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# Detection and Quantification of Chlorpyrifos in Soil, Milk, Dip Wash, Spray Race Residues Using High Performance Liquid Chromatography in Selected Dairy Farms in Kenya

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**Abstract:** Organophosphate acaricides are well known for their extensive use in livestock for the management of Ticks and Tick borne diseases. However, the intensive use of Chlorpyrifos causes environmental pollution due to their residues accumulation. The study was aimed at detection and quantification of Chlorpyrifos in soil, dip wash, spray race residues, milk and milk products from Kilifi, Nakuru and Kajiado Counties. A baseline survey was conducted through a cross-sectional study using questionnaire, formal interview and personal observation to collect data and information on the use and type of acaricides. Thereafter soil, dip wash, spray race residues, milk and milk products from the farmers using acaricides containing Chlorpyrifos as the active compound were collected, analyzed and quantified for the presence of Chlorpyrifos using HPLC. Data obtained was stored in excel spread sheets coded and analyzed using Statistical Package for social Scientists (SPSS). Chemicals used for killing ticks included TRIATIX (12), DUODIP (11), and STELADONE (7) among others with majority of the farmers spraying once a week. Out of 11 samples collected from spray race and dip wash, 7 samples were positive for Chlorpyrifos. Nine (9) samples from the analyzed 27 samples of milk and milk products were Chlorpyrifos positive. Chlorpyrifos was also detected in 6 samples out of the 28 soil samples whereas 5 water samples from the 25 collected sample were positive of chlorpyrifos. Chlorpyrifos was not detected in milk and milk product from Kajiado County. However, the concentration of Chlorpyrifos ranged between 1.000±0.242 $mgL^{-1}$ and 2.854±0.149 $mgL^{-1}$ in Nakuru County and between 1.930±0.106 $mgL^{-1}$ and 2.017±0.049 $mgL^{-1}$ in Kilifi County. The positive soil samples were from Nakuru County with concentration ranges between 0.915±0.048 $mgL^{-1}$ to 8.556±0.549 $mgL^{-1}$. The Nakuru water samples had chlorpyrifos concentration ranging between 0.888±0.180 $mgL^{-1}$ to 1.870±0.0243 $mgL^{-1}$. The dip wash and spray race samples had a Chlorpyrifos ranges of 0.918±0.217 $mgL^{-1}$ (Kajiado County) and 3.282±0.140 $mgL^{-1}$ (Nakuru County). The study concludes that there is accumulation of Chlorpyrifos in soil, water, dip wash and spray race and milk and milk products beyond the acceptable limit set at 0 to 0.01 mg/kg body weight by WHO. The concentration of Chlorpyrifos in Nakuru County were found to be higher cozampared to Kilifi and Kajiado County. Surveillance, monitoring and regulation on the use of Chlorpyrifos in manufacturing acaricides is highly recommended.

**Keywords:** Chlorpyrifos, HPLC, Acaricides, Accumulation, Dip Wash, Spray Race Residues

# 1. Introduction

The ingestion of milk and milk products is increasing throughout the world by entire population humans of all ages [1, 2]. Milk and milk related products are good sources of proteins, fat and minerals thus are essential components in the nutrition of humans of entire ages. In Kenya, 60% of the country is occupied by livestock farmers especially the pastoralists whose livelihood depends mostly on livestock production. This sector contributes about 42% and 10% for the agricultural Gross Domestic Product (GDP) and the entire GDP respectively [3]. Therefore, the adulteration of milk and milk based products has become a problem of public health concern. Livestock productivity has played a major role in poverty eradication programs. Urbanization and population growth has led increased demand for food supplies as well as economic growth. The dairy farming is mostly done in rural areas which usually serve as suppliers of milk and milk products to the urban consumers. The population in Kenya has increased from 25.7% in year 1991 to 31.16% in year 2019 [10, 3]. To meet the increasing demands of food supply for human and animal feed for both lactating animals and animals for milk and beef production respectively, the agricultural improvements are gearing towards modern and industrialized farming [4]. Moreover, to reduce the prevalence of vector borne diseases and for control of ectoparasites in the large scale farming system, acaricides are often used. Ticks cause three major threats to livestock: they are vectors for disease transmission, they cause tick paralysis or tick toxicosis and also physical injury that lowers the quality of hides and also discomfort.

