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Pesticide residues in drinking water and associated risk to consumers in Ethiopia

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HIGHLIGHTS

- Diazinon, 2,4-D, malathion and fenpropimorph were detected in drinking water sources of Jimma and Addis Ababa.
- All consumers are at chronic risk of all pesticides but acute risk was not observed.
- Pesticide residues were detected from source up to community taps from Jimma and Addis Ababa water sources.
- Wells, streams and ponds have higher concentration of all pesticides under study than the community taps.

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ABSTRACT

Access to safe and reliable drinking water is vital for a healthy population. However, surface water may be contaminated with pesticides because of the nearby agricultural areas as well as from household application. Water samples were collected from water sources in Jimma zone and Addis Ababa, Ethiopia. The extraction and clean up of the samples were undertaken using liquid-solid and liquid-liquid methods. Human exposure was assessed by calculating the estimated daily intake (EDI) of pesticides in water and compared with the acceptable daily intake (ADI) and the acute reference dose (ARfD). The mean concentrations of 2,4-D, malathion, diazinon and fenpropimorph were 1.59-13.90 μg/l and 0.11-138 μg/l in Jimma and Addis Ababa water sources, respectively. The residue level of some of the pesticides were above the European drinking water guide line values, which is an indication of an illegal use of pesticides in the study areas. Concerning human health risk estimation, there was no acute risk (EDI < ARfD). However, chronic risks to human health were observed from exposure to diazinon and fenpropimorph (EDI > ADI) for Jimma and Addis Ababa populations, respectively. A comprehensive monitoring is required to reduce the level of pesticide residues in the water and to minimize particularly the long term human health risks.

1. Introduction

Access to clean water is a fundamental human right and vital to sustain healthy life. Reports, however, indicate that residues of pesticides occur in different water sources (Sankararamakrishnan et al., 2005; Ntow, 2001; Chowdhury et al., 2012; Flores-García et al., 2011; Varca, 2012). Environmental contamination of natural water by pesticide residues during and after field applications is of a great concern. Water is an important component of public health and failure to supply safe drinking water will cause a heavy health burden to humanity (van der Kooij, 2014). The contamination of surface and ground water by pesticides is discussed by different authors (Varca, 2012; Donald et al., 2007). For example, a study done by Teklu et al. (2015), detected 2,4-D, malathion, deltamethrin, atrazin, chlorothalonil and endosulfan in surface water samples from Ethiopia.

Pesticides may enter into the aquatic system by diffusion to the surface or subsurface hydrological pathways. Pesticide transport to

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surface water, is mainly caused by spray drift, runoff water and drainage water (Ikehata and Gamal El-Din, 2005). This may happen, due to improper operations such as filling of sprayers, washing of measuring utilities, disposing of packing materials and cleaning of spraying equipment. The pesticide sprayers in Ethiopia can do mixing/loading or dilution of pesticides near to water sources, which contaminate the water as well as the irrigated crops. In turn, such practices affect the health of the communities living around these areas. Additionally, applications on lawns and runoff during rain events are prone to be flushed into the sewerage channels and end up in the receiving water bodies (Gerecke et al., 2002).

Due to the persistence of some pesticides, such as DDT and its metabolites, in the environment and their potential adverse health effects for consumers, contamination of surface and ground water has long been recognized as an important issue in many countries. In developing countries, the need to ensure local agricultural production and food security while simultaneously protecting the population against health effects from pesticide exposure, remain a major public health challenge. According to Kesavachandran et al. (2009), developing countries use only small amount of the world's agrochemicals, but they suffer from 99% of deaths from unsafe application of pesticides and poor handling due to illiteracy and poverty status of the users. Even if Ethiopia has a huge potential of surface and ground water sources, the country utilizes a small portion of these resources. About 48.9% of the population obtains unprotected drinking water (Central Statistical Agency, 2012).

Some of the water sources in the rural communities around Jimma, in southwestern Ethiopia, are springs, rivers, streams, wells and ponds. Jimma town, which is located at 353 km southwest of Addis Ababa, suffers from shortage of clean water supply due to power interruption and limited capacity of the existing treatment plant and inefficient water distribution system. Currently, new treatment plant is being operational. However, there is no continuous treated water supply to all communities of the town which forces them to fetch water from unprotected sources. The dwellers of the town use water from different sources such as tap water, springs, wells and rivers for drinking and other domestic purposes. Before 2014, the town has only one conventional water treatment plant in the town which supplies purified water (Kifle and Gadisa, 2006). Other parts of the communities in Jimma zone do not have a conventional water treatment plant but rely on the different water sources.

Addis Ababa, the capital of Ethiopia and the diplomatic center of Africa, is one of the fastest growing cities in the continent. Its population has nearly doubled every decade. The city is subdivided into 10 sub-cities with a total population of 3,048,631. The main water supply sources of Addis Ababa are generated from the three ponds (Geferesa, Legedadi, and Dire) and ground water source (Akaki). Water coverage of the city is about 94% in 2012 with a daily supply of 374,000 cubic meters (City Government of Addis Ababa, 2013).

