

Organochlorine Pesticides Residue Levels in Air and Soil from Nairobi and Mount Kenya regions, Kenya

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Abstract: The study investigates the organochlorine pesticides residue level in air and soil at sites in Nairobi and Mount Kenya regions, Kenya. Air and soil samples from four sites were collected and analysed for selected organochlorine pesticides (OCP) using gas chromatography equipped with electron capture detector and confirmed using GC/MS. The targeted pesticides were α -HCH, β -HCH, γ -HCH (lindane), α -endosulfan, β -endosulfan and Endosulfansulfate. The samples were collected seasonally between the months of July 2012 and April 2013. The residue levels of organochlorine pesticides in air samples during month of October ranged between 0.027 ± 0.004 to 5.735 ± 0.575 ng/M³, while during the Month of February the concentration ranged between 0.013 ± 0.00 to 9.375 ± 1.65 ng/M³ and the levels during the month of April ranged between 0.013 ± 0.00 to 11.508 ± 0.26 ng/M³. Organochlorine pesticide detected in soil during month of October ranged between BDL to 131.206 ± 14.41 ng/Kg, while during the Month of February the concentration ranged between 0.418 ± 0.01 to 38.361 ± 5.39 ng/Kg and the levels during the month of April ranged between 0.406 ± 0.00 to 26.877 ± 8.89 ng/Kg. The residue levels of the analysed POPs in air and soil were generally high at the Dandora and Industrial area sites. This indicates that industrial activities such as Tetra-Pac, general plastics, Phillips industries waste and stock piles are the main sources of the new POPs in Nairobi. The high concentration level poses a health risk to residents of Dandora and Industrial area workers.

Keywords: Dandora, Kabete, Industrial area, Mount Kenya, organochlorine pesticide residues, air, soil

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I. Introduction

Persistent organic pollutants (POPs) are a group of semi-lipophilic chemicals, including polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), polychlorinated dibenzo-p-dioxins (dioxin) and polybrominated diphenyl ethers PBDE [1]. Persistent organic pollutants (POPs) are globally distributed and found in environmental media like sediment, air, soil and biota [2]. They are toxic compounds of anthropogenic origin that resist degradation in environmental compartments and may undergo long-range transport [3]. In 2002, a global treaty, the Stockholm Convention (SC) on Persistent Organic Pollutants, was adopted by the world's governments to protect human health and the environment from POPs in line with the aims of the Stockholm convention to protect humans and the environment from hazardous and persistent chemicals by reducing or eliminating their production and introduction to the environment [4]. In 2004 the first twelve POPs to be listed in annexes to the Stockholm convention on POPs were; aldrin, chlordane, dieldrin, endrin, heptachlor, hexachlorobenzene (HCB), mirex, toxaphene, polychlorinated biphenyls (PCB), DDT, dioxins and furans [5]. The convention also defined criteria for including new chemicals basing on their persistence, bioaccumulation, and potential for long-range transport and adverse effects [6]. Accordingly, the conference of parties to the convention agreed in May 2009 to add nine new POPs to the convention's annexes. The nine new POPs include; pentabromodiphenylether (PentaBDE), octabromodiphenylether (Octa-BDE), perfluorooctanesulfonate (PFOs), pentachlorobenzene, and chlordecone, hexabromobiphenyl, lindane (gamma hexachlorocyclohexane, γ -HCH) alpha hexachlorocyclohexane (α -HCH) and beta hexachlorocyclohexane (β -HCH). At its fifth meeting held in May 2011, the Conference of Parties adopted an amendment to annex A to the Stockholm convention to list technical Endosulfan and its related isomers [7]. The new POPs are categorised as; pesticides: chlordecone, endosulfan, alpha hexachlorocyclohexane (α -HCH), beta hexachlorocyclohexane (β -HCH), lindane (γ -HCH), pentachlorobenzene; Industrial chemicals: hexabromobiphenyl, hexabromodiphenyl ether and heptabromodiphenyl ether, pentachlorobenzene, perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride, tetrabromodiphenyl ether and penta bromodiphenylether; By-products: alpha-hexachlorocyclohexane, beta-hexachlorocyclohexane and pentachlorobenzene [7]. This study was undertaken in Nairobi, the capital city of Kenya which is also an industrial city and Mt. Kenya which is a remote site near Nairobi to provide evidence for long range transport of the new POPs. Due to urbanisation, industrialisation and

