Effect of Conventional and Household Water Treatment Technologies on Pesticide Residues in Drinking Water, Southwestern, Ethiopia

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Abstract

Water resources have been contaminated by pesticides due to the different activities of human beings. From different studies advanced water treatment systems can eliminate these chemical pesticides while conventional and household treatment technologies are not well studied. The main aim of the present study is to determine the effect of conventional and household water treatment technologies on pesticides residue in drinking water. Water samples were collected from Gibe River (intake point) for Jimma conventional water treatment plant, from each treatment process, and from distribution system. To determine the effect of household water treatment process (solar disinfection and boiling) pesticides were spiked into distilled water then passed through solar disinfection (SODIS) and boiling. The extraction of samples was conducted by following low density based dispersive liquid-liquid micro extraction procedure. The result of the study revealed that almost all studied pesticides (p'p-DDD, p'p-DDE, p'p-DDT, γ -Chlordane, dimethachlor, lindane, heptachlor, cypermethrin and deltamethrin) except o'p-DDT were detected in water samples. The percent reduction of pesticide residue after post chlorination by conventional water treatment ranges from 11.7% (p'p-DDD) to 97.29% (Dimethachlor) and percent reduction of pesticide residue by SODIS and boiling ranges from 2.31% (o'p-DDT) to 54.45% (Cypermethrin) and 27.13% (γ -Chlordane) to 38.9%(p'p-DDE) respectively. This indicates the treatment technologies are important for the reduction of pesticides in water. Treatment technologies improvement is necessary to allow further removal of pesticides.

Introduction

Various types of pesticides are widely used in Ethiopian due to agricultural intensifications. Even banned or severely restricted pesticides in other countries like Dichlorodiphenyltrichloroethane (DDT) and others are used illegally. Moreover, much misuse (abuse and overuse) of pesticides is practiced by Ethiopian farmers, particularly when storing, mixing (dosage), and applying them, unwearing protective cloths and disposing of empty containers. These problems can be attributed to farmers' lack of technical knowledge, the absence of extension services, and lack of training on safe pesticide use (Mengistie et al. 2017). Besides their intensive use, pesticides may leach from the irrigation of plants into the ground and surface water sources (Elfikrie et al. 2020). Moreover, only 0.1% of the pesticides reach the target during application, while the remaining 99.9% has the potential to move to the different environmental matrices, including surface and groundwater sources (Costa et al. 2018). Pesticide residues were found in drinking water sources around the world including Ethiopia (Elfikrie et al. 2020; Majd et al. 2017; Loha et al. 2020; Mekonen et al. 2016). Profenofos was detected at the highest concentration in the Bulbula River and tap water at the Batu Drinking Water supply in Ethiopia (Loha et al. 2020). In the other study, Diazinon 2, 4-D, Malathion, Fenpropimorph, and Pirimiphos methyl were detected in water samples collected from different drinking water sources at Jimma zone and the study concluded that, there was a decline of pesticide residues concentration from the source (river) to tap water except for Diazinon (Mekonen et al. 2016). Consuming of such polluted water may result in health problem for the humans. Acute exposure to pesticides can lead to serious illness or death. Chronic exposure can impair the function of the

endocrine, nervous, renal, immune, reproductive, respiratory and cardiovascular systems (Sherpa Awasthi 2019). The chronic effect also include neurotoxic effects, carcinogenic, oncogenic, genotoxic, and teratogenic effects on the human being (Singh et al. 2018). From a study done by (Mekonen et al. 2016) the pesticide residues detected in drinking water have no acute health risk to consumers. However, chronic risks to human health were observed from exposure to some pesticides for Jimma and Addis Ababa populations. Considering the toxicity of pesticides and its metabolites, the removal of pesticides from contaminated aquatic systems is necessary. From different studies, advanced water treatment technologies, such as reverse osmosis, ozonation and advanced oxidation processes, adsorption, and nano filtration, are effective in removing pesticide residues from water (Chelme-Ayala et al. 2011; Thuy et al. 2012; Khoshnood and Azizian 2012; Lin et al. 2012; Moussavi et al. 2013; Zhao et al. 2016; Cruz-Alcalde et al. 2017). Despite this, advanced water treatment technologies are expensive especially for countries like Ethiopia; however, conventional and household water treatment technologies can be an alternative. Very few studies in other countries showed that conventional water treatment technology has an impact on reducing the levels of pesticides from water (Majd et al. 2017; Elfikrie et al. 2020). However, data were scares with regard to the effect of household water treatment technologies. In most developing countries such as Ethiopia, there is lack of studies conducted on the effect of the both conventional and household water treatment process on pesticide residues. Therefore the main aim of the present study is to determine the level of pesticides from sources, up to point of use and effect of the conventional and household treatment technologies on pesticide residues.