The Legedadi pond is the largest water supply source which contributes 40% of the town water. The water treatment capacity of the plant is 150,000 cubic meters per day (UNEP/UNESCO/UN-HABITAT/ECA, 2003). The catchment area of Legedadi is about 206 square kilometers and is surrounded by farm lands. These farm lands are owned by smallholder farmers who use different crop protection products (pesticides). During application they may contaminate drinking water sources. The other possible sources of pesticide contamination in the drinking water sources may be attributed to leaks of pesticides from obsolete stockpiles near the study area ("Sireguyo pesticides store") (personal observation). Inappropriate storage, poor handing practice, inappropriate labeling (labels are in English rather than the local language), and illegal use of pesticides due to poor knowledge of farmers may aggravate the contamination of the water sources (Haylamicheal and Dalvie, 2009).

A study conducted in the rift valley region of Ethiopia indicates that, organochlorine pesticides such as endosulfan and DDTs were detected in the soils. This can pose a risk of contamination to the surrounding water bodies (Westbom et al., 2008). In Ethiopia, the health hazards associated with pesticide handling are not well understood by both the sprayers and consumers. Misuse of pesticides, lack of awareness towards the proper handling of pesticides and poor monitoring systems and the presence of high amounts of pesticides are the main contributors of water source contamination (Mekonnen and Agonafir, 2002). Consumption of water and other consumer products that are contaminated with pesticides could expose individuals to different acute and chronic illnesses, such as cancer. In Ethiopia, the prevalence of cancer is increasing. This has dictated the government to establish cancer treatment centers in selected referral hospitals. On the contrary, there is little effort to investigate the major underlying causes of such illnesses. Consequently, a study such as ours, could help in tracing major possible causes of chronic illnesses.

To date, there are no comprehensive assessments of pesticide residues from different drinking water sources upon which consumer risk could be estimated. Therefore, the present study aims at investigating pesticide residues from different drinking water sources that are used for human consumption and to undertake consumers risk assessment.

2. Materials and methods

2.1. Study area

One of the water sample source is the Addis Ababa water supply system. Addis Ababa lies 9°1′48″N latitude and 38°44′24″E longitude. The city is located at the heart of the country at an altitude of 2100 m. The city occupies a total area of 540 km^2 and has a complex mix of highland climate regions with annual average temperature of 22.2 °C. The study area encompasses the Legedadi pond which is the main water supply source for Addis Ababa. The catchment area of Legedadi pond is about 206 square kilometers, which has similar rainfall and temperature conditions compared to Addis Ababa (Fig. 1).

The other water sample source is Jimma zone in southwestern Ethiopia. The study area includes ten districts of Jimma zone (Jimma, Dedo, Seka, Kersa, Tiro Afeta, Mana, Limu kossa, Shebe, Omo-Nada and Gomma) in which water samples were collected. Jimma zone is located in Oromia region, 1744 m above sea level, at a latitude of 7°40′0.01″ and longitude of 37°0′0″ (Fig. 2).

2.2. Sampling

A total of 50 sep-pak and 45 raw water samples were collected from springs (n = 19), well water (n = 7), river water before treatment (n = 5), community taps (n= 17) and distribution reservoirs (n= 2) located in different districts and Jimma town. Most of the water sources are surrounded by agricultural fields where chemical pesticides were applied (personal observation). The water samples from Jimma zone were classified into treated (samples taken immediately after treatment, community taps and reservoir) and untreated water (samples taken from surface water, springs and wells).

The water samples were also collected from Legedadi water treatment plant which is the main water supply source to Addis Ababa city. Two small streams that pass through agricultural fields and join the pond were considered as sampling sites. Before the

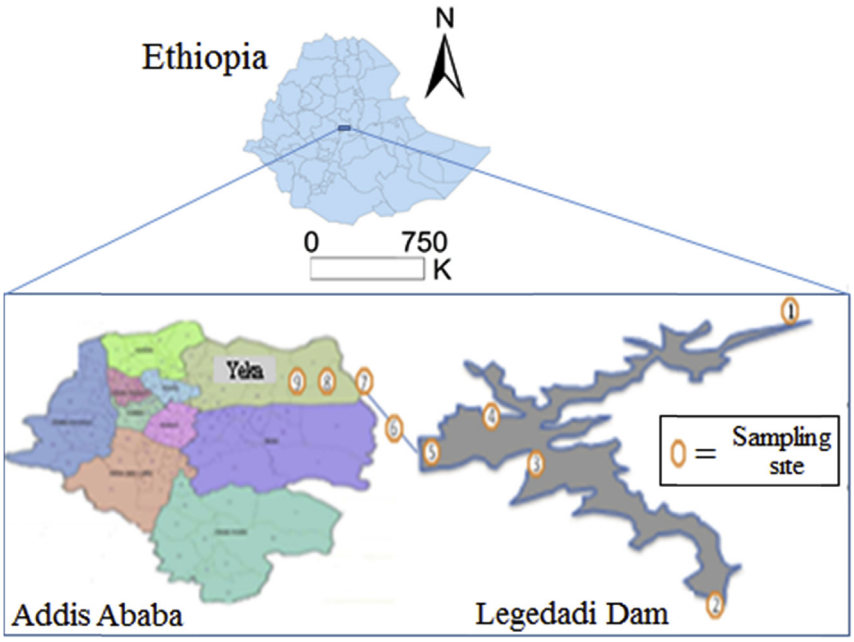

Fig. 1. Map of the study area in Addis Ababa water supply from Legedadi pond.

water treatment plant, three different sampling points were considered. In the distribution system four sampling sites were considered (one from just after the treatment, one from central reservoir and two from community taps). A total of nine sampling points were considered from the source up to the distribution points. Water samples were collected two weeks after the pesticide application. After collection the water samples were transported to the laboratory and stored at 4 °C until the extraction was done.