rapid population growth, Kenya requires data on the current state of pollution with regard to the new POPs. The aim of this study was to determine the levels of selected new POPs; Endosulfan, and its isomers and metabolite, Lindane (γ -HCH), alpha hexachlorocyclohexane (α -HCH) and beta hexachlorocyclohexane (β -HCH) in air and soil in designated sites in Nairobi and Mount Kenya region, Kenya.

II. Materials And Methods

2.1 The Study Area

Nairobi, the capital city of Kenya is located at the south-eastern end of Kenya's agricultural heartland, at approximately 1° 9'S, 1° 28'S and 36° 4'E, 37° 10'E. It occupies an area of about 696 km² and the altitude varies between 1,600 and 1,850 metres above sea level [8]. The western part of Nairobi is on high ground (approximately 1700–1800 m) with rugged topography, the eastern side is generally low (approximately 1600 m) and flat [9]. It is the administrative, commercial and industrial city of Kenya. Commercial and administrative activities are concentrated at the commercial business centre while most of the industrial activities are located to the south East. According to a report by the Japanese International cooperation Agency, Nairobi is the most industrialized urban centre in Kenya and in East Africa in general [10]. A total of 338 industries have registered with the Directorate of Occupational Health and Safety (DOHS) (JICA, 2004). Out of these, 123 are located in the industrial area, 53 in the central business district (CBD), 28 along Mombasa road and the rest dispersed in other parts of the city [10].

Mt. Kenya was considered as a remote area in this study. It is located east of the great rift valley about 175 km north-east of Nairobi with its flanks across the equator. It is situated at 037° 17'84"E, 00° 03' 75"S. Vegetation varies with altitude and rainfall. Continuous vegetation stops at about 4500 m although isolated vascular plants have been found at over 5000 m. As the climate warms, the vegetation is expected to shift higher up the mountain. The samplers were installed at an altitude of about 4500m. They were suspended on metal frames at a height of 1.5m above the ground. Figure 1 shows the map of the study area.

