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Applications of Active and Passive Sampling Techniques in Environmental Monitoring of Organochlorine Pesticides (OCPs) in Kenya

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Abstract: *This study evaluated the efficiency of using active sampling to estimate the environmental levels of bioavailable persistent organic pollutants (POPs) by introducing graded filters. Long-term passive sampling was combined with scheduled active sampling in monitoring the levels organochlorine pesticides in the Industrial Area of Nairobi City. Triolein-filled semipermeable membrane devices (SPMDs) were deployed for 28 days in air and surface waters. During the same period, air samples were collected weekly using low-volume samplers, through graded filters, onto polyurethane foam (PUF) sorbents. Similarly water samples were collected using grab sampling, passed through graded filters, and extracted using silica-gel cartridges. The SPMDs were extracted by dialysis while the PUF samplers were extracted in soxhlets, using n-hexane. Cleanup and fractionation was achieved using adsorption chromatography, analytes identified by GC-MS and quantified using the internal standard method. From the results, the levels of OCPs sampled by SPMDs were significantly higher ($P \leq 0.05$) than those from active sampling. Further, the standard deviations of DDTs, DDDs and chlordane in air, and those of DDDs, endrin, heptachlor and γ–HCH in surface waters, from active sampling were much larger compared to those of SPMDs samples. These resulted in high percentage coefficients of variance (CV %). The standard errors of differences of means (S.E.D) values for DDTs, DDDs, chlordane, endrin, heptachlor and γ-HCH were very high. This indicated that repeated collection of the two sets of data would result in high variability in the means. This was attributed to the possibility of loss of some of the free-phase OCPs due to use of graded filters, and to lack of time-integration during active sampling. This study concluded that though use of graded filters in active sampling could resolve questions regarding the bioavailability the sampled contaminants, the data presented the possibility of underestimation of the levels of the contaminants.*

Key Words: *Organochlorine pesticides (OCPs); Passive sampling; Active sampling; Graded filters*

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I. Introduction

Data from the Nairobi Cancer Registry shows that the annual age standardized cancer incidence rates among men were 161 per 100,000 and 231 per 100,000 among women in Nairobi City [1]. The percentage of the cases with morphological verification of diagnosis (overall 85.7% in males, 87.0% in females) was higher than those in the other registries of sub-Saharan Africa [1]. Though tobacco and alcohol have been shown to be clear risk factors in South Africa [2], they do not obviously explain the high rates in Nairobi, where smoking among women is extremely very low, compared with other regions. Thus, the reasons for the high burden of cancers in Nairobi City are not fully understood.

Persistent organic pollutants (POPs) are known carcinogens [3, 4, 5]. This class of pollutants includes organochlorinated pesticides (OCPs), among others. International regulations have been focused on reducing emission of POPs into the environment (UNECE, 1998), risk assessment and modeling efforts on the ambient distribution of POPs [6]. In Kenya, the National Implementation Plan for POPs recommended the need to expand air monitoring assessment to capture high gradient sites [7]. However, the sampling method employed for any environmental monitoring program dictates the type of data obtained. This in turn determines the usefulness of the data collected. For instance, to assess the risks posed by a contaminant, the bioavailable fraction of the contaminant in the environment has to be determined.

Passive sampling refers to any sampling technique based on free flow of molecules of the analyte from the sampled medium to a receiving phase in a sampling device [8], due to the difference between the chemical potential of the analyte in the two media [9]. Passive samplers include filter papers, polyurethane foam (PUF), as well as Semipermeable membrane devices (SPMDs). SPMDs consist of an additive free lay-flat tube, made of low-density polyethylene (LDPE), with pore diameter approximately 10^{-9} m [10]. The most widely used filling material in SPMDs is the synthetic triolein 1,2,3-tri-[cis-9-octacenoyl]-glycerol [11]. The membrane is permeable for small environmental pollutant molecules but not for triolein and particulate matter. Because triolein is highly lipophilic, the pollutants cannot penetrate back to the environment. SPMDs have been widely used as passive samplers in the monitoring of environmental levels of POPs [12, 13, 14, 15, 16, among others]. However, SPMDs are not readily available on the Kenyan market and the cost of importation could be prohibitive to many researchers.

The active sampling technique, on the other hand, involves collection of discrete amounts of samples for extraction. Form the literature surveyed, all the studies on POPs in Kenya employed this method Kenya [17, 18, 19, 20, among others], except Aucha et al., [21]. However, data collected by active sampling only gives information about the total concentrations of the POPs, but do not provide any information on what fraction of the POPs is bioavailable [10, 22]. Further, the data is not time- integrated and hence it is not representative of the actual environmental levels of the contaminants [13, 22]. In Kenya, Aucha et al., [21] employed polyurethane foam (PUF) disks in long term monitoring of OCPs in Nairobi City. However, the study made no effort to separate the particulate-phase OCPs from those in gas-phase OCPs. Burgess et al., [23], observed that the uptake of contaminants from environmental sorptive phases, like colloids or suspended particles, was often limited. Thus data such as that reported by Aucha et al., [21] could not be used to evaluate the human health risks posed by OCPs. Graded filters could be used to remove the particulate matter from the samples. However, it is not known how the use of these graded filters, would affect the reported levels of the POPs from the samples.