2.3. Chemicals and reagents

Acetonitrile (99.9%), *n*-hexane (99%), methanol (100%) and anhydrous sodium sulfate, sodium chloride and HPLC (high-performance liquid chromatography) water were used for the extraction and clean up of the pesticides. Anhydrous sodium sulfate was used to remove water from the hexane solution and sodium chloride was used to facilitate the separation of water and hexane solution. Methanol and HPLC water were used to activate the Sep-Pak cartridges before extraction of the water samples. Five point calibration curves were obtained from solutions containing the standard mixture of the pesticide under study (2,4-D, malathion, diazinon, fenpropimorph and pirimiphos methyl). The standard curves were prepared using a concentration range of 0.001–0.1 mg/l.

2.4. Extraction and clean up of the samples

The extractions of the water samples were made in two different ways: liquid-solid and liquid-liquid extractions.

2.4.1. Liquid-solid extraction procedure

The Sep-Pak cartridge C18 column was used to extract the samples. The Sep-pak was first activated with 1 ml methanol passing through the bonded phase and rinsing with 1 ml HPLC water, sequentially. Then one liter of water sample passed through the cartridge. The Sep-Pak samples were rolled with teflon, well labeled and stored at −21 °C until the extraction with solvents was done. The extraction procedures were as follows: the Sep-Pack cartridges, in which a 1000 ml of water sample passed through, were opened. 10 ml of *n*-hexane as extraction solvent was pushed through the sep-pak cartridge using 10 ml syringe into a flask. Five to 6 g of sodium sulfate (Na_2SO_4) was added to the flask which is to separate water from the solvent. Then the *n*-hexane was evaporated to dryness using a rota-vapor at 40 °C and reconstituted with 10 ml of acetonitrile to make the samples amenable for LC-MS/MS injection. Then the extract was put into vials for LC-MS/MS analysis.

2.4.2. Liquid-liquid extraction procedure

In addition to the Sep-Pak samples, raw water samples were collected from each of the sampling sites. A 250 ml plastic bottle (two bottles for each site) was used to collect raw water samples, which were rinsed well with distilled water and dried in the air. The bottles were carefully filled with the water samples to overflow without trapping air bubbles in the bottle. The samples were sealed in black sheets and kept at low temperature to reduce degradation of the pesticide and to transport them to the lab for extraction.

The liquid-liquid extraction procedure was as follows: a 500 ml of water sample was added into a 1 L separator funnel and 100 ml of *n*-hexane was added followed by 10 ml of sodium chloride (NaCl). Samples were agitated by hand to enhance the contact of the solvent with the pesticides. After 10 min, the hexane and water medium were separated and the water phase was removed at the bottom of the separator funnel. The hexane solution passed through 15 g anhydrous sodium sulfate into a 250 ml flask in order to absorb any remaining water from the hexane solution. For the completeness of the extraction, this procedure was repeated once; again the hexane solution was diluted up to 250 ml *n*-hexane and then evaporated to dryness using rota-vapor at 40 °C and reconstituted with 10 ml of acetonitrile. The extract was then transferred to LC-MS/MS vials for analysis.

2.5. Analytical equipment and chromatographic separation

For the determination of the pesticides under study, high performance liquid chromatography with double mass spectrometer (HPLC-MS/MS), with water acuity UPLC instrument was used. The

