Sources, distribution, and risk assessment of organochlorine pesticides in Nairobi City, Kenya

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A B S T R A C T

The distribution and sources of organochlorine pesticides (OCPs) in air and surface waters were monitored in Nairobi City using triolein-filled semipermeable membrane devices (SPMDs). The SPMDs were extracted by dialysis using *n*-hexane, followed by cleanup by adsorption chromatography on silica gel cartridges. Sample analysis was done by GC-ECD and confirmed by GC–MS. Separation of means was achieved by analysis of variance, followed by pair-wise comparison using the *t*-test ($p \leq 0.05$). The total OCPs ranged between 0.018 – 1.277 ng/m^3 in the air and <LOD – 1391.000 ng/m^3 in surface waters. Based on the results, the means of Industrial Area, Dandora and Kibera were not significantly different ($p \leq 0.05$), but were higher ($p \leq 0.05$) than those of City square and Ngong' Forest. The results revealed non-significant ($p \leq 0.05$) contribution of long-range transport to OCP pollution in Nairobi City. This indicated possible presence of point sources of environmental OCPs in the city. The water-air fugacity ratios indicated that volatilization and deposition played an important role in the spatial distribution of OCPs in Nairobi City. This indicated that contaminated surface waters could be major sources of human exposure to OCPs, through volatilization. The incremental lifetime cancer risks (ILCR) determined from inhalation of atmospheric OCPs were $2.3745 \times 10^{-13} – 1.6845 \times 10^{-11}$ (adult) and $5.5404 \times 10^{-13} – 3.9306 \times 10^{-11}$ (child) in the order: Dandora > Kibera > Industrial Area > City Square > Ngong' Forest. However, these were lower than the USEPA acceptable risks, $10^{-6} – 10^{-4}$. This study concluded that atmospheric OCPs did not pose significant cancer risks to the residents.

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Introduction

The chlorine-carbon bonds in organochlorine compounds are strong, and as a result are not easily broken. Due to this, organochlorine pesticides (OCPs) have long persistence in the environment. Previously, OCPs were widely used to control pests and as formulations of other pesticide products, such as mosquito coils (Afful et al., 2010). Due to high persistence in the environment, the Stockholm Convention on persistent organic pollutants (POPs) banned the use of most organochlorine pesticides (UNEP, 2009). The OCPs include aldrin, chlordane, dichlorodiphenyltrichloroethane (DDT), dieldrin, endrin, heptachlor, hexachlorobenzene (HCB) and hexachlorocyclohexanes (HCHs). Acute exposure to aldrin has been reported to result in death to birds, fish, and humans. Dieldrin, endrin and chlordane, on the

other hand, are suspected of either damaging and/or suppressing the human immune system. Similarly, chlordane, DDT and its metabolite DDE and heptachlor are listed as possible human carcinogens, especially with regard to hormonal cancers, such as breast cancer. Despite the ban, OCPs are still found in the environment in significant levels (Afful et al., 2010).

From the National Inventory of POPs, Kenya is still grappling with the management of stockpiles of obsolete pesticides and other persistent chemicals, some of which were banned under the Stockholm Convention (UNEP-GEF Project, 2012). As at 2012, there were over 15,000 tons of obsolete pesticides in Kenya, distributed countrywide (UNEP-GEF Project, 2012). Since the environmental protection laws in Kenya are generally weak, with poor enforcement of even the existing weak ones, some of the obsolete pesticides could be finding their way into the environment, causing high levels of human exposure to these environmental pollutants.

In Kenya, cancer is ranked third as a cause of death after infectious and cardiovascular diseases, accounting for about 7% of total
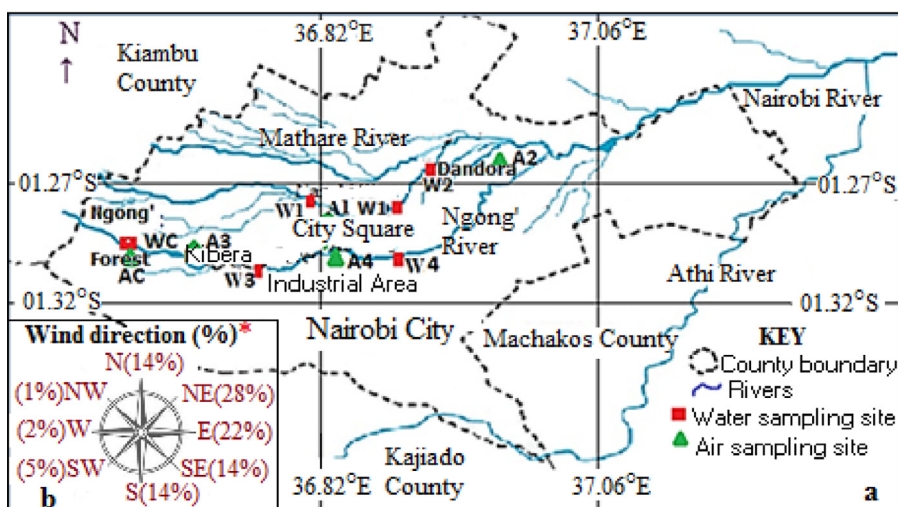
Fig. 1 – (a) Map showing the sampling Area in Nairobi City, Kenya and (b) Wind direction in Nairobi City between May 2017 and December 2017 (Meteorological Department of Kenya, 2017).
W: water sampling site; A: air sampling sites (1-City Square; 2-Dandora; 3-Kibera; 4-Industrial Area; c-Ngong' Forest).
✱Wind direction in hours (%) during the sampling period.