Some previous studies have employed a combination of both active sampling and passive sampling in environmental monitoring of POPs: For instance, Yao [24] combined long-term passive sampling with meteorological conditions-triggered active sampling in monitoring atmospheric pollutants. Similarly, Crump et al., [25] used a photoionization detector monitoring device to trigger a sorbent-based volatile organic compound sample in an aircraft cabin. Ke et al., [26], on the other hand combined long-term passive sampling with caged fish in monitoring OCPs in Taihu Lake in China; the study reported that SPMDs gave much higher concentration factors for OCPs than the fish. This study combined active sampling and passive sampling in monitoring the environmental levels of gas-phase and dissolved-phase OCPs in the industrial Area of Nairobi City of Kenya. The study aimed to investigate the relative efficiency of using active sampling integrated with graded filters, in monitoring the levels of gas-phase and dissolved OCPs in air and surface waters respectively.

II. Materials And Methods

Materials

Standard length 92 cm performance reference compound semipermeable membrane devices (PRC-SPMDs), filled 99.9% pure grade triolein, were acquired from Sampling and Testing Department, E&H Services Inc., in Prague, Czech Republic along with 5-SPMD carrier deployment cages made of stainless steel. Stevenson screens, made of untreated wood and 1-1.5 m above the ground, were fabricated in a carpentry workshop (Embakasi, off Outering Road, Nairobi City, Kenya). Analytical grade solvents and reagents were acquired from Sigma-Aldrich (St. Louis, Missouri, USA). On the other hand, Standards and Certified Reference Materials were acquired from Industrial Analytical (PTY) Ltd, (Part of LGC Standards), (Vorna Valley, 1686, Republic of South Africa).

Study design

The experiments were set up in a two factor randomized design with four replications, on the eastern part of Nairobi's Industrial Area. The main factor in this study was the sampling method: active sampling versus passive sampling. The sub-factor was the environmental medium: Air and surface waters. Water sampling was carried out on Ngong' River at various sites between, W_1 (-1.3109, 36.8776) and W_4 (-1.3102, 36.8809). Similarly, air sampling was done at various sites between Nandunu close off LungaLunga Road, A_1, (-1.3078, 36.877) to the west, Bridge International Academy – Sinai, A_2, (-1.3068, 36.8819) to the north, Deliverance Church – Sinai, A_3, (-1.3088, 36.8802) to the East and bordered to the south by the section of Ngong' River where water sampling was done, A_4 (-1.3092, 36.8815) (Figure 1).

Since the daily patterns of the various industries and distribution of the industrial activities that probably lead to environmental pollution could not be established with certainty, this was considered to be a probable source of variation during sampling. To mitigate these possible variations, the weekly sampling days were staggered: During first week, sampling was done on the Monday; during the second week sampling was

done on the Wednesday and in the third week sampling was done on the Friday; the sampling during the fourth week was carried out on the Tuesday. To mitigate the uncertainty probably resulting from possible variations in the times of release of effluents during the day, two sets of samples were collected on each sampling day; the first set of samples was collected between 9.00 am and 12.00 am, and the other set collected between 2.00 pm and 5.00 pm, on the sampling days.