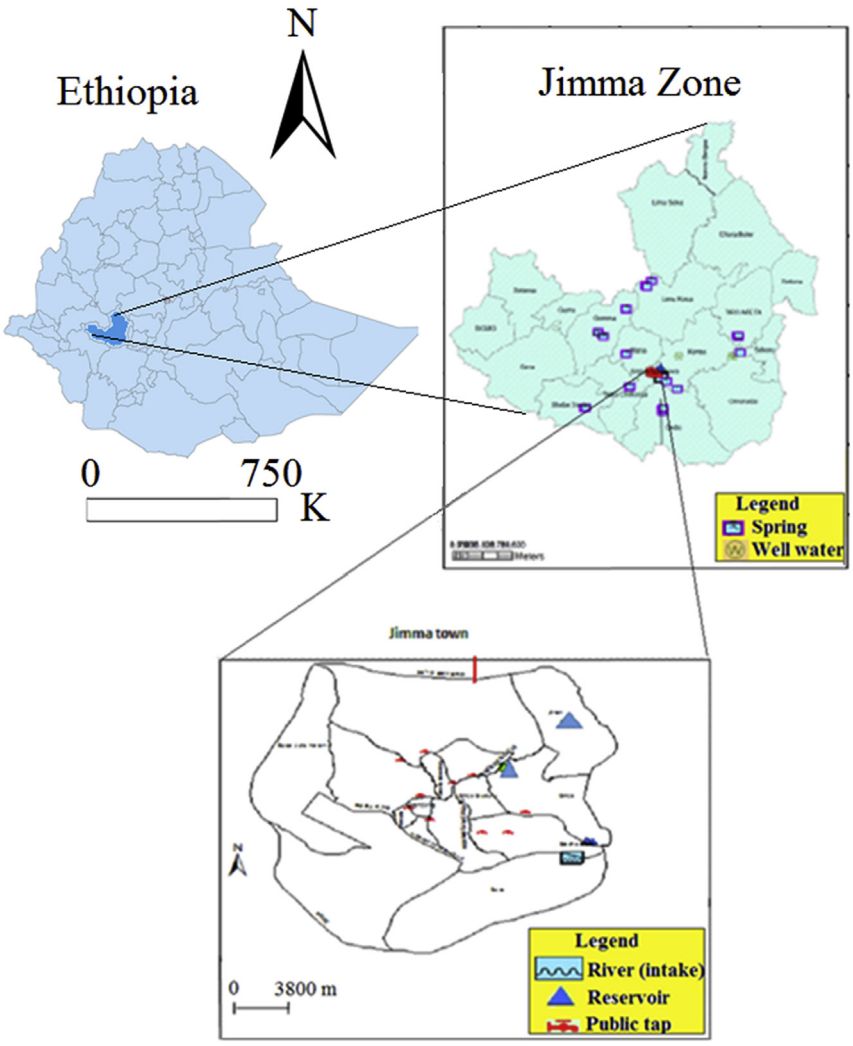

Fig. 2. Map of the study areas in Jimma zone, southwestern Ethiopia.

respective chromatographic conditions were as follows: The column was water HSS T3 (1.8 μm) and an injection volume of 5 μl. The oven temperature was 40 °C and a flow rate of 0.4 ml min^{-1}. The detector was triple quadruple mass spectrometer with Electrons Spray Ionization (ESI), and with a potential of 500 V and a temperature of 500 °C. The scan type was Multiple Reactions Monitoring mode (MRM). The respective ESI, Ions (parent and daughter ions) of the pesticides under study (Table 1).

Not all the pesticides are detected in all the water samples. Analyte concentrations below the limit of detection (LOD), but showed signals were reported as less than the LOD. Moreover, the observed concentrations from the instrument were compared with the norm value of 0.1 μg/l set for single pesticides by the European Commission and the World Health Organization guidelines (Northern Ireland Environment Agency, 2011; World Health OrganizationHO, 2008; World Health Organization, 2011).

2.6. Pesticide screening

Screening was carried out before all samples were completely analyzed to determine which pesticide was presented in the samples. The screening was performed by mixing a small portion of sample from each site and passing it through the sep-pak. Subsequently, the quantitative determination and identifications of each pesticide was worked out for all the samples. The quantification and identification of the pesticides in water samples were done

Table 1
The parent and daughter ions for each pesticide analyzed in water samples using LC-MS/MS.

Pesticide	Parent ions *m/z*	Daughter ion *m/z*	ESI Charge	Cone voltage (eV)	Collision energy (eV)
2,4-D	218.9/220.9	160.7/162.7	Negative	20/20	11/11
Diazinon	305	95/169	Negative	31/31	35/22
Malathion	331	99/127	Positive	20/20	24/12
Fenpropimorph	304.2	57/147	Positive	50/50	30/28
Pirimiphos methyl	306	100.1/164.1	Positive	30/30	32/22

m/z = mass to charge, eV = electron volt, ESI = Electron Spray Ionization.

using peak area and retention time, respectively.

2.7. Quality control

Representative samples were collected in clean materials for the extraction and analysis. Sep-Pak C18-column extraction was made within 48 h of sample collection, which helped to avoid the degradation of the pesticides and to determine the accurate quantity of the residue of the pesticides. Both the Sep-Pak cartridges and the raw water samples were transported in a cold box with ice pack to the Laboratory and were stored at low temperature (below 4 °C) until the extraction was made. The glass-ware materials used were kept clean to avoid cross contamination and all the reagents used were analytical grade.

Before the analysis of the samples, method validation was undertaken by determining the recovery of pesticides, limit of detection and quantification and the regression coefficient. To determine the accuracy of the method, recovery studies were performed by spiking a known amount of the standard mixture of pesticides in ultra pure water. The average percent recovery was estimated by spiking 0.1 mg/l of each pesticide under study. The percent recovery was calculated by dividing the recovered concentration by the spiked concentration. The limit of detection (LOD) and the limit of quantification (LOQ) were also determined by taking the signal to noise ratio (S/N) into account. For LOD the lowest concentration when S/N ratio is over 3 was considered, while for LOQ the lowest concentration when S/N ratio is over 10 was considered.

2.8. Statistical analysis

Statistical analysis was performed using SPSS (Version 20). Before the actual data analyses, normality of the data was checked using the histogram. The concentration of all the four pesticides (2,4-D, malathion, diazinon and fenpropimorph) showed skewness. As the result non-parametric statistical analyses was followed. The Kruskal-Wallis test was applied to compare the distribution of pesticides residues among the water sources. The level of significance was set at P-value = 0.05. The results were presented using a box and whisker plot.

2.9. Risk assessment

To understand the intake of pesticides under study from consumption of water, the risk was assessed for human population with different groups (Adult, Children and Infants).

