chlorodanes”; p,p′-DDT, breakdown products o,p′- and p,p′-DDE and -DDE, and the isomer o,p′-DDT as “DDX”; and, Endosulfan I, II and sulfate as “endosulfans”. Because ambient temperatures varied among sites during sampling (21–55 °C), sample volumes (m³) were corrected to 298 K and 1 atmosphere pressure using data from local airport meteorology stations near each site (Meteorological Terminal Aviation Routine data).

2.6. Statistical analysis

Random numbers were generated between zero and estimated detection limits and substituted for non-detects in the dataset (Aruga, 1997). To compare SOC profiles among samples, Principal Component Analysis (PCA) was performed on individual SOC concentrations normalized to total SOCs. PCA and cluster analysis were executed using PRIMER 6® software. Differences in TSP concentrations among source and downwind dust and non-dust conditions were tested using a Student’s t-test (Zar, 2004). Data were further analyzed using non-parametric descriptive statistics (Tables S3–5) because number of samples varied among sites and few non-dust-condition samples were collected.

2.7. Air mass origin

A weight of evidence approach was used to establish if each air mass sampled at downwind sites was of Saharan origin by using field observations, analytical data (32 elements), an aerosol forecast/hindcast model, and an atmospheric transport and dispersion model. All samples from Mali were considered of Saharan-Sahelian origin. In the field, a Saharan dust air mass incursion at downwind sites was indicated by (1) degradation of visibility (Fig. S1); (2) wind direction between east-northeast to southeast; (3) presence of reddish-brown particles on filters; and, (4) dust forecast by the Navy Aerosol Analysis and Prediction System Global Aerosol Model (NAAPS, http://www.nrlmry.navy.mil/aerosol_web/Docs/globaer_model.html).

Air mass origin of each sample was further investigated based on elemental composition of samples. Specifically, sample iron (Fe) content (ppm), lanthanum–scandium–thorium (La–Sc–Th) ratios (Muhs et al., 2007), and enrichment profiles of 30 elements were compared to Saharan-Sahel dust literature values, source-region samples from this study, local soils (TOB, VI), and Montserrat volcanic ash (Supplementary material). Element enrichment factors were calculated against average upper continental crust elemental composition as in Wedepohl (1995). Because aluminum (Al) environmental enclosures housed
3. Results and discussion

3.1. Air mass origin

Trace metal composition, elemental enrichment factors, and La–Sc–Th ratios of total suspended particles (TSP) confirmed that all downwind samples (CV, TOB, TRIN and VI) collected during Saharan dust-event conditions were of Saharan origin and not local or regional (Figs. 2 and S2). La–Sc–Th ratios of BKO and KATI dust samples, Mauritanian and KATI soils, BKO dry deposition, and downwind dust-incursion samples clustered together, whereas downwind samples collected during non-dust conditions (air mass origin not Saharan), soils from downwind sample sites, and Montserrat volcano (Caribbean) ash were distinct from samples of Saharan origin (Fig. 2). The La–Sc–Th analysis suggested the presence of Montserrat ash in one VI sample of an air mass that originated over West Africa (7–9 July 2006; Fig. 2). HYSPLIT back trajectories confirmed possible regional input from Montserrat volcanic ash in that sample (Fig. S3). NAAPS models and HYSPLIT back trajectories provided additional substantiation of a Saharan origin of downwind samples of dust-incursions and transport of North American, European or marine influence in non-dust period samples. Regional sources likely contributed SOCs to two downwind samples: a Saharan dust air mass that moved over northeastern South America (Fig. S4) and a non-dust air mass that traversed the northeastern Caribbean (Fig. S5) within the boundary layer and within 24-h of sample collection. In a non-dust period sample, the movement of boundary layer air from SW Europe directly to the Lesser Antilles exemplifies the Atlantic “shortcut” proposed by Gangoiti et al. (2006) (Fig. S6).

3.2. Total suspended particulates

TSP concentrations ranged from 93 to 657 μg/m³ (mean = 336 ± 150) in Mali, 10–319 μg/m³ (mean 112 ± 81) at downwind sites during dust conditions, and 28–63 μg/m³ (mean = 40 ± 16) at downwind sites in non-dust conditions (Fig. 3). Atmospheric dust concentrations were significantly greater in Mali than downwind sites during dust conditions (p < 0.0005) and in downwind dust than nondust period samples (p = 0.0005). None of the sampling periods coincided with intense dust events at source or downwind sites. TSP concentrations in Mali were 20–200-fold lower than the maximum (13,735 μg/m³) during an intense dust episode but similar to the mean background concentrations (575 μg/m³) during the Spring dust season (April) in Mali reported by Gillies et al. (1996). Downwind site TSP concentrations during dust incursions were similar to other reports from the eastern Caribbean (e.g., Perry et al., 1997; Prospero, 1999). Following LRT to the eastern Caribbean, 30–50% of dust particles are PM2.5 (Li-Jones and Prospero, 1999; Perry et al., 1997), a result of gravitational settling of large particles or aggregates, rainout, and air mass subsidence removing larger particles during transport (Reid et al., 2003). The U.S. Environmental Protection Agency (USEPA) and the World Health Organization (WHO), among other health organizations, set regulatory limits for PM2.5 and particulate matter < 10 μm aerodynamic diameter (PM10) concentrations, because they are strongly associated with increased mortality and morbidity from cardiorespiratory diseases (e.g., Dockery et al., 1993; Wang et al., 2013). PM2.5 and PM10 were estimated from the literature and an ongoing study in Bamako, Mali (Table S1): PM10 reported as 68% of TSP in Mali and the northwest Sahara (Gillies et al., 1996; Ozer et al., 2007; unpublished data, Garrison et al.); and, PM2.5 reported as 16–20% of TSP in Mali (d’Almeida and Schütz, 1983; Gillies et al., 1996; Weinzierl et al., 2009; unpublished data, Garrison et al.) and 43% of TSP at Caribbean sites (Li-Jones and Prospero, 1998).