Despite the strict regulation on the use of pesticides many countries of the world are still using them injudiciously leading to the occurrence of residues in both biotic and abiotic sections of the surrounding [5]. Organophosphates (OPs) and Synthetic Pyrethroid (SPs) based acaricides has amplified in the past three decades in many parts of the world due to the restrictions on the use of Organochlorides (OCs); dichloro-diphenyl trichloroethane (DDT), hexachlorocyclohexane (HCH) and endosulfan in the late 1990s [6]. This is evidenced by the presence of the OPs and SPs in in vegetables, animal feeds, milk and milk products and even in human breast milk [7].

The use of acaricides is not only beneficial to livestock production but also play a substantial role in management and control of vector-borne human and animal diseases [8]. However, the incidence of acaricide residues in various components of the surroundings and food commodities has elevated unattractive concerns about their usage [9]. However, the remains of these acaricides in food chain has been a major public health concern worldwide and brought debatable issues related to international trade [10]. Pesticides are lipophilic in nature resulting to their magnification in fat-rich tissues of animals. Furthermore, during lactation the conscription of deposited contaminants in animal fats leads to their elimination in milk [11].

The increasing accumulation of acaricides contaminate the environment and is considered to be potentially toxic to human and animal health and to the environment [12]. Long-term exposure has been associated kidney and liver complications, disorder of the endocrine system nervous and immune system ailments and higher risk of lungs, breast, cervix and prostate cancer [13]. Further, environmental pollution with pesticides also affect aves, wildlife, water and domestic animal’s inhabitants [14].

Chlorpyrifos (CP) has been widely used as an active compound in OPs containing acaricides to control ticks and tick bone diseases to boost livestock productivity [15]. Currently, use of OPs acaricides containing CP is most preferred method of control ticks. However, when used extensively, its accumulation contaminates soils, air and water sources become a major public health problem [16]. Chlorpyrifos affects the central nervous system (CNS) by inhibiting acetylcholine esterase, teratogenic, toxic to the liver and cause immunological impairment. The Chlorpyrifos residues in the soil and water results in biodiversity loss, alter its quality and productivity [17]. The estimated acceptable daily intake (ADI) of CP for humans was set at 0 to 0.01 $mgL^{-1}$ and the acute reference dose (ARD) at 0.1 $mgL^{-1}$ as evaluated by [18-20]. Gas Chromatography (GC) and High Performance Liquid Chromatography (HPLC) have been used to identify and quantify CP and its residues. Further, simple HPLC methods have been established and authenticated in the laboratory for residue analysis of CP in soil, water, dip wash and spray race residues [21]. At the same time, the incidence of OCs residues in food of animal origin including meat, milk and their products has been broadly documented. However, limited studies have reported multiple pesticide residue contamination comprising of OPs and SPs [22], with none of these studies conducted in the livestock farming regions of Kenya.

The poisonous effects of acute contact to OPs in animals and humans are easily acknowledged, but the long term contact to low doses through dietary intake are not easy to distinguish. Further, the problem is exacerbated by the fact that the effects of a consistent intake of OPs residues over food are hard to identify and quantify [23]. Because of constant ingestion of OPs residue in food, the contact as well as risk assessments are necessary to determine the origin of effects. Therefore, it is obligatory to ascertain the levels of contamination of food matrices, so that human contacts to these contaminants by dietary intake, do not rise beyond the acceptable limits for health [24]. There are comprehensive studies that are representative of different livestock farming regions of Kenya in terms of tendency as well as health risks linked with ingestion of milk contaminated with OPs residues. As a result of improper and changing consumption patterns of OPs based acaricides, due to restricted use of OCs and the inadequate information and attentiveness on impurity of water, milk and milk products with OPs based acaricides, the present study intended to detect and quantify CP in soils, dip wash and spray races residues, water, milk and milk products collected from livestock farming regions of Kenya namely, Kilifi, Kajiado and Nakuru counties using high performance liquid chromatography (HPLC).