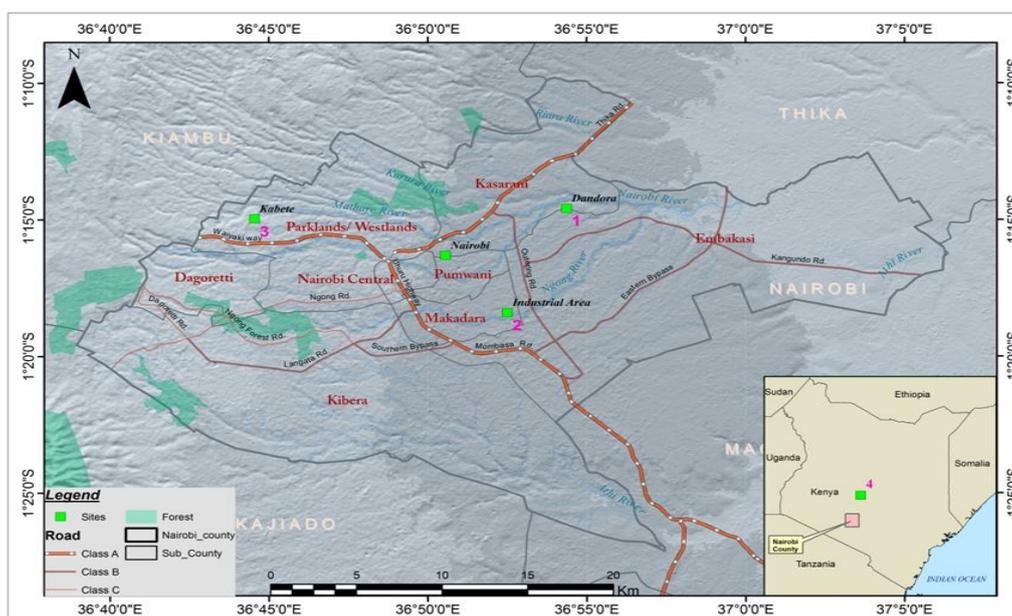


Figure 1: Map of the sampling sites in Nairobi and Mt. Kenya for the air and soil samples.

2.2 Sample Collection

Passive air samplers consisting of polyurethane foam disks housed in protective stainless steel chambers were employed in this study. Passive samplers were deployed over three-month periods (July -October 2012, October 2012- January 2013, January 2013- April - 2013). Sampling chambers were prewashed and solvent-rinsed with acetone prior to installation. All filters were prewashed, cleaned (8 hours extraction in acetone and 8 hours in dichloromethane), wrapped in two layers of aluminum foil, placed into zip-lock polyethylene bags and kept in a freezer prior to deployment. Exposed filters were wrapped in two layers of sterile aluminum foil, labeled and placed in self-sealing polythene bags and stored in polyurethane cool-boxes containing dry ice. In the laboratory samples were kept in a freezer at ≤ -19 °C to await extraction. Pesticide residue levels analysis was done within 7 days.

Soil samples were collected from under the air samplers within an area of 16 m². Grass or vegetation from the soil surface was removed and soil dug up to about 10 cm of relatively homogenous soil in vertical direction. 200 g of soil from four different points in one sampling site of the 16 m² were dug. These were then put on aluminum foil mixed to form a composite sample from which 500 g were taken to the laboratory for analysis. A cleaned stainless shovel was used. Roots, leaves and stones were removed from each sample. The soil samples were then packed in two layers of aluminum foil, placed in zip-lock plastic bags and placed in cooling boxes at 4 °C and transported to the laboratory for storage in a freezer at -18 °C awaiting extraction.

2.3 Sample Extraction and Clean-up

The PUF sorbents initially stored in the freezer at -19 °C were removed and allowed to attain room temperature. The polyurethane foams were placed in the Soxhlet extractor and were extracted for 16-18 hours using 200ml of dichloromethane. The extracts were then stored at 4 °C in a refrigerator prior to sample clean-up. The extracts were cleaned by passing through Al₂O₃ chromatographic column topped with anhydrous sodium sulphate. Pesticide residues were sequentially eluted with 175 ml n-hexane. The elutes were concentrated to 1 ml using a rotary evaporator at 40°C, and reconstituted in 0.5 ml HPLC grade isooctane for GC analyses.

EPA method 3540 Soxhlet extraction of soil was applied. The soil samples were allowed to thaw for 4 hours in the laboratory prior to mixing. Triplicates of 10 g samples were dried overnight with activated anhydrous sodium sulphate (Na₂SO₄) before transferring to the Soxhlet thimble. This sample was extracted with 200 ml of hexane: acetone (3:1 v/v) in a 250 ml round bottomed flasks for at least 16 hours. The extracts were then stored at 4 °C in a refrigerator prior to sample clean-up. Sulphur was removed using copper powder. Clean-up was accomplished by eluting through Al₂O₃ topped with anhydrous sodium sulphate. The elute was concentrated to 1ml using a rotary evaporator at 40°C, and reconstituted in 0.5 ml HPLC grade Isooctane for GC analyses.