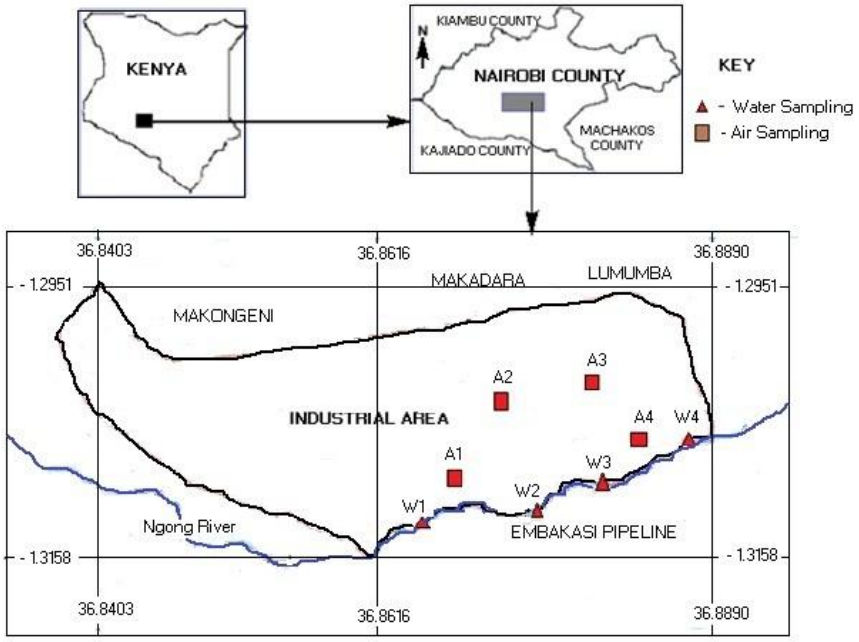

Figure 1: Map showing the sampling sites in the Industrial Area of Nairobi City

Sampling

Active sampling of air and surface water was done weekly, in four replications, by active sampling: air samples were collected using a low-volume air sampler, with a stainless steel funnel of 25 cm diameter. The funnel was fitted to a vent (sampling tube) of 7.0 cm internal diameter, standing at a height of 1.5 m above the ground level. The sampling tube was tightly fitted with a 0.45 μm glass-fiber air filter. The air was sucked, through the filter, onto polyurethane foam (PUF) sorbent for 20 minutes at each sampling unit. After each sampling, the PUF was removed and sealed in pre-extracted aluminum foil and kept in a cooler-box. A new filter was then fitted onto the pump before the next sampling, to avoid cross-contamination. Similarly, water samples were collected from Ngong River in pre-cleaned 1.0 L brown bottles. The sampling bottles were immediately sealed, wrapped in pre-cleaned aluminum foil and transported to the laboratory for extraction. The temperature and the pH of the water were determined at the sampling site.

Passive sampling experiments were also set up concurrently over the same period (mid-May 2017 - mid-June 2017), for 28 days. The SPMDs used in air sampling were placed in Stevenson's screens, to avoid precipitation and direct sunlight. Another set of SPMDs in stainless steel cages were deployed for 28 days in the surface waters on Ngong' River.

Quality Control

The quality control measures during included the use of field blanks and laboratory blanks: The field blanks and the laboratory blanks, used in passive sampling, were transported according to the method described by Alvarez [13]. The field blanks were used to account for contamination during transportation of the samplers, during the deployment and retrieval periods, as well as from storage, processing and analysis. On the other hand, the laboratory blanks were used to account for any contamination resulting from processing and analysis of the samples.

Extraction

The PUF samplers were extracted in soxhlet apparatus according to the USEPA method TO-13A [27]; the PUF plugs were extracted in soxhlets using 300 mL of a mixture of diethyl ether: n-hexane (1:9 v/v), at 40℃ for 7 hours. On the other hand, the water samples were filtered through a 0.5μm filter to remove particulate matter and subsequently through a 0.2μm cellulose acetate filter to remove colloidal particles. The samples were then extracted using adsorption chromatography on silica cartridges.

Extraction of the SPMDs was based on the methods reported in literature [13, 22, 28, 12, 29]: Each SPMD was removed from the metal cage and immediately cleaned to remove any particulate matter on its surface and extracted by dialysis using 300 mL aliquot of analytical grade hexane for 24 hours. The extract was decanted off, a second aliquot 300 mL of analytical grade hexane added to the flask and extracted for 12 hours. The extracts from both dialyses were combined followed by clean-up and concentration.

Sample clean-up and Concentration

Each of the extracts was concentrated to about 2 ml in a rotary evaporator at 35°C, prior to the cleanup and fractionation. About 2g of analytical grade sodium sulfate was added at the top of every SPE cartridge before sample addition to remove any moisture present in the sample. The samples were cleaned according to USEPA Method 3630C: The samples were quantitatively transferred onto preconditioned silica gel cartridges and eluted with 5.0 mL hexane. An additional 5.0 mL of hexane was added to the cartridge, retained for 1 minute and then allowed to elute. This eluate was collected as Fraction 1 and discarded. A 5-mL aliquot of diethyl ether/hexane (50/50, v/v) was added to the cartridge and the eluate collected as Fraction 2. This fraction was analyzed for OCPs.

The samples were finally concentrated and prepared for GC-analysis according to the method used by Lalah and Kaigwara[30], as modified by Lisouza et al., [19]: To each of the cleaned samples, 0.5 mL of analytical grade toluene was added, and the sample reduced to 0.5 mL in a rotary evaporator at 35℃. The extract was then transferred to a 2-mL amber coloured agilent vial wrapped in pre-cleaned aluminum foil. Internal standards were then added into each of the extracts according to the US EPA method 8100/8015 [31].

Instrumental analysis and characterization

The PAHs and OCPs samples were analyzed according to the methods used by Zhu et al., [14], Wang et al., [15], and Schramm et al., [16]. The extracts were analyzed using an Agilent Gas Chromatograph instrument coupled with mass spectrornetry (GC-MS). Splitless 1µL injections were made onto a 30m DB5-MS column with 0.250 mm internal diameterand 25 µm film thickness. The instrument was run is selected ion monitoring (SIM) mode. The analytes were characterized using the method used by Lalah and Kaigwara[30] as modified by Lisouza et al., [19]. Identification was achieved by comparing the peak retention times on the sample chromatograms with the chromatograms of the authentic standards and confirmed by mass spectrometry.