# 2. Materials and Methods

### *2.1. Sampling Site*

A baseline survey was conducted through a cross-sectional study design on livestock farmers in the purposively three selected counties (Kilifi, Kajiado and Nakuru) based on the intensity of livestock farming (low, medium and high respectively). Kajiado County borders Nairobi and extends to the Tanzania border further south and it is located in the following geographical co-ordinates 1° 50' 31.463" S 36° 47' 30.696" E in the former Rift valley province. This county represented medium scale milk producers. Kilifi county is on the coast of Kenya and it is located in the following geographical co-ordinates 3°37'49.62" S 39°50'59.71" E. This region represented small scale milk producers. Nakuru County is in the former Rift Valley province where farmers practice high intensive milk production. This region is located in the following geographical co-ordinates 0° 18' 11.1564" S and 36° 4' 48.0900" E. *Purposive Sampling* technique was applied by establishing a list of farmers' names from each of the selected counties. Questionnaire, informal face-to-face interview and personal observations were used to collect primary data on the various acaricides used. Thereafter soil, water, raw and processed milk, milk products and dip wash were collected from farmers using Organophosphate acaricides.

### *2.2. Sample Collection*

Processed milk and milk products were collected from different milk pens, automatic teller machine, shops and supermarkets whereas raw milk were collected from different farmers in the selected counties. After homogenization, samples were placed in bags then put in cool boxes and maintained frozen (-20°C) on reaching the laboratory until analysis. About 10 mL of dip wash were collected from inside the dips effluent and streams around farm using labelled separate sterile dark bottles, then transported in cool boxes to the laboratory and preserved in the refrigerator until analysis. The pre-concentration samples were prepared one day after sampling. For soil samples, the vegetation and the residues were removed from the soil surface. Using an auger, soil were collected at a depth of 0-15 cm. About 10g of soil was mixed and collected in plastic bags which were sealed, branded accordingly and then stored in the refrigerator until analysis. Each sampling station comprised of three soil samples from a rooting depth of 150 mm which were composed randomly to form a composite sample which were labelled accordingly.

### *2.3. Sample Preparation*

Samples were prepared according to the method described by [25] with slight modifications. Briefly, one gram for solid samples and 1mL for liquid samples was accurately weighed using analytical balance (Adventurer Pro) and measured using measuring cylinder respectively into a 50 mL screw top glass vial was suspended 5.0 mL of a premixed solution of 90% acetonitrile and 10% 1mM $PO_4$ buffer (pH 4.5) was mixed gently by hand followed by sonication and vortexing for 10 minutes. The samples were then shaken at high speed (200rpm) for 15 minutes on mechanical shaker before centrifugation at 2000rpm for 5 minutes, and the supernatant was removed and transferred to a 10 mL tube. Addition of second 5.0 mL of the premixed solvent was done to each of the original samples, and the extraction procedure was repeated. The first 5 mL extracts of each sample were added again into each of the original sample tubes, and were mixed using a vortex and centrifuged again at same speed. The final supernatant of each sample were taken back to the 10 mL tubes, which had held each of the first extract, and vortexed at high speed. An aliquot of each of the extracts were filtered into HPLC vial using a 0.45mm teflon syringe filter.

### *2.4. Chromatographic Conditions*

The Soil, Water, Milk, Dip wash and spray race extracts were analyzed using an 1100 series HPLC (Shimadzu 110 CHT) equipped with a UV/Vis detector (UV at 230nm). A Phenomenex (Torrance, CA) Prodigy ODS/3, C18, 5 mm, 250 mm 4.6 mm i.d. analytical column was used, along with a Phenomenex Security Guard column (4 mm 2 mm, C18). Soil, Water, Milk, Dip wash and Spray race extracts were analysed with a pre-mixed mobile phase contained 75% acetonitrile/25% 1 mM $PO_4$ (pH 4.5) at room temperature. Injection of 25µL of each extract at a flow rate of 1mL.min$^{-1}$ for 25 min.

### *2.5. Accuracy*

Stock solutions of 100 mg L$^{-1}$ of chlorpyrifos were prepared in HPLC grade acetonitrile.

Working solutions of 2, 4, 6, 8 and 10 mg L$^{-1}$ were set by successive dilution in the same solvent. The calibration curve for chlorpyrifos were found undeviating in the range of 2 to 10mg L-1 concentrations.

### *2.6. Data Analysis*

The different data were analyzed using mean separation by GenStat discovery 14$^{th}$ Edition [26] through Fischer least significance difference. Comparisons of multiple means was done by Analysis of variance (ANOVA) followed by Duncan's test, $P < 0.05$ considered statistically significant. The results were expressed as mean ± standard error of the mean.