Materials And Methods

Description of Study area

The study was conducted in Jimma, southwestern Ethiopia. Jimma is the largest city in southwestern Ethiopia (Fig. 1). It has a latitude and longitude of (7°40'N36°50'E) and is located at 350 km southwest of Addis Ababa at an average altitude of 1780 m above sea level. One of the sampling areas was the Jimma town's drinking water treatment plant. Gilgel Gibe River is the source of raw water for the Jimma town water treatment plant. The treatment plant has an intake structure with four low-lift pumps and the aerator structure is a concrete cascade. It consists of treatment processes such as aeration, coagulation and flocculation unit, sedimentation, filtration, and chlorination structures. The final treated water is lifted via high-lift pumps to a reservoir for the distribution to the town. It served the town for about 20 years and was renovated in 2014 (Sisay et al. 2017).

Sampling of water

Purposive sampling was used in this study. Water samples were collected using grab sampling into 1 L of bottles, which were rinsed with ultrapure water and then, the bottles were flushed three times with the water to be sampled. After collection, the samples were labeled and transported to Jimma University Environmental Health laboratory and stored at 4°C until further analysis. Before the extraction process, all

water samples were filtered using Whatman filter paper with a pore size of 8µm to remove any particulate matter.

To assess the fate of pesticide residues during conventional water treatment, from each treatment process three water samples were collected. The samples were collected from the raw water source (Gibe River), aeration effluent, coagulation, and flocculation effluent, sedimentation basin effluent, filtration effluent, and post-chlorination (disinfection) effluent. In total 18 water samples were collected from the conventional water treatment plant, from Jimma southwestern Ethiopia.

To determine the concentration of pesticide residues in the water distribution system of Jimma town, water samples were collected from five water reservoirs, and from each reservoir three water samples, a total of 15 samples were collected which is located in treatment plant compound, Ginjo, Jimma University medical center, Abajifar, and Jiren. And 10 water samples were collected from the community tap,

Effect of water treatment technologies on pesticide residues

The effect of water treatment technologies on pesticide residues were measured by calculating percent reduction and processing factor.

Pesticides reduction at each water-treatment process were calculated using Equation by (Elfikrie et al. 2020).

Percent reduction=

$$\frac{\text{concentration of pesticide in the raw water} - \text{concentration of pesticide under treatment } x}{\text{Concentration of pesticide in the raw water}} * 100 \dots \text{Equation (1)}$$

Where x is treatment process (aeration, coagulation and flocculation, sedimentation, filtration, post chlorination SODIS, and boiling)

OR Percent reduction= (1-PF)*100

Percent reduction expressed as percentile. Positive sign of present reduction indicated that reduction factor, whereas negative sign of percent reduction indicated that concentration factor

Processing factor (PF) was calculated as the ratio between the pesticide concentrations in processed water sample (µg/L) to the pesticide concentration in unprocessed water sample (µg/L). PF of < 1 indicated that there is reduction of pesticides by the processing (reduction factor) whereas, PF > 1 indicated no reduction by the processing (PF > 1 = concentration factor)

$$\text{Processing factor (PF)} = \frac{\text{concentration of processed sample}}{\text{concentration of pesticide in unprocessed(raw) sample}} \dots \text{Equation (2)}$$

(Mekonen et al. 2015)

Experimental Procedure for Solar Disinfection (SODIS) and boiling as household water treatment methods

SODIS and boiling was selected as household treatment methods to see if they have an effect on the concentration of pesticides in drinking water. This is because of other treatment mechanism (filtration, sedimentation, and chlorination) were investigated under conventional treatment process. A 1ppm concentration of each pesticides were spiked into distilled water to assess the effect of SODIS and boiling on pesticide level in water. The SODIS intervention was designed according to the Swiss Federal Institute of Aquatic Science and Technology published guideline (Meierhofer and Wegelin 2002) as follow

✓ 1 liter PET bottle was filled three fourths with sampled water, thoroughly shake the bottles to increase dissolved oxygen, and was filled fully, covered it with an air-tight lid, and placed it horizontally on a reflective corrugated iron sheet. The bottle was exposed to the sun from morning until evening for at least 6 hours.