Quantification of the analytes

The relative response factors of the analytes were determined according to the US EPA method 8100/8015 [31]. The peak area responses of the identified analytes were tabulated against their concentration and that of the internal standard, and the relative response factors (RRF) for each of the analytes calculated using the equation:

$$RRF = \frac{A_S \ x \ C_{IS}}{A_{IS} \ x \ C_S} \qquad (Equation\ 5)$$

Where, A_S = Peak Area for the target analyte measured; A_{IS} = Peak Area for the internal standard; C_{IS} = Concentration of the internal standard; C_S = Concentration of the target analyte

The amount of the analytes in the SPMDs was determined using the internal standard method, according to the US EPA method 8100/8015 [31]. Equation 6 was used in the calculations:

$$Amount, N, (ng/SPMD) = \frac{A_S \ x \ W_{IS} \ x \ D \ x \ F}{A_{IS} \ x \ RRF \ x \ W_S} \qquad (Equation\ 6)$$

Where, A_S = Peak Area for the analyte in the sample; A_{IS} = Peak Area for the internal standard in the sample; W_{IS} = Amount (ng) of internal standard added to the sample; D = Dilution factor; since no dilution was made on the sample prior to analysis, D = 1; W_S = Final volume of extract from SPMD; F = Factor if the samples are split in half for analyses.

Method Recovery

The recovery study experiments were set up in three replications. The blank matrices were spiked with 1.0 ppm authentic standards. The extraction, clean-up, instrumental analysis and quantification was achieved using the same methods used for the field samples. The percentage recovery was calculated using Equation 7.

$$Percentage\ Recovery = \frac{\text{Amount (⍰g/vol)in spiked sample} - \text{Amount (⍰g/vol) in unspiked sample}}{\text{Amount (⍰g/vol) spiked}} \ x\ 100$$

$$(Equation\ 7)$$

The mean percentage recovery rate was used to correct all the analyte concentrations calculated for method recovery.

Sampling rate (Rs) and Concentrations for SPMDs

The release rate (K_e) of the performance reference compound (PRC) was determined comparing the amount of compound initially added to the SPMD (N_o) to the amount remaining (N_t) time t days (*Equation 8*). Samples of the SPMDs used for sampling were analyzed using a head-space gas chromatograph instrument coupled with mass spectrometer.

$$K_e = \frac{[\ln(\frac{N_t}{N_0})]}{t} \qquad (Equation\ 8)$$

Then, *Log* K_{pw} is determined from a regression model of the compound's Log K_{ow}using Equation 9$LogK_{PW} = a_0 + 2.321logK_{OW} - 0.1618(logK_{OW})^2$ $(Equation\ 9)$

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

The sampling rate of the SPMDs was subsequently calculated using Equation 10.

$$R_S = V_S K_{PW} K_e \qquad (Equation\ 10)$$

Where; *V*s is the volume of the SPMD (L)

In passive sampling, the sampling rate for a passive sampler is the volume of water or air cleared of analyte per unit of time by the passive sampling device. The time-weighted average concentration of the analyte in the gas phase or water phase was then calculated, using a non-linear kinetic uptake model, Equation 11 [32],

$$C_{W(SPMD)} = \frac{M_S(t)}{R_S t} \qquad (Equation\ 11)$$

Where *M*sis the amount of an analyte sampled after exposure for time, t days.

The SPMD-based analyte concentrations in the air or surface waters were therefore calculated using a non-linear kinetic uptake model, Equation 12 [32].

$$Concentration = \frac{N}{K_{SW} V_s [1 - \exp(-k_e t)} \qquad (Equation\ 12)$$

Statistical analysis of data

Analysis of variance of the data, for a two factor completely randomized design was subsequently used to separate means for sampling method, and means for environmental media. This was followed by pair-wise comparison of means using t-test was used to determine if there exist significant differences between the means at $P \leq 0.05$. Further, the standard errors of differences of means (S.E.D) were determined to provide information on the sampling distribution of the differences between means. This was used to evaluate the accuracy of the methods in estimating the environmental levels of bioavailable OCPs.

III. Results And Discussion

Weather Data in Nairobi city during the sampling period

Daily weather information was collected during the sampling periods, between mid-May and mid-June 2017. The mean daily temperatures ranged between 19.4±0.7℃ - 21.9±2.7℃. Similarly, the means of daily humidity were in the range of 63.1±10.3 % - 79.0±4.5 %. During the sampling period, the average daily wind speeds were between 10.5±2.4 Km/hr - 12.0±3.7 Km/hr. The accumulated monthly precipitation was 51.2 mm in May, over nine precipitation days in the month, and 2.0 mm in June on a single precipitation day.

Comparison between the levels of OCPs collected by active sampling and SPMDs

The percentage recoveries of the OCPs in this study were in the range 74.5% - 91.0%. Figure 1 shows the relative levels of OCPs in air and surface waters, collected by active sampling and passive sampling, in Nairobi City of Kenya.