# 3. Results

### *3.1. Acaricides Used by Farmers*

A total of 72 farmers were visited where information regarding the brand names and active compound of the acaricides used by the farmers were gathered as presented in Table 1. The most common used brand name of the acaricides was TRIATIX 12.5, which contains 12.5% Amitraz as the active compound used by 12 farmers followed by DUODIP, a mixture of organophosphate (Ops) and synthetic pyrethroids used by 11 farmers and STELADONE EC an organophosphate containing Chlorfenvinphos 300 g/L used by 7 farmers. Other brands are also used but with low frequency (Table 1).

***Table 1.*** *List of brand name and active compounds of acaricides used to control ticks in Kilifi, Kajiado and Nakuru Counties.*

| **Brand Name** | **Active Compound** | **Number of farmers using the brand** | | |
|---|---|---|---|---|
| | | **Kilifi** | **Kajiado** | **Nakuru** |
| DUODIP | OPs and synthetic pyrethroids | 1 | 2 | 8 |
| STELADONE EC | Organophosphate (Chlorfenvinphos) | 4 | 1 | 3 |
| NEOCIDOL | Diazinon 600g/l | 0 | 1 | 0 |
| TIXFIX E.C | Amitraz 12.5 w/v | 2 | 0 | 1 |
| BAYTICOL | Flumethrin (synthetic pyrethroid) | 1 | 0 | 1 |
| ACTRAZ | Amitraz 125g/L | 2 | 0 | 0 |
| ECTOMINE | Cypermethrine (High-cis) (pyrethiod) | 1 | 0 | 3 |
| DELETE | Deltamethrin 50g/l | 0 | 2 | 4 |
| DOMINEX | Alphacypermethrin | 0 | 1 | 1 |
| GRENADE | Cyhalothrin 5% | 0 | 0 | 2 |
| NOROTRAZ | Amitraz 12.5% | 0 | 1 | 1 |
| ECTOPOR | Cypermethrin 20g/l | 0 | 0 | 1 |
| FARMTRAZ | Amitraz 12.5% | 0 | 0 | 1 |
| MONSTRAZ | Amitraz 12.5% | 0 | 0 | 1 |
| ALMATIX 125 | Amitraz 12.5% w/v | 0 | 3 | 0 |
| BYE BYE | Amitraz 125g/l | 0 | 3 | 0 |
| Total | | 18 | 22 | 32 |

### *3.2. Detection of Chlorpyrifos in Milk, Soil and Water Using HPLC*

The HPLC chromatograms of the identified chlorpyrifos from a water sample collected in Nakuru County alongside with the standard are presented in figures 1 and 2 respectively. A total of 28 (soil), 12 (dip wash and spray race), 22 (water) and 27 (milk and milk products) as samples were collected from Kilifi, Kajiado and Nakuru Counties (Table 2). However, all the soil and water samples from Kilifi and Kajiado Counties were negative of Chlorpyrifos. The positive soil samples were 6 whereas the positive water samples were 5. Further, out of 12 samples collected from dip wash and spray race residues, 6 samples tested positive for the presence of Chlorpyrifos. Twenty-seven (27) milk and milk products samples were analyzed for the presence of Chlorpyrifos and only 9 tested positive. The Chlorpyrifos was also detected in 6 samples out of the 28 soil samples whereas 5 water samples from the 25 collected sample were positive of Chlorpyrifos. The Chlorpyrifos was not detected in milk and milk product from Kajiado County.