All Mali samples (BKO and KATI) exceeded WHO PM10 24-h limit (50 μg/m³), 74% > USEPA 24-h (150 μg/m³), 84% > WHO PM2.5 24-h (25 μg/m³), and 74–84% > USEPA 24-h limits (35 μg/m³) (Fig. 3). At downwind sites in the Caribbean, one half of samples exceeded WHO and none exceeded USEPA PM10 24-h limits; 67% of Caribbean samples exceeded WHO and 52% were greater than USEPA PM2.5 24-h limits (Fig. 3). These findings concur with Perry et al. (1997), Li-Jones and Prospero (1998) and Prospero (1999) that fine particle concentrations in the majority of Saharan dust incursions in the eastern Caribbean exceed levels known to be harmful to human health. The situation in the dust source region is more severe.

3.3. SOCs

SOCs were detected in all samples [19 source-region and 30 downwind sampling periods of which 26 were from dust and 4 from non-dust (December and January) periods]. Thirteen banned or current-use pesticides, six PAHs, and six PCB congeners were identified, including five of the Dirty Dozen persistent organic pollutants: chlordane, dieldrin, DDT and breakdown products (DDX), heptachlor and PCBs. Dust source-region samples contained a larger number of SOCs and in higher concentrations compared to downwind samples, with total SOC concentrations one-to-three orders of magnitude higher in source-region than downwind sites in dust conditions (source: 1.9–126 ng/m³, mean = 25 ± 34; and downwind: 0.05–0.71 ng/m³, mean = 0.24 ± 0.18). SOC concentrations were generally an order of magnitude higher in the source region river valley (BKO, mean = 75 ± 31 ng/m³) than at the escarpment site 8.6 km distant and 170 m higher elevation (KATI, mean = 6.9 ± 3.4 ng/m³). Not only is greater use of pesticides expected in the urban center with small-scale...
agriculture, but an inversion in the river valley (BKO) traps local pollution from numerous small fires, vehicle exhaust, unpaved roads, small garden plots, and industry. PCA and cluster analysis of individual SOC concentrations grouped samples generally by site/region: BKO; Kati, Cape Verde (CV), Tobago (TOB), Trinidad (TRIN), Trinidad local contamination (TRIN-LC), Trinidad non-dust period (NTRIN), Virgin Islands (VI), and non-dust period Virgin Islands (NVI). USEPA and WHO 24-h limits for PM2.5 and PM10 shown.

Fig. 3. Box plot with minimum, maximum, 75% and 25% percentile, arithmetic mean (dashed line) and median (mg/m³) of: measured total suspended particles (no fill); estimated PM2.5 (gray fill). Bamako (BKO), Kati, Cape Verde (CV), Tobago (TOB), Trinidad (TRIN), Trinidad local contamination (TRIN-LC), Trinidad non-dust period (NTRIN), Virgin Islands (VI), and non-dust period Virgin Islands (NVI). USEPA and WHO 24-h limits for PM2.5 and PM10 shown.

Fig. 4. PCA biplot of individual SOCs in samples. All Bamako sites cluster; Kati sites cluster; TRIN-LC ⬤ clusters with Kati sites; TR050702 ⬤ clusters with but differs from other downwind sites; and, all downwind sites (except TRIN-LC) cluster. PC1 accounts for 51.6% and PC2 accounts for 13.3% of variation (64.9% total).

Fig. 5. Box plots showing minimum, maximum, 75% and 25% percentile, arithmetic mean (dashed line) and median sum of SOCs (log pg/m³) by site. Random number between zero and estimated detection limit substituted for no detection.
3.3.1. Banned and current-use pesticides

Seven of the 13 banned and current-use pesticides and their isomers and degradation products identified in air samples in this study [chlor-danes, chlorpyrifos, daethyl, dieldrin, endosulfans, hexachlorobenzene (HCB), and trichlorfluorin] were found at all sites and chlorpyrifos, endosulfans, and HCB were detected in most samples (Fig. 6). Nine [those listed above plus DDX, and γ-hexachlorocyclohexane (γ-HCH)] occurred at both source and downwind sites. Source region samples contained one-to-multiple orders of magnitude higher concentrations of chlor-danes, chlorpyrifos, daethyl, dieldrin, DDX, endosulfans, and trichlorfluorin than downwind sites (Fig. 6). Heptachlor and α-HCH were detected only at downwind sites (TOB; TRIN, TOB and non-dust VI, respectively), whereas diazinon and profenofos were identified only in the source region (BKO). Endosulfans, HCB and chlorpyrifos were the most abundant OCPPs detected in this study and with the exception of endosulfans, differed from two investigations of atmospheric SOCs in the northwestern U.S., an area impacted by LRT from Asia as well as local and regional sources: HCB, endosulfans, and α-HCH (Genualdi et al., 2009); and daethyl, endosulfans, and γ-HCH (Primbs et al., 2008).