2.9.1. Chronic risk assessment

The estimated daily intake (EDI) was calculated from the residue of pesticides in water and the water consumption and was compared with the acceptable daily intake (ADI) for each pesticide. The ADI is an estimate of the daily maximum intake of a substance over a lifetime that will not result in adverse effects at any stage in human life span. It is expressed on a body weight bases (Food and Agriculture Organization, 2009). The estimated daily intake EDI (mg/kg bw/day) is found by multiplying the residual pesticide concentration in drinking water (μg/l) with the daily intake of water and by dividing it with the average body weight of consumers based on the equation below (Mahmood et al., 2014). The average daily intake of drinking water for a 60 kg adult, 10 kg child and 5 kg infant were 2 L, 1 L and 0.75 L per day, respectively (Younes and Galal-Gorchev, 2000). EDI is calculated by the following formula:

Table 2
The regression coefficient, average percent recovery, limit of detection (LOD) and limits of quantification (LOQ).

Pesticides	r^2	% Recovery	LOD (μg/l)	LOQ (μg/l)
2,4-D	0.9998	85.4	0.0030	0.010
Diazinon	0.9995	83.0	0.0003	0.001
Malathion	0.9997	92.0	0.0003	0.001
Pirimiphos methyl	0.9999	82.0	0.0150	0.050
Fenpropimorph	0.9998	77.2	0.0003	0.001

$$EDI = Cw*Iw/Bw$$

Where:Cw = concentration of the pesticide in water (μg/l).Iw = daily intake of water (l/day) for adults, children and infants.Bw = Body weight.

To calculate the EDI the maximum concentration in water was considered (worst case scenario). Results were compared with the ADI. An EDI greater than ADI indicates a potential chronic human health risk for consumers according to (Darko and Akoto, 2008).

2.9.2. Acute risk assessment

The short term exposure to pesticide residues was assessed via oral intake of drinking water containing the pesticides under study. The acute reference dose (ARfD) is an estimate of an oral exposure of a chemical for short term duration (24 h or less). The ARfD is used as a measure of acute toxicity of the pesticides. The non-uniform distribution of residues within water may result in some individuals being exposed to above average levels for short periods of time resulting in an acute risk (Renwick, 2002). The EDI for short term exposure of the pesticides under study was calculated by the same equation of the chronic exposure and compared with ARfD.

3. Results

3.1. Method validation results

The method validation results are described in Table 2. The regression coefficient (r^2) was greater than 0.995 for all the

Table 3
Summary statistics for the pesticide residue (μg/l) in drinking water sources of Jimma zone.

Pesticides	Water source	Min	Max	Mean	StDv
2,4-D	River water	1.590	3.971	2.666	0.796
	Spring	1.574	5.703	2.690	0.931
	Tap water	1.412	3.472	2.270	0.517
	Well water	1.559	5.797	2.939	1.361
	Distribution reservoir	1.368	3.365	2.354	0.583
Diazinon	River water	3.000	7.477	5.646	1.321
	Spring	0.0001	15.633	1.592	3.229
	Tap water	0.0001	9.644	2.023	2.187
	Well water	0.0001	11.491	2.197	3.863
	Distribution reservoir	0.0001	24.734	3.280	6.997
Fenpropimorph	River water	1.854	9.042	5.028	1.940
	Spring	0.008	7.036	1.711	1.622
	Tap water	0.008	7.773	2.681	2.279
	Well water	0.008	11.491	2.408	3.290
	Distribution reservoir	0.008	8.085	3.300	2.088
Malathion	River water	0.0001	50.162	7.658	11.945
	Spring	0.0001	67.439	7.252	12.707
	Tap water	5.1000	11.948	7.713	2.745
	Well water	0.0001	105.031	13.947	27.839
	Distribution reservoir	0.0001	33.844	12.165	13.302

StDv = Standard deviation, river water = intake for treatment.