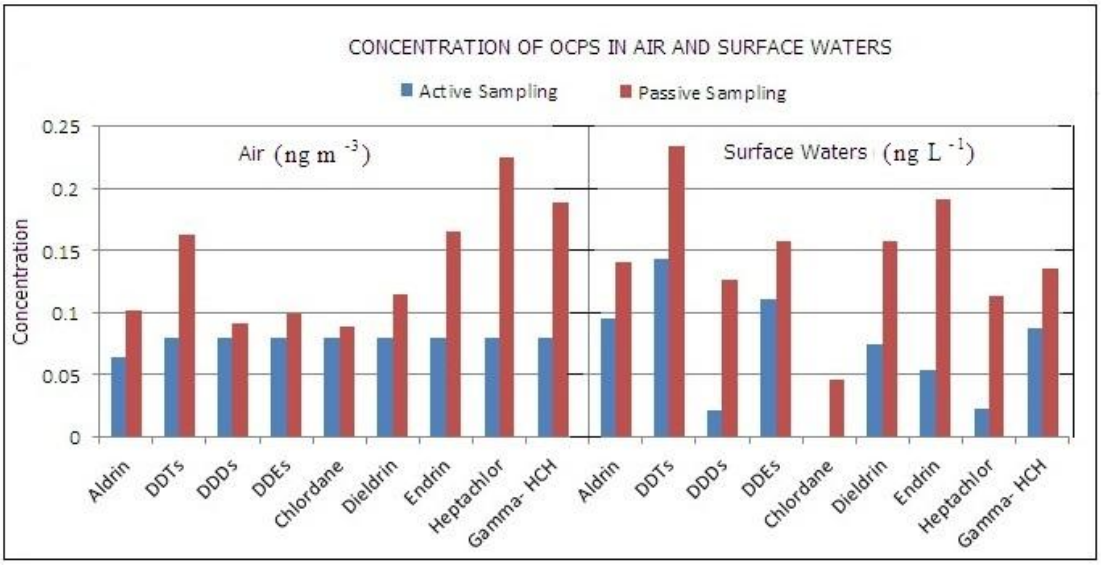

Figure 1: Bar chart showing the levels of OCPs in air and surface waters by active and passive sampling

The levels of OCPs collected using SPMDs were higher than those sampled by active sampling in both the air and surface waters. From the data, heptachlor gave the highest concentrations in air from passive sampling. But this was not the case from the active sampling data. Similarly, the levels of DDTs, endrin and γ-HCH collected by passive sampling were much higher than those from active sampling. In surface waters, the levels of DDTs, DDDs, Chlordane dieldrin, endrin and heptachlor from passive sampling were also much higher than those collected by active sampling. These results show the sampling method used play an important role on the reported levels of the contaminant. These results were consistent with those of Sun et al., [33] who reported that heptachlor had the highest concentration, among OCPs, in soils in Kenya yet the species had low detection frequencies. These results point to a possibility of periodical contaminant release from point sources resulting from either anthropogenic activities or change in weather.

Distribution of the means of the data from Active and Passive sampling

Table 1 gives the means, coefficients of variation (CV %), standard errors of differences of means (S.E.D) and the frequencies of detection of the individual OCPs in the collected samples (n = 8).

Table 1: Levels of OCPs obtained from the air (ng m^{-3}) and surface waters (ng L^{-1}) using both active and passive sampling

OCP	Environ. medium	Sampling method*		Mean	CV%	LSD (P ≤ 0.05)	S.E.D	Detection frequency (n = 8)
		Active	Passive					
Aldrin	Air	0.064±0.015	0.102± 0.001	0.083± 0.027	11.4	0.021	0.007	8
	S. Waters	0.096±0.012	0.141±0.001	0.119± 0.032	6.9	0.018	0.006	8
DDTs	Air	0.080±0.007	0.163±0.007	0.122± 0.058	35.0	0.096	0.030	7
	S. Waters	0.144± 0.059	0.234±0.003	0.189± 0.064	22.5	0.097	0.030	8
DDDs	Air	0.021±0.047	0.092±0.004	0.056± 0.051	50.2	0.064	0.020	5
	S. Waters	0.021±0.041	0.127±0.005	0.074± 0.075	30.5	0.059	0.019	5
DDEs	Air	ND	0.099±0.006	0.050± 0.070	8.4	0.009	0.003	4
	S. Waters	0.111±0.013	0.158±0.019	0.134± 0.033	5.4	0.017	0.005	8
Chlordane	Air	0.021± 0.050	0.089± 0.005	0.055± 0.048	58.7	0.073	0.023	5
	S. Waters	ND	0.046± 0.053	0.023± 0.032	164.0	0.084	0.026	2
Dieldrin	Air	0.103± 0.010	0.115± 0.003	0.109± 0.008	3.5	0.009	0.003	8
	S. Waters	0.074± 0.010	0.158± 0.004	0.116± 0.059	8.6	0.023	0.007	8
Endrin	Air	0.112± 0.020	0.166 ± 0.006	0.139± 0.038	12.3	0.038	0.012	8
	S. Waters	0.054± 0.064	0.192± 0.013	0.123± 0.097	40.1	0.111	0.035	6
Heptachlor	Air	0.206± 0.015	0.225± 0.008	0.215± 0.013	8.2	0.040	0.012	8
	S. Waters	0.023± 0.046	0.114± 0.001	0.068± 0.064	46.6	0.072	0.023	6
γ - HCH	Air	0.135± 0.023	0.189± 0.004	0.162± 0.038	7.0	0.026	0.008	8
	S. Waters	0.087± 0.062	0.136± 0.006	0.111± 0.034	41.3	0.104	0.033	7