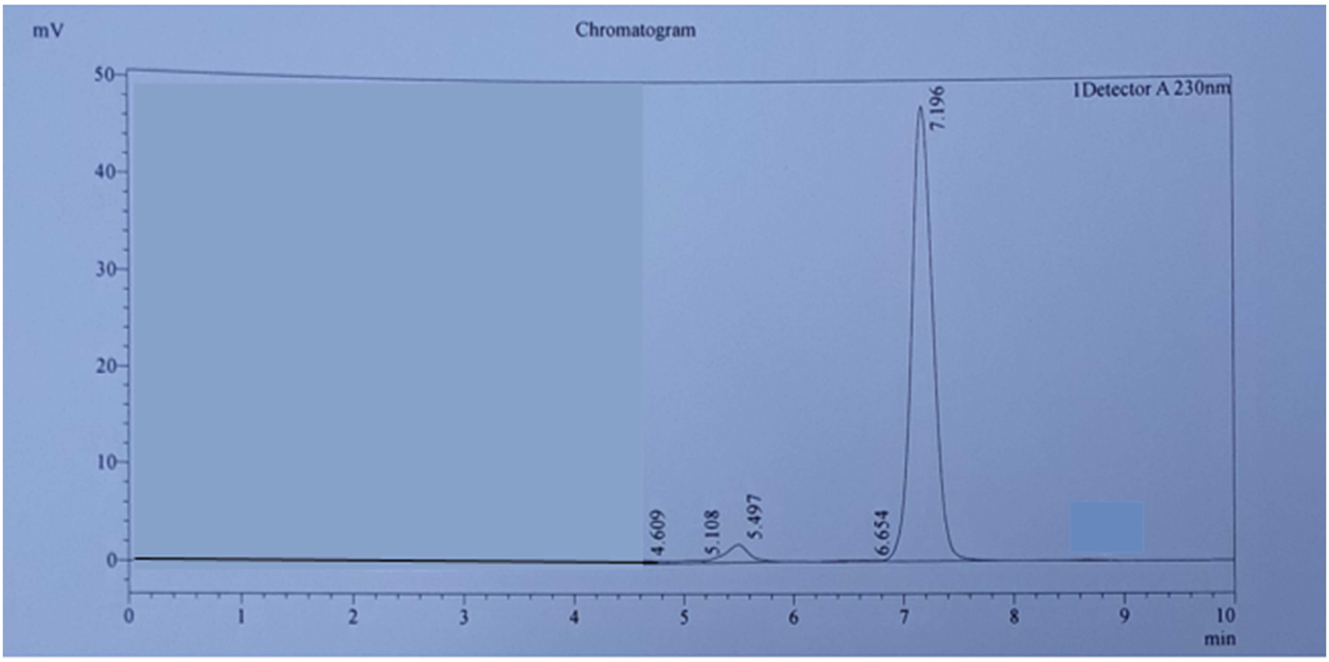


***Figure 1.*** *HPLC Chromatogram for chlorpyrifos standard.*

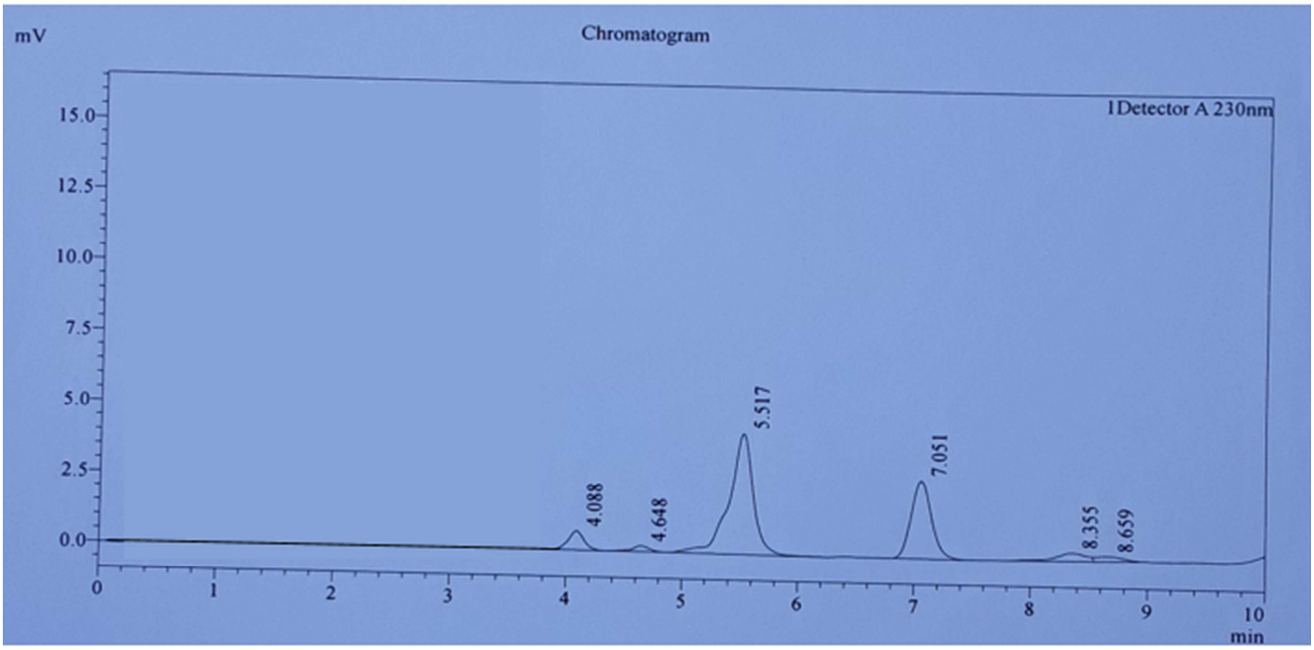


***Figure 2.*** *HPLC chromatogram for chlorpyrifos positive water sample.*

***Table 2.*** *The samples in which Chlorpyrifos was detected positive from selected dairy farms in Kilifi, Kajiado and Nakuru Counties.*