national mortality every year (MOH, 2011). The risk of getting cancer before the age of 75 years in Kenya is estimated at 14%, while the risk of dying of cancer is estimated at 12% (MOH, 2011). However, possible causes of the high cancer incidences have not been established. A number of persistent organic pollutants are carcinogens. Analysis of human milk samples from breastfeeding mothers in Nairobi City revealed presence of high levels of DDTs, dieldrin, furans, dioxins, and PCBs (UNEP-GEF Project, 2012). This is an indication of human exposure to bioavailable persistent organic pollutants in Nairobi City, including OCPs. However, the level of pollution in Nairobi City with reference to bioavailable OCPs is not documented.

This study characterized and quantified the OCPs in air and surface waters at various sites in Nairobi City, Kenya using a passive sampling technique. The water-air fugacity ratios of OCPs were also determined to evaluate the potential sources of the gas-phase OCPs in the city. This study found no evidence of direct use of the waters of Nairobi River by the residents for either domestic uses such as drinking, cooking, and bathing, or recreational activities such as swimming and fishing. The carcinogenic human health impact of OCPs in Nairobi City was therefore evaluated by determining the Incremental Lifetime Cancer Risks (ILCR) from inhalation of the atmospheric OCPs.

1. Experimental

1.1. Sampling site

Nairobi City occupies 696 square kilometers (Fig. 1a). This study was conducted in City Square (sites A1 and W1), Dandora (sites A2 and W2), Kibera (sites A3 and W3), Industrial Area (sites A4 and W4), and Ngong' Forest (control site, AC and WC), within Nairobi City (1°09′S 36°39′E and 1°27′S 37°06′E), Kenya (Fig. 1a and b).

The Ngong' Forest lies to the extreme West of Nairobi City (Fig. 1a) and is the source of Nairobi River, which flows into the city. The Ngong' Forest sampling site was carefully chosen based on the predominant wind directions; the movement of wind in the Western direction, from the city towards Ngong' Forest, accounted for only 2% of all the hours during the sampling period (Fig. 1b) (Meteorological Department of Kenya, 2017). This indicated minimal OCP contamination of the Ngong' Forest sampling site by pollutants emitted in the city through environmental transport. Sam-

pling in this study was done between October 23 and November 19, 2017. The results from this site were used to evaluate the possible contribution of long-range transport to OCP pollution in Nairobi City.

1.2. Materials and methods

1.2.1. Materials

The materials used in these experiments included: Standard length 92 cm performance reference compound semipermeable membrane devices (PRC SPMDs) made of low-density polyethylene (LDPE) and filled with 99.9% pure grade triolein, were acquired from the Sampling and Testing Department, E&H Services Inc. (Prague, Czech Republic), along with 5-SPMD carrier deployment canisters made of stainless steel; Stevenson screens, made of untreated wood, 1–1.5 m above the ground, which were used in air sampling; Analytical grade solvents and reagents were acquired from Sigma-Aldrich (St. Louis, Missouri, USA); Standards and Certified Reference Materials were acquired from Industrial Analytical (PTY) Ltd., Republic of South Africa. The other general laboratory equipment was cleaned, dried, and then rinsed with analytical grade solvents before use.

1.2.2. Sampling

Sampling of surface waters was based on the methods used in previous studies (Alvarez, 2010; Zhu et al., 2013). The SPMDs were placed in metal cages suspended in water at the five sampling sites (Fig. 1a) on Nairobi River and its tributaries, over 28 continuous days in three replicates. During deployment, the metal cages were secured at the sampling sites to a fixed point using galvanized steel cables. Sampling for air monitoring was based on previous methods (Söderström and Bergqvist, 2004; Zhu et al., 2013). The SPMDs were placed in Stevenson screens, made of untreated wood, 1–1.5 m above the ground, at the five sampling sites (Fig. 1a). The SPMDs were also exposed for 28 days continuously in three replicates during the same period, over which sampling of surface waters was carried out. Fig. 2 shows the deployment of SPMDs for air sampling and sampling of surface waters.