ND = not detected

Aldrin was detected in all the water and air samples with relatively high atmospheric concentrations of 0.064 ± 0.015 ng m^{-3} and 0.102 ± 0.001 ng m^{-3} from active and passive sampling respectively. These values were within the range of those reported in the air in Alexandria, Egypt (>LOD – 147 pg m^{-3}) [34. The levels of dissolved aldrin in surface waters were 0.096 ± 0.012ng m^{-3} and 0.141 ± 0.001 ng m^{-3} from active and passive sampling respectively. The most significant observation here was that the levels of aldrin in both air and surface water samples collected by passive sampling were significantly higher ($P \leq 0.05$) than those collected active sampling. This trend was also observed in both the atmospheric and dissolved phase levels of DDDs, DDEs, chlordane, dieldrin, endrin and heptachlor, as well as the atmospheric levels of γ-HCH. However, though the atmospheric and dissolved phase levels of DDTs collected by active sampling were lower than those collected by passive sampling, they were not significantly different ($P \leq 0.05$). This was also observed in the levels of dissolved phase γ-HCH sampled by the two methods.

DDE and chlordane were not detected in the air samples collected by active sampling. Similarly, a number of the OCPs were not detected in all the replicates of air samples collected by the active method: this included DDD which was found in one replicate; chlordane in one; and DDT in three replicates. In the water samples collected by the active method, DDD was detected in one replicate; heptachlor in one; and γ-HCH in three replicates. This was attributed to the uncertainties and hence the variances resulting from choice of the sampling time, which are inherent in active sampling. On the other hand, chlordane was only detected in two of the SPMDs used in the passive sampling of the surface water. For the purpose of this study, the levels of the analytes in the samples in which they were below detection limit were assumed to be zero.

Generally, the results show that the levels of OCPs obtained by passive sampling were significantly higher ($P \leq 0.05$) than those from active sampling. However, for DDE and dieldrin the means from active sampling were significantly higher ($P \leq 0.05$) than those from passive sampling. One of the advantages of using SPMDs, over other sampling methods, is that SPMDs can be deployed for extended time periods to integrate long-term data as noted by Esteve-Turrillas et al., [35]. Since passive sampling methods give time-averaged concentrations. Soderstrom and Bergqvist, [36] further noted that the risk of underestimation or overestimation of total pollutant mass flows due to accidental sampling is reduced. This indicates that the results obtained by passive sampling could be more reproducible than those obtained by active sampling.

The coefficients of variation percentages (CV %) across all the analytes monitored in the all the samples ranged between 3.5 % (dieldrin) to 50.2% (DDD). However, chlordane showed extremely high CV% (164%). This was attributed to the non-detection of chlordane in some of the replicates, resulting in non-homogeneous sample variances. This high CV% values in a number of the analytes was an indication of non-homogeneity in the variance of the experimental errors [37, 38, 39], in the collected data. The high CV% values further indicated that the data variances were significantly different [37, 38, 39, 19]. This study attributed this non-homogeneity to the difference in the sampling methods:

The standard errors of differences of means (S.E.D) values for DDTs, DDDs, chlordane, Endrin, heptachlor and γ-HCH were very high, especially when considered as a percentage of the differences between the means. The indicated that collection of the two sets of data was repeated many times would result in high variability in the means. In the design of this study the span of the sampling area was reduced in order to minimize the variations resulting from probable source distribution. This was meant to establish a near-homogenous sampling block. Further, to make the data collected more representative, the number of replications was increased. This study attributed these high SED values to the possibility of loss of some of the dissolved OCPs due to use of graded filters to remove particulate matter and colloidal particles [40]. The study further attributed the high variations in the distributions to the fact that data from active sampling was not time-integrated [13, 22].

IV. Conclusions And Recommendations

From the results obtained, modification of active sampling to include graded filters resolved questions regarding the bioavailability the sampled contaminants. However, the data still presented the possibility of underestimation of the bioavailable contaminants. This study recommends that, in the absence of SPMDs, integration of graded filters in active sampling could provide an insight into probable levels of bioavailable POPs in the environment. However, the frequency of sampling should be increased to make up for the variances resulting from lack of time-integration.

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References

[1]. Korir, A., Okerosi, N., Ronoh, V., Mutuma, G., &Parkin, M. (2015). Incidence of cancer in Nairobi, Kenya (2004–2008).*International Journal of Cancer*, ***137***, 2053–2059.

[2]. Pacella-Norman, R., Urban, M.I., &Sitas, F. (2002). Risk factors for oesophageal, lung, oral and laryngeal cancers in black South Africans.*British Journal of Cancer, 86*, 1751–56.

[3]. Çok, İ., Donmez, M. K., Hakan, S. M., Aydınuraz, B., Henkelmann, B., Kotalik, J., & Schramm, K.-W. (2007). Concentration of polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans and dioxin-like PCBs in human adipose tissue from Turkish men.*Chemosphere***,** *66*, (10), 1955-1961.