| County | Soil | | Dip wash and spray race residues | | Water | | Milk/milk products | |
|---|---|---|---|---|---|---|---|---|
| | +ve samples | -ve samples | +ve samples | -ve samples | +ve samples | -ve samples | +ve samples | -ve samples |
| Nakuru | 6 | 4 | 3 | 2 | 5 | 3 | 7 | 7 |
| Kilifi | 0 | 11 | 1 | 4 | 0 | 10 | 2 | 6 |
| Kajiado | 0 | 7 | 2 | 0 | 0 | 7 | 0 | 5 |
| Total | 6 | 22 | 6 | 6 | 5 | 17 | 9 | 18 |

The concentration of Chlorpyrifos in the collected raw milk and milk products is presented in Table 3. The concentration was in the ranges of 1.930±0.106 $mgL^{-1}$ to 2.017±0.049 $mgL^{-1}$ in Kilifi County. In Nakuru County, the concentration of Chlorpyrifos was in the range between 1.000±0.242 $mgL^{-1}$ and 2.854±0.149 $mgL^{-1}$. However, Chlorpyrifos was not detected from the raw milk and milk products from Kajiado County. The concentration of Chlorpyrifos between the Counties and at different sites within the County differed significantly ($p<0.05$) with Nakuru County milk and milk products having the highest concentration of 2.854±0.149 $mgL^{-1}$.

***Table 3.*** *Concentration of Chlorpyrifos ($mgL^{-1}$) in raw milk collected from Nakuru and Kilifi Counties.*

| Nakuru County | | Kilifi County | | Detection limits |
|---|---|---|---|---|
| Sample code | Concentration | Sample code | Concentration | Concentration |
| NF4SI | $2.163^{e}$±0.281 | KFIS1 | $1.930^{e}$±0.106 | 0-0.01 |
| NF1S1 | $2.622^{bd}$±0.200 | KF4S1 | $2.017^{a}$±0.049 | |
| NF10S1 | $1.861^{a}$±0.404 | | | |
| NF8S1 | $1.528^{c}$±0.238 | | | |
| NF7S1 | $1.518^{c}$±0.280 | | | |
| NF3S1 | $1.000^{a}$±0.242 | | | |
| NF2S1 | $2.854^{b}$±0.149 | | | |

Mean values (n=3) ± SEM. Values appended by different superscript letters within a raw and column are significantly different ($p<0.05$).

***Table 4.*** *Concentration of Chlorpyrifos ($mgL^{-1}$) in soil and water samples collected from Nakuru County.*

| Soil samples | | Water samples | | Detection limits |
|---|---|---|---|---|
| Sample code | Concentration | Sample code | Concentration | Concentration |
| NF10S3 | $1.452^{a}$±0.273 | NF8S4 | $0.888^{b}$±0.180 | 0-0.01 |
| NF2S3 | $2.070^{b}$±0.145 | NF2S4 | $1.093^{ab}$±0.071 | |
| NF5S3 | $1.826^{d}$±0.058 | NF10S4 | $1.320^{a}$±0.044 | |
| NF7S3 | $8.556^{e}$±0.546 | NF6S4 | $1.364^{a}$±0.045 | |
| NF6S3 | $0.915^{c}$±0.048 | NF1S4 | $1.870^{c}$±0.0243 | |
| NF4S3 | $2.017^{b}$±0.053 | | | |

Mean values (n=3) ± SEM. Values appended by different superscript letters within a raw and column are significantly different ($p<0.05$).

The Chlorpyrifos was detected in water sources of Nakuru County only (Table 4). The concentration of Chlorpyrifos of water samples in Nakuru County was in the ranges of 0.888±0.180 $mgL^{-1}$ and 1.870±0.0243 $mgL^{-1}$. The soil samples from Nakuru County had higher concentration of Chlorpyrifos ranging between 0.915±0.048 $mgL^{-1}$ and 8.556±0.546 $mgL^{-1}$. Further, the concentration of Chlorpyrifos of the water and soil samples from different sites of Nakuru County differed significantly (P<0.05).