Meteorological data for each day during the sampling period was obtained from the Meteorological Department of Kenya in Nairobi.
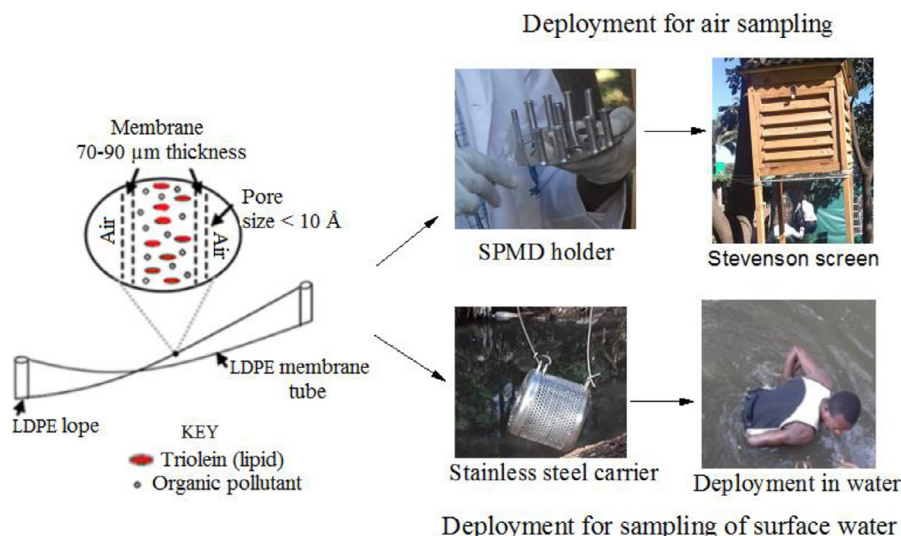
Fig. 2 – Schematic diagram for semipermeable membrane device sampling
LDPE: low density polyethylene.

1.2.3. Quality control during sampling

The quality control measures during sampling from the air and water bodies included the use of field blanks and laboratory blanks: The blanks were prepared according to the method described by Alvarez, (2010). The field blanks were used to account for contamination during transportation of the samplers and the deployment and retrieval periods. The laboratory blanks, on the other hand, were used to account for any possible contamination resulting from processing and analysis of the samples.

1.2.4. Extraction, clean-up and concentration

The SPMD field samplers, field blanks, and laboratory blanks were cleaned and extracted by dialysis (Alvarez, 2010; Alvarez et al., 2008; Huckins et al, 2006): Each SPMD was removed from the metal cage and cleaned immediately with a gloved hand using a pre-cleaned soft brush, to remove any particulate matter and any bio-film on its surface. The SPMD was then submerged in dilute nitric acid to remove salts embedded on the surface of the sampler.

The pre-cleaned SPMDs were extracted by dialysis in 300 mL analytical grade *n*-hexane for 24 hr. in a 500 mL conical flask. After this first dialysis period, the hexane extract was transferred into a clean 1 L beaker wrapped in aluminum foil. A second 300 mL portion of analytical grade *n*-hexane added to the conical flask and a second dialysis performed for 12 hr. The two hexane extracts were combined and the SPMD discarded. The volume of each of the sample extracts in hexane was reduced to about 2 mL in a rotary evaporator at 35 °C, prior to cleanup and fractionation procedures.

The concentrated samples were cleaned according to USEPA Method 3630C: The sample was quantitatively transferred to preconditioned silica gel cartridges and eluted with 5 mL analytical grade *n*-hexane at a rate of 1 mL/min. An additional 5 mL of analytical grade *n*-hexane was added to the cartridge and the solvent was allowed to soak for 1 min. The solvent was eluted and the eluent collected in a vial as Fraction 1, which was discarded. The cartridge was then extracted using 5 mL diethyl ether/hexane (50/50, *V/V*) mixture and the eluent collected as Fraction 2, which was prepared for analysis of OCPs. Fraction 2 was concentrated in a rotary evaporator to about 2 mL and 0.5 mL analytical grade toluene added. Finally, the volume of the mixture was reduced to 0.5 mL in the rotary evaporator at 35 °C.

1.2.5. Analysis of the samples, characterization and quantification

The cleaned and concentrated OCP extracts were analyzed using an Agilent Technologies 7890A gas chromatograph instrument equipped with an electron capture detector (GC-ECD) and a mass spectrometer (Agilent Technologies Model 5975) (Zhu et al., 2013; Wang et al., 2009). Splitless 1 μL injections were made onto a 30 m DB5 capillary column with 0.250 mm internal diameter and 25 μm film thickness. During the analysis, the GC instrument was run in selected ion monitoring (SIM) mode. Characterization was done by comparing the peak retention times of the sample with those of authentic standards and confirmed by mass spectrometry. Quantification of the analytes was the done using the internal standard method (US EPA method 8100/8015).