2.4 Quantification and Analysis of the Samples

Analysis of OC Pesticides residue in air and soil samples was carried out using Agilent 6890N gas chromatograph (equipped with an auto sampler (Agilent 7683 Series injector) and a micro-electron capture detector (μECD). The injector and detector temperatures were maintained at 250 °C and 300 °C, respectively. Helium gas was used as the carrier gas and nitrogen as make-up gas with a constant flow rate of 1 ml/min. The injection volume was 1 μl with a pulsed splitless injection mode. The following injection temperature program was applied: 90°C (3 min), 90 °C to 200 °C (at 30 °C/ min and hold time of 15 min), 200 °C to 275 °C (at 30 °C/min and hold time of 5 min). The column used was HP capillary column with the following dimensions: 30 m long, internal diameter of 0.25 mm and film thickness of 0.25 μm). Data processing was done using Chemstation software version A. 09.03(1417).

Quality control and quality assurance procedures included Analysis triplicate samples, sample blanks; spiked samples were included in the sample extraction.

2.5 Data Analysis

The data obtained was analyzed using Statistical Package for Social Science (SPSS) to establish relationship between pesticide residue levels in the samples from different sampling sites and the seasonal variability. Bivariate correlation coefficients were established using Pearson product moment correlation coefficient, “r”, which is a dimensionless index, whose value is in the range -1.0 ≤ r ≤ 1.0.

III. Results And Discussion

Analysis was done for four out of the ten new POPs; alpha-hexachlorocyclohexane (α-HCH), beta-hexachlorocyclohexane (β-HCH), lindane (γ-HCH), endosulfan, its isomers and metabolite. Recoveries were higher than 70% for all samples respectively. Recovery factors were not applied to any of the data [11]. The correlation coefficients for the calibration curves ranged between 0.989- 0.9996. Table 1 shows the percentage recovery, detection limit and the correlation coefficient for the calibration curves (r²).

Table 1: Percentage recovery, Detection limit and the Correlation coefficient for the calibration curves (r²)

| New POP | Recovery | Detection limit | Correlation coefficient for calibration curve (r ²) |
|--------------------|-------------|-----------------|---|
| Alpha HCH | 94.82±8.31 | 1.1 | 0.9994 |
| Beta HCH | 87.52±4.09 | 1.6 | 0.9983 |
| Gamma HCH | 92.06±9.58 | 1.6 | 0.9990 |
| Endosulfan | 102.58±4.95 | 1.5 | 0.9996 |
| Endosulfan II | 93.23±7.13 | 1.1 | 0.9986 |
| Endosulfan sulfate | 78.25± 6.00 | 2.1 | 0.9890 |

3.1 New POPs in Air

Beta-hexachlorocyclohexane (β -HCH) dominated the composition of the new POPs in the four sampling sites and was followed by endosulfan sulfate and α -endosulfan as shown in Figure 2. The levels of β -HCH were highest at the Industrial area (5.735 ± 0.575 ng/M³) and Kabete (3.607 ± 0.276 ng/M³) sites while endosulfan sulfate and α -endosulfan were high at Industrial area and Dandora sites. The levels of Σ new POPs were highest at the Industrial area site (7.528 ng/M³) and lowest at the Mt. Kenya site (1.154 ng/M³). This may indicate production or use of these compounds in industries in the industrial area site.