The Chlorpyrifos was detected in the dip wash and spray race residues from the three selected counties (Nakuru, Kilifi and Kajiado) (Table 5). The lowest concentration of Chlorpyrifos found in Kajiado County in the ranges of 0.918±0.217 $mgL^{-1}$ and 0.949±0.23 $mgL^{-1}$ followed by only One sample in Kilifi County with a concentration of 1.142±0.123 $mgL^{-1}$. The dip wash and spray race residues from Nakuru County had highest concentration of Chlorpyrifos ranging between 1.508±0.185 $mgL^{-1}$ and $3.282^{b}$±0.140 $mgL^{-1}$. Further, there concentration of Chlorpyrifos of the dip wash and spray race samples from the three county and within different sites of the three Counties differed significantly (P<0.05).

***Table 5.*** *Concentration of Chlorpyrifos in Dip wash and spray race samples collected from Kilifi, Kajiado and Nakuru counties.*

| Nakuru County | | Kilifi County | | Kajiado County | | Detection limits |
|---|---|---|---|---|---|---|
| **Sample code** | **Concentration** | **Sample code** | **Concentration** | **Sample code** | **Concentration** | **Concentration** |
| NF1S2 | $3.282^{b}$±0.140 | KF2S2 | $1.142^{a}$±0.123 | JF4S2 | $0.949^{c}$±0.23 | 0-0.01 |
| NF8S2 | $2.035^{a}$±0.176 | | | JF5S2 | $0.918^{b}$±0.217 | |
| NF4S2 | $1.508^{c}$±0.185 | | | | | |

Mean values (n=3) ± SEM. Values appended by different superscript letters within a raw and column are significantly different (p<0.05).

# 4. Discussion

### *4.1. Acaricides Used by the Farmers*

Organophosphorus pesticides were used instead of Organochlorine (OCs) pesticides because of being less stable and persistent than Organochlorine [27] and also due to the restriction in the use of OCs [28]. The acaricides residue analysis of soil, water, dip wash, spray race milk and milk products from different sites in the three selected Counties (Nakuru, Kilifi and Kajiado) indicated contamination with OPs (CP) residues. The study showed a significant difference at (p<0.05) between the three counties in presence of OPs residues. Among the 12 dip wash and spray race residue samples collected from different sites of the selected three Counties, 6 (50%) were noticed with detectable residues of CP (>limit of detection) while 6 (50%) were noticed to be below the limit of detection). Nakuru County had the highest percentage (3 samples out of the 12 collected samples representing 25%) of CP positive samples whereas Kajiado and Kilifi Counties had 2 positive samples (16.67%) and 1 positive sample (4.55%) respectively. This could to be accredited to the fact that Nakuru is an intensive farming zone in Kenya characterized by high usage of the acaricides with most of the farmers using DUODIP containing a combination of OPs and SPs and STELADONE EC an OPs acaricide whose active compound is Chlorfenvinphos (Table 1). The concentration of CP in dip wash and spray race residue samples was high in Nakuru County (3.282±0.140 $mgL^{-1}$) followed by Kilifi County (1.142±0.123 $mgL^{-1}$) and finally Kajiado County (0.949±0.23 $mgL^{-1}$).

### *4.2. Detection of Chlorpyrifos in Milk Soil and Water Using HPLC*

A total of 28 soil samples and 22 water samples were collected from the selected three counties (Nakuru, Kilifi and Kajiado). There were no positive CP soil and water samples from Kilifi County and Kajiado County. Out of the 28 collected water samples, 21.42% (6 samples) were positive of CP while out of the 22 collected water samples, only 22.73% (5 samples) were positive of CP. Furthermore, deposition of CP occurred in the soil than in water as evidence by high concentration of the CP highest value at 8.556±0.546 $mgL^{-1}$ and 1.870±0.0243 $mgL^{-1}$ in the soil samples and water samples respectively. The nonfunctional cattle dips and none-practice of intensive zero and fenced grazing and free range grazing in the pastoral community in Kilifi County and Kajiado County respectively [29] could have led to the undetected levels of CP in collected soil and water samples in Kilifi and Kajiado Counties. The low frequency in the use of DUODIP by the farmers in Kilifi County (1 farmer) and Kajiado County (2 farmers) compared to high frequency use in Nakuru County (8 farmers) as presented in Table 1 could have contributed to the undetected/not detected (<limit of detection) of CP in collected soil and water samples. Despite the use of STELADONE EC in Kilifi County (3 farmers) and Kajiado County (1 farmer), CP was not detected in the soil and water samples from these Counties. The reason may be due to the fact that STELADONE EC is an Ops based acaricide containing Chlorfenvinphos instead of CP as the active compound.

