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Legacy and currently used pesticides in the atmospheric environment of Lake Victoria, East Africa

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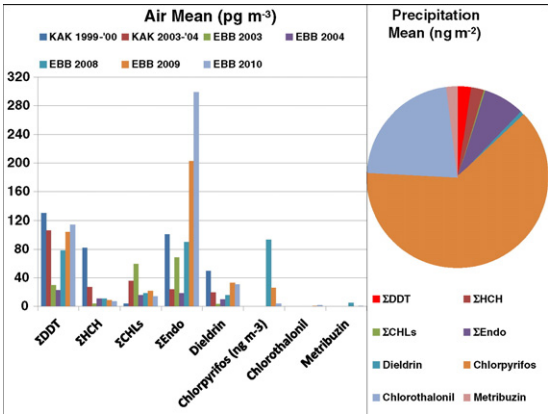
HIGHLIGHTS

- Chlorpyrifos was the most abundant in the 2008–2010 air and precipitation samples.
- Profiles of endosulfan, DDT and HCHs suggested recent fresh emissions.
- The pesticides abundant in air samples also predominated in precipitation.
- Pesticide residues increased in rainy periods.
- Backward air trajectories suggested transboundary and local emission sources.

GRAPHICAL ABSTRACT



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ABSTRACT

The Lake Victoria watershed has extensive agricultural activity with a long history of pesticide use but there is limited information on historical use or on environmental levels. To address this data gap, high volume air samples were collected from two sites close to the northern shore of Lake Victoria; Kakira (KAK) and Entebbe (EBB). The samples, to be analyzed for pesticides, were collected over various periods between 1999 and 2004 inclusive (KAK 1999–2000, KAK 2003–2004, EBB 2003 and EBB 2004 sample sets) and from 2008 to 2010 inclusive (EBB 2008, EBB 2009 and EBB 2010 sample sets). The latter sample sets (which also included precipitation samples) were also analyzed for currently used pesticides (CUPs) including chlorpyrifos, chlorthalonil, metribuzin, trifluralin, malathion and dacthal. Chlorpyrifos was the predominant CUP in air samples with average concentrations of 93.5, 26.1 and 3.54 ng m^{-3} for the EBB 2008, 2009, 2010 sample sets, respectively. Average concentrations of total endosulfan (ΣEndo), total DDT related compounds (ΣDDTs) and hexachlorocyclohexanes (ΣHCHs) ranged from 12.3–282, 22.8–130 and 3.72–81.8 pg m^{-3}, respectively, for all the sample sets. Atmospheric prevalence of residues of persistent organic pollutants (POPs) increased with fresh emissions of endosulfan, DDT and lindane. Hexachlorobenzene (HCB), pentachlorobenzene (PeCB) and dieldrin were also detected in air samples. Transformation products, pentachloroanisole, 3,4,5-trichloroveratrole and 3,4,5,6-tetrachloroveratrole, were also detected. The five most prevalent compounds in the precipitation samples were in the order chlorpyrifos >

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chlorothalonil > ΣEndo > ΣDDTs > ΣHCHs with average fluxes of 1123, 396, 130, 41.7 and 41.3 ng m^{-2} $sample^{-1}$, respectively. PeCB exceeded HCB in precipitation samples. The reverse was true for air samples. Backward air trajectories suggested transboundary and local emission sources of the analytes. The results underscore the need for a concerted regional vigilance in management of chemicals.

1. Introduction

The Lake Victoria basin (about 193,500 km^2) is spread over five countries (Kenya, Uganda, Tanzania, Rwanda and Burundi) and is home to over 30 million people (Odada et al., 2006). The basin has a high level of commercial and subsistence agriculture activity. Historically, cash crops such as cotton, coffee and sugarcane and animal husbandry (mainly cattle and goats) have characterized the agricultural sector in Uganda. These sections of the agricultural sector account for the majority of the historical pesticide uses in the lake's basin. For instance, in Kenya, organochlorine pesticides have been in use since the 1940s (Wandiga, 2001) when they were imported for use on animal farms while pesticides, such as DDT and dieldrin were largely used in Uganda to control mosquitoes, tsetse flies, termites and banana weevils (Ejobi et al., 1996). A host of other pesticides listed under the Stockholm Convention on Persistent Organic Pollutants (POPs) have previously been used and some continue to be used in the East African region. For instance, DDT has recently been used in Uganda for control of mosquitoes (UNEP, 2010) while endosulfan is still largely used in food growing. Following the global ban on a number of organochlorine pesticides, production and use of alternative pesticides with varying persistence and toxicity has occurred. For example, the use of pesticides that are less persistent and bioaccumulative in the East African region has been on the rise in recent years as exemplified by the annual pesticide importation profiles for Uganda and Kenya (e.g. see Fig. S1). The depletion of the forest cover in the East African region, the high rate of biomass combustion (Arinaitwe et al., 2012), current and historical pesticide use in agriculture, existence of stockpiles of obsolete pesticides in the region (Elfvendahl et al., 2004), a warm tropical climate and atmospheric transfer contribute to the exposure of Lake Victoria to atmospheric loading of pesticide residues. Organochlorine pesticide residues have been detected in varying levels in compartments of the lake's environment (Kasozi et al., 2006; Wasswa et al., 2011). The large surface area of the lake makes atmospheric deposition a significant loading route. In spite of this fact, there are no significant data from atmospheric measurements of POPs in the watershed of the lake, except a recent report of flame retardants in air and precipitation samples (Arinaitwe et al., 2014). In fact, atmospheric measurement of banned and currently used pesticides (CUPs) on the African continent is very limited (Batterman et al., 2008; Karlsson et al., 2000; Pozo et al., 2009; Garrison et al., 2013; Klanova et al., 2009; Adu-Kumi et al., 2012). This study provides the largest dataset, to-date, on atmospheric prevalence and wet deposition of old and currently used pesticides in the immediate environment of Lake Victoria. The observed levels are compared with results from other similar studies done in Africa.