[4]. Bordajandi, L. R., Abad, E., & González, M. J. (2008). Occurrence of PCBs, PCDD/Fs, PBDEs and DDTs in Spanish breast milk: Enantiomeric fraction of chiral PCBs. *Chemosphere***,** *70*, (4), 567-575.

[5]. Field, J. A., & Sierra-Alvarez, R., (2008). Microbial degradation of chlorinated dioxins.*Chemosphere***,** *71*, (6), 1005-1018.

[6]. Klecka, G., Boethling, B., Franklin, J., Graham, G., Grady, L., Howard, P., Kannan, K., Larson, R., Mackay, D., Muir, D.,& van de Meent, K. (2000). Evaluation of persistence and long-range transport of organic chemicals in the environment.SETAC Special Publication Series: Pensacola, FL, USA.

[7]. UNEP-GEF Project (2012). Supporting the global monitoring plan on persistent organic pollutants - National Report from Kenya: United Nations Environment Programme Chemicals. East Southern African Region Project GFL 4A80, report.

[8]. Hazrati, S., &Harrad, S. (2007). Calibration of polyurethane foam (PUF) disk passive air samplers for quantitative measurement of polychlorinated biphenyls (PCBs) and polybrominateddiphenyl ethers (PBDEs): Factors influencing sampling rates. *Chemosphere, 67***,** 448–455.

[9]. Vrana, B., Allan, I. J., Greenwood, R., Mills, G. A., Dominiak, E., Svensson, K., Knutsson, J. & Morrison, G. (2005). Passive sampling techniques for monitoring pollutants in water.*Trends in Analytical Chemistry, 24*, (10), 845-868.

[10]. Huckins, J. N., Tubergen, M. W., &Manuweera, G. K. (1990). Semipermeable membrane devices containing model lipid: A new approach to monitoring the bioavailability of lipophilic contaminants and estimating their bioconcentration potential. *Chemosphere, 20*, 533-552.

[11]. Kočí, V., Mlejnek, M., &Kochánková, L. (2003). Toxicological evaluation of exposed SPMD membranes.*Central European Journal of Chemistry 1*, 28-34.

[12]. Huckins, J.N., Petty, J.D., &Booij, K. (2006). Monitors of organic chemicals in the environment semipermeable membrane devices. Springer Science, LLC (pp223), New York.

[13]. Alvarez, D.A. (2010). Guidelines for the use of the semipermeable membrane device (SPMD) and the polar organic chemical integrative sampler (POCIS) in environmental monitoring studies.*U.S. Geological Survey, Techniques and Methods 1-D4*, 28.

[14]. Zhu, X., Zhou, C., Henkelmann, B., Wang, Z., Ma, X., Fiester, G., & Schramm, K.-W. (2013). Monitoring of PAHs profiles in the urban air of Dalian, China with active high volume sampler and semipermeable membrane devices. *Polycyclic Aromatic Compounds*, *33*(3), 265-288.

[15]. Wang, J., Bi, Y., Pfister, G., Henkelmann, B., Zhu, K., & Schramm, K-W. (2009). Determination of PAH, PCB and OCP in water from Three Gorges Reservoir accumulated by semipermeable membrane devices (SPMD). *Chemosphere, 75*, 1119-1127.

[16]. Schramm, K-W., Bi, Y., Temoka, C., Pfister, G., Henkelmann, B., &Scherb, H. (2012). Chemical and effect-oriented exposomics: Three Gorges Reservoir. *Environmental Science &Polution Research*.DOI 10.1007/s11356-012-1319-9.

[17]. Onyango, A.A., Lalah, J.O., Wandiga, S.O., &Gichuki, J. (2012). Assessment of Polycyclic Aromatic Hydrocarbons in Latesniloticus, Oreochromisniloticus and Rastrineobolaargentea as Sources of Human Exposure in Kisumu Bay, Winam Gulf of Lake Victoria. *Bulletin of Environmental Contamination & Toxicology*, Bulletin of Environmental Contamination & Toxicology, 88(5), 747-51.

[18]. Kwach, B.O., Lalah, J.O., &Wandiga, S.O. (2009). Spatial and seasonal variations in concentrations of polycyclic aromatic hydrocarbons in water and sediment of Kisumu City Bay of Winam Gulf, Lake Victoria-Kenya.*Bulletin of Environmental Contamination & Toxicology*, *83*, 722–733.

[19]. Lisouza, F.A., Owuor, P.O., & Lalah, J.O. (2011). Variation in indoor levels of polycyclic aromatic hydrocarbons from burning various biomass types in the traditional grass-roofed households in Western Kenya. *Environmental Pollution, 159*, 1810 -1815.

[20]. Omwoma, S., Lalah, J. O., Virani, M., Schramm, K-W., &Henkelmann, B. (2015). Dioxin-like PCBs and PCDD/Fs in surface sediments near the shore of Winam Gulf, Lake Victoria.*Chemosphere, 118*, 143–147.

[21]. Aucha J.K., Wandiga S.O., Abong'o D.A., Madadi V.O., &Osoro E.M., (2017).Organochlorine pesticides residue levels in air and soil from Nairobi and Mount Kenya regions, Kenya. *IOSR Journal of Applied Chemistry (IOSR-JAC), 10*, 2278-5736.