The presence of CP in milk and milk products may be explained by their extensive use as they are of great significance in pest control [30]. Among all the 27 milk and milk product samples collected from Nakuru County (14 Samples), Kilifi County (8 samples) and Kajiado County (5 samples), 9 (33.33%) were noticed with detected residues levels of CP whereas 18 (66.67%) were noticed to be undetected/not detected (<limit of detection) of CP (Table 2). Nakuru County had the highest number of CP positive samples (6 samples equivalent to 25.93%) compeered to

Kilifi County (2 samples equivalent to 7.41%). The milk and milk products collected from Kajiado County (5 Samples equivalent to 18.52%) had undetected/not detected (<limit of detection) of Chlorpyrifos. The concentration of Chlorpyrifos was found to be higher in Nakuru County (2.854±0.149 $mgL^{-1}$) compared to Kilifi County (2.017±0.049 $mgL^{-1}$). Therefore, number of milk and milk products samples positivity for Chlorpyrifos reflected highest contamination in Nakuru County (25.93%) followed by Kilifi County (7.41%), and none in Kajiado County (Table 2). However, the study indicates the use of other chemicals in control of tick and tick-borne diseases in the three selected Counties of Kenya (Table 1). The concentrations of all examined raw milk and milk products samples collected from the three different Counties exceed European Union (EU) or European Commission (EC) limits set at 0.01 $mgL^{-1}$ [31].

The soil, dip wash and spray race, water, milk and milk products samples were collected from individual farms in the selected counties. Therefore, the site and/or sample level prevalence was calculated based on each type of sample positivity. Soil samples had 21.43, 0 and 0 per cent sites were positive for CP in Nakuru, Kilifi and Kajiado Counties respectively compared to 22.73, 0 and 0 per cent site positivity for CP in Nakuru, Kilifi and Kajiado Counties respectively in water samples. For milk and milk products, the level prevalence in Nakuru, Kilifi and Kajiado Counties, out of 27 samples at each site was 25.93, 7.41 and 0 per cent sites were positive for CP respectively.

In recent past, many researches performed elsewhere in the world have noticed the presence of residues of OPs in milk. Other authors attribute the presence of Ops residues in milk due to their ability to covalently link with the milk proteins [32]. This study corroborates with studies conducted by [33], among others who reported the presence of CP in milk and milk products samples with concentrations exceeding the MRL values set by European Commission at 0.01 mgL-1 [34]. The overall residue pattern of CP as an OPs based acaricide observed in present study in soil, dip wash and spray race residues, water, milk and milk products samples in Kilifi, Kajiado and Nakuru counties corroborates with other findings where farmers in these counties use OPs base acaricides among other types of acaricides [29]. Thus, the present results may indicate the shifting trends in usage of OPs as an alternate for OCs which is also apparent in some latest studies performed in other countries such as India, Egypt among others [34]. Although, other studies have been conducted to detect the presence of chlorpyrifos in soil samples [35], this current study was the first attempt to look for contamination of water and milk and milk product for CP in Kenya. Therefore, the observed contamination the present study can form the basis of screening for OPs based acaricides to establish the exact concentration, status and Prevalence in Kenya.

# 5. Conclusion and Recommendation

From the survey results, Chlorpyrifos is most used acaricide in the three Counties and it could be concluded that soil, milk, dip wash, water and spray race residues collected from selected farms in Nakuru County was the most contaminated with chlorpyrifos. It can also be concluded that this County is a highly intensive livestock and dairy farming region applying the compound on their animals to control ticks and tick-bone diseases. On the other hand, soil, milk, dip wash, water and spray race residues sampled from Kilifi County and Kajiado County are least contaminated with Chlorpyrifos as they are medium and low livestock and dairy farming regions of Kenya. Therefore, there is need to enhance safety precautions during applications and disposal to avoid contamination of the environment and milk and milk products from the outlook of human food security.

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