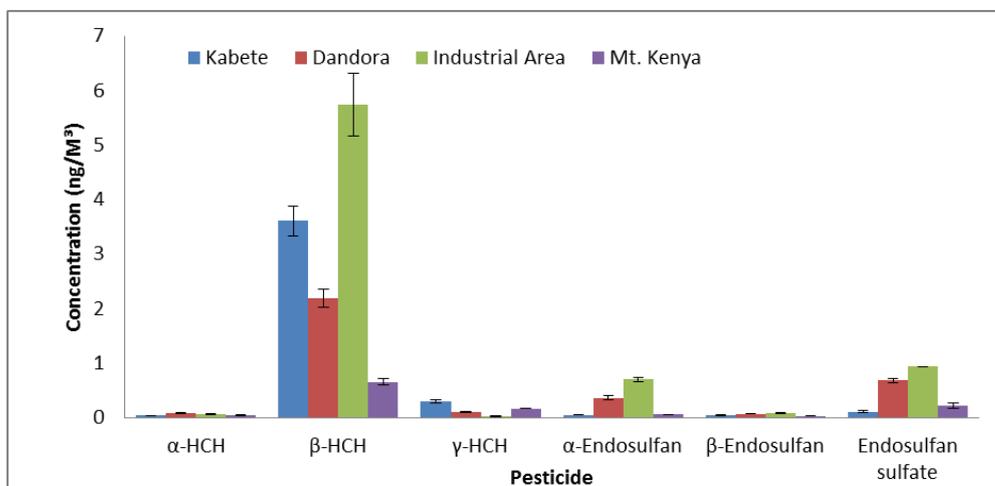


Figure 2: The spatial distribution of the new POPs residue levels in air in July-October sampling period

The average new POPs residue levels were high in air during the warm-dry season (October-January). β -HCH was in high levels at three sites and was followed by endosulfan sulfate and γ -HCH (lindane). The levels of β -HCH were highest at the Industrial area (9.376 ± 0.404 ng/M³); Dandora (7.097 ± 0.332 ng/M³); and Kabete (3.002 ± 0.216 ng/M³) sites while endosulfan sulfate and γ -HCH were high at Kabete and Dandora sites respectively (Figure 3). The Mt. Kenya site recorded the lowest levels of β -HCH, γ -HCH, β -endosulfan and endosulfan sulfate. During this sampling session, Industrial area recorded the highest level of Σ new POPs of 11.457 ± 0.512 ng/M³ followed by Dandora (8.767 ± 0.423 ng/M³) then Kabete (5.633 ± 0.309 ng/M³) and lastly Mt. Kenya with the sum of all the new POPs during that session at 0.687 ± 0.055 ng/M³. This shows that Industrial area and Dandora are point sources of this POPs.

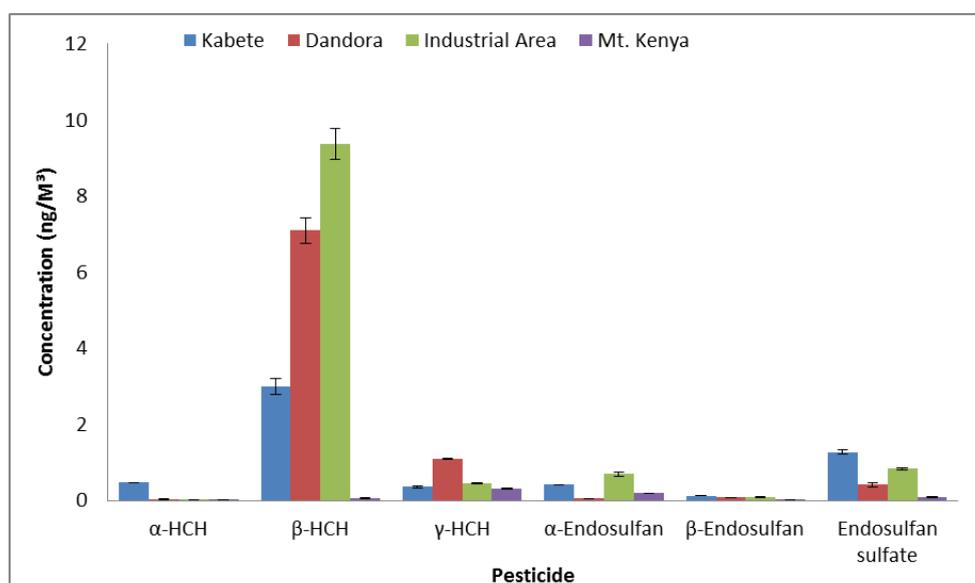


Figure 3: The spatial distribution of the new POPs residue levels in air in October-January sampling period.

The average new POPs residue levels in air during the third sampling session (January-April 2015) are indicated in Figure 4. During the third sampling session which represented the wet season (January-April),

Dandora had highest \sum new POPs residue levels (14.374 ± 0.197 ng/M³) followed by Industrial area (8.061 ± 0.094 ng/M³), Kabete (4.795 ± 0.165 ng/M³) and Mt. Kenya (1.334 ± 0.154 ng/M³) sites.