3.3.1.1. Source and downwind sites. Chlor-danes, carcinogenic and mutagenic organochlorine insecticides, occurred in up to 3-fold higher concentrations in urban BKO (19–86 pg/m³, mean = 48 ± 28, median = 28) than KATI (not detected (nd) – 4.1 pg/m³, mean = 1.5 ± 1.3, median = 1.2) and downwind sites (nd – 27 pg/m³, mean = 2.5 ± 4.9, median = 1.4; Fig. 6). BKO appears to be a source of chlor-dane for regional and LRT. trans-Chlordane and trans-nonachlor were detected in most samples, whereas cis-chlordane was not detected and cis-nonachlor was detected only at the VI site (Garrison et al., 2011). Chlor-dane levels at downwind and KATI sites were within the lower range of concentrations reported from the eastern Atlantic (Gioia et al., 2012), similar to an industrial site in Turkey (Bozlaker et al., 2009), and lower by 2–3 orders of magnitude in residences in three U.S. cities (Offenberg et al., 2004). A single high downwind concentration (27 pg/m³ in TRIN) was similar to some remote sites, including Barbados in the 1970s when chlor-dane was still in use (e.g., Bidleman et al., 1981; Bidleman and Leonard, 1982) and within the range reported in the eastern north Atlantic off West Africa (Gioia et al., 2012), pointing to a possible local or regional source. Back trajectory results showed the air mass primarily within the boundary layer over the Atlantic, with short periods over the Sahara–Sahel within the mixed layer, briefly transiting northeastern South America within the boundary layer (Fig. S.4), and over the Atlantic above the boundary layer. The Sahara, South America and/or local re-emission or use all are possible chlor-dane sources.

The MONET passive sampling network detected little chlor-dane at Mali stations, including Bamako (Klánová et al., 2009). However, their estimates in Ghana (Adu-Kumi et al., 2012) bracketed BKO concentrations in this study. In contrast, Pozo et al. (2009) did not detect chlor-danes in Ghana in 2005. Overall, chlor-danes in BKO appear to be in line with other urban centers with current use and re-emission and would be expected to be a source of particle-associated (from soil resuspension) and volatilized chlor-danes for regional and LRT. Downwind site concentrations were generally at background levels with occasional increases from long-distance and likely, regional transport.

Chlorpyrifos, a current-use organophosphate insecticide that binds strongly to soil (Verschueren, 1996), also volatilizes and exists primarily in the gas phase in air (Majewski et al., 2008). It is used on cotton, peanuts, and vegetable crops and against fleas, cockroaches, mosquitoes, termites and other pests around dwellings, and on pets. Chlorpyrifos was one of the most abundant and frequently detected pesticides (75% of samples) and occurred at all sites except TOB. Chlorpyrifos in BKO (urban and close to cotton and maize growing areas) reached nearly 30,000 pg/m³, with mean concentrations (9960 ± 11,000, median = 3500) 200-fold greater than the neighboring rural and non-agricultural KATI site (nd = 220 pg/m³, mean = 44 ± 63, median = 22), and 3 orders of magnitude greater than in downwind samples during dust (nd – 8.3 pg/m³, mean = 2.1 ± 1.9, median = 2.2) and non-dust conditions (nd – 20 pg/m³, mean = 5.7 ± 9.4, median = 1.3) (Fig. 6). A single non-dust period sample (TRIN-LC) that captured local contamination from a nearby garbage dump fire contained 20 pg/m³ chlorpyrifos likely volatilized by the fire. Chlorpyrifos levels in BKO were similar to those reported in a use area in California (LeNoir et al., 1999) and orders of magnitude greater than those reported at an industrial site in Turkey (Bozlaker et al., 2009). Air concentrations in the mid-continental U.S.A. in the 1990s (a high use area; Majewski et al., 1998, 2008) and in both agricultural and non-agricultural areas in Quebec (Sadiki and Poissant, 2008) were greater than KATI and less than BKO. KATI levels were similar to locations impacted by regional transport: remote tropical and subtropical mountains of Brazil (estimates from passive samplers; Meire et al., 2012) and far less than in Costa Rica close to local use (Gouin et al., 2008b). Although chlorpyrifos occurred in 70% of downwind samples, its concentrations were low as would be expected from LRT.