1.2.6. Determination of sampling rate (R_s) and concentration

The PRC release rate, K_e (day^{-1}), was determined by comparing the amount of PRC initially added to the SPMD (N_0) to the amount remaining (N_t) after a sampling time (t) in days (Eq. (1)) (Huckins et al., 2002). This was determined by analyzing a set of SPMDs deployed in the same sampling cages as those used in the study for the same duration, using a head-space gas chromatograph instrument.

$$K_e = \frac{\left[\ln\left(\frac{N_t}{N_0}\right)\right]}{t} \tag{1}$$

logK_{PW} was determined from a regression model of the PRC's logK_{OW} using Eq. (2), which was empirically derived (Huckins et al., 2006).

$$\log K_{PW} = a_0 + 2.321\log K_{OW} - 0.1618(\log K_{OW})^2 \tag{2}$$

where, a_0 is the intercept, determined to be -2.61 for PCBs, OCs, and PAHs.

The PRC-based sampling rates, R_S (m^3/day), were then calculated using Eq. (3) (Huckins et al., 2006; Wang et al., 2009); where V_S is the volume of the SPMD (in L or mL).

$$R_S = V_S K_{PW} K_e \tag{3}$$

The sampling rate for the passive sampler in this study referred to the volume of water or air cleared of analyte per unit time by the passive sampling device. From the data obtained, the concentration of the analyte in the SPMD samplers did not attain equilibrium levels. Thus, the time-weighted average concentrations of the analytes in the gas phase (C_A, ng/m^3) or water phase (C_W,

ng/m^3), were calculated, using a non-linear kinetic uptake model (Huckins et al., 1999), Eq. (4):

$$C_{W(SPMD)} = \frac{M_S(t)}{R_S t} \quad (4)$$

where, M_S (ng) is the amount of an analyte accumulated in the sampler after exposure for time, t (day).

1.2.7. Statistical analysis of data

Analysis of variance of the data for a two-factor completely randomized complete design was used to separate the means for site, and the means for environmental media. Thereafter, pair-wise comparison of means using the t-test was used to determine significant differences between the means at $p \leq 0.05$.

1.2.8. Water-air fugacity ratios

The gaseous exchange was determined using the fugacity approach (Mackay, 1979). The contaminant fugacity in air (f_A) was calculated using the ideal gas law, Eq. (5) (Bidleman and McConnell, 1995; Wania et al., 1998).

$$f_A = \left(\frac{n}{V}\right) RT = C_A RT \quad (5)$$

Similarly, the contaminant fugacity in water (f_W) was calculated by Eq. (6) (Bidleman and McConnell, 1995; Wania et al., 1998).

$$f_W = C_W H \quad (6)$$

where, C_A (mol/m^3) and C_W (mol/m^3) are the concentrations of the contaminant exclusively in gas-phase and dissolved-phase respectively (Devi et al., 2011; Odabasi et al., 2008); while f_A and f_W were in atmospheres; H ((m^3·atm)/mol) is Henry's law constant for the contaminant; R (8.2057 × 10^{-5} ((m^3·atm)/(K· mol)) is the ideal gas constant and T (K) was the average temperature during the sampling period in Kelvin (Devi et al., 2011; Odabasi et al., 2008).

The ratio between the fugacities in air and surface waters were then calculated using Eq. (7) (Wania et al., 1998; Mackay 1979).

$$f_W/f_A = C_W H / C_A RT \quad (7)$$

where, H/RT is the compound-specific temperature-corrected Henry's law value (Tidwell et al., 2015; Odabasi et al., 2008).

The following fugacity decision rules (Eq. (8)) were adopted to determine the net gas exchange direction (Devi et al., 2011; Odabasi et al., 2008; Wania et al., 1998; Mackay, 1979):

$$
\begin{aligned}
f_W/f_A &> 1 \text{ Net volatization} \\
f_W/f_A &= 1 \text{ Equilibrium (no net exchange)} \quad (8) \\
f_W/f_A &< 1 \text{ Net deposition}
\end{aligned}
$$

The net exchange provided vital information concerning the possible sources of the contaminant in a given environmental location (Meire et al., 2016). The results were used to evaluate the possible sources of the gas-phase OCPs in the city.