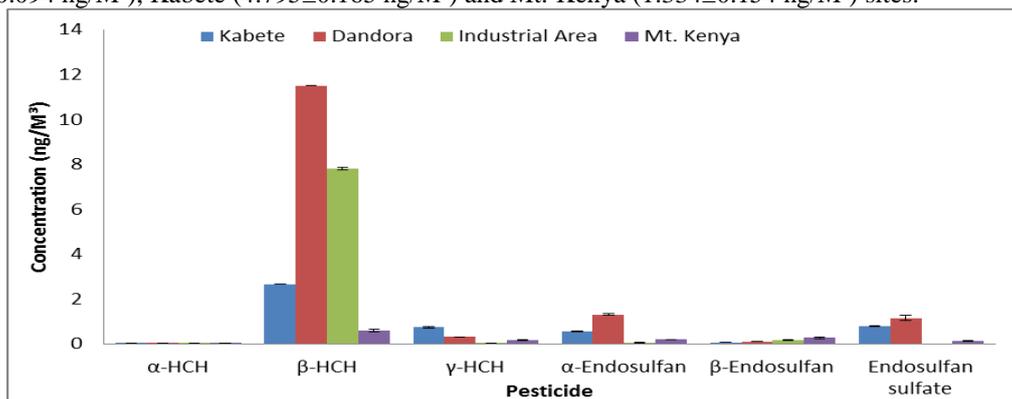


Figure 4: The average new POPs residue levels in air in January-April sampling period

The highest mean of alpha-hexachlorocyclohexane was detected at the Kabete site (0.174 ng/M³) while the lowest levels were detected at the Mt. Kenya site (0.028 ng/M³). The high levels at Kabete could be attributed to application and post application volatilization due to the agricultural activities at the site [12]. The concentrations of beta-hexachlorocyclohexane (β -HCH) were the highest among all the new POPs analyzed in study. They ranged between 7.643 ng/M³ at the Industrial area site and 0.433 ng/M³ at the Mt. Kenya Sites. The high levels of β -HCH mostly result from extensive use, former production, disposal sites and stockpiles [13]. The chemical structure of β -HCH also confers the greatest physical and metabolic stability hence its high concentrations at the Dandora, Industrial area and Kabete sites [13]. Alpha and beta hexachlorocyclohexane are also unintentionally produced as by-products of lindane production [7]. Lindane (γ -HCH) was detected at all the four sampling sites. Its production and agricultural use are the main causes of environmental contamination [14]. It is still in use as a second-line pharmaceutical treatment for lice and scabies [15]. Since it relatively persists in the environment and is transported long distances by global distillation, it was detected at all the sites though in low levels ranging from 0.497 ng/M³ at the Dandora site and 0.169 ng/M³ at the Industrial area site [13]. Endosulfan is degraded in the environment and metabolized in living beings [16]. The endosulfan isomers; α -endosulfan, β -endosulfan and the metabolite; endosulfan sulfate were detected in all the sites in relatively low concentrations. The concentrations for α -endosulfan ranged between 0.142 ng/M³ at the Mt. Kenya site and 0.571 ng/M³ at the Dandora site. The average concentrations of β -endosulfan ranged between 0.075 ng/M³ at the Kabete site and 0.104 ng/M³ at the Industrial area site. Those for the metabolite endosulfan sulfate ranged between 0.144 ng/M³ at the Mt. Kenya site and 0.750 ng/M³ at the Dandora site. The low concentrations of endosulfan suggest that the four sites may not be point sources of this POP. Since it is applied to crops using air-blast or ground boom sprayers, it may have drifted or long-range transported from other point sources [16]. Endosulfan-I (α -endosulfan) and endosulfan-II (β -endosulfan) persist in the environment for 800 and 60 days respectively [13]. There is a continuous degradation of isomer β -endosulfan to the metabolite in soil and sediment [17]. This explains the very low concentrations of β -endosulfan in all the sites compared to the concentrations of α -endosulfan and endosulfan sulfate. The relatively high concentration of β -endosulfan at the Mt. Kenya site could be attributed to the halting of the degradation of the same during winter [17] considering the cool climatic conditions at the Mt. Kenya sampling site.