The organochlorine insecticide DDT is licensed for use against disease transmitting insects and some crop pests in the Sahara/Sahel. DDT and/or its breakdown products (DDX) were found in 80% of source region but only 3% of downwind samples (p,p′-DDT in a single TRIN dust-condition sample). Concentrations in BKO samples (2450–3800 pg/m³; mean = 2900 ± 590, median = 2600) were 2–3 orders of magnitude greater than at the KATI escarpment site (1.6–1010 pg/m³; mean = 110 ± 260, median = 42; Fig. 6). Higher concentrations in the river valley likely are due to a concentrated population using DDT on crops and against malarial mosquitoes, volatilization from a pesticide formulation and repackaging facility in BKO, trapping by an inversion layer, and/or greater use during the time period sampled (2001–2003) in BKO than KATI (2004–2008). DDE/DDT ratios generally increased from 0.6 (2001) to 1.0 (2003) in BKO and from 0.5 (2004) to 2.6 (2006) in KATI with no DDT detected after 2006 (Garrison et al., 2011). This could be year-to-year variability or indicative of decreasing DDT use. Mixtures of detected DDX components changed over time. All six DDT isomers and degradates were present from 2001 to 2004 in the source region (p,p′-DDE > p,p′-DDT > p′,o′-DDT > p′,p′-DDE > p,p′-DDD > o,p′-DDE), whereas only three (p,p′-DDE > p,p′-DDT > o,p′-DDE) were detected from 2006 to 2008. DDX concentrations in BKO were considerably higher than most values reported since DDT was banned (e.g., Klánová et al., 2009; Pozo et al., 2009), except in areas where DDT was in use at the time (e.g., Alegria et al., 2000, 2008; Karlsson et al., 2000; Weber and Montone, 1990). KATI values were: higher than those reported in the eastern Atlantic off West Africa (Gioia et al., 2012), as would be expected of a continental source to windward; consistent with those reported from some oceanic sites and non-agricultural areas (Jaward et al., 2004a; Klánová et al., 2009; Pozo et al., 2009); and, lower than some urban and agricultural regions (Alegria et al., 2000, 2008; Karlsson et al., 2000; Weber and Montone, 1990). The TRIN sample p,p′-DDE concentration (0.7 pg/m³) was 1–3 orders of magnitude lower than KATI and BKO, 2–20 fold lower than estimates in Ghana (Adu-Kumi et al., 2012; Pozo et al., 2009), but similar to values from the eastern Atlantic off West Africa that were attributed to LRT (Gioia et al., 2012). This pattern is consistent with LRT from West Africa. p,p′-DDT and p,p′-DDE estimates from particles only in Barbados in the late 1960s when DDT was still in wide use (mean = 0.1 pg/m³; Prospero and Seba, 1972; Seba and Prospero, 1971) were lower than the single TRIN detection in this study. Measuring both gas and particle associated phases, Bidleman et al. (1981) reported up to 5 pg/m³ of p,p′-DDT and -DDE and DDT/DDE ratios indicative of current use. In this study, o,p′-DDE was detected only in the source region (Table S.3), indicating recent use. All source region sampling occurred during the dry (dust) season when pesticide use is relatively low, whereas the single downwind sample that contained DDX (TRIN p,p′-DDE) was collected during the West African rainy season (July) when DDT application against mosquitoes and other disease vectors occurs. Seba and Prospero (1971) suggested that DDT detected in Saharan dust incursions in the eastern Caribbean originated in Europe or North America, not Africa, at that time and was
Fig. 6. Box plots showing minimum, maximum, 75% and 25% percentile, arithmetic mean and median pesticide concentrations (pg/m³) in source region and downwind by site. Random number between zero and estimated detection limit substituted for no detection. Number of samples in which analyte was detected/number of samples analyzed shown to the right of y-axis.
scavenged from the atmosphere over the Atlantic by Saharan dust. However, in this study, a Sahara/Sahel source is suspected based on air mass back trajectories, the presence of active SAL dust transport from Africa (Mali and Mauritania) to the Caribbean (including TRIN) during the sampling period, La–Sc–Th ratios of dust, and, detection of p, p’-DDE only and at a low concentration. Current use of DDT in West Africa makes the region a likely source for LRT.

Dieldrin, an organochlorine insecticide, is currently used against disease vectors such as malarial mosquitoes and other insect pests (e.g., termites, locusts, and cotton pests) in the Sahel. It was detected in all BKO samples and one third of KATI and downwind site samples. BKO concentrations (91–1800 pg/m³, mean = 1100 ± 840, median = 1700) exceeded KATI levels (nd – 47 pg/m³, mean = 10 ± 16, median = 2.0) by >2 orders of magnitude and downwind sites (nd – 21 pg/m³, mean = 2.6 ± 4.2, median = 0.6) by 2–3 orders of magnitude. Levels in BKO were similar to those reported from an inland agricultural area of Belize (Alegria et al., 2000) but greater than mid-continental U.S.A. sites (Majewski et al., 2008), and were multiple orders of magnitude higher than estimated from the MONET passive sampling network in Mali, Senegal (Klánová et al., 2009) and Ghana (Adu-Kumi et al., 2012). The KATI dieldrin concentrations exceeded the highest MONET passive sampler estimates in Mali (urban Bamako; Klánová et al., 2009) and Ghana (Adu-Kumi et al., 2012) but were within those reported from Lake Malawi, a site with small-scale agriculture (Karlfsson et al., 2000). Data from our study do not show a decrease in dieldrin in source site samples over time, indicating that the difference between BKO and KATI levels is likely a function of greater use in urban-agricultural BKO. The comparatively low levels reported by MONET could be an artifact of mass per volume estimates from passive samplers in conditions of extreme temperatures and humidity. Concentrations at downwind sites appeared to be at background levels, similar to remote sites when dieldrin was more widely in use (e.g., Atlas and Giam, 1981; Bidleman et al., 1981; Bidleman and Leonard, 1982) and at background sites near urban centers today (Adu-Kumi et al., 2012). Soils contaminated by dieldrin spills at staging sites for locust-control in northern Mali are another source of dieldrin. West Africa appears to be a source for regional and LRT of dieldrin.