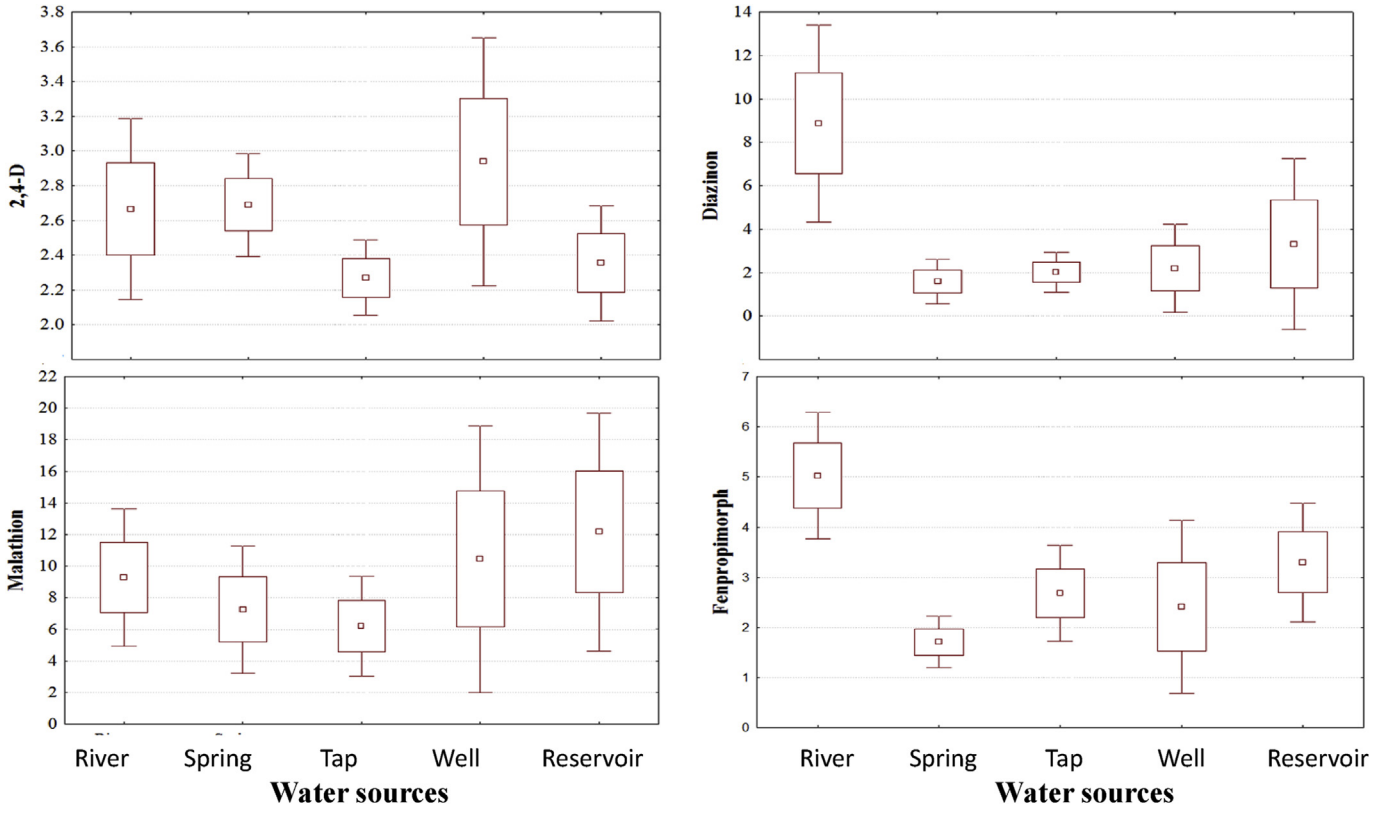

Fig. 3. The distribution of the pesticides under study (μg/L) among different water sources. The inner box indicates the mean, the outer box indicates mean ± standard error and the whiskers indicate the 95% confidence interval.

pesticides under study which indicates a perfect linearity of the standard curves. The mean percent recovery (% recovery) was in the range of 72.2–92.0%. The results showed that the recovery of the pesticides were in the acceptable analytical range which is 70–120%. The validation results met the requirements of European Commission, document No SANCO/12571/2013 (2013). The LOD and LOQ were in the range of 0.0003–0.0150 and 0.001–0.050 μg/l, respectively. Hence, the method is able to detect up to a minimum concentration.

3.2. Pesticide residue in drinking water sources in Jimma zone

Water samples collected from all drinking water sources were screened for pesticides. In the screening process only five pesticide 2,4-D, diazinon, malathion, fenpropimorph and pirimiphos methyl were detected. Pirimiphos methyl was not detected in all the water samples except for well water and spring water with concentrations of 0.33 and 168.20 μg/L, respectively. A summary of the residues of the pesticides in the water samples is given in Table 3. The

Table 4
Estimated daily intake of pesticides under study by Jimma zone population from consumption of drinking water. The ADI and ARfD were obtained from (FOOTPRINT-IUPAC-PPDB, 2015).

Pesticides	Water sources	Max. conc. (μg/l)	EDI (μg/kg bw/day			ADI (μg/kg bw/day	ARFD (μg/kg bw/day
			Adult	Children	Infants		
Fenpropimorph	River water	9.042	0.301	0.904	1.356	3	30
	Spring	7.036	0.235	0.704	1.055		
	Tap water	7.773	0.259	0.777	1.166		
	Well water	11.491	0.383	1.149	1.724		
2,4-D	River water	3.971	0.132	0.397	0.596	50	750
	Spring	5.703	0.190	0.570	0.856		
	Tap water	3.472	0.116	0.347	0.521		
	Well water	5.797	0.193	0.579	0.869		
Diazinon	River water	7.477	0.249	0.748	1.122	0.2	25
	Spring	15.633	0.521	1.563	2.345		
	Tap water	9.644	0.321	0.964	1.447		
	Well water	11.491	0.383	1.149	1.724		
Malathion	River water	50.162	1.672	5.016	7.524	20	300
	Spring	67.439	2.248	6.744	10.116		
	Tap water	11.948	0.398	1.195	1.792		
	Well water	105.031	3.501	10.503	15.755		

EDI = Estimated Daily Intake, ADI = Acceptable Daily Intake, ARfD = Acute Reference Dose.

Table 5
Concentration (μg/l) of 2,4-D, diazinon and fenpropimorph for each sampling point.

Pesticides	Water sources	Min	Max	Mean	StDv
2,4-D	Stream	11.200	127.000	69.100	81.800
	Pond	7.040	30.200	14.900	13.200
	Distribution	4.800	6.590	5.700	1.250
	Reservoirs	5.810	6.120	5.970	0.200
	Community taps	0.230	4.730	0.597	1.260
Diazinon	Stream	0.0002*	0.0002*	0.0002*	0.0002*
	Pond	0.014	96.230	32.100	55.500
	Distribution	0.065	11.000	5.500	7.770
	Reservoirs	0.250	1.240	0.633	0.800
	Community taps	0.034	0.132	0.083	0.600
Fenpropimorph	Stream	112.000	164.000	138.000	36.760
	Pond	0.430	76.900	26.000	44.000
	Distribution	0.173	0.335	0.254	1.100
	Reservoirs	0.107	0.110	0.109	0.020
	Community taps	0.105	0.126	0.116	0.140

* indicates ND = 1/2LOD, StDv = Standard Deviation.

average concentrations of 2,4-D ranged from 2.27 to 2.94 μg/L among the different water sources, where the highest concentration was found in the well water. The highest concentration of diazinon (~5.65 μg/L) was registered in the river water sample of which Jimma town receives water for its municipal water treatment. The mean concentration of malathion ranged from 7.25 to 13.95 μg/l, in which the highest concentration was observed in the well water. Fenpropimorph was mainly observed in the river water.

Kruskal-Wallis test indicated that, the distribution of diazinon and fenpropimorph among the water sources were significantly differed (p-value < 0.004). But other pesticides had no statistical difference between the water sources. On the other side, water samples taken from the Gilgel Gibe River before treatment, contaminated by high concentrations of diazinon and fenpropimorph compared to the well and spring water sources (the source of these two pesticides seems to be the Gilgel Gibe River). As it can be depicted from the box and whisker plot, 2,4-D and malathion residues were much higher in the well water samples (Fig. 3) compared to other pesticides under study.

3.3. Exposure assessment of population in Jimma zone to pesticides residues in water

Human exposure was assessed based on the residue of each pesticide in the water sources and the average water consumption (Table 4). Exposure assessment was not done for pesticide residues found from the distribution reservoirs as communities were not directly consuming water from it. From the findings, the EDI for adults, children and infants were below the ARfD for all the pesticides under study. The EDI for diazinon was above ADI for adults, children and infants, while all other pesticides under study were below the ADI. Values in bold indicate EDI above health based guidance values.

3.4. Pesticide residues in Addis Ababa water source

The findings of the present study showed the presence of 2,4-D, diazinon and fenpropimorph consistently from the source up to the distribution points in the Addis Ababa water supply system (Table 5). The maximum concentration of fenpropimorph (164 μg/l) and 2,4-D (127 μg/l) were observed in samples collected from two streams. The maximum concentration of diazinon was observed in the Legedadi pond. Among the community taps the maximum concentration recorded for 2,4-D (4.728 μg/l) followed by diazinon (0.132 μg/l) and fenpropimorph (0.126 μg/l). The concentration of 2,4-D was high in community taps, while there were only trace amounts of diazinon and fenpropimorph detected.

3.5. Exposure assessment of pesticides in water for the population in Addis Ababa

The human exposure for adults, children and infants in Addis Ababa is expressed as the EDI and is presented in Table 6. Adults, children, and infants consuming water from the streams and children and infants from the Legedadi pond were exposed above the health based reference value (EDI > ADI), but less than the acute ARfD. The EDI for 2,4-D from source up to the community taps were below the ADI and ARfD. Regarding diazinon, the EDI was above the ADI but below the ARfD for adults; children and infants consuming water from the pond. For the exposure assessment the results of the two streams were combined assuming that the farmers applied similar pesticides as they produced similar crops (personal observation). This hypothesis was confirmed by the obtained study results.

4. Discussion and conclusions

The result of the present study confirmed the presence of 2,4-D, malathion, diazinon, pirimiphos methyl and fenpropimorph in drinking water sources from Jimma zone, southwestern Ethiopia. 2,4-D was detected in all water samples and this may be due to the time of sample collection (during July–August), in which weed control pesticides are applied in agricultural fields. Higher concentration of 2,4-D and malathion were detected in well water, while diazinon and fenpropimorph occurred more in river water. This may be due to the rainy season in which erosion may bring pesticides to the water sources from the surrounding agricultural fields.

The results from the Addis Ababa drinking water sources indicate the presence of 2,4-D, diazinon, and fenpropimorph from

Table 6
Estimated daily intake of the detected pesticides in Jimma and Addis Ababa water sources.

Pesticides	Water sources	Max. Conc. (μg/l)	EDI (μg/kg bw/day)			ADI (μg/kg bw/day	ARfD (μg/kg bw/day
			Adult	Children	Infants		
Fenpropimorph	Stream	164	**5.467**	**16.400**	**24.600**	3	30
	Pond	76.868	2.562	**7.687**	**11.530**		
	Community Taps	0.126	0.004	0.013	0.019		
2,4-D	Stream	126.597	4.220	12.660	18.990	50	750
	Pond	30.247	1.008	3.025	4.537		
	Community Taps	4.728	0.158	0.473	0.709		
Diazinon	Stream	*	*	*	*	0.2	25
	Pond	96.198	**3.207**	**9.620**	**14.430**		
	Community Taps	0.132	0.004	0.013	0.020		

* = Values less than LOD, ND = Not Detected, NA = Not Applicable, ADI = acceptable daily intake, ARfD = acute reference dose, values in bold indicate EDI > ADI.

source up to the community taps. The highest concentration of 2,4-D and fenpropimorph were found in the stream water passing through the agricultural fields. This may be attributed to the high amount of rainfall that occurred during the months preceding pesticide applications and the lack of buffer zones around the Legedadi pond, which may prevent the contamination of the water body. The herbicide 2,4-D is used mainly to control dicotyle weeds in crops such as teff and wheat, which are mostly grown around the studied water basin.

In addition to this, the presence 2,4-D is explained by its high water solubility (900 mg/l, at 25 °C), its low potential to move from the water into the air and its stability in water. Concerning 2,4-D, the result of this study was found to be inconsistent with earlier results obtained in Canada (0.123 μg/L) (Donald et al., 2007). This discrepancy may be attributed to the difference in the size of the water body, the pesticide handling systems, the scale of application, the climatic conditions and the amount and duration of the application.

Diazinon and malathion are organophosphate insecticides mainly applied for the control of cockroaches, ants and fleas. Their presence in the water bodies from Jimma and Addis Ababa may be explained by transport from the point of application by drifting (high volatilization) to the water and its stability and persistency (up to six weeks) in the natural water (Howard, 1991). Diazinon and malathion were also detected in drinking water sources in a similar study done in Iran (Shayegehi et al., 2007). The residue of diazinon in the present study was lower than what is detected in surface water of Iran (Fadaei et al., 2012) and Venezuela (Flores-García et al., 2011). However, the concentration was higher than what is observed in Lebanon (Kouzayha et al., 2013).

Fenpropimorph is a fungicide which is mainly used for the control of fungal diseases like rust in cereals and in barley leafs. Its presence in drinking water may be explained due to leakage from obsolete pesticide stocks, biological desorption of fenpropimorph residues and its stability in the water. The residue of fenpropimorph was present in all Jimma water sources while, streams and ponds in Addis Ababa. The residues from Addis Ababa were considerably higher than the result obtained in Demark drinking water sources (Schriever et al., 2007). This may be attributed to the lack awareness of Ethiopian farmers to follow good agricultural practices (GAP) and pesticide handling in addition to application condition and local geological, hydrological and meteorological condition.

The mean concentration of the pesticides from the Jimma and Addis Ababa drinking water sources exceeds the European drinking water standard of 0.1 μg/l for individual pesticide and 0.5 μg/l for the sum of all the detected pesticides except for the mean concentration of diazinon in streams. Based on WHO guidelines, the maximum allowable concentration for 2,4-D, diazinon and fenpropimorph in the drinking water is 30 μg/l, 1 μg/l and 0.1 μg/l, respectively (World Health Organization, 2008). The concentrations of 2,4-D and diazinon from Jimma drinking water sources appear to be below the WHO standard, while diazinon and fenpropimorph were above the guide line in the Addis Ababa water sources.

From the results, in the Jimma zone, high concentration of the pesticides were detected in untreated water sources (well and river water). Once pesticides enter into the well water, the concentration may remain unchanged for a certain period, due to longer water residence time. This could be the reason for the elevated pesticide concentration in the well water samples. While for river water, the eroded soil from the surrounding agricultural areas may directly enter, which may keep the concentration high. Regarding the Addis Ababa water sources, there is a continuous reduction of the residues of each pesticide starting from the source up to the community taps. This may be due to the longer distance of Addis Ababa from the agricultural field area. In addition, the results may be attributed to the larger volume of water in the pond and the deposition of the pesticides with the sediment. The treatment facilities in the Legedadi treatment plant, may contribute to further reduce the pesticide residue in the water.

The detection of these chemical pesticides in drinking water sources may affect the health of consumers in Ethiopia. From the results in the present study, the EDIs for 2,4-D, malathion and fenpropimorph, were below the ADI and ARfD for all the considered population groups. This indicates that, there are no acute and chronic health problems expected for consumers. The EDI for diazinon for adults, children and infants consuming water from the river, well, spring and even in community taps, however, were above the ADI but below the ARfD. This indicates a chronic health problem will happen for the population in Jimma zone. A similar chronic risk of diazinon and malathion from drinking water is also reported for the Iranian population (Shayegehi et al., 2007).

From the results of Addis Ababa water sources, the EDIs of fenpropimorph for adults, children and infants consuming water from the streams and for children and infants consuming water from the pond were above the ADI, while below the ARfD. The EDI for 2,4-D for the three populations who consume water from sources up to the community taps were below the ADI and ARfD. Regarding diazinon, the EDI was above ADI but less than the ARfD for adults; children and infants consuming water from the pond. As is described, the EDI for all the pesticides under study were below the ARfD. This indicates that there is no short term risk for consumers. However, this does not grantee safety for the chronic risk of these pesticides.

Due to cumulative effects of pesticides, adverse human health effects may occur through chronic exposure. This raises the need for a greater attention to create awareness about the use of pesticides by farmers across the watershed, both in the aquatic and terrestrial environment. Care should be taken to decrease the risk of these pesticides by respecting the buffer zone of Legedadi pond and establishment of buffer strips to the different water sources, specifically to those which are used as drinking water source. Moreover, raising the awareness of applicators and different pesticide users, maintaining the application equipment in good working condition, and avoidance of poorly timed application of pesticides is important for decreasing contamination of water as explained by Waskom (2010). In conclusion, a comprehensive monitoring and source oriented remediation action is required to reduce the level of pesticide residues and to minimize in particular the long term health risks on human health.

Conflict of interest

The authors declare that there is no conflict of interest.

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