3.2 Levels of New Pops in Soil

During the month of October the highest residue levels were recorded at the Dandora site (230.48 ng/kg) while the lowest residue levels were recorded at the Mt. Kenya soil (15.02 ng/kg) (Figure 5).

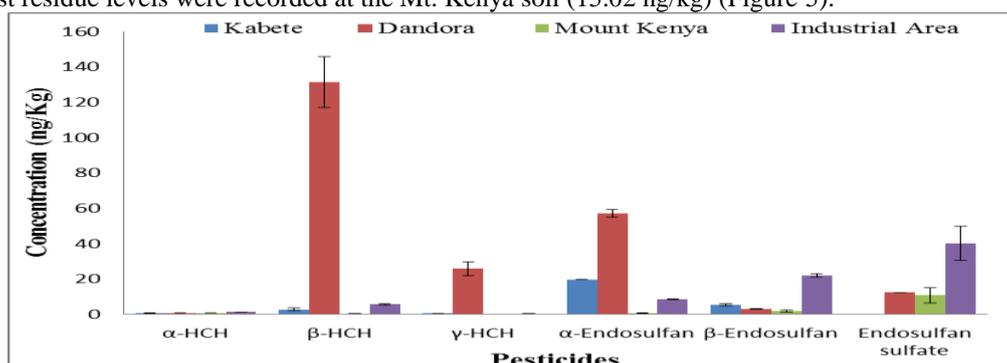


Figure 5: Spatial distribution of the New POPs residue level soil in October

In January, the highest levels of Σ new POPs were recorded at the Industrial area site (52.18 ng/kg) while Mt. Kenya recorded the lowest levels of 5.76 ng/kg) (Figure 6).

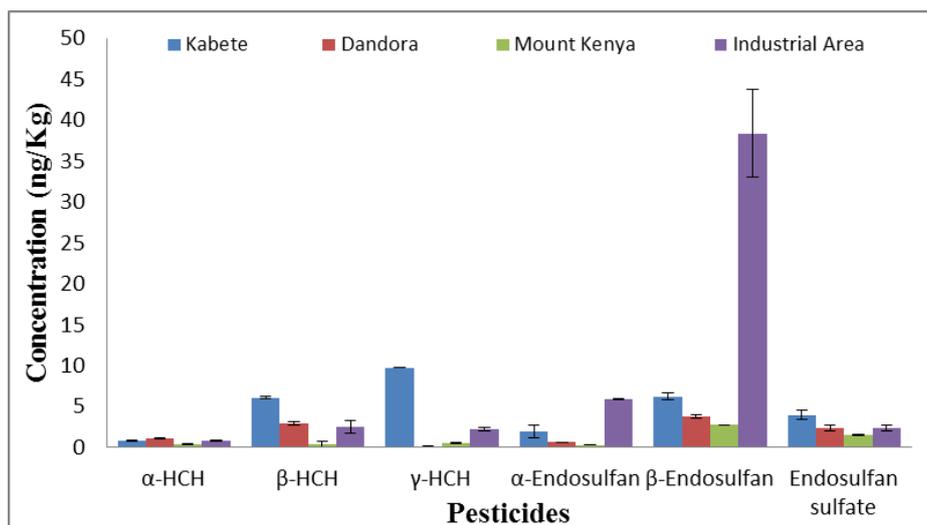


Figure 6: Spatial distribution of the New POPs residue level soil in January

The residue levels ranged between 51.68 ng/kg in soil from Dandora site and 1.71 ng/kg in soil from Mt. Kenya site (Figure7).