Endosulfan (ENDO), an organochlorine insecticide and acaricide, was the most abundant pesticide detected, as has been reported by investigations in other regions of the world (e.g., reviewed in Weber et al., 2010). Total ENDO concentrations followed patterns observed for other SOCs: BKO (11,200–15,900 pg/m³, mean = 13,100 ± 1800, median = 12,400) exceeded KATI (19–460 pg/m³, mean = 180 ± 140, median = 140) which exceeded downwind sites (nd – 45 pg/m³, mean = 8.6 ± 9.5, median = 4.7; Fig. 6). Concentrations at downwind sites during dust incursions on average were twice those in non-dust conditions. BKO concentrations were within recent values reported from use areas in Central America (e.g., Daly et al., 2007; Wong et al., 2009) and higher than estimates from passive samplers in Ghana, Senegal and Mali (Klánová et al., 2009; Pozo et al., 2009), Bermuda and the Canary Islands (Shunthisharingham et al., 2010). KATI levels were similar to areas affected by regional transport (e.g., Hayward et al., 2010; Pozo et al., 2004; Shunthisharingham et al., 2010), lower than other West African countries (Klánová et al., 2009; although these are estimates from passive samplers), and greater than values reported from a site (Lake Malawi; Karlsson et al., 2000) with small-scale agriculture.

ENDO I, II and sulfate occurred in all source region samples at 80, 16, and 16%, respectively, of downwind samples. The ENDO I:II ratios in source samples (1.0–5.6, mean = 2.7) indicated local use of technical ENDO (ratios 2:1 to 7:3) (Herrmann, 2002). Lower concentrations and ENDO I:II ratios at downwind sites (3.3–26, mean = 14, with no ENDO II detection in 83% of samples) were consistent with isomerization of I to II in an aged air mass, as would be expected with LRT (e.g., Weber et al., 2010). Of 20 pesticides applied in the cotton-growing area of Mali from 1997 to 2007, ENDO was the most widely used, followed by profenofos, and chlorpyrifos (Dem et al., 2007). ENDO II was the most commonly detected pesticide in soil in four cotton growing regions in Mali (Dem et al., 2007) likely due to greater volatileization of ENDO I than II from soils (Antonious et al., 1998). Other than HCB which was identified in all samples, ENDO and chlorpyrifos were the most frequently detected OCPPs at downwind sites and reflect OCPP use in the dust source region. West Africa continues to be a source of ENDO available for regional and LRT.

HCB, one of the most abundant chlorinated hydrocarbons in the atmosphere in the late 1980s (Duque et al., 1991), was detected in 96% of samples at generally low concentrations (nd – 113 pg/m³, mean = 8.6 ± 16, median = 5.6) similar to reported global background levels (e.g., GenuaLdi et al., 2009; Gioia et al., 2012; Jaward et al., 2004c; Klánová et al., 2009; Shen et al., 2005). Two KATI samples at higher concentrations (26 and 110 pg/m³) indicated local use.

Technical hexachlorocyclohexene (HCH), no longer in use, contained five HCH isomers: γ-HCH (lindane), the active isomer (10–15%); α-HCH (60–70%); and β-, ω-, and ε-HCH. Today, lindane, composed primarily of γ-HCH, is banned from use in 52 countries, restricted in many more since 2009, and is currently licensed for use in Mali and other Saharan/Sahelian countries. It is used primarily to treat seeds such as sorghum (the major cultivated crop in Mali) against insect pests and to control external parasites of humans, livestock, and pets, although it also has been used to preserve fish in Mali (Tingle, 2008). γ-HCH was detected more frequently in downwind dust-condition (50%) than source-region samples (5%), with TOB concentrations 6–20 fold higher than VI, TRIN, and the single source region (KATI) samples (Fig. 6). TOB γ-HCH values (30–52 pg/m³, mean = 41 ± 9.1, median = 42) were an order of magnitude lower than those reported in some areas with local use (e.g., Dvorská et al., 2009; Hoff et al., 1992; Karlsson et al., 2000) but similar to others with current use [an agricultural area in Belize in the 1990s (Alegria et al., 2000), urban and rural areas in Canada (Gouin et al., 2008a), and an urban area in Chile (Pozo et al., 2004)]. Local use in TOB appears probable, despite the relatively low concentrations. Concentrations from all sites in this study (nd – 52 pg/m³) were within the range reported in the eastern Atlantic off West Africa (~3.6–100 pg/m³) (Jaward et al., 2004a), where West Africa is considered the probable source. TRIN and VI concentrations were similar to those reported from remote sites (e.g., Atlas and Giam, 1981; Atlas and Schaufler, 1990; Bidleman and Leonard, 1982; GenuaLdi et al., 2009; Jaward et al., 2004c) and lower than areas with current agricultural and urban use (e.g., Alegria et al., 2000; Hoff et al., 1992; Jaward et al., 2004c; Karlsson et al., 2000), further strengthening the case for a remote source. Zhang et al. (2008) reported trans-Atlantic atmospheric transport of lindane from Western Africa/Western Europe to the Caribbean, southern and eastern U.S. Considering the documented current use of γ-HCH in Mali (Diarra, 1997), the concentrations and low frequency of detection in BKO and KATI samples might be a reflection of the time of year sampling occurred. All source region sampling occurred from Dec–May, during the primary dust season in Mali but prior to the planting (and rainy) season when most pesticide application occurs (June–Sept). All TOB and VI half of TRIN dust air mass sample collection occurred during the source region rainy season (June to October), the period of maximum pesticide use. LRT from West Africa is one source of γ-HCH at downwind sites, with probable local use in TOB.