[22]. Alvarez, D.A., Petty, J.D., &Huckins, J.N. (2004). Development of a passive, in situ, integrative sampler for hydrophilic organic contaminants in aquatic environments.*Environmental Toxicology & Chemistry*, *23*, 1640-1648.

[23]. Burgess, R. M., Lohmann, R., Schubauer-Berigan, J. P., Reitsma, P., Perron, M. M., Lefkovitz, L., & Cantwell, M. G. (2015).Application of passive sampling for measuring dissolved concentrations of organic contaminants in the water column at three marine superfund sites.*Environmental Toxicology and Chemistry, (9999), 1-14*

[24]. Yao, Y. (2007): Sources and occurrence of dacthal in the Canadian atmosphere. *Environmental Science & Technology* 41:688–694.

[25]. Crump, D., Harrison, P., & Walton C. (2011). *Aircraft Cabin Air Sampling Study: Part 1 of the Final Report*. Cranfield University Institute of Environment and Health, Bedfordshire, UK.https://dspace.lib.cranfield.ac.uk

[26]. Ke R., Xu Y., Huang S., Wang Z., &Huckins J.N., (2007): Comparison of the Uptake of Polycyclic Aromatic Hydrocarbons and Organochlorine Pesticides by Semipermeable Membrane Devices and Caged Fish (*CarassiusCarassius*) in Taihu Lake, China. *Environmental toxicology and chemistry, (26) 6*, 1258–1264

[27]. Ozcan, S., Aydin, M.E. & Tor, A. (2008). Chromatographic separation and analytic procedure for priority organic pollutants in urban air, *Clean: Soil, Air, Water. (*36), 969-977.

[28]. Alvarez, D.A., Cranor, W.L., Perkins, S.D., Clark, R.C., & Smith, S.B. (2008). Chemical and toxicological assessment of organic contaminants in surface water using passive samplers.*Journal of Environmental Quality*, *37*, 1024–1033.

[29]. Petty, J.D., Orazio, C.E., Huckins, J.N., Gale, R.W., Lebo, J.A., Meadows, J.C., Echols, K.R., &Cranor, W.L. (2000). Considerations involved with the use of semipermeable membrane devices for monitoring environmental contaminants: *Journal of Chromatography, 879*, 83–95.

[30]. Lalah, J.O., &Kaigwara, P.N. (2005). Polynuclear aromatic compounds in kerosene, diesel and unmodified sunflower oil and in respective engine exhaust particulate emissions. *Toxicological & Environmental Chemistry,10*, 1-17.

[31]. USEPA, (1997). Polynuclear aromatic hydrocarbons/nonhalogenated organics using GC/FID.Method 8100/8015. Test Methods for Evaluating Solid Waste, Physical/ Chemical Methods EPA SW-846 [Version 2] (December 1997): Integrated Manual Through Update III. U.S. EPA,Washington, DC.

[32]. Huckins, J.N., Petty, J.D., Orazio, C.E., Lebo, J.A., Clark, R.C., Gibson, V.L., Gala, W.R., & Echols, K.R. (1999). Determination of uptake kinetics (sampling rates) by lipid containing semipermeable membrane devices (SPMDs) for polycyclic aromatic hydrocarbons (PAHs) in water.*Environmental Science and Technology, 33*, 3918–3923.
[33]. Sun H., Qi Y., Zhang D., Qing X. Li Q.X., & Wang J. (2016): Concentrations, distribution, sources and risk assessment of organohalogenated contaminants in soils from Kenya, Eastern Africa. Environmental Pollution (209) pp 177-185
[34]. Khairy M.A., &LohmannR., (2013): Feasibility of using low density polyethylene sheets to detect atmospheric organochlorine pesticides in Alexandria, Egypt. *Environmental Pollution (181)*: 151-158
[35]. Esteve-Turrillas, F.A, Yus`a, V., Pastor, A., & Guardia, M. (2008). Review: New perspectives in the use of semipermeable membrane devices as passive samplers. *Talanta 74*, 443–457.
[36]. Soderstrom, H.S., &Bergqvist, P.-A. (2004). Passive air sampling using semipermeable membrane devices at different wind speeds in situ calibrated by performance reference compounds (PRC).*Environmental Science & Technology, 38*, 4828–4834.
[37]. Gomez, A.K., & Gomez, A.A., (1983). Statistical Procedures of Agricultural Research. John Wiley & Sons, New York, pp. 294 - 315.
[38]. Hopkins, W.G., (2000). A New View of Statistics.Internet Society for Sports Science.http://www.sportssci.org/resource/stats/ (Last accessed November 2018).
[39]. Osborne, J., (2002). Notes on the use of data transformations.Practical Assessment, Research & Evaluation 8 (6).http://PAREonline.net (Last accessed December 2018).
[40]. Carlson M. &Thompson R. D., (2000). Analyte loss due to membrane filters adsorption as determined by high-performance liquid Chromatography.Journal of Chromatographic Science, **38**, 77 – 83.

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