Environmental risk assessment of pesticides in Ethiopia:

A case of surface water systems

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Environmental risk assessment of pesticides in Ethiopia: A case of surface water systems

Berhan Mellese Teklu

Thesis

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‘’Risk assessment is the mark of an instructed mind to rest easy with the degree of precision which thenature of the subject permits and not to seek an exactness where only an approximation of the truth is possible.’’

(Aristotle**)**

Dedicated to my Beloved Mother Fana Kidane

Contents:

Chapter 1

General Introduction

Agriculture and pesticides

Over the past five decades, pesticides have played a major role in ensuring food security by helping to increase agricultural production and control vectors of disease (Matthews, 2006). Nevertheless, there has been increasing criticism of the negative impacts, ever since Rachel Carson alerted the world to the side-effects of some pesticides in the environment (Carson, 1962). Pesticides are most commonly used as plant protection products. Their main benefits are increasing crop yields or productivity by protecting crops from diseases, pests and weeds, and preventing the deterioration of crop products in storage and extending the shelf-life of fruits and vegetables to maintain marketability (Aktar et al 2009). When carefully applied only when needed, pesticides can contribute to increased productivity and allow us to feed and protect the growing human population (Matthews, 2006). The recent introduction of a number of different chemical groups to pesticides has enhanced agricultural production by providing crop producers with a variety of options for better control of pests on the one hand, while minimising their side-effects on the other (Taylor et al. 2007).

Agricultural intensification and pesticide use in Ethiopia and the global trend

Agriculture in Ethiopia forms the basis of the country's economy. About 84% of the country’s population are engaged in agriculture and generate income for their households to sustain their livelihood. The government has committed itself to intensifying the sector through technological advancement and the use of state-of-the-art agricultural inputs such as fertilisers and pesticides. Ethiopia’s agriculture used to be mainly dominated by small-scale farmers practicing subsistence farming, which are dominated by low inputs and low technology farming systems. This was considered to be the main cause of the low production and productivity of farmers; hence the government is promoting the use of agrochemicals throughout the country to increase production and productivity (CSA, 2012).

The use of pesticides in Ethiopia to control crop pests can be traced back to the mid-1940s, when arsenic and later on BHC in bran bait were used to control desert locust outbreaks. The use of agricultural inputs including pesticides was introduced to smallholder farmers since the 1960s via agricultural extension systems. Since then the use of pesticides has shown a steady growth and with the current development of the flower-growing sector, average imports of pesticides have grown to over 2400 tons per annum (Assefa, 2010) (Fig 1). In recent years, the import and use of pesticides in Ethiopia has grown rapidly, as this is also part of a development plan to intensify agriculture with the objective of increasing food production and expanding the floriculture industry (Amera and Abate, 2008; PHRD, 2015).

Commercial farmers, as the main users of pesticides, account for the use of about 80% of the pesticides imported into Ethiopia. The remaining 20% of the total import is used for small-scale farming, household, health and industrial purposes (EPA, 2004). Of the total of 4125 metric tons of active ingredients that were used in Ethiopia in 2010, the largest proportion (75%) were herbicides, followed by insecticides (15%) and fungicides (9%) (http://faostat3.fao.org/browse/R/RP/E; Fig. 1). At the same time, horticulture in East Africa is undergoing a tremendous development, and in Kenya the recorded pesticide use in 2005 was 7047 metric tonnes, with insecticides accounting for 40% of the total (Tsimbiri et al. 2015). Similar trends in pesticide use have been reported in Tanzania (PAN-UK 2006).

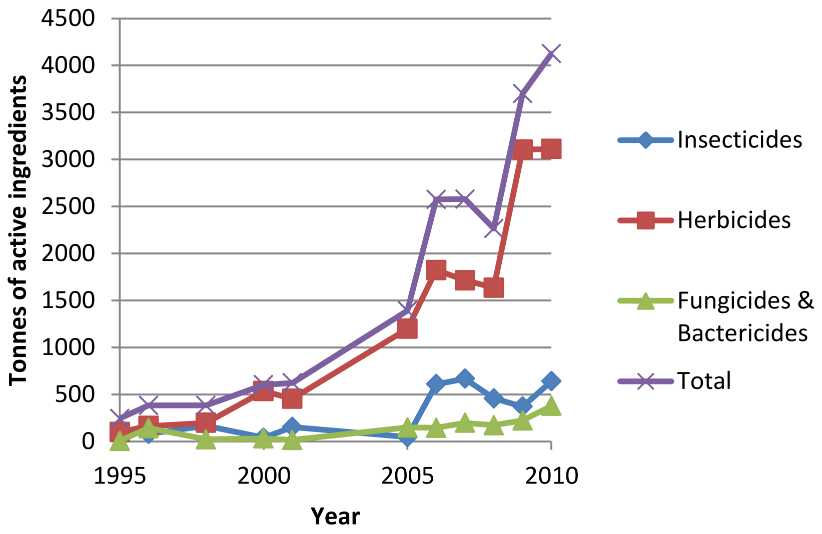

Fig 1: Pesticide use in Ethiopia (1995-2010) source http://faostat3.fao.org/browse/R/RP/E.

Impacts of pesticides on humans and the environment

Although it is known that pesticides enhance crop production through improved control of pests, herewith contributing to the overall regional and global economy, there is a great deal of evidence for impacts of pesticides on humans and the environment, as well as unintended side-effects on non-target organisms (Aktar, 2009). The impact may be serious in high-risk groups exposed to pesticides, like production workers, formulators, sprayers, mixers, loaders and agricultural farm workers. Although great efforts are being made to minimise the hazards of pesticides, complete protection of the human population against pesticide exposure is very difficult. Developing countries are prone to risks from pesticides due to lack of awareness and finances to support proper precaution measures to safely handle pesticides (WHO, 1990). Toxic effects of pesticides in humans can occur through direct or indirect exposure. Direct or primary exposure normally occurs when one comes into direct contact with the chemicals during application, transport or storage. Indirect or secondary exposure comes from exposure through polluted environments or the ingestion of food treated with pesticides (Tadeo, 2008). Pesticide exposure is associated with a wide range of human health hazards, ranging from short-term impacts like headaches and nausea to chronic impacts such as cancer, reproductive disorders, endocrine disruption, birth defects and immune system disorders (Perry et al. 2015; Bouman 2004; 2006 ;Olaya - Contrras et al. 1998; Oesterlund, 2014).

The environmental impact of pesticides consists of the negative effects of pesticides on non-target species. Pesticide residues may contaminate surface waters, e.g. through runoff from treated plants and soil, or through spray drift during application (Konstantinou et al., 2006). This implies that aquatic flora and fauna may be subject to damage by pesticides when concentrations exceed the threshold levels in the surface water systems. Moreover pesticide use may also impact groundwater, soil and beneficial soil organisms, as well as on airborne organisms like birds and bees, and can damage non-target terrestrial plants and animals. All of these have been reported in many scientific studies (Vijver and van den Brink, 2014; Diepens et al., 2014; Cole and Bagchi 1995; Andreu and Pico 2004). Investigations in eastern and other parts of Africa have reported similar health and environmental impacts of pesticides (Macharia 2015; Ansara-Ross et al 2008).

Pesticide registration in Ethiopia: adoption of risk assessment as a registration tool

The first Pesticide Registration and Control Special Decree No. 20/1990 was issued in Ethiopia in 1990 to regulate imports, sales, distribution and use of pesticides. Pesticide registration was started in 1996, six years after the decree was issued. Between the years 1996 and 2011 a total of 274 pesticides were registered, the majority being insecticides (PHRD, 2015). Registration of agrochemicals in Ethiopia involves one simple efficacy trial and a quick first-tier assessment of the pesticide’s properties, e.g. their basic physicochemical properties and WHO classification status, supplied by the registrant from databases like the WHO risk classification, EPA classification of active ingredients or the European Pesticides Properties Database (PPDB). According to an assessment based on the WHO classification, it has been reported that of the 231 pesticides assessed for registration, 133 (58%) were found to be in the low-risk category in the WHO classification, and 16 (7%) in the extremely hazardous classes Ia and Ib (Fig 2) (Assefa 2010).

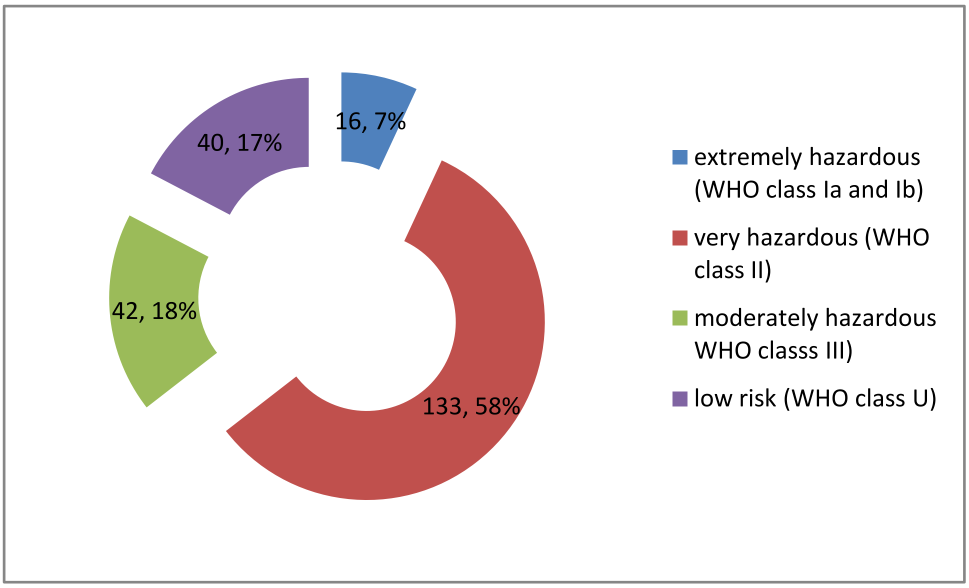

Fig 2. Risk categories of registered pesticides in Ethiopia based on WHO classification (Assefa 2010)

Realising the increased need for more pesticide imports both in type and quantity, there was a need to adopt a better registration system, which gives fast and reliable results. The system should also improve the current situation, which allows pesticides to be used that are believed to be risky to endpoints that were formerly not considered, including the protection of non-target organisms like bees and birds, aquatic ecosystems, non-target arthropods, terrestrial ecosystems and non-target plants. Other endpoints that need to be considered include occupational health issues like risks to indoor applicators and outdoor/indoor workers and the protection of groundwater and surface water as a source of drinking water and shelter for aquatic organisms.

This was the reason why the Pesticide Risk Reduction Programme (PRRP)-Ethiopia was launched in 2010. This is a programme for pesticide registration and post-registration jointly set up by the Ministry of Agriculture of the Federal Republic of Ethiopia (MoA), the State of the Netherlands, represented by the Ministry of Foreign Affairs/ForeignTrade and Development Cooperation, and the Technical Cooperation Programme (TCP) of the Food and Agricultural Organisation of the United Nations (FAO). It generally concerns pesticide registration and management. The programme covers all aspects of pesticide legislation in the agricultural and public health sectors, setting up a sustainable system, and capacity building for pesticide registration, as well as a holistic plan for post-registration measures: monitoring, inspection, quality control, storage and capacity building.The present PhD project, together with two others on human health effects and policy issues, was part of this programme, coming under work package D. This package concerns the sustainability of the developed systems, and involves capacity building for the development of a technical and scientific platform.

After a series of consultation workshops with relevant stakeholders and background studies including an inventory of agro-environmental characteristics and existing environmental standards in Ethiopia, the project introduced a tool called PRIMET_Registration_Ethiopia_1.1. This tool can be used to assess the risks for all the endpoints in a relatively short time, as long as the data needed as input for the software is provided by the importer (Deneer et al 2014; Wipfler et al 2014). The present PhD project tried to evaluate the applicability of this risk assessment tool, using the case of surface water systems in Ethiopia as an example. Surface water was selected since the country is endowed with plenty of surface water resources which may be subject to contamination by pesticide residues.

Overall aim of the thesis

Current developmental activities in Ethiopia are resulting in intensified agricultural activity both at small-scale and commercial levels. It is believed that both the types and amounts of pesticides used in Ethiopia are increasing at an alarming rate (Fig. 1). Whereas the country has huge water resources, and is sometimes even referred as the water tower of Africa, there are clear indications that all of the country's surface water systems, especially the river and pond systems, are under a clear and present threat from possible pesticide contamination. This PhD project therefore aimed to assess the environmental risks posed by the extensive use of pesticides in the surface water systems in Ethiopia.

Research Objectives

The following research objectives are discussed in this thesis

1. Investigating the applicability of model-based risk assessment to predict environmental concentrations in the Ethiopian surface water systems, as part of the PRIMET_Registration_Ethiopia_1.1.
2. Performing simple chemical monitoring programmes to show the status of residues in Ethiopian surface waters and undertake single-species toxicity tests to compare sensitivity with European species.

Outline of thesis

Chapter 2 describesscenarios for future use in the pesticide registration procedures in Ethiopia, designed for 3 specific Ethiopian locations, which should be protective for the whole of Ethiopia. The scenarios estimate pesticide concentrations in surface water resulting from agricultural use, for a small stream and for two types of small ponds. Seven pesticides were selected since they were estimated to carry the highest risk to humans on the basis of volume of use, application rate and acute and chronic human toxicity, assuming exposure as a result of the consumption of surface water. Potential ecotoxicological risks were not considered as a selection criterion at this stage. Estimates of exposure concentrations in surface water were established using modelling software also applied in the EU registration procedure (PRZM and TOXSWA). Input variables included physicochemical properties and data such as crop calendars, irrigation schedules, meteorological information and detailed application data which were specifically tailored to the Ethiopian situation.

Chapter 3discusses the feasibility of undertaking single-species toxicity testing by circumventing the need for analytical verification of the test solution concentration. Experiments were performed with three aquatic arthropods; one crustacean (*Diaphanosoma brachyurum*) and two insects (*Anopheles pharoensis* and *Culexpipiens*). Two pesticides (endosulfan and diazinone) were tested. All species–pesticide combinations were used in duplicate to estimate the intra-laboratory variation in test results. *Daphnia magna* was also tested, to compare the test results directly with values from the literature. The studies were conducted at Addis Ababa University, AratKillo Campus, in the Fisheries and Limnology Laboratory. Species for the experiment were either collected from fresh undisturbed water bodies in the periphery of Addis or brought in from a Fisheries Research Centre of the Ethiopian Institute of Agricultural Research (EIAR), which rears them for scientific purposes.

Chapter 4presents results of water quality monitoring in Lake Ziway in Ethiopia. The objective of this study was to assess the possible change in water quality variables in the Lake Ziway area due to expanding agricultural activity, including very large-scale flower farming practices close to the lake. In addition to analysing the residues of more than 300 pesticides by taking water samples to the Altic laboratory in the Netherlands twice between the years 2014 and 2015, this study made a risk assessment using additional data from previous work by (Jansen and Harmsen, 2011). Both acute and chronic risks were determined for humans using surface water as a source of drinking water, using the acceptable daily intake(ADI) and the acute reference dose (ARfD) values.Pesticide residues detected in each sampling period were first used to determine the acute ETR (exposure toxicity ratio) using predicted no effect concentrations (PNECs). Species sensitivity distribution (SSDs) and HC5 concentrations (hazardous concentration protective of 95% of the population) were determined in a second-tier risk assessment.This paper also discusses values of the physicochemical parameters of the lake for the year 2011-2015 and compares them with the Ethiopian or WHO standard for drinking water.

Chapter 5 Discusses the status of organo-chlorine pesticides (OCPs) in samples from rivers and temporary ponds near agricultural activities. The study was done at the Wedecha and Belbela irrigation system, by taking samples from the Belbela and Wedecha rivers and temporary ponds formed at the end of the rainy season close to the rivers and agricultural plots. The study also assessed the risks posed by the current use of pesticides by small-scale farmers, using the PRIMET_Ethiopia_1.1. model. It includes a worst-case scenario protective of the Wedecha and Belbela irrigation system, using the actual application rate and frequency reported by farmers in the area as input data. Further first- and second-tier risk assessments were performed to assess the risks posed by the measured OCP levels to humans and aquatic organisms. Similar risk assessment was performed for the reported current pesticide use by small-scale farmers

Chapter 6 presents a general discussion of the results reported in the previous chapters in order to describe the overall status of the pesticide risk assessment for surface water systems in Ethiopia. It also indicates a way forward for future risk assessment and monitoring studies in Ethiopia.

Chapter 2

Surface water risk assessment of pesticides in Ethiopia

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Abstract

Scenarios for future use in the pesticide registration procedure in Ethiopia were designed for 3 separate Ethiopian locations, which are aimed to be protective for the whole of Ethiopia. The scenarios estimate concentrations in surface water resulting from agricultural use of pesticides for a small stream and for two types of small ponds. Seven selected pesticides were selected since they were estimated to bear the highest risk to humans on the basis of volume of use, application rate and acute and chronic human toxicity, assuming exposure as a result of the consumption of surface water. Potential ecotoxicological risks were not considered as a selection criterion at this stage. Estimates of exposure concentrations in surface water were established using modelling software also applied in the EU registration procedure (PRZM and TOXSWA). Input variables included physico-chemical proper-ties, and data such as crop calendars, irrigation schedules, meteorological information and detailed application data which were specifically tailored to the Ethiopian situation.

The results indicate that for all the pesticides investigated the acute human risk resulting from the consumption of surface water is low to negligible, whereas agricultural use of chlorothalonil, deltamethrin, endosulfan and malathion in some crops may result in medium to high risk to aquatic species.The predicted environmental concentration estimates are based on procedures similar to procedures used at the EU level and in the USA. Addition of aquatic macrophytes as an ecotoxicological endpoint may constitute a welcome future addition to the risk assessment procedure. Implementation of the methods used for risk characterization constitutes a good step forward in the pesticide registration procedure in Ethiopia.

Introduction

Agriculture is often referred to as the backbone of the Ethiopian economy. Over 80% of the people living in the rural areas are dependent on agriculture. Recent developments in the country brought about intensification of farming activities, both in acreage and in the use ofextrinsic inputs like pesticides and fertilisers (Ethiopia Investment Agency, 2012). This is evidenced by the latest increase in intensive commercial agricultural activities, including large scale flower farming in the country. The pesticide consumption of small-scale farmers is also in-creasing at a high rate despite the poor knowledge about the (eco-) toxicological properties of pesticides and inappropriate handling of agrochemicals (Taddese and Asferachew, 2008).

Ethiopia has 11 fresh and 9 saline lakes of major importance, 4 crater lakes, over 12 major swamps or wetlands and more than 96 rivers, and is for that reason sometimes referred to as the water tower of Africa. The majority of the lakes are found in the Rift Valley Basin. The total surface area of these natural and artificial lakes in Ethiopia is about 7500 km^2, and most of Ethiopian lakes are rich in fish (Awulachew et al., 2007). Besides these larger water bodies many small rivers and (temporary) ponds exist. Because small water bodies are more vulnerable for pesticide contamination than larger water bodies, the risk assessment focusses on these smaller water bodies.

In view of the current intensification of agricultural activities and increased intensity of pesticide use, in combination with the abundance of surface water bodies in the country, the risk posed to humans and the environment from application of pesticides may be increasing. Hence there is a growing need for the adoption of a scientifically sound pesticide registration procedure that filters out pesticides causing damage to humans and the environment. So, a sound risk assessment tool for quantifying risks is essential. In this light the Pesticide Risk Reduction Programme — Ethiopia (PRRP-Ethiopia), a joint collaborative project on pesticide registration and post-registration aiming to develop a sound tool for quantitative risk assessment, was initiated in 2010 (www.prrp-ethiopia.org).

Pesticide risk assessment is typically based on a framework as depicted in Fig. 1, comparing estimated exposure to toxicologically relevant values of a compound. Generally, application scenarios and pesticide properties, as well as data on pesticide use and data obtained through toxicological studies, are used as input for models. Despite the many challenges faced in the implementation and acceptance in risk assessment, adoption of this framework is essential to make a scientific informed decision on the admittance of a pesticide on the market (Brock et al., 2006; Van den Brink, 2013).

Aquatic risk assessment in Ethiopia has until now not included such tools. Some of the few monitoring studies undertaken (Prabu, 2009;Prabu et al., 2011) concentrate on heavy metal pollution and assessment of the physico-chemical characteristics of the Awash tributary rivers Akaki (Small and Greater) in Addis Ababa and Huluka and Aleltu Rivers of Ambo. These studies indicated an increased heavy meal pollution downstream the rivers Huluka and Aleltu and increased concentration of heavy metals in waters of Akaki rivers and residues in vegetables produced using these rivers as a source of irrigation. Investigation by Jansen and Harmsen (2011) on samples taken from surface waters around agricultural fields and effluent waters from commercial farms showed concentrations of pesticides above 0.1 µg/L, hence not meeting the European standards for drinking water(URL: http://eur-lex.europa. eu/legal-content/EN/TXT/PDF/?uri=CELEX:31998L0083&from=EN).

This study presents results on risk assessment for humans and aquatic life for 7 pesticides currently in use in Ethiopia. The risk assessment is based on principles underlying the EU aquatic risk assessment and is presently being implemented in the registration procedure for pesticides in Ethiopia.

The objectives of this study are (i) to assess the suitability of the pro-posed protection goals and scenario locations for risk assessment procedures under development in Ethiopia, (ii) to evaluate the applicability of the combination of PRZM and TOXSWA exposure models for assessing the exposure concentration in a realistic worst-case acute surface water risk assessment of agricultural chemicals in Ethiopia, (iii) to evaluate the risk posed by a few of the already registered pesticides to surface water organisms and humans, based on Exposure Toxicity Ratios (ETR) calculations and (iv) to gain a preliminary perspective on the feasibility of pre-registration risk assessment, using the outlined principles, in Ethiopia.

Materials and methods

Selection of protection goals and scenario locations

The selection of protection goals was discussed in workshops with Ethiopian experts of the Animal and Plant Health Regulatory Directorate (APHRD), Addis Ababa University (AAU), Institute of Biodiversity Conservation (IBC) and Ethiopian Institute of Agricultural Research (EIAR) (www.prrp-ethiopia.org). The selected protection goals were humans directly using surface water as drinking water (especially in surface water that is used for consumption without prior purification) and aquatic organisms living in surface water. Highest priority was given to streams and small rivers above 1500 m altitude, used for irrigation of horticultural crops in areas with intensive pesticide use. Such streams are often also used as drinking water sources, both for humans and cattle from the nearby villages. Second priority was given to temporary lakes or ponds or swamps used in a similar fashion as the small streams. These may be typically found below 1500 m, but sometimes also between 1500–2000 m.

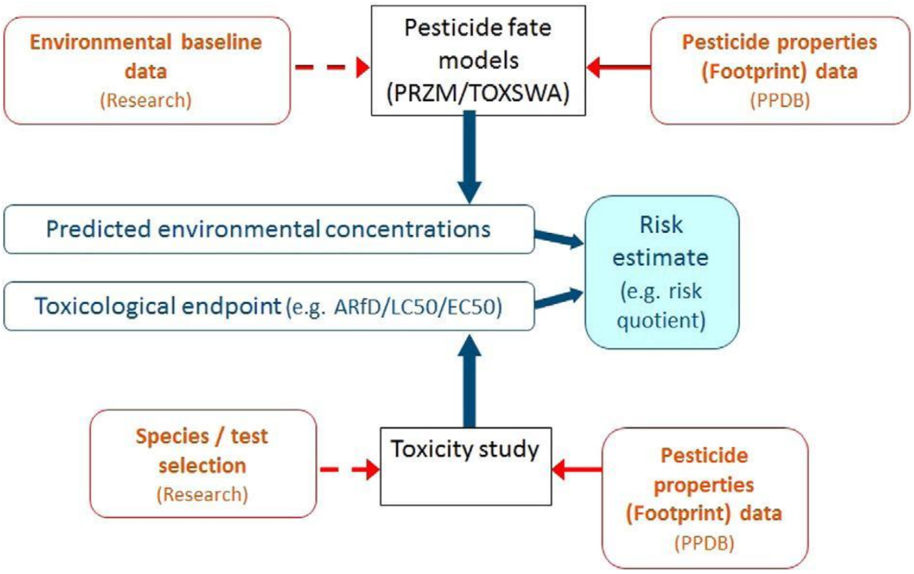

Fig. 1. General approach of the proposed risk estimation (Source:Adriaanse et al., 2014).

Preliminary calculations demonstrated that surface runoff in the surplus of rainfall was the main driving factor for the target variable concentration in surface waters in Ethiopia. Since daily precipitation amounts >20 mm per day are a good indication for the occurrence of runoff events (Blenkinsop et al., 2007), the meteorological data was taken from the ERA Interim dataset (Dee et al., 2011), which is a re-analysis of all available observations from different sources (e.g. satellite, ground observations) made by the ECMWF (European Centre for Medium-Range Weather Forecasts), to create an analysis field on a regular grid. The ERA Interim dataset runs from 1979 up to 2011 (33 years). Candidate locations were selected out of the population of relevant grids for each protection goal (e.g. all grids above 1500 m altitude for small streams in the highlands) by considering the temporal as well as spatial distribution of the number of days with daily rainfall exceeding 20 mm over the available 33 years. The overall probability of occurrence (i.e. spatial and temporal probability combined) aimed for was the 99 percentile for the concentration in surface water used for drinking water. Out of the selected candidate locations final scenario locations were selected with the aid of additional criteria: (i) presence of the protection goal within the selected (80 * 80 km^2) location (grid), (ii) the presence of crops with high use of pesticides within the grid and (iii) well populated. In this way three locations were selected for the protection goals of small streams in the highlands (grid 191, Table 1, Fig. 2) and of temporary ponds in the highlands and in the Rift Valley (grids 373 and 217, respectively). For simplicity the same scenario locations were used to estimate realistic worst-case exposure concentrations for the aquatic ecosystem. For the aquatic ecosystem a less strict standard than for drinking water for humans was judged to be acceptable and therefore a 90 percentile overall probability (i.e. the EU standard) was obtained by lowering the temporal probability, while selecting one of the 33 maximum yearly concentrations. Further details on selection of protection goals and scenario locations are provided in Adriaanse et al. (2014).

Selection of models and calculation of exposure concentrations

The models chosen to calculate the runoff and fate of the pesticides in the surface water were the Pesticide Root Zone Model (PRZM) and the TOXic substances in Surface WAters model (TOXSWA), respectively. These models are also used in the EU registration procedures (FOCUS, 2001; EC, 2011). PRZM is a one-dimensional, dynamic, compartmental model that can be used to simulate pesticide movement in unsaturated soil systems within and immediately below the plant root zone (Carsel et al., 1998). TOXSWA is a pseudo-two-dimensional numerical model describing pesticide behaviour in the water layer and its underlying sediment at the edge-of-field scale (Adriaanse, 1996, 1997; Adriaanse et al., 2013). These models were parameterized using the EU-FOCUS R4 scenario characteristics for PRZM (the scenario with worst case soil properties for runoff of the 4 EU Runoff scenarios) and the EU FOCUS R1 pond scenario for TOXSWA (FOCUS, 2001), but using Ethiopiancrop data (MOARD, 2006–2011), irrigation data (Adriaanse et al., 2014) and meteorology data (Dee et al., 2011). The EU Drift calculator was used to estimate drift deposition (FOCUS, 2001), relatively low depositions, representing 70 percentile probability, were used to avoid stacking extreme entry route occurrences in the ponds, which would result in unrealistically high exposure estimates.

Table 1 Surface water protection goals and their scenario locations.

Protection goal	Scenario	Location (grid no.)
Surface water used as a source of drinking water without prior purification.	1.Small streams in areas above 1500 m altitude	191 (W of Lake Tana); 1682 m altitude; 2581 mm rain[a]
	2.Temporary ponds below 1500 m altitude and with more than 500 mm rain (long term, annual average)	373 (W of Arba Minch); 1288 m altitude; 1702 mm rain[a]
	2. Temporary ponds between 1500 – 2000 m altitude	217 (SE of Bure); 1705 m altitude; 2779 mm rain[a]

[a] Long term annual average.

For the stream scenario, PECs (Predicted Environmental Concentrations) were estimated using the PRZM model, plus a meta-model for TOXSWA, mixing the runoff of the 20 pesticidetreated ha with the base flow, the subsurface drainage flows (both without pesticides) and the pesticide-free runoff water from the remaining 80 untreated ha of the upstream catchment (for details, see Adriaanse et al., 2014). For the two pond scenarios PRZM and TOXSWA were used to calculate the PECs. For each of the stream and pond scenarios, the 33 annual maximum concentrations were determined, for the entire period (1979– 2011) covered in the simulation. From the ranked list of annual maxi-mum concentrations, the second highest concentration was used as the exposure concentration for the human risk assessment, whereas the sixth highest annual maximum concentration was used as the expo-sure concentration in the aquatic risk assessment. The second and sixth highest concentrations correspond to the 96 and 83 temporal percentile concentrations, and result in 97, 84 and 96 (drinking water, for grids 191, 373 and 217, respectively) and 91, 78 and 90 (aquatic ecosystem, for grids 191, 373 and 217, respectively) overall probability of occurrence concentrations, as referred elsewhere in this paper. The difference in temporal percentile used for the two protection goals reflects the protection level desired by the protection goals workshop (see above). Details on the preparation of post-processing programmes and designing meta-models and calculation of the temporal 83th and 96th percentile concentrations are given in Adriaanse et al. (2014). The meteorological data were obtained from a commercial party and can for that reason not be included in the paper.

Crop data

Crop data were gathered for the types of crops that from an agronomic point of view may grow in the three grids with their altitudes and precipitation rates. Moreover, the crops should be relevant with respect to pesticide use. The crop selection was done through consultation with APHRD and EIAR experts. For other input parameters needed for the PRZM model, like Pan Evaporation factor, canopy interception, Run-off Curve Numbers for fallow and cropping and residue, a translation table was used to link the crops specific for Ethiopia to the FOCUS crops (Table 2) in order to base the Ethiopian scenarios as much as possible on internationally accepted parameters.

For other scenario dependent crop calendar parameters like maxi-mum rooting depth, maximum cropping height, emergence date, maturation date, harvest date and fallow date, data specific to Ethiopia were gathered from references from the Ministry of Agriculture (MoA) crop variety register issues 9 through 14 (MOARD, 2006–2011). Further information was obtained from agronomic books and personal communications with experts at APHRD. Crops were then further classified as either growing in two cycles, i.e. both in the main rainy season (Kiremt) and with the help of irrigation during dry season (Bega), or growing only in one cycle during the main rainy season (Kiremt).

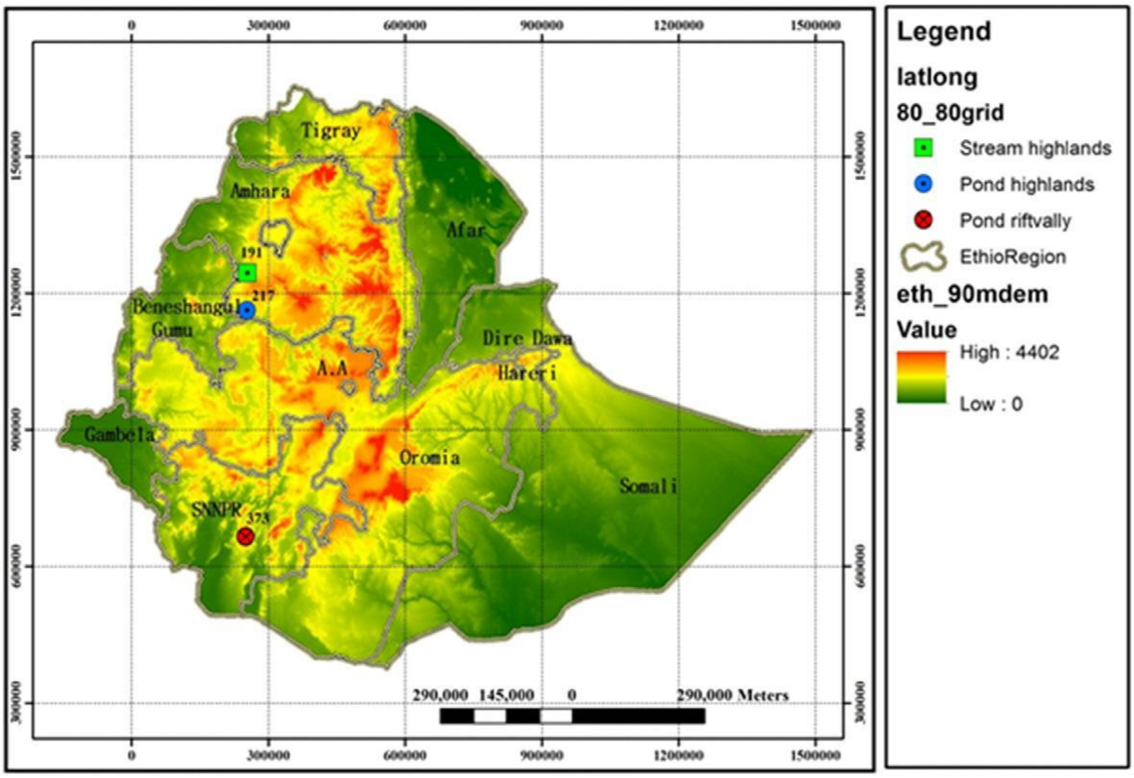

Fig. 2.Selected grids for risk calculations in Ethiopia, denoted by the square and circles.

Choice of compounds

Some pesticides to use as case studies were chosen from a list of more than 100 actives in more than 200 formulated products, based on Ethiopian sales volumes in 2010 (kindly provided by the Ethiopian Ministry of Agriculture) in combination with human toxicity data, by making prior rankings based on the ratio of sales volume to Acute Reference Dose (ARfD) or the Acceptable Daily Intake (ADI), when the ARfD was not available (2,4-D). Additional requirements were the availability of necessary data with regard to pesticide properties and that the compound is potentially used at these selected locations (Table 3).

Physico-chemical properties of pesticides

Pesticide data including their molar mass, saturated vapour pressure at 20 °C, water solubility, half-life of transformation in soil (DT_{50soil}), half-life of transformation in water ($DT_{50water}$), dissociation constant (pKa), coefficient for sorption on soil based on organic carbon content (K_{oc}), and their Freundlich exponent (1/n) were taken from the footprint Pesticide Properties Database (Lewis et al. 2016) (Appendix A).

Table 2 Main Ethiopian crops on which the 7 studied pesticides are used and their corresponding FOCUS crops.

Ethiopian crop	FOCUS crop
Cabbage	Vegetables, leafy
Potato	Potatoes
Teff	Cereals, spring
Wheat	Cereals, spring
Maize	Maize
Barley	Cereals, spring
Faba bean	Field beans
Sweet potato	Potatoes
Cotton	Sunflowers
Sugar cane	Maize

Values of saturated vapour pressure which were given at a temperature of 25 °C were converted into the corresponding value at 20 °C and were subsequently used to estimate the dimensionless Henry constant. K_{om} values needed by TOXSWA were calculated as K_{om} = 1.724 K_{oc}, with K_{om} and K_{oc} expressed as L/kg and the K_{om} standing for coefficient for sorption on soil (and sediment) based on organic matter content (Beltman et al., 2006). TOXSWA and PRZM calculations internally both use temperature corrected values for physico-chemical properties, using an Arrhenius type of equation. During actual registration of a pesticide, properties of pesticides would be obtained from the registration file required by the registration authorities, enabling a more rigid data quality check. For this paper the data were taken from footprint for demonstration purposes only.

Table 3 Selected pesticides with volume and ARfD values from footprint pesticides properties database (Lewis et al. 2016).

Compound	Volume (tons) 2010	ARfD(mg/Kg BW/day)	ADI(mg/Kg BW/day)	Type[a]
2,4-D	1824	Not applicable	0.05	HB
Atrazine	40	0.1	0.02	HB
Chlorothalonil	b1	0.6	0.015	FU
Deltamethrin	30	0.01	0.01	IN
Dimethoate	63	0.01	0.001	IN
Endosulfan	84	0.02	0.006	IN
Malathion	193	0.3	0.03	IN

[a] IN = Insecticide; HB = Herbicide, FU = Fungicide and BW = Body Weight (kg).

Application pattern

For all crop-pesticide combinations data for an application pattern including number of applications, rate of application in kg a.i./ha and application interval in days was determined in consultation with Experts at the Ministry of Agriculture Ethiopia and FAO data (FAO, 2011). The possible dates of application were set using the maximum number of applications and minimum application intervals and dates from the crop calendar as a reference (Appendix B), resulting in worst-case estimates of emissions.

Human risk assessment

Risks for drinking water were assessed using the water concentration aimed at representing the 99th percentile of probability of occurrence in Ethiopia as explained in a previous section. This high percentile is used because risks to humans are considered to be non-acceptable. As small water bodies are vulnerable, concentrations are calculated in water drawn from small streams or temporary ponds. Acute risk assessment consists of comparing the concentration in surface water to the acute human toxicity value. The Acute Reference Dose (ARfD) was used for all the selected pesticides except 2,4-D where the chronic toxicity value ADI was used because no ARfD was available. Only acute toxic effects are considered in the risk assessment, i.e. reproductive effects, carcinogenicity or endocrine disruptive effects are not considered in the risk assessment. The Estimated Short Term Intake (ESTI) was calculated with Eq. (1), using a body weight of 60 kg and assuming a large portion (LP) of intake of 6 L drinking water per day. The value of 6 L is triple the amount indicated by WHO (WHO, 2011) and is used because of high temperatures and possible high physical exertion. ESTI expresses the intake of a pesticide as a percentage of the total acceptable intake for one person in one day for acute toxicity.

$$\mathrm{ESTI} = \frac{\mathrm{LP\_dw} \times \mathrm{PEC}_{99\mathrm{th}}}{\mathrm{ARfD} \times \mathrm{BW}} 100\% \qquad \text{eq. (1)}$$

With:

ESTI = Estimated Short Term Intake (-)

LP_dw = Large Portion of drinking water (L/day;

PEC_{99th} = 99th percentile concentration in the selected surface water (µg/L);

ARfD = Acute Reference Dose (µg/Kg BW*d) and

BW = Body Weight (kg).

Environmental risk assessment

Risks for aquatic organisms were estimated using the water concentration aimed at representing the 90th percentile of probability of occurrence in Ethiopia as explained in a previous section. This percentile is commonly used in EU registration procedures for risks for the aquatic ecosystem, and reflects a somewhat less strict need for protection of aquatic organisms compared to humans. The No Effect Concentrations (NEC) values for aquatic organisms were estimated from the acute ecotoxicity data (LC50 and EC50) values for Daphnia, algae and fish taken from the footprint pesticides properties database (Lewis et al. 2016). Toxicity to-wards rooted macrophytes, possibly a useful future addition to the risk assessment procedure, is not yet considered. NEC was calculated for each species by multiplying its EC/LC50 by an extrapolation factor, which was species dependent (Eqs. (2)–(4)). These values were calculated in correspondence with the calculation of NEC values (µg/L) for the surface water system as is commonly done in lower tiers of the EU registration procedure and also applied by Peeters et al. (2008) (Appendix C).

NEC Fish = 0.01 * (LC50 Fish) eq. (2)

NEC Daphnia = 0.01 * (EC50 Daphnia) eq. (3)

NEC Algae = 0.1 * (EC50 Algae) eq. (4)

Acute toxicity risks for surface water organisms were calculated for each of the three locations, using the estimated predicted environmental concentrations (PECs) for the stream at grid 191 and for ponds at grids 217 and 373. Risk assessment was performed by comparing PEC values to NEC values for each of the organisms (Eq. (5)).

$$\mathrm{ETRwater-org} = \frac{PEC_{90th}}{\mathrm{NECorg}} \qquad \text{eq. (5)}$$

With:

ETRwater-org = Exposure Toxicity Ratio for the water organisms fish, daphnia or algae (-)

PEC_{90th} = 90^{th} percentile concentration in the selected surface water (μg/L);

NECorg = No Effect Concentration for the water organisms fish, daphnia or algae (μg/L)

For each of the organisms risk was classified according to the calculated ETR using a scheme as given in Table 4. For fish a 10 times stricter criterion was used than for Daphnia and algae, implying a somewhat stricter protection for vertebrates than for the invertebrates.

Results and discussion

PRZM, TOXSWA and TOXSWA meta model simulations

Fig. 3A and B show the concentration over time for an example pesticide-crop combination, i.e. 2,4-D in maize, for the entire 33 year period covered in the simulation (1979–2011). In the streams concentrations increase sharply, and also decrease sharply due to the relatively high flows resulting in rapid outflow of the pesticide (Fig. 3A). So, once the pesticide has entered the stream water, it is rapidly displaced due to inflow of clean water (base flow plus subsurface drain flow), resulting in short-time exposure generally lasting less than a day. As soon as runoff is greater than 0.1 mm the incoming runoff water of the 100 ha upstream catchment dominates the pesticide-free base flow and subsurface drainage flows in the stream and concentrationsin the stream are in essence the concentration in the runoff water of the 20 ha treated fields, divided by the dilution factor of 5. The magnitude of concentration in the runoff water of treated fields is heavily influenced by (i) the time between application and occurrence of therunoff event, due to the degradation of 2,4-D in soil in the intermediate period (DT50soil = 14d) and (ii) rainfall occurring between application and the first runoff event, because such intermediate rainfall makes the pesticide leach out of the upper millimetres of soil before it can runoff and thus, the concentration in the runoff decreases.

Table 4 Risk intervals and categories used in risk assessment for aquatic organisms.

ETR value	Risk Category	
	Algae and Daphnia	Fish
<1	Low risk	Low risk
1-10	Possible risk	Possible risk
10-100	Possible risk	High risk
>100	High risk	High risk

The ponds, on the other hand, are modelled as ideally mixed reservoirs with a relatively small inflow of clean water and small outflow of pond water, which results in a more gradual decrease of concentration as a result of dilution and of degradation in the water (DT50water = 1000d) and sorption into and later desorption from the pond sediment (K_{oc} = 88.4 L/kg) (Fig. 3B).

For streams, differences in concentration profiles between years are mostly caused by differences in meteorology, and the resulting differences in the size and occurrence of runoff events. The fluctuations in concentrations seen for the pond scenario reflect not only runoff events, but also reflect the yearly recurring drift events occurring at each application.

For most pesticide-crop combinations the PEC_{90th} calculated for the stream scenario is higher than the corresponding concentration calculated for the pond scenarios. This indicates that for most pesticide-crop combinations investigated in this paper, the acute risk calculated for aquatic life is higher in the stream scenario than in the pond scenarios under similar circumstances (Appendix D). Considering that the concentration peaks in streams are only transient in nature, the risk for pond scenarios may in reality be higher due to the longer exposure duration. This shows the need to perform a chronic risk assessment.

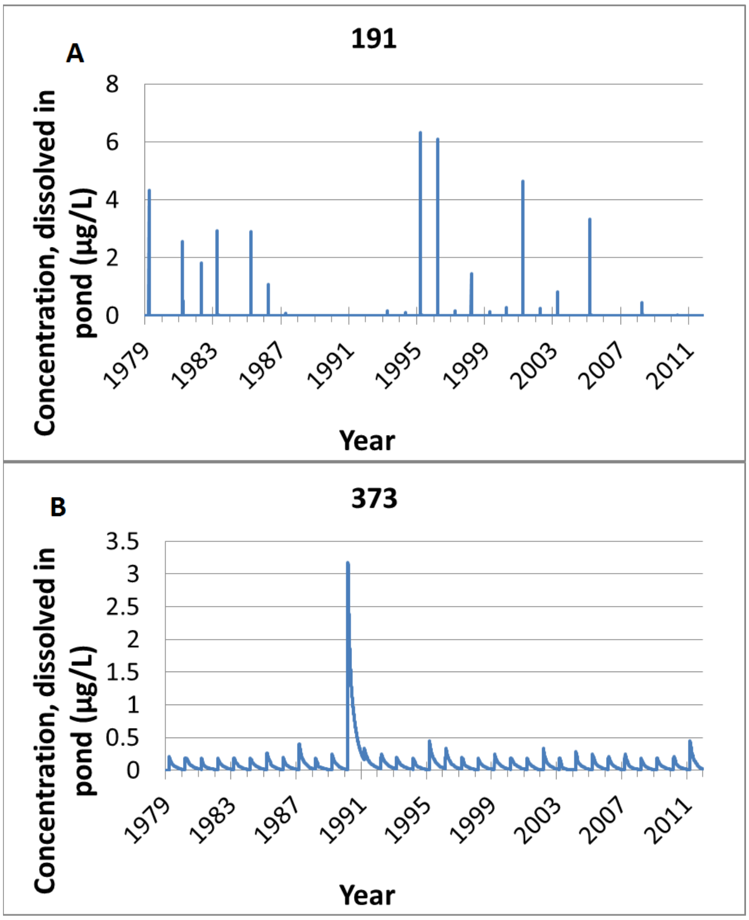

Fig. 3.Concentrations as a function of time for the stream (A, grid 191) and pond (B, grid373) scenario for 2,4-D in maize.

PECs for the same pesticide may differ significantly between their use on different crops, even when application rates are similar. For example the PEC_{99th} for 2,4-D of the crops maize and teff for the stream scenario are 2.9 and 58.4 respectively, i.e. differing by a factor 20. This difference is mainly the result of the differences in the moment of pesticide application which is 10th of March for maize while it is 10th of July for teff. This brings about a huge difference in the size of runoff water and pesticide fluxes entering the streams, since for these crops and their timing of application, the meteo-irrigation data for the 33years interval vary significantly between March (dry season) and July (rainy season). When application times are close, PECs are also close, which is for instance obvious from the PEC_{90th} results of 2,4-D for teff and wheat, 58.4 and 49.2 respectively (application dates are 10th of July for teff and 5th of July for wheat) (Tables 6 and 9).

Although the realistic worst case PECs are based upon a scenario se-lection procedure going beyond the current state-of-the-art for surface water scenarios in e.g. the EU and the USA, the scenario selection procedure can be considerably improved using simulated PECs for the entire country, instead of days with daily rainfall above 20 mm. This is already common practice in e.g. scenario definition for exposure of soil organ-isms to pesticides in the EU (Tiktak et al., 2013). Parameterisation and running the suite of runoff and surface water fate models, including more detailed information on e.g. soils, land use and hydrology would result in geographically distributed PECs for the series of 33 years for Ethiopia. After repeating the procedure for a range of pesticides, candidate grids can be selected according to the wished overall probability of occurrence of the PEC, valid for the highest possible number of compounds.

Little validation of the PRZM and TOXSWA models has been done in the sense that for a range of situations (the validation domain) the validity of simulated mechanistic processes has been tested for a defined target output parameter for a range of compounds. Singh and Jones (2002) demonstrated that PRZM provides a reasonable estimate of pesticide runoff at the edge of a field, by analysing nine different runoff field studies. However, Young and Carleton (2006) proved that random se-lection of the daily Runoff Curve Number from a distribution performed better than the Curve Number calculation based on soil moisture, currently implemented in PRZM. The variability in rainfall-runoff relation-ship for a 1.75 acre catchment in Oklahoma was better characterized by the modified PRZM model than by the original model (Young and Carleton, 2006). For the TOXSWA model Adriaanse et al. (2013) demonstrated that measured concentration-time profiles in water and sediment of a stagnant ditch can only be well mimicked after calibration of the laboratory-measured degradation rate in water and properties of the upper millimetres of sediment instead of using 5-cm averaged values. So, continuing validation efforts are needed, involving adequate experiments with measured site-specific system parameters and pesticide properties and that include situations and compounds representing Ethiopia.

Sound validation of models requires a careful measurement of all relevant system and physico-chemical input parameters, preferably established by an uncertainty and sensitivity analysis (Jones and Mangels, 2002; Carbone et al., 2002; Westein et al., 1998). If relevant input parameters may not be correctly estimated or cannot be verified comparing model output (and certainly output from a suite of coupled models), to field measurements raises concerns about its usefulness and validity, especially if contributions from non-modelled point sources cannot be excluded for the field measurements. In addition, if populations of simulations and field measurements are compared, it is crucial to demonstrate that the compared populations of simulations and field measurements represent similar environmental conditions and that for each comparison the application regimes are identical (Knäbel et al., 2012 and two ensuing rebuttals: Bach and Hollis, 2013; Reichenberger, 2013).

Results human risk assessment

Estimated risks for humans indicate that all the pesticide-crop combinations have Estimated Short Term Intake (ESTI) values less than 100% at all locations (Table 10). This indicates that the daily intake from consuming a large portion (6 L) of drinking water per day is below the acceptable total daily intake. These results indicate that for the investigated combinations of pesticides and crops, direct surface water consumption is associated with low acute health risks for humans in Ethiopia (Table 5).

Table 5 Summary of risk assessment results for humans for grids 191, 217 and 373.

Pesticide	**Crop**	**ESTI (%)**	**ESTI (%)**	**ESTI (%)**	**Risk category**		
		191	**217**	**373**	**191**	**217**	**373**
2,4-D	Maize	1.22	0.08	0.1	low	low	Low
2,4-D	Sugar cane	[a]	[a]	0.12	[a]	[a]	Low
2,4-D	Teff	12.26	3.86	0.12	low	low	Low
2,4-D	Wheat	11.52	4.36	0.18	low	low	[a]
Atrazine	Maize	2.78	0.05	0.05	low	low	Low
Atrazine	Sugar cane	[a]	[a]	0.03	[a]	[a]	Low
Chlorothalonil	Potato (cycle 1)	0.51	0.68	0.05	low	low	Low
Chlorothalonil	Potato (cycle 2)	0.58	0.26	0.29	low	low	Low
Deltamethrin	Cabbage (cycle 1)	0.00019	0.00079	0.00084	low	low	Low
Deltamethrin	Cabbage (cycle 2)	0.00019	0.00084	0.00084	low	low	Low
Deltamethrin	Cotton	[a]	[a]	0.01	[a]	[a]	Low
Deltamethrin	Maize	0.000041	0.00029	0.00029	low	low	Low
Deltamethrin	Sweet potato	[a]	[a]	0.0029	[a]	[a]	Low
Dimethoate	Barley	27.4	21.7	[a]	low	low	[a]
Dimethoate	Faba beans	22.6	15.6	[a]	low	low	[a]
Endosulfan	Cotton	[a]	[a]	0.25	[a]	[a]	Low
Endosulfan	Maize	0.70	0.45	0.80	low	low	Low
Malathion	Sweet potato	[a]	[a]	0.007	low	low	Low

[a] No simulation result since the crop is not expected to be grown on the specified location.

A closer look at the results of the ESTI and the 99th percentile PEC concentrations indicates that the pesticides 2,4-D, atrazine, chlorothalonil and dimethoate are the compounds with the highest PEC_{99th} results (Appendix D), but only dimethoate has an ESTI value >20% (Table 5). The relatively low human toxicity of 2,4-D, atrazine and chlorothalonil causes the risks for humans to be low (Table 3), despite the relatively high exposure concentrations calculated for these com-pounds. The short term risk for deltamethrin is estimated to be very low resulting from a very low (negligible)

PEC_{99th} concentration calculated for both the stream and the pond scenarios.

The highest uncertainty in the human risk assessment is that the contribution of other foodstuffs to the ESTI is unknown. So it is un-known whether an ESTI value of 20% is posing a risk to humans in combination with exposure through foodstuffs from a normal Ethiopian diet or the Ethiopian diet. An example of such a diet is the one defined by the WHO GEMS (Global Environmental Monitoring System) cluster diets (WHO, 2005). In this classification all countries of the world are classified in 13 diets for different regions, based on agricultural and trade data. The Ethiopian diet is clustered together with central African coastal countries and this diet composition could be used to perform an initial risk assessment using MRLs (Maximum Residue Levels) or measured residues to evaluate the contribution of drinking water to the overall exposure through foods. Van den Brink et al. (2013) performed a similar analysis of the toxicity of using surface

Table 6. Summary of risk assessment results for aquatic organism grids 191 (stream highland), 217 (pond highland) and 373 (pond lowland).

Pesticide	Crop	ETR values for grid 191			ETR values for grid 217			ETR values for grid 373		
		Algae	Daphnia	Fish	Algae	Daphnia	Fish	Algae	Daphnia	Fish
2,4-D	Maize	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
2,4-D	Sugar cane							<0.1	<0.1	<0.1
2,4-D	Teff	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
2,4-D	Wheat	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Atrazine	Maize	2.64	<0.1	0.35	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Atrazine	Sugar cane							<0.1	<0.1	<0.1
Chlorothalonil	Potato (cycle 1)	8.58	33.69	74.47	9.69	38.09	84.21	0.48	1.90	4.21
Chlorothalonil	Potato (cycle 2)	10.09	39.64	87.63	4.30	16.90	37.34	4.79	18.81	41.58
Deltamethrin	Cabbage (cycle 1)	<0.1	<0.1	<0.1	<0.1	0.14	0.30	<0.1	0.16	0.33
Deltamethrin	Cabbage (cycle 2)	<0.1	<0.1	<0.1	<0.1	0.15	0.32	<0.1	0.15	0.32
Deltamethrin	Cotton							<0.1	1.18	2.54
Deltamethrin	Maize	<0.1	<0.1	<0.1	<0.1	<0.1	0.12	<0.1	<0.1	0.11
Deltamethrin	Sweet potato							<0.1	0.52	1.11
Dimethoate	Barley	<0.1	1.31	<0.1	<0.1	0.83	<0.1			
Dimethoate	Faba beans	<0.1	1.09	<0.1	<0.1	0.64	<0.1			
Endosulfan	Cotton							<0.1	<0.1	13.0
Endosulfan	Maize	<0.1	0.25	55	<0.1	0.13	29.5	<0.1	0.14	31.5
Malathion	Sweet potato							<0.1	30.0	1.17

water as drinking water, as well as the consumption of fish and macrophytes obtained from this surface water, for Thailand and Sri Lanka. They concluded that no single food item caused the exceedences of human toxicity reference values and that the risks are not associated with a single crop. Therefore it is of importance to assess the risk of the total diet and not only for single items in order to obtain an estimation of the overall risk (Van den Brink et al., 2013).

Results aquatic ecosystem risk assessment

The ETRs for all the compounds and crops along the three locations (grids) indicates that 2,4-D and deltamethrin are low risks for all the aquatic organisms (algae, Daphnia and fish) at the stream scenario 191. However atrazine, chlorothalonil, dimethoate and endosulfan, have possible and high risks across the representative organisms (Table 6).

For the highland pond scenario 217, the pesticides 2,4-D, atrazine, deltamethrin and dimethoate pose low risks for algae, Daphnia and fish, while chlorothalonil and endosulfan have possible risks for algaeand Daphnia and high risk for fish (Table 6). In the lowland pond scenario (grid 373), 2,4-D and atrazine are with low risks for all the representative organisms, while chlorothalonil, deltamethrin, endosulfan and malathion pose possible and high risks for some of the pesticide-crop combinations (Table 6). All the high risks recorded for fish are mainly due to the implementation of a ten times stricter risk categorization for fish which was considered necessary for the stricter protection of fish and other surface water vertebrates. The highest estimated risk category is taken as representative for the overall risk for all the aquatic organisms within a grid.

One of the challenges of the aquatic risk assessment of pesticides in (sub-)tropical regions is the absence of sensitivity data of local species (Rico et al., 2011). Daam and Van den Brink (2010) reviewed the literature on the differences in sensitivity between (sub-) tropical and temperate species and concluded that no systematic difference in sensitivity could be found. Teklu (pers. comment) performed toxicity tests with three invertebrate species indigenous to Ethiopia and concluded that the sensitivity of these species to the pesticides endosulfan and diazinon was comparable to values present in the literature for taxonomically related species. This means that toxicity data from other geographical areas can probably be used to perform a risk assessment for an Ethiopian situation. NEC estimates based on single species toxicity data of Daphnia magna will result in a conservative risk assessment for the compounds evaluated in this study, but might underestimate the risks to invertebrates for neonicotinoids and insect growth regulators (Brock and Van Wijngaarden, 2012). It is, therefore, recommended to include other invertebrate species like *Chironomus riparius* and *Americamysis bahia* in the NEC calculations when these pesticide groups are considered.

Conclusion and recommendation

For the pesticide-crop combinations investigated, estimated short term risks for humans from using surface water as a source of drinking water are quite small. Possible and high risks are estimated for aquatic organisms for some pesticides-crop combinations. The ESTI and ETR calculations and risk estimates are based on a procedure very similar to the risk assessment procedure at EU level, as outlined by EFSA (2013). Input on crops, meteorology, irrigation and application pattern were tailored to the Ethiopian situation, including the distinctly innovative use of a 33-year meteorological data series, thus increasing the reliability of the results obtained. A close look at the comparison between PECs with-in pesticides, crops and locations, and pond versus stream scenario indicates that results are logical and differences can be explained. However, ultimately the usefulness of model calculations for registration purposes requires validation of model outcomes using field measurements and validation studies on, especially the fate assessment, are needed.

Protection goals were set after discussion with the appropriate stakeholders; small water bodies close to intensive agriculture and relatively densely populated areas were selected, in order to simulate realistic, vulnerable situations. Evaluating the spatial and temporal variation of the main driving factor, runoff, for concentrations in the small water bodies, 99th and 90th percentile probability of occurrence scenario locations were selected, that thus protect the large majority of the aimed small water bodies across Ethiopia. The final decision on adoption of the model calculations for a formal pre-registration risk assessment of pesticides depends upon agreement by the Ethiopian government and all the stakeholders participating in the pesticide import and distribution channel. As the accuracy of results depends on the availability and quality of the available input data retrieval of pesticide application pattern and quality control of all submitted pesticide physico-chemical and ecotoxicological properties for all the registered pesticides in Ethiopia is recommended. Performing the risk assessment for all registered pesticides accordingly is a possible next step, which will give insight in the impact on the number of registered pesticides in Ethiopia after implementation of the proposed pre-registration risk assessment procedure.

Implementation of the methods described for risk characterization constitute a good step forward in the pesticide registration procedure in Ethiopia. Addition of aquatic macrophytes as an ecotoxicological endpoint may constitute a welcome future addition to the risk assessment procedure.

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Appendix A. Supplementary data

Appendices for Chapter 2

Appendix A. An overview of the physic-chemical pesticide properties data used in models: all the data were taken from footprint pesticides properties database (Lewis et al. 2016)

Pesticide	**Molar Mass (g/mol)**	**Saturated vapour pressure (20^oC ,Pa)**	**Water solubility (20^oC, mg/L)**	**Henry coefficient (-)**	**DT50soil (d)**	**DT50water (d)**	**Koc (L/kg)**	**1/n (-) Freundlich exponent**
2,4-D	221.04	0.97E-05	23180	0.38E-10	14	1000	88.4	1
Atrazine	215.68	0.20E-04	35	0.51E-07	75	86	100	1
Chlorothalonil	265.91	0.39E-04	0.081	0.53E-05	15.7	1000	850	0.9
Deltamethrin	505.2	0.64E-10	0.0002	0.67E-05	26	1000	10240000	1
Dimethoate	229.26)	0.13E-3	39800	0.30E-9	2.6	68	28.3	1
Endosulfan	406.93	0.43E-03	0.32	0.23E-03	39	20	11500	0.9
Malathion	330.36	0.16E-02	148	0.15E-05	0.17	10.4	1800	0.94

Appendix B. Data on pesticide application patterns for different crop pesticide combinations

Pesticide	Use	Crop	Number of applications	Rate of application (kg a.i./ha)	Application interval (days)	Possible crop stage during application
Dimethoate	Russian wheat aphids	Barley	2	0.6	7	E-1/2 M (29 July, 5 Aug)
		Faba beans	2	0.48	7	E-1/2 M (23 July, 30 July)
Endosulfan	African bollworm, Leafhoppers	Cotton	6	1.05	7-10	E-1/2M (12 July, 19 July, 26 July, 2 Aug, 9 Aug, 16 Aug)
		Maize	2	0.7	7-10	E-1/2M (10 April, 17 April)
Deltamethrin	African bollworm Leafhoppers	Cotton	5	0.18	7	E-1/2 M (12 July, 19 July, 26 July, 2 Aug, 9 Aug)
		Maize	1	0.021	-	E-1/2 M (17 April)
		Cabbage	5	0.025	10	E-1/2 M 1st (4 June, 14 June, 24 June, 4 July, 14 July) 2nd (21 Nov, 1 Dec, 11 Dec, 21 Dec, 31 Dec)
		Sweet potato	4	0.09	7-10	E-1/2 M (19 July, 26 July, 2 Aug, 9 Aug)
2,4-D	Broad leaf weeds	Wheat	1	1.44	-	E-1/2M (10 July)
		Teff	1	1.44	-	E-1/2M (5 July)
		Maize	1	1.44	-	E-1/2M (10 March)
		Sugar cane	1	2.88	-	E-1/2M (2 Jan)
Malathion	Sweet potato butterfly	Sweet potato	7	1	10	E-1/2 M (10 July, 20 July, 30 July, 9 Aug, 19 Aug, 29 Aug, 8 Sept)
Atrazine	Both grass and broadleaf weeds	Maize	1	1.75	-	(10 March)
		Sugar cane	1	1.75	-	(2 Jan)
Chlorothalonil	Late blight	Potato	3	1.5	7-14	E-1/2E 1st(12 July, 19 July, 26 July) 2nd (19 Jan, 26 Jan, 1 Feb)

E = before emergence; E - ½M = emergence to halfway maturation; ½M – M = halfway maturation to maturation; M – H = maturation to just before harvest

Appendix C. Acute ecotoxicological data used for risk calculations. All data in µg/L and taken from foot print pesticides properties database (Lewis et al. 2016).

Pesticide	LC50 Fish	EC50 Daphnia	EC50 Algae	NEC fish[a]	NEC Daphnia[a]	NEC Algae[a]
2,4-D	63,400	100,000	100,000	634	1,000	10,000
Atrazine	4,500	85,000	59	45	850	5.9
Chlorothalonil	38	84	33	0.38	0.84	3.3
Deltamethrin	0.26	0.56	9,100	0.0026	0.0056	910
Dimethoate	30,200	2,000	90,400	302	20	9,040
Endosulfan	2	440	2,150	0.02	4.4	215
Malathion	18	0.7	13,000	0.18	0.007	1,300

[a] NEC values calculated from the LC50/EC50 values.

Appendix D. PRZM, TOXSWA and TOXSWA meta model simulation results (overall 90th and 99th probability of occurrence Predicted Environmental Concentrations in µg/L) for the small stream (grid 191), and the two ponds (grid 217 and 373).

Pesticide	**Crop**	**191**		**217**		**373**	
		90th	**99th**	**90th**	**99th**	**90th**	**99th**
2,4-D	Maize	2.9	6.1	0.24	0.4	0.33	0.5
2,4-D	Sugar cane	[a]	[a]	[a]	[a]	0.37	0.6
2,4-D	Teff	58.4	61.3	11.4	19.3	0.22	0.6
2,4-D	Wheat	49.2	57.6	11.0	21.8	0.26	0.9
Atrazine	Maize	15.6	27.8	0.28	0.5	0.41	0.5
Atrazine	Sugar cane	[a]	[a]	[a]	[a]	0.21	0.3
Chlorothalonil	Potato (cycle 1)	28.3	30.8	32.0	40.5	1.6	2.7
Chlorothalonil	Potato (cycle 2)	33.3	34.8	14.2	15.5	15.8	17.1
Deltamethrin	Cabbage (cycle 1)	1.8E-04	1.9E-04	7.8E-04	7.9E-04	8.7E-04	8.8E-04
Deltamethrin	Cabbage (cycle 2)	1.8E-04	1.9E-04	8.3E-04	8.4E-04	8.4E-04	8.4E-04
Deltamethrin	Cotton	[a]	[a]	[a]	[a]	6.6E-03	6.6E-03
Deltamethrin	Maize	3.3E-05	4.1E-05	2.8E-04	2.9E-04	2.9E-04	2.9E-04
Deltamethrin	Sweet potato	[a]	[a]	[a]	[a]	2.9E-03	2.9E-03
Dimethoate	Barley	26.2	27.4	12.7	21.7	[a]	[a]
Dimethoate	Faba beans	21.82	22.6	12.9	15.6	[a]	[a]
Endosulfan	Cotton	[a]	[a]	[a]	[a]	0.26	0.5
Endosulfan	Maize	1.1	1.40	0.59	0.9	0.63	1.6
Malathion	Sweet potato	[a]	[a]	[a]	[a]	0.21	0.2

[a] no simulation result since the crop is not expected to be grown on the specified location.

Chapter 3

Sensitivity of Ethiopian aquatic macroinvertebrates to the pesticides endosulfan and diazinon, compared to literature data.

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Abstract

The aims of the present study were to present a methodology for toxicity tests that can be used when analytical resources to verify the test concentrations are limited, and to evaluate whether the sensitivity of a limited number of Ethiopian species to pesticides differs from literature values for, mainly, temperate species. Acute toxicity tests were performed using three Ethiopian aquatic invertebrate species, one crustacean (*Diaphanosoma brachyurum*) and two insects (*Anopheles pharoensis* and *Culex pipiens*)and using the pesticides endosulfan and diazinon