Atmospheric concentrations of α-HCH have declined since 2000 (Li et al., 2003) in response to decreased use of technical HCH and lindane, and changes in lindane production that reduced the amount of α-isomer. Surprisingly, α-HCH was detected in TOB only and in low concentrations (<1.4 pg/m³) similar to those reported in the eastern Atlantic by Gioia et al. (2012), but lower than those reported in the eastern Atlantic off West Africa by Jaward et al. (2004c) and in the Indian Ocean and Western Pacific (Gioia et al., 2012), and at the lowest concentrations reported from urban and suburban Ghana (Adu-Kumi et al., 2012), where lindane remains in use. α-HCH detected in Tobago may have come from photolysis of γ-HCH or re-emission from soil treated
decades ago (reviewed in Walker et al., 1999). The low α-γ-ratio (<0.04, n = 2) in TOB is indicative of LRT (α- and γ-isomers) and local use (γ-HCH). However, identification of a probable local source has been elusive. Lindane use in TRIN-TOB is limited to treating head lice and for external parasites of household pets (UNEP/POPS/POPRC.6/13/Annex II); however, no dwellings or roads were windward of the TOB and for external parasites of household pets (UNEP/POPS/POPRC.6/13/Annex II); however, no dwellings or roads were windward of the TOB.

Some PAHs enter the atmosphere from: incomplete combustion of fossil fuels, wood, waste, and other substances; volatilization from soils (anaerobic degradation of organic matter); the petroleum refining process, flares, and spills; and other sources. Most PAHs have been shown to be sorbed primarily on the respirable fraction of particles (Manichini, 1992). The sum of six PAHs (ΣPAH) detected in West Africa in this study (Fig. S.8) was similar to levels reported in the eastern Atlantic off the West African coast (Jaward et al., 2004c; Nizzetto et al., 2008) and concentrations at downwind sites were similar to ΣPAHs in the relatively pristine southeastern Atlantic (Nizzetto et al., 2008). ΣPAHs in this study were 1–3 orders of magnitude higher in source region samples and a single non-dust sample from Trinidad (TRIN-LC) than in downwind samples (Fig. S.8). This is consistent with the continual burning of biomass and garbage throughout the dust source region and the rapid increase in use of two-stroke engines in the TRIN-LC sample, a dump fire 42 km to the north coincided with non-dust condition sampling. The high ΣPAH concentrations in this sample were within the range of KATI and BKO values and provided PAH concentrations from a substantiated regional source (Fig. S.8). ΣPAH levels were not significantly different among the other downwind site samples. CV levels were marginally higher than other downwind sites overall (TOB, TRIN and VI) but lower than source sites with local/regional sources (BKO, KATI and TRIN-LC), conforming with a LRT model.

Phenanthrene, fluoranthene and pyrene, were detected at all sites and were the most frequently detected PAHs (Fig. 7), as reported in other investigations (e.g., Halsall et al., 1994; Jaward et al., 2004b). Nizzetto et al. (2008) found phenanthrene, fluoranthene, and pyrene dominated atmospheric PAHs in the eastern Atlantic off West Africa but not Europe and attributed that to oil extraction (and reprocessing), flares, spills, etc.), biomass burning, and natural sources in West Africa. Rodriguez et al. (2011) concluded that oil refineries and other Northwest African industries were probable sources of industrial pollutants in the SAL. Phenanthrene levels reported in the eastern Atlantic off West Africa (mean = 1.6 ng/m³; Nizzetto et al., 2008) were lower than sites with local and regional sources [BKO (mean = 13 ± 10 ng/m³), KATI (mean = 3.2 ± 1.6 ng/m³) and TRIN-LC (3.8 ng/m³)]; and higher than sites affected by LRT [downwind dust-condition sites in this study (mean = 0.1 ± 0.2 ng/m³)]. Benzo[a]pyrene is strongly carcinogenic (U.S. Centers for Disease Control, 1995) and its concentrations were higher in source sites than the few downwind samples (TOB and TRIN) in which it was identified (Fig. 7). Anthracene, a combustion product with a short half-life, was detected in 11 of 19 source samples but in only one downwind sample (12 pg/m³) at a concentration close to the method detection limit (Fig. 7). Anthraquinone, a photodegradation of anthracene, also has industrial (dye manufacturing, pulp bleaching) and other sources (http://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?db=hdb&term=β-DCNO+1-2074); it occurred in source region samples only. Cloth and leather dying occurs at small- and medium-scale enterprises throughout the BKO area.

Individual PAH concentrations at downwind sites (excepting TRIN-LC) in this study (Fig. 7) were consistently within or below the low range of values reported from remote sites (Atlas and Schaufler,
1990; Genualdi et al., 2009) and considerably lower than other published studies (e.g., Del Vento and Dachs, 2007; Jaward et al., 2004b; Manichini, 1992; Masclet et al., 1988). Source site PAH (anthracene, benzo[a]pyrene, fluoranthene, phenanthrene) values were higher than most reports from remote sites (Atlas and Schäffer, 1990; Genualdi et al., 2009; Jaward et al., 2004b) and within the range of or higher than a remote Mediterranean location (Masclet et al., 1988), an urban area in Florida, U.S. (Poor et al., 2004), and West Africa-impacted sites in the Atlantic (Del Vento and Dachs, 2007; Jaward et al., 2004b).