1.2.9. Cancer risk assessment

Human exposure to OCPs occur mainly through three pathways: inhalation, dermal contact and consumption. This study found no evidence of direct use of the waters of Nairobi River by the residents for either domestic uses such as drinking, cooking, and bathing, or recreational activities such as swimming and fishing. The carcinogenic human health impact of OCPs in Nairobi City was therefore evaluated by determining the Incremental Lifetime Cancer Risks from inhalation (ILCR$_{Inhalation}$) of the atmospheric free-phase OCPs using Eq. (18) (Sruthi et al., 2016).

$$ILCR_{Inhalation} = \frac{C_{Air} \times CSF \times InhR \times ET \times EF \times ED \times IUR}{BW \times AT} \quad (9)$$

where C_{Air} (mg/m^3) is the concentration of the OCPs in air; CSF (mg/(kg•day)) is the Inhalation cancer slope factor of the OCP, which is equal to 0.007 mg/(kg•day) (USEPA, 1991); InhR (m^3/hr) is the inhalation rate, equal to 0.6 m^3/hr for standing adult males and 0.48 m^3/hr for standing adult females, and 0.27 (USEPA, 1997), equal to an average of 0.54 m^3/hr, for both standing males and females (Jin et al., 2018); ET (hr/day) is the daily exposure duration: For this study, the times spent outdoors in the sampling sites were taken to be from 8.00 am – 6.00 pm, which gave 10 hr/day; EF (day/yr) is the exposure frequency, equal to 365 days/yr; ED (yr) is the lifetime exposure duration: In this study this was taken as 30 years, as adopted from USEPA (1989). IUR is the inhalation unit risk of the contaminant (0.057 (mg/m^3)$^{-1}$ for OCPs), BW (kg) is the body weight; in this study average body weights of 70 kg and 15 kg for an adult and child, respectively, were used, as adopted from USEPA (1989). AT (day) is the averaging time leading to a Lifetime Average Daily Dose (LADD) of 365 days/yr × 70 yr for a carcinogenic contaminant (USEPA, 1989). This study considered the average hours spent outdoors for an average resident of Nairobi to be between 8.00 am and 6.00 pm, which gave a daily exposure duration to outdoor inhalable OCPs in the air of 10 hr. During the computations, the concentrations of OCPs were converted to mg/m^3.

2. Results and discussion

2.1. Identity of the sampled OCPs

Nine OCPs were identified in the extracts from the air and surface waters. These included; aldrin, p,p'-DDT, p,p'-DDD, p,p'-DDE, chlordane, dieldrin, endrin, heptachlor, and gamma-HCH. Although a previous study (Aucha et al., 2017) reported the presence of the endosulfan isomers, α-endosulfan, β-endosulfan and the metabolite, endosulfan sulfate, in the Dandora, Industrial Area and Kabete sites of Nairobi City, in relatively low concentrations, these isomers were not detected in any of the sites in this study. This could be in part due to the differences in the types of samplers employed: In the previous study (Aucha et al., 2017), polyurethane foam (PUF) disks were used as passive samplers, which sampled both particulate-phase and gas-phase OCPs. No procedure was put in place to separate the particle-phase and gas-phase OCPs (Aucha et al., 2017). Consequently, such data could not be used to evaluate the human health risks posed by OCPs. In the current study, only the gas-phase OCPs were sampled. The findings of this study are therefore very useful for evaluation of the level of human exposure to bioavailable OCPs within Nairobi City, and hence in the assessment of human health risks posed by OCP pollution in the city. Such information would shed light on the possible causes of the many cancer cases in Kenya.

2.2. Method detection limits (MDL) for OCPs

The blank samples were analyzed in the same manner as the real samples. In almost all the blanks, no peaks of the target compounds were found. Thus, the method detection limit (MDL) for each of the OCPs was estimated from the instrument detection limit (IDL), set at a signal-to-noise ratio (S/N) of three (Keith et al., 1991; Ozcan et al., 2008) using the sampling rate of the compound. Table 1 gives the IDLs and the estimated method detection limits (EMDLs) of the sampled OCPs.

2.3. Sampling rates of the SPMDs

Table 2 shows the PRC-based sampling rates of the OCPs identified and quantified in the air and surface waters. The data obtained
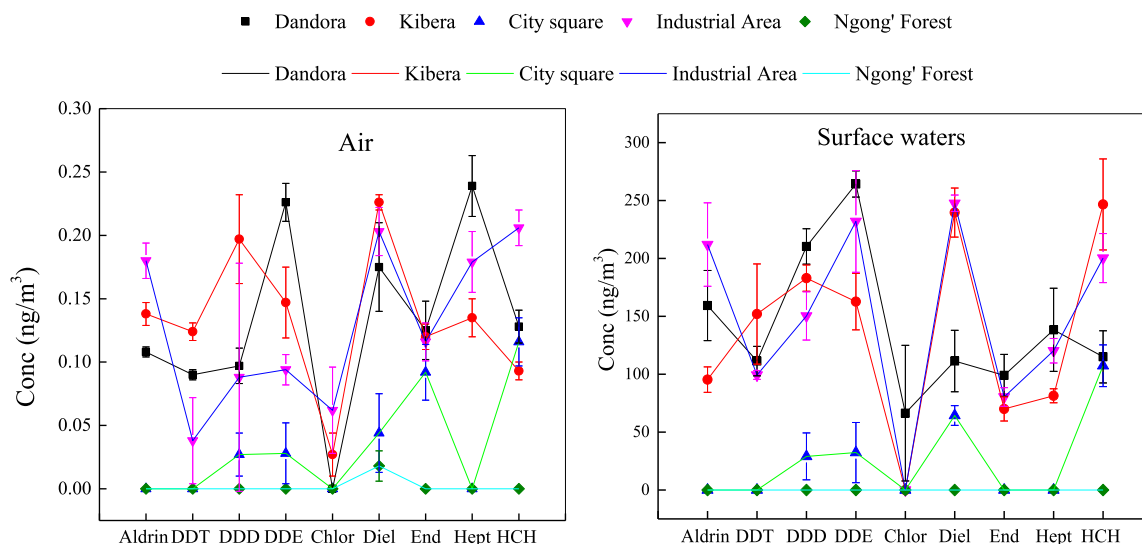
Fig. 3 – Variation in levels of the bioavailable fraction of organochlorine pesticides in air and surface waters in Nairobi City, Kenya.

Table 1 – Method detection limits for organochlorine pesticides*.

OCP	IDL (ng/L)	EMDL Air (pg/m³)	EMDL Water (pg/L)
Aldrin	0.090	13.56	20.46
p,p'-DDT	0.086	14.07	21.21
p,p'-DDD	0.086	13.42	20.23
p,p'-DDE	0.090	13.93	21.01
Chlordane	0.086	13.20	19.91
Dieldrin	0.090	16.48	24.85
Endrin	0.096	17.56	26.49
Heptachlor	0.086	13.52	20.39
γ-HCH	0.077	17.03	25.68

IDL: instrument detection limit; EMDL: Estimated method detection limit.

* The limit of quantification (LOQ) for each of the sampled OCPs was determined as three times the MDL.

Table 2 – Sampling rates of OCPs in surface waters $R_{s(Water)}$ and air $R_{s(Air)}$*.

OCP	$R_{s(Water)}$ (L/day)	$R_{s(Air)}$ (m³/day)
Aldrin	0.156	0.236
p,p'-DDT	0.145	0.219
p,p'-DDD	0.152	0.230
p,p'-DDE	0.152	0.230
Chlordane	0.155	0.234
Dieldrin	0.129	0.194
Endrin	0.129	0.195
Heptachlor	0.151	0.228
Gamma-HCH	0.107	0.161
Means	0.142 ± 0.017	0.214 ± 0.025

* The sampling rates obtained were used together with the concentrations of the analytes in the SPMDs to determine the concentration of each of the OCPs in air and surface water using Eq. (4).

show that the concentration of the analytes in the SPMDs did not attain equilibrium levels.

2.4. Levels, and distribution of OCPs in air and surface waters in Nairobi City, Kenya

Fig. 3 shows the levels, and distribution of bioavailable OCPs in the air in Nairobi City, Kenya and the waters of Nairobi River and its tributary, Ngong' River, traversing through the city at the Dandora, Kibera, City Square, Industrial Area, and Ngong' Forest sampling sites. The concentrations of dissolved OCPs were reported in ng/m³ to enable calculation of the fugacity ratios of individual OCPs.

The levels of total gas-phase OCPs ranged from 0.018 ng/m³, in Ngong' Forest, to 1.277 ng/m³ in Dandora in the order: Dandora > Industrial Area > Kibera > City Square > Ngong' Forest. On the other hand, the levels of total dissolved-phase OCPs in surface waters ranged from non-detection in Ngong Forest to 1297.667 ng/m³ in the order: Industrial Area > Dandora > Kibera > City Square > Ngong' Forest. Though the levels of total OCPs in Industrial Area, Dandora and Kibera were not significantly different ($p \leq 0.05$), they each were significantly higher ($p \leq 0.05$) than those in the City Square. In Kenya, DDTs were banned from agricultural use in 1986, but the other OCPs remained in use till 2004, when a ban or restrictions on their use were put in place (Kenya NIP, 2007). Some OCPs were still in use for public health purposes by 2007 (Kenya NIP, 2007). Since OCPs persist in the environment, it is possible that OCPs from previous as well as current use, if any, could still be available in the environment in Kenya. This suggestion is supported by the findings of previous studies, which reported the presence of OCPs in soils, air, and human milk samples in Kenya (Aucha et al., 2017; Sun et al., 2016; UNEP-GEF Project, 2012). OCPs have also been reported in air, dust, soil, sediment, surface waters and biota by several studies (Odabasi et al., 2008; Ssebugere et al., 2010), in other parts of the world. The studies attributed the sources of these OCPs to anthropogenic activities coupled with environmental transport into surface waters and the atmosphere through industrial discharge, surface runoff from non-point sources, volatilization and atmospheric deposition, among others. These lead to cross-contamination (Feng et al., 2011; Yang et al., 2013). The results of the current study indicated that Industrial Area, Kibera and Dandora could be possible point sources of bioavailable OCPs in Nairobi City of Kenya.

On the other hand, the levels of OCPs in Ngong' Forest were significantly lower ($p \leq 0.05$) than those of the rest of the sampling sites. In general, the results obtained showed that Ngong' Forest could fairly be described as pristine ($p \leq 0.05$) with reference to gas-phase or dissolved OCP pollution when compared to the other parts of the city. These results indicated that the contribution of long-range environmental transport to the levels of total gas-phase and dissolved OCPs in Nairobi City was not significant ($p \leq 0.05$).

Table 3 – Water-air fugacity ratio for the quantified organochlorine pesticides.

OCP	f_W/f_A				
	Dandora	Kibera	City Square	Industrial Area	Ngong' Forest
Aldrin	2.511	1.176	nd	2.005	nd
p, p'- DDT	0.664	0.658	nd	1.404	nd
p, p'- DDD	0.361	0.155	0.179	0.290	nd
p, p'- DDE	1.022	0.967	1.009	2.157	nd
Chlordane	nd	nd	nd	nd	nd
Dieldrin	1.536	2.560	3.530	2.945	nd
Endrin	0.016	0.012	nd	0.014	nd
Heptachlor	0.554	0.577	nd	0.644	nd
γ - HCH	0.131	0.386	0.135	0.142	nd

f_W/f_A: Water – air fugacity ratio; nd: could not be determined

These findings also pointed to the possibility of the presence of point sources of OCP pollution in air and surface waters within the city. To evaluate the strength of this suggestion, this study determined the fugacity ratios of individual OCPs at the various sampling sites to help elucidate the possible sources of these OCPs in the city.

The levels and distribution of individual OCPs also varied with the sampling site. Though aldrin was not detected in the City Square and Ngong Forest, its levels in the other three sampling sites were in the order: Industrial Area > Dandora > Kibera. The levels of aldrin in Industrial Area and Dandora were, however, not significantly different ($p \leq 0.05$), but its levels in Industrial Area were significantly higher ($p \leq 0.05$) than those in Kibera. These results indicated that Industrial Area and Dandora could be possible point sources of bioavailable aldrin in Nairobi city, with Kibera as a minor point source. The levels of *p,p'*-DDD, *p,p'*-DDE, chlordane, endrin and heptachlor, on the other hand, were in the order: Dandora > Industrial Area > Kibera > City Square, except for *p,p'*-DDD, where the levels in City Square were higher than those in Kibera. However, none of the five OCPs was detected in either surface waters or air in Ngong Forest. These results ruled out the possibility of contamination of the city by any of the five pollutants from non-point sources outside the city, through either inflow of contaminated surface waters or atmospheric transport. The results further confirmed the possibility of the existence of point sources of these contaminants within Nairobi City. This suggestion was in agreement with a previous study by Grimalt et al. (2004), who also suggested that environmental contamination by persistent organochlorine pesticides could be related to the presence of point sources within the environment under investigation.

2.5. Fugacity ratios and source apportionment of OCPs in air and surface waters in Nairobi City

The water-air fugacity ratios (f_W/f_A) were calculated from the concentrations of dissolved-phase and gas-phase OCPs using their compound-specific temperature-corrected Henry's law constants (Tidwell et al., 2015; Odabasi et al., 2008), corrected to 292.8 K (Eq. (7)). The calculated f_W/f_A values were then used to assess the equilibrium state of individual OCPs between the air and surface waters (Eq. (8)). The calculated f_W/f_A values of each of the OCPs quantified in this study at each of the sampling sites are shown in Table 3.

The determined fugacities of *p,p'*-DDT, *p,p'*-DDD, endrin and gamma-HCH gave $f_W/f_A < 1$ in Dandora, Industrial Area and Kibera, except for *p,p'*-DDT, which had $f_W/f_A > 1$ in Industrial Area. These results indicated net deposition of the gas-phase OCPs into surface waters at the sites. These observations raised a fundamental question as to the possible sources of these high levels of these OCPs in the atmosphere. Since recent studies have reported high levels of OCPs in soils in the region (Aucha et al., 2017; Sun et al., 2016; Ssebugere et al., 2010), this study suggested the possibility of

volatilization of these OCPs from contaminated soils and surfaces into the atmosphere. This suggestion is in agreement with other recent studies (Qu et al., 2016, 2019), which suggested that soils could be a re-emission source of OCPs. The studies subsequently postulated a secondary distribution pattern for some OCPs based on volatilization of the OCPs from contaminated soils during warm seasons, as reported by other studies (Tao et al., 2008; Wang et al., 2011). Dandora hosts the largest dump site in Nairobi City, where most of the waste from all around the city is disposed. Most of this waste is incinerated and the rest is allowed to decompose. Frequent dredging through the decomposing wastes and dump-site soils could lead to volatilization of the OCPs from the soils into the atmosphere. Surface run-off during storms could also result in contamination of surface waters with OCPs. Possible current use of these OCPs could be another source of atmospheric OCPs. For instance, Kibera, the second largest slum dwelling in Africa, is home to a huge population living in temporary housing made of wood, mud and/or iron sheet walling. The slum has extremely poor drainage. Possible use of pesticides by the residents to control termites, mosquitoes, and other pests, as well as surface run-off during storms, could be a major source of OCPs in the air and surface waters.

While the fugacity ratios of chlordane could not be determined due to non-detection of the pollutant in some of the environmental matrices, *p,p'*-DDE in Dandora, Kibera and City Square gave $f_W/f_A \approx 1$. This indicated the existence of an equilibrium state between gas-phase and dissolved *p,p'*-DDE in the three sites. On the other hand, Aldrin, *p,p'*-DDE and dieldrin in Dandora, Industrial Area and Kibera had $f_W/f_A > 1$. Similarly, *p,p'*-DDT and *p,p'*-DDE had $f_W/f_A > 1$ in Industrial Area. These results indicated net volatilization (Eq. (8)) of the OCPs from surface waters into the atmosphere (Devi et al., 2011; Odabasi et al., 2008; Wania et al., 1998; Mackay, 1979) at the three sites. Henry's Law constant (H_C) is an index of partitioning for a compound between the atmospheric and the aqueous phase (Mackay et al., 1982). The relative volatility (α) of a hydrophobic contaminant is useful in estimating the change in the concentration of the contaminant in surface waters (Mackay and Shiu, 1981). OCPs have H_C values less than the H_C value for water, which implies that, in dry weather, the OCPs become more concentrated in the water phase, because water volatilizes into the atmosphere faster than the OCP. However, when it is humid, such as during wet weather conditions, the evaporation of water into the atmosphere is greatly reduced. However, this does not affect the evaporation of the OCP. This presents an interesting scenario regarding the possible environmental behavior of the OCPs, in which the OCPs can still have high volatility relative to water. This is due to their highly hydrophobic nature, during the wet conditions. This alters the spatial environmental distribution of OCPs. More than 40% of all the industries in Kenya are in Nairobi City, the majority of which are situated in the city's Industrial Area. Many of these industries discharge their effluents into Nairobi River and its tributary, Ngong' River. Surface run-off

during storms as well as discharge of untreated sewage into the river could be other major sources of OCP pollution in these waters in Kibera, Industrial Area and Dandora.

From the results obtained, this study concluded that though contaminated surface waters may not be used directly for drinking, cooking, and fishing, they could still be major sources of gas-phase OCPs through volatilization. Further, this study observed that volatilization of OCPs from contaminated soils and surfaces into the atmosphere probably contribute to the presence of gas-phase OCPs in the environment in Nairobi City, which increases human exposure to bioavailable OCPs.

2.6. Human health risk assessment

The lifetime cancer risks of the residents of Nairobi City resulting from outdoor inhalation of gas-phase OCPs in the atmosphere were in the range 2.3745×10^{-13} – 1.6845×10^{-11} for adults and 5.5404×10^{-13} - 3.9306×10^{-11} for a child. The risks determined were in the order: Dandora > Kibera > Industrial Area > City Square > Ngong' Forest. The cancer risks in Dandora, Kibera and Industrial Area for both adults and children were not significantly different, falling within a narrow range of 1.6278×10^{-11} - 1.6845×10^{-11} for an adult and 3.7983×10^{-11} - 3.9306×10^{-11} for a child. However, the cancer risks in the three sites were about two and three orders of magnitude higher than those in the City Square and Ngong' Forest, respectively. Since the inhalation exposure risks in all the five sampling sites were lower than the acceptable risk range (10^{-6} - 10^{-4}) set by the USEPA (1997), this study concluded that atmospheric OCPs in Nairobi City did not pose significant cancer risks to the residents of the city.

3. Conclusions

The results of this study indicated that Industrial Area, Kibera and Dandora were possible point sources of environmental OCPs in Nairobi City of Kenya. The calculated fugacity ratios indicated that though contaminated surface waters may not be used directly for domestic and/or recreational activities, they may be major sources of gas-phase OCPs through volatilization; this increases human exposure to bioavailable OCPs. However, the determined ILCR values were lower than the USEPA acceptable risk level range. This study concluded that the atmospheric OCPs in Nairobi City did not pose significant cancer risks to the residents of the city.

Declaration of Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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