✓ For boiling, water was brought to a rolling point for 1 minute (CDC 2009)

After treatment of spiked distilled water by SODIS and boiling, then extraction procedure was followed using low density based dispersive liquid- liquid micro-extraction.

Chemicals and reagents

All chemicals and reagents were analytical and HPLC grade. n-hexane (99%purity), methanol (99% purity), acetone (99.9%purity) obtained from biochem pharm, France, and Sodium chloride was used to improves the extraction of analytes due to the salting-out effect. N-hexane was used as extraction solvents. As disperser solvents, acetone was used because it is partially miscible with water. High purity analytical pesticides reference standards ($\geq 98\%$) such as o'p-DDT, p'p-DDT, p'p-DDD, p'p-DDE lindane, heptachlor, dimethachlor, γ-Chlordane, cypermethrin, deltamethrin were used as an analyte for this study.

Preparation of standard solutions

Stock solutions of 1000 mg/L for each pesticide were prepared by dissolving accurately weighed 50 mg of each pesticide in a volumetric flask with acetone (except heptachlor, cypermethrin, and deltamethrin which were dissolved in methanol) and stored at 4⁰C. An intermediate solution of 100 mg/L was prepared by taking 1ml of stock solution and diluting in 9 ml of the corresponding solvent. Working standard solutions were prepared at concentration ranges of 0.001 to 10 mg/L by serial dilution of the intermediate solution and then, the solution was stored in the refrigerator at 4 °C. Calibration curves were drawn by running the working standard solutions for each pesticides.

Instruments

Separation and quantification of the target pesticides were performed using Agilent Gas chromatography equipped with an electron capture detector (GC-ECD), autosampler, pump, and column compartment model 7890A (Agilent technologies, Singapore). An HP-5 capillary column (30 m, 0.25 mm inner diameter; and 0.25-mm film thickness) coated with 5% phenyl methyl siloxane model 7890A was also obtained from Agilent technologies. Other instruments applied were 15mL centrifuge tube, analytical balance, 5mL syringe, and the centrifuge were used for this study.

Sample extraction procedures

The low density-based dispersive liquid-liquid microextraction (LD-DLLME) method which was earlier applied by (Dejene et al. 2020) was used with minor modification for extraction of the target pesticide residues from water samples. Accordingly, a 5 mL water sample was taken into a 15 mL centrifuge tube and then, a mixture of 100 μ L N-hexane and 500 μ L acetone as extraction and disperser solvents respectively were rapidly injected using a 5 mL medical syringe. Subsequently, after the addition of 0.5 g NaCl, the content was shaken by hand until the salt was completely dissolved. Then the content was centrifuged for 5 min at 5000 rpm to facilitate the phase separation. A 50 μ L of the floating organic phase was carefully withdrawn via a syringe and then transferred into vials. Finally, 1 μ L of the extract was injected into the Gas chromatography system.

Pesticide identification and quantification

Analyses of the pesticide residues were performed using GC-ECD. GC-ECD was connected to a nitrogen gas generator of 99.99% purity used as a carrier and makeup gas. The instrument condition was set by the following conditions. ALS (auto liquid sampler) with 10 μ L syringes was used and the injection volume was 1 μ L. Splitless injection mode was used with an inlet temperature of 250°C and a carrier nitrogen gas flow of 45 ml/min and a pressure of 10.04 Psi. A column of (30 m x3.20 mm) internal diameter and 0.25 μ m film thickness was used following the oven temperature program with the initial temperature was set at 80°C, ramp at a rate of 30°C/min to 180°C, then ramp at a rate of 3°C/min 205°C for 4 min holding time and then ramp at a rate of 20°C/min 290°C and 8 min holding time. The total run time was 27.92 min. μ ECD detector temperature was 300°C using nitrogen as a makeup gas at a flow rate of 60 ml/min.

Quality control

All glass wares were washed with solvents before used to remove any contaminants. The quantitative determination of pesticide residue in water was done on the basis of the external standard method. Identification of the pesticides was undertaken by running specific concentrations for each pesticide and by looking at the retention time. And then, the linearity of the standard solutions was measured at five different concentrations of 10 mg/L, 1 mg/L, 0.1 mg/L 0.01 mg/L, and 0.001 mg/L from the mixture of all standards by their corresponding working concentration. Calibration curves were plotted by taking concentration against the peak area of the individual pesticides and the linearity of the calibration curve

was validated using a coefficient of determination (r^2). Coefficients of regression (r^2) were greater than 0.995 for all pesticides which indicate that linearity of standard curves.