Overall, PAH concentrations near sources (BKO, KATI, TRIN-LC) were similar to those reported from other PAH-source locations, whereas concentrations in the eastern Caribbean were similar to remote sites and regions impacted by LRT. Based on the findings from a study of seawater/air partitioning of PAHs in the eastern Atlantic, atmospheric transport from primary sources drives atmospheric PAH concentrations in the Atlantic, with little to no influence from volatilization from seawater (Nizzetto et al., 2008). The pattern of PAH presence/absence and concentrations, rare earth "tracers" in atmospheric dust showing a West African origin of sampled air masses, meteorological conditions, and air mass back trajectories in this study indicate LRT from the Sahara/Sahel as the primary source of PAHs during Saharan dust conditions in the eastern Caribbean.

### 3.3.3. PCBs

More PCB congeners (101, 118, 138, 153, 183, 187) were detected and occurred in higher concentrations in dust source locations than at downwind sites (Fig. 8), similar to patterns seen for OCPs and PAHs. Congener concentrations decreased from BKO > KATI > TRIN > CV, TOB, VI. Higher concentrations in TRIN than other downwind sites suggest an upwind regional PCB source — possibly from ships passing to windward or offshore gas platforms to the SSE. Source region sample $\Sigma_6$PCBs (nd = 52 pg/m$^3$, mean = 14 ± 12, median = 10) were nearly an order of magnitude higher than in downwind dust (nd = 11 pg/m$^3$, mean = 2.3 ± 238, median = nd) and non-dust samples (nd = 6.0 pg/m$^3$, mean = 2.3 ± 2.5, median = nd). The downwind sample with local contamination from a dump fire (TRIN-LC) contained elevated PCB concentrations (5.7 pg/m$^3$) that were similar to dust source sites (Fig. 8). PCB 183 was detected in the source-region only and co-planar PCB (118), a product of open

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![Box plots showing minimum, maximum, 75% and 25% percentile, arithmetic mean and median individual PAH concentrations (pg/m$^3$) by site. Random number between zero and estimated detection limit substituted for no detection. Number of samples in which analyte was detected/number of samples analyzed shown to the right of y-axis.](image-url)
burning, was detected at all sites except CV. Lack of PCBs in CV samples could be a consequence of the short period sampled and/or the altitude of the SAL.

Individual congener concentrations along an eastern Atlantic transect off Africa (Gioia et al., 2012) were within the range observed in this study in West Africa (BKO and KATI) and at downwind sites, as would be expected with transport from West Africa to the west. BKO and KATI congener concentrations were similar to those reported in West Africa by Gioia et al. (2011), higher than along a N–S eastern Atlantic transect (Gioia et al., 2008, 2012), but lower than another N–S eastern Atlantic transect (Jaward et al., 2004c). The spatial pattern of PCB concentrations seen in our study and compared to other investigations supports LRT of PCBs from the Sahara/Sahel to the Caribbean. PCB concentrations in downwind dust-condition samples were similar to those reported from the remote SE Atlantic (Gioia et al., 2008) and lower than other remote sites (e.g., Dachs et al., 1999).

Detection of PCB 101 only at CV and at a lower concentration than in other studies (Gioia et al., 2008, 2011; Schreitmüller and Ballschmiter, 1994) may be a function of time of year, altitude of the SAL and mixing depth during sampling, and/or differences in air mass pollution load when sampling occurred. Considerably lower PCB concentrations in the Caribbean than West Africa are to be expected from dilution during LRT. West Africa has previously been identified as a source of PCBs available for LRT (Gioia et al., 2011). Sources in West Africa include electrical equipment such as transformers, plastics manufacturing (such as in Bamako, Mali; Diarra, 1997), and open burning of waste, including contaminated soils and vegetation (Eckhardt et al., 2007). PCB reemission from the ocean has been suggested as a secondary source to the atmosphere (Jaward et al., 2004a) and could contribute to background levels in the insular Caribbean.

3.4. Implications for Saharan dust source regions and the eastern Caribbean

What does the presence of atmospheric SOCs that are toxic to organisms (biotoxic) and inhalable particles mean for humans and other organisms in the Sahara/Sahel and in the eastern Caribbean during Saharan dust incursions? To begin to address this important but unstudied question, we used the concentration data to estimate quantities of SOCs that could be inhaled by a person in one day (ng/d) at each sampling location. This provides an approximation of SOCs that could enter

Fig. 8. Box plots showing minimum, maximum, 75% and 25% percentile, arithmetic mean and median PCB concentrations (pg/m³) by site. Random number between zero and estimated detection limit substituted for no detection. Number of samples in which analyte was detected/number of samples analyzed shown to the right of y-axis.
the body through the nose and eventually reach the lungs (gas-phase and sorbed on PM_{10}) or stomach (PM_{10-100} trapped in mucus) (Johnson and Vincent, 2003). Assumptions are: (a) reported SOC concentrations (both gaseous and particle-associated SOCs) are inhaled, even though some fraction is sorbed to particles too large to be inhaled (> PM_{100}); (b) the amount of SOCs sorbed to > PM_{100} fraction is small because most detected SOCs were likely in the gas-phase and no particles > 80 μm were reported in Mali by Gillies et al. (1996), indicating a low > PM_{100} fraction in the source region and downwind; (c) estimates represent inhalable maximums during the light-to-moderate dust conditions sampled; and, (d) a conservative normal respiration rate for a resting adult (12 breaths/min) and an average tidal volume of 0.5 L/breath was used (des Jardins, 2008). Estimates of PM_{10} from TSP were based on literature values and an ongoing study (Table S.1).

We estimated that a scientist sampling in the dust source region could have inhaled 17–1100 ng/d (mean = 200 ± 300) SOCs and 0.4–6 ng/d (mean = 2 ± 2) at downwind sites during dust conditions. During the periods sampled, estimated inhalable SOCs were an order of magnitude greater at the urban dust source region site (BKO, 440–1100 ng/d, mean = 650 ± 300) than at a more rural location 8.6 km distant and 170 m higher in elevation (KATI, 17–110 ng/d, mean = 60 ± 30). For individual analytes, estimated inhalation was 1–3 orders of magnitude greater in source than downwind sites.

As discussed in Section 3.2, USEPA and WHO PM_{10} 24-h limits were exceeded 74–100% of days sampled in the source region and 0–50% of days in the eastern Caribbean during dust conditions, respectively. USEPA and WHO PM_{2.5} 24-h limits were exceeded 74–84% of days sampled in the source region and 52–67% of days in the eastern Caribbean during dust conditions, respectively. Elevated PM_{10} and PM_{2.5} concentrations present recognized adverse effects on human cardiorespiratory health (e.g., Dockery et al., 1993; Pope et al., 1995; Wang et al., 2013).

People (and other organisms) in the Sahara/Sahel are exposed to considerably higher concentrations of inhalable particles as well as biotoxic synthetic compounds than at downwind sites following LRT. Presently, no information exists on the effects of SOCs or fine particles and associated metals on health in the source region (de Longueville et al., 2010) or at downwind sites in the eastern Caribbean and elsewhere. Investigations to elucidate the effects of chronic exposure to atmospheric SOCs, fine particles, and mixtures on human health are needed.

4. Conclusions

The Sahara/Sahel region of Africa is a source of OCPs, PAHs, and PCBs exported via the SAL to the eastern Caribbean, a seemingly remote region considered to have unimpaired air quality. Most SOC concentrations were orders of magnitude higher in the dust source region than at downwind sites during dust incursions but also were orders of magnitude lower than the few existing regulatory limits. Inhalation limits do not exist for many of the SOCs detected in this study and no guidelines exist for mixtures. Mixtures of SOCs and respirable particles containing bioactive and biotoxic metals were present in all dust-condition samples. PM_{2.5} and PM_{10} concentrations in sampled dust air masses often exceeded existing air quality standards above which there are recognized adverse effects on human cardiorespiratory health. Little is known about toxicity or effects of SOC mixtures or in combination with bioactive/biotoxic metals on organism health and ultimately on ecosystems. Are there SOC–SOC and SOC–metal interactions? If so, are they synergistic, additive or antagonistic? Are there adverse health effects from: chronic, low level exposure to multiple biotoxic compounds; or, periodic exposure to biotoxic compounds and fine particles that can be inhaled into the lungs? Is there an urgent need to elucidate the long-term effects and mechanisms by which real-world mixtures of biotoxic and bioactive synthetic compounds and mineral dust in the atmosphere impact human health and ecosystems.

Conflict of interest statement

The authors declare that they have no competing financial or other conflicting interests.

Acknowledgments

The authors thank the following individuals and agencies who were essential to the project in Africa, the Caribbean, and the U.S.: S. Coulibaly, M. Dandara, O. Konipo, D. Maiga, B. Nadio, M. Ranneberger, R. Smith, American International School, Ministry of Communication (ORTM) and staff at emettet Kati, Ministry of Geology and Mines, U.S. Embassy Bamako (Mali); P.J.P. Gomes, J. Pimente, E. Santos Suarez, Institute of Meteorology and Geophysics, International Airport and Security Authority (Sal Island, Cape Verde); J. Agard, S. Mahabir, L. Thomas, Environmental Management Authority, Maritime Services, Tobago House Assembly, University of the West Indies (Trinidad and Tobago); R. Berey, H. Tonnenmacher, R. Van Heckman (St. Croix, U.S. Virgin Islands); and P. Lamotho, J. Schraul, S. Skaates, and G. Wilson (sample analysis). The NOAA Air Resources Laboratory (ARL) is acknowledged for the provision of the HYSPLIT transport and dispersion model website (http://ready.arl.noaa.gov) used in this publication. Deep thanks to the Friends of Virgin Islands National Park, National Aeronautic and Space Administration, and the U.S. Geological Survey for providing project financial support and the U.S. Embassy Bamako for in-kind support. Funding sponsors supported performance of the research and article preparation only and had no involvement in: study design, sample collection, analysis and interpretation of data; report preparation or submission for publication. Any use of trade names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2013.08.076.

References


Bidleman TF, Christensen EJ, Billings WN, Leonard R. The determination of 42 elements in geological materials by ICP MS.

Briggs PH, Meier AL. The determination of 42 elements in geological materials by ICP MS.


des Jardins TR. Cardiopulmonary anatomy & physiology. 5th ed. NY, USA: CENGAGE LEARNING; 2008.