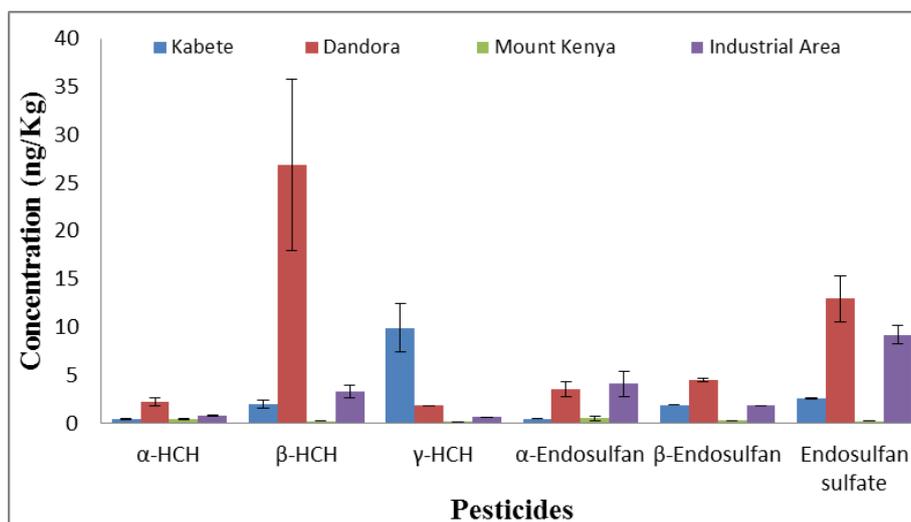


Figure 7: Spatial distribution of the New POPs residue levels in soil in April

There were more significant variations in the levels of the Σ new POPs in soils at the Dandora and Industrial area sites than at Mt. Kenya and Kabete sites. On average, β -HCH was the most abundant of the new POPs analyzed because of its stability in the environment while α -HCH was the least abundant. The use of alpha hexachlorocyclohexane as an insecticide was phased out many years ago but it is still produced as a by-product of lindane (EPH, 2008). There were relatively higher concentrations of endosulfan isomers and metabolite in the soils compared with HCHs because β -endosulfan and endosulfan sulfate persist in soil for over two years [17]. POPs may not change significantly during chemical storage but dehydrochlorinations of α and β -HCH may occur [18] resulting in low levels in soil. The levels of the new POPs were high in the Dandora and Industrial area soils over the sampling period than in the Kabete and Mt. Kenya soils. This is attributed to their release into the environment by the industrial activities and dumping of contaminated wastes at the two sites, respectively. On average, the concentrations of β -endosulfan and endosulfan sulfate were higher than the concentrations of α -endosulfan. This is explained by the persistence of β -endosulfan and endosulfan sulfate in soil for over two years while α -endosulfan disappears within 60 days in soil and 7 days in river water [17]. The residue levels of endosulfan isomers and metabolites at the Mt. Kenya are higher than those of HCHs confirming drift and long range-transport of this POP to the site.

IV. Conclusions and Recommendations

The study documents new POPs residue levels in air and soil in Nairobi and Mt. Kenya areas for the 2012-2013 sampling period. The results reveal that β -HCH was the most abundant of the new POPs analyzed in air and soil while α -HCH was the least abundant. Most new POPs residue levels detected in the sampling area were high in Dandora > Industrial area > Kabete > Mt. Kenya. Since most new POPs residue levels were detected in Dandora and Industrial areas in ambient air during short rain and the dry seasons, it implies that in Nairobi area these pesticides are in high active releases from the waste and industrial activities during the period between July and December.

The high prevalence of the new POPs pesticides such as α -HCH, β -HCH, γ -HCH, α -Endosulfan, β -Endosulfan and endosulfan sulfate in ambient air reinforces the need to strengthen POPs management and control activities to reduce releases of these chemicals into the environment. Although these chemicals have been banned or restricted in Kenya, the management of contaminated sites and soil and treatment of obsolete stocks remain top priority activity hence there is need to strengthen the Nairobi County's capacity for management of the county's waste at the Dandora dumpsite, Industrial waste and medical waste.

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