2. Methods

2.1. Sampling and sample preparation

High volume (24 h) air samples were collected with a TE-1000 PUF high volume air sampler (Tisch Environmental Inc., OH, USA) at Kakira sugarcane plantation in Jinja (KAK, 0°30′40.53′ N, 33°16′48.97′ E) and at the Directorate of Water Resources Management (DWRM) at Entebbe (EBB, 0°02′55.38′ N, 32°28′19.50′ E), both located near the northern shoreline of Lake Victoria. The Kakira (KAK) and Entebbe (EBB) sampling sites and sampling procedures have been described in detail elsewhere (Arinaitwe et al., 2012; Arinaitwe et al., 2014). In brief, the samples were collected over two sampling campaigns. In the first campaign, samples were collected at various intervals at KAK from 1999 to 2004 and at EBB from 2003 to 2004. In the second campaign, samples were collected from EBB from October 2008 to July 2010.

The precipitation samples were collected at EBB between October 2008 and April 2010 using a Meteorological Instruments of Canada (MIC) type sampler which had a stainless steel rain collection funnel. The sampler opened automatically during rain events and the trapped precipitation flowed from the funnel through a column packed with an XAD-2 resin. Every resin column was deployed for a period of one month. The detailed description of the precipitation sample collection, including description of the sampler and the individual resin column deployment period have been previously reported (Arinaitwe et al., 2014).

The sample extraction and cleanup procedures have been previously described in detail (Arinaitwe et al., 2014). In brief, the air samples (PUF + filter combined) were extracted by pressurized fluid extraction (ASE 200, Dionex Instruments) with Hexane/Acetone 70:30 v/v. The concentrated extract was eluted over deactivated (10%) silica gel with 5% methanol in dichloromethane (DCM) for initial analysis for CUPs before fractionation on an activated silica column using hexane (fraction A) and hexane/DCM 1:1 v/v (fraction B). Both fractions were concentrated, the solvent changed to isooctane, and brought to the final volume (200 μl) for GC analysis for pesticide residues.

For precipitation samples, the XAD resin was successively eluted with methanol and DCM. The organic layer was separated, dried over anhydrous Na_2SO_4, concentrated and processed further for analysis as for the air sample extracts.

2.2. Quality control

The high volume air samplers were regularly calibrated following the manufacturer's manual. Field PUF/filter and XAD resin column blanks were included, along with laboratory procedure and recovery blanks. All the samples were spiked with recovery standards, δ-HCH and ^{13}C-mirex, during sample preparation. The average recoveries of δ-HCH and ^{13}C-mirex were 73 ± 6% and 94 ± 11% for air samples and 73 ± 5% and 95 ± 6% for precipitation samples, respectively. The detection limits and recoveries of the analytes reported here are given in Table S1.

2.3. Sample and data analysis

Organochlorine pesticide analysis for all the KAK samples and EBB (2003–2004) samples was achieved with an Agilent 5890 GC (Agilent Technologies Inc., U.S.A.) equipped with dual ECDs. For the EBB 2008–2010 air and rain samples, a Gas Chromatograph Agilent 6890 Series, equipped with an Electron Capture detector (μECD) was used. HP-5, HP-5MS and HP-1MS columns (30 m × 0.25 mm × 0.25 μm, Agilent Technologies Inc., U.S.A) were used. The CUPs were analyzed by GC–MS (Agilent 5975C Series GC–MSD, transfer line at 295 °C) in splitless mode using single ion monitoring (SIM) following negative chemical ionization (NCI). An HP-5MS 30 m × 0.25 mm × 0.10 μm column (Agilent Technologies, Mississauga, ON) was used for GC analysis. The detailed GC settings are given in the supporting information. Data processing was done using Agilent Chemstation software.