Statistical analysis

Excel sheet was used for the calculation of pesticide residues using the equation of the calibration curves. Mean and standard deviation was analyzed using SPSS ® V, 23. Shapiro-Wilk was used to check the normality of the data at $P < 0.05$ was used. The one-way ANOVA test was used to examine the significant differences (Tukey's test) ($p < 0.05$) for the data which were normally distributed. In contrast Kruskal -Wallis nonparametric test was used for the data which were not normally distributed. P -value < 0.05 were considered as significant.

Results And Discussion

The concentration of pesticides detected in the water samples from Jimma conventional water treatment plants in southwestern, Ethiopia at different processing stages as illustrated in Table 1. The pesticides under study were DDT with its metabolites (p,p'-DDE, p,p'-DDD, p,p'-DDT and o,p'-DDT), heptachlor, γ -Chlordane, lindane, dimethachlor, cypermethrin, and deltamethrin. From our findings, except o,p'-DDT all the pesticides under study were detected at the intake point (Gibe River which is the source of water for the treatment plant) of the Jimma conventional treatment plant. This may be due to current or historical illegal use of those banned pesticides or previously used pesticides by farmers could contaminate the source of water. Since this pesticides are highly persistent, the residue may exist for long period of time in the water sources. Farmyard runoff, sewer overflows, and accidental spills (Vryzas 2018) may contribute for the contamination of water in the study area. The mean concentration of p,p'-DDD, p,p'-DDE, and p,p'-DDT in Gibe River were 70.83 $\mu\text{g/L}$, 0.31 $\mu\text{g/L}$, and 158.1 $\mu\text{g/L}$, respectively, this is due to, since Jimma zone in southwest Ethiopia was malaria endemic area these pesticides may be sprayed for public health purpose. The mean concentration of cypermethrin and deltamethrin in Gibe River was 81.78 $\mu\text{g/L}$ and 28.07 $\mu\text{g/L}$, respectively. This findings were lower relative to a study done in Nigeria by (Akan et al. 2015), mean concentration of p,p'-DDD, p,p'-DDE, and p,p'-DDT in River Water Benue in Vinikilang, Yola, Adamawa State, Nigeria was 2160 $\mu\text{g/L}$, 300 $\mu\text{g/L}$, and 3750 $\mu\text{g/L}$ respectively. The concentration of cypermethrin and deltamethrin in River Water Benue in Vinikilang, Yola, Adamawa State, Nigeria was 930 $\mu\text{g/L}$ and 1140 $\mu\text{g/L}$, respectively. The mean concentration of lindane in the Gibe river of our study area was 1585.45 $\mu\text{g/L}$ which is higher than river water which is located at northern Greece detected at concentration of 0.252 $\mu\text{g/L}$ (Papadakis et al. 2018). This may be due to residence area variation, preferences of users/farmers to different types of pesticides.

The mean concentration of pesticide residue in each processing stage of the conventional water treatment plant is investigated. Kruskal-Wallis test result showed that there is significant difference ($p < 0.05$) in the mean concentration of p,p'-DDE in raw water (0.31 $\mu\text{g/L}$) and post chlorination (2.42 $\mu\text{g/L}$) unit. This is may be due to a reaction between chlorine (post-chlorination) and the chlorinated pesticides. Addition of chlorine can produce the transformation of parent compounds to its metabolites according to

(Costa et al., 2018). From one way ANOVA test results there is a significant difference ($p < 0.05$) between the mean concentration of raw water (158.1 $\mu\text{g/L}$) and aeration (ND), coagulation (ND), sedimentation (18.24 $\mu\text{g/L}$), and filtration unit (55.31 $\mu\text{g/L}$) for p'p-DDT. This may be due to evaporation, photodecomposition, microorganisms and the hydrophobicity characteristics of this pesticide contribute for the reduction of concentration by the above mentioned water treatment processes

Table 1
Mean concentration ($\mu\text{g/L}$) of pesticides residue in a different stage of the treatment process

Mean $\pm$ SD						
Pesticides	Raw Water	Aeration	Coagulation and Flocculation	Sedimentation	Filtration	Post-chlorination
p'p-DDD	70.83 $\pm$ 55.49	69.27 $\pm$ 15.29	78.05 $\pm$ 49.18	107.98 $\pm$ 45.15	148.81 $\pm$ 85.18	62.54 $\pm$ 6.86
p'p-DDE	0.31 $\pm$ 0.11	ND	ND	ND	0.06 $\pm$ 0.11	2.42 $\pm$ 0.34**
p'p-DDT	158.10 $\pm$ 58.38	ND*	ND*	18.24 $\pm$ 0.54*	55.31 $\pm$ 0.43*	75.92 $\pm$ 22.80
γ -Chlordane	12.21 $\pm$ 1.10	1.00 $\pm$ 0.15	1.53 $\pm$ 1.38	3.06 $\pm$ 2.60	3.09 $\pm$ 1.58	3.11 $\pm$ 1.02
Dimethachlor	5510.10 $\pm$ 723.41	342.83 $\pm$ 73.73	367 $\pm$ 208.7	6372.45 $\pm$ 1249	1266.74 $\pm$ 1047.4	149.50 $\pm$ 127.99**
Lindane	1585.45 $\pm$ 1337.5	809.53 $\pm$ 146.8	356.17 $\pm$ 194.7	223.18 $\pm$ 99.3	663.11 $\pm$ 405.89	135.47 $\pm$ 101.27
Heptachlor	49.28 $\pm$ 10.67	4.89 $\pm$ 2.43	42.22 $\pm$ 30.95	51.78 $\pm$ 5.62	232.87 $\pm$ 134.26	246.73 $\pm$ 196.19
Cypermethrin	81.78 $\pm$ 71.44	45.84 $\pm$ 0.09	81.45 $\pm$ 6.83	76.09 $\pm$ 13.04	59.93 $\pm$ 18.28	217.39 $\pm$ 175.42
Deltamethrin	28.07 $\pm$ 25.94	3.18 $\pm$ 1.78	24.24 $\pm$ 2.90	46.96 $\pm$ 36.83	29.70 $\pm$ 6.80	31.84 $\pm$ 4.35

Note: *represents ANOVA with Tukey post-hoc test results with $P < 0.05$ and **represents Kruskal-Wallis test result with $P < 0.05$, ND = Not Detected

The mean concentration of the pesticides under study was analyzed from Jimma water distribution system. Table 2 revealed that, except for o,p'-DDT all studied pesticides are detected. p'p-DDE and p'p-DDT were not detected in Jiren and Abajifar reservoirs. Maximum mean concentration of p'p-DDD, p'p-DDT, dimethachlor, cypermethrin, and lindane were detected at Gingo and Jimma University medical

center reservoirs. But the minimum mean concentration of p'p-DDD, p'p-DDE, dimethachlor, lindane, heptachlor, cypermethrin, and deltamethrin was detected in Jiren and Abajifar reservoirs. This indicates most maximum mean concentration of pesticides are detected at Gingo and Jimma University medical center reservoirs, in contrast most minimum mean concentration of pesticides are detected in Jiren and Abajifar reservoirs. The one way ANOVA test results showed that there is a significant difference ($p < 0.05$) in mean concentration of dimethachlor between Jimma university medical center reservoir and other reservoirs. These all might be due to the location variation of reservoirs, variation in distribution line, and the difference in being near to the different agricultural activities and areas. Jiren and Abajifar reservoirs in Jimma in southwestern, Ethiopia are located in the mountainous area and also there are no agricultural practices near these reservoirs so the residues of pesticide became low. Since Ginjo and Jimma University medical center reservoirs are located at the lowland there might be farmyard runoff and sewer overflows that contribute to the increment of pesticide residue. Reservoir that located at Jimma University medical center has no cover on the top. This may contribute for the contamination of this reservoir with different pesticides coming from different activities.

The mean concentration of p,p'-DDE, p,p'-DDD, p,p'-DDT, heptachlor, and lindane in the tap water of our study area were 0.68 µg/L, 95.91 µg/L, 55.44 µg/L, 126.78 µg/L, and 126.78µg/L respective. According to Bulut et al., (2010) in Afyonkarahisar, Turkey the concentration of heptachlor 0.041 µg/L, DDE 0.021 µg/L, DDD 0.036 µg/L. Lindane(0.03 µg/L), heptachlor (0.02 µg/L) and p'p-DDT(0.03 µg/L) were detected in Ghana drinking water (Fosu-Mensah et al. 2016a). The mean concentration of cypermethrin and deltamethrin were 179.34 µg/L and 37.78 µg/L in water samples collected from taps. our finding was higher than the study done by (Fosu-Mensah et al. 2016b) in Ghana which is mean concentration of cypermethrin was 0.03 µg/L and the mean concentration of deltamethrin was 0.05 µg/L. According to world health organization (WHO) and Netherlands government maximum residue level (MRL) value for total DDT, γ-Chlordane and lindane is 2 µg/L, 0.2 µg/L and 2 µg/L respectively, and for Australia the limit is 20 µg/L for total DDT. MRL value for heptachlor is 0.03 µg/L, 0.3 µg/L, 0.4 µg/L and 0.04 µg/L according to WHO, Australia, United States of America(USA) and Netherlands guideline respectively (Hamilton et al. 2003). Most pesticides which were detected in water samples from our study areas exceeded the maximum residue limits (MRL) set by this organizations except for p,p'-DD. The exceedance of MRL confirm that the previous use or continuous illegal use of the pesticide in the study area as both parent and metabolites exceeds the legal limit (MRL).

Table 2
Pesticide residue concentrations (mean $\pm$ SD) in ($\mu\text{g/L}$) in Jimma town water distribution system

Pesticides	TPR	GR	JUMCR	AR	JR	Tap
p'p-DDD	90.83 $\pm$ 58.85	128.55 $\pm$ 76.26	114.24 $\pm$ 39.02	79.0 $\pm$ 33.82	63.47 $\pm$ 40.66	95.91 $\pm$ 63.31
p'p-DDE	0.24 $\pm$ 0.01	0.43 $\pm$ 0.09	0.25 $\pm$ 0.05	0.1 $\pm$ 40	0.33	0.68 $\pm$ 0.65
p'p-DDT	3.88 $\pm$ 2.49	43.05 $\pm$ 28.22	62.14 $\pm$ 39.63	ND	ND	55.44 $\pm$ 43.22
γ -chlordane	2.75 $\pm$ 2.59	3.96 $\pm$ 2.62	4.63 $\pm$ 0.77	3.36 $\pm$ 0.5	9.78 $\pm$ 8.5	3.41 $\pm$ 2.58
Dimethachlor	223.63 $\pm$ 171.9	294.87 $\pm$ 157.55	1153.55 $\pm$ 210.4*	85.47 $\pm$ 30.8	109.74 $\pm$ 1.53	359.56 $\pm$ 249.27
Lindane	52.04 $\pm$ 23.74	180.91 $\pm$ 120.35	181.04 $\pm$ 68.94	21.35 $\pm$ 1.6	42.98 $\pm$ 14.43	126.97 $\pm$ 118.45
Heptachlor	73.62 $\pm$ 12.29	96.32 $\pm$ 77.67	83.77 $\pm$ 10.27	47.22 $\pm$ 2.4	50.02 $\pm$ 32.9	129.78 $\pm$ 91.58
Cypermethrin	98.81 $\pm$ 62.66	181.22 $\pm$ 58.14	119.51 $\pm$ 85.08	131.71 $\pm$ 92.35	80.28 $\pm$ 1.9	179.34 $\pm$ 161.37
Deltamethrin	21.14 $\pm$ 10	33.14 $\pm$ 14.65	34.7 $\pm$ 9.16	22.54 $\pm$ 8.66	15.75 $\pm$ 2.63	37.78 $\pm$ 21.93
<i>Where TPR: Treatment plant reservoir, GR: Ginjo reservoir, JUMCR: Jimma university medical center reservoir, AR: Abajifar reservoir, JR: Jiren reservoir, ND: not detected, SD: Standard deviation, * represents ANOVA with Tukey post-hoc test result with $P < 0.05$</i>						

The water treatment process may have an effect on the level of pesticides. According to this study during the aeration process, the concentration of studied pesticides was decreased. The percent reduction ranges from 2.21% (p'p-DDD) to 100% (p'p-DDE, p'p-DDT) by aeration process (Table 3). This may be due to evaporation and photodecomposition process which will have a role in loss of pesticide residues. During coagulation and sedimentation, some pesticide residues became more concentrated like dimethachlor, deltamethrin, heptachlor, and p'p-DDD. This may be due to a reaction with chlorine which originates from prechlorination process. There is an addition of chlorine as prechlorination with coagulant in the Jimma water treatment process. Addition of chlorine can result in the reaction of pesticides which will produce the transformation of parent compounds to metabolites (Costa et al. 2018) This may increase the concentration of pesticides during chlorination process or resulted in concentrated pesticide level.

During sedimentation, the percent reduction of pesticides ranged from 88.46% (p'p-DDT) to 6.87% (cypermethrin). Reduction in the concentration of pesticide during coagulation and sedimentation is due

to the hydrophobic characteristics of organochlorine pesticides. these chemical pesticides preferably bound to the particle phase in the aquatic system then accumulates to the sediment or floc which is supported by a study done by (Akan et al. 2015). According to Ormad et al., (2008) DDT metabolites were degraded around 70% by the coagulation process, and also 60% removal was obtained for heptachlor by peroxidation of chlorine. During the filtration process the percent reduction ranges from 80.11% (p'p-DDE) to 26.72% (cypermethrin). The reason for reducing the concentration of pesticide residues in the filtration processing stage might be due to microorganism that is found in a biological layer on the sand surface and is known as the schmutzdecke might have a role in the reduction of pesticide residues. Pesticides used as mainly microbial nutrient, and ultimately decomposed into some small molecules, such as CO₂ and H₂O. The progress is called enzymatic reaction, which included that the compound got into microorganism' body through a certain way firstly, and then through a series of physiological and biochemical reactions under the action of various enzymes, finally pesticide would be completely degraded or broken down into smaller molecular compounds which have non-toxic or less toxic (Huang et al. 2018; El-Gendy et al. 2021). Overall p'p-DDD (11.7%), p'p-DDT (51.98%), γ-Chlordane (74.55%), dimethachlor (97.29%), and lindane (91.46%) was reduced their concentration through entire treatment process. Even if their concentration decreased, they exceed MRL set by WHO, Australia, USA, and Netherland. While, the concentration of p'p-DDE was below MRL even if the concentration become increased during the entire process. This might be due to the concentration of p'p-DDE at the intake point was very low. In another study in Iran the concentration of chlorinated organic pesticides were decreased in most of the conventional water treatment process. However, Metoxychlor were concentrated from raw water in the sedimentation process (Majd et al. 2017).

Table 3
Percentage reduction of pesticide residue (%) through the conventional water treatment process

Pesticides	Aeration	Coagulation & flocculation	Sedimentation	Filtration	Post-chlorination
p'p-DDD	2.21	-10.2	-52.45	-110.09	11.70
p'p-DDE	100	100	100	80.11	-688.28
p'p-DDT	100	100	88.46	65.02	51.98
γ- Chlordane	93.78	87.46	74.95	74.70	74.55
Dimethachlor	93.78	93.34	-15.65	77.01	97.29
Lindane	48.94	77.53	85.92	58.18	91.46
Heptachlor	90.07	14.33	-5.07	-372.54	-400.67
Cypermethrin	43.95	0.4	6.87	26.72	-165.82
Deltamethrin	88.67	13.62	-67.33	-5.81	-13.4 6
<i>NB; negative sign indicated that the concentration of pesticides were increase during treatment process relative to raw water</i>					

The effect of the household water treatment process (boiling and solar disinfection) was investigated by this study. Boiling was not efficient for the removal of p'p-DDD, p'p-DDT, dimethachlor, lindane, heptachlor, cypermethrin, and deltamethrin. This is might be due to, most studied pesticides are chlorinated and are highly thermal resistant (Lozowicka et al. 2016). Only three pesticides concentrations were reduced by boiling treatment process namely; p'p-DDE, o'p-DDT, and γ -Chlordane. This may be due to relatively these three pesticides has lower boiling point than the other studied pesticides. O'p-DDT, p'p-DDE, and were removed 100%, 38.9%, and 27.13% respectively by boiling process. Boiling point of DDT isomers and γ -Chlordane is 260°C and 175°C respectively. The rest pesticides have a boiling point of in range between 300°C-350°C.

Using the SODIS treatment, the two pyrethroids (cypermethrin and deltamethrin) were removed by 54.45% and 15%, respectively. This may be due to photodegradation plays a significant role in the degradation of the product on leaf surfaces and in surface waters especially for pyrethroids (cypermethrin and deltamethrin) according to International Programme on Chemical Safety et al., (1989). γ -Chlordane, heptachlor, lindane, p'p-DDD, and o'p-DDT were reduced by 44.81%, 26.2%, 14.45%, 5.38%, and 2.31%, respectively (Table 4).

Table 4
Mean concentration, percentage reduction, and PF of pesticides in the different household water treatment process

	Untreated	Boiled			SODIS		
Pesticides	Mean $\pm$ SD ($\mu\text{g/L}$)	Mean $\pm$ SD ($\mu\text{g/L}$)	Percent reduction (%)	PF	Mean $\pm$ SD ($\mu\text{g/L}$)	Percent reduction (%)	PF
p'p-DDD	668.65 $\pm$ 134.07	863.97 $\pm$ 113.53	-29.21	1.29	632.68 $\pm$ 451.69	5.38	0.95
p'p-DDE	14.23 $\pm$ 12.39	8.69 $\pm$ 3.27	38.90	0.61	24.34 $\pm$ 12.03	-71.02	1.71
p'p-DDT	221.41 $\pm$ 156.76	312.32 $\pm$ 254	-41.06	1.41	347.35 $\pm$ 195.31	-56.88	1.57
o'p-DDT	89.69 $\pm$ 67.47	ND	100.00	0.00	87.62 $\pm$ 75.89	2.31	0.98
γ -Chlordane	64.46 $\pm$ 26.44	46.97 $\pm$ 34.25	27.13	0.73	35.58 $\pm$ 18.8	44.81	0.55
Dimethachlor	1096.22 $\pm$ 331.13	1857 $\pm$ 593.35	-69.42	1.69	1290.41 $\pm$ 312.42	-17.71	1.18
Lindane	192.93 $\pm$ 38.85	457.77 $\pm$ 314.83	-137.27	2.37	165.05 $\pm$ 74.5	14.45	0.86
Heptachlor	418 $\pm$ 102.11	796.92 $\pm$ 660.01	-90.64	1.91	308.52 $\pm$ 161.7	26.20	0.74
Cypermethrin	12211 $\pm$ 8650.81	14428.2 $\pm$ 2371	-18.15	1.18	5563 $\pm$ 380	54.45	0.46
Deltamethrin	200 $\pm$ 137	370 $\pm$ 120	-85	1.85	170 $\pm$ 40	15	0.85

Conclusions

Organochlorine pesticides (p,p'-DDE, p,p'-DDD, p,p'-DDT, heptachlor, γ -Chlordane, lindane, and dimethachlor) which were banned for agricultural use and two pyrethroids (cypermethrin and deltamethrin) were detected in Gibe river (intake point), in distribution system and in tap water. The presence of OCP in water samples indicates that there is previous or recent illegal use of pesticides in the study area. Conventional water treatment processes reduce the concentration of p'p-DDT, p'p-DDD, γ -Chlordane, dimethachlor, and lindane to some extent. However, their concentration still exceeds the MRL set by a different organization. This indicates there were not complete removal of these pesticides through the entire conventional water treatment process. Therefore this may need additional intervention to protect the health of consumers. In addition other alternative pesticides which are less harmful pesticides should be supplied to the farmers and applying other advanced treatment mechanisms to reduce the level of pesticide residues in drinking water is important. The other results indicates that

pesticides such as p,p'-DDE, p,p'-DDD, and o,p'-DDT, heptachlor, γ -Chlordane, lindane, cypermethrin, and deltamethrin were reduced through the household water treatment process such as boiling or solar disinfection methods. However, p,p'-DDT, and dimethachlor were not reduced during both household water treatment methods (SODIS and boiling). Other household water treatment method by changing different parameters and SODIS which is not commonly applicable by the public should be recommended to assure the safety of the community. Generally, strict regulation is necessary especially for those pesticides which are not removed by both treatment processes for keeping the people safe and healthy.

Declarations

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Ethical Approval

Not applicable

Consent to Participate

Not applicable

Consent to Publish

Not applicable

Authors Contributions

Temima Jemal and Seblework mekonen contributed starting from the inception of the idea up to the submission of the manuscript, data analysis, and interpretation of results, drafting and editing the manuscript.

Higemengist Astatke designed the method, writing the methodology, chemical analysis, reviewing, and editing of the manuscript.

Amare Terfe contributed in conducting sample collection, laboratory analysis, data entry, data analysis, reviewing and editing of the manuscript.

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Competing Interests

The authors declare no competing interests.

Availability of data and materials

Will be available upon the request.

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Figures

Figure 1

Map of the study area in Jimma town, southwestern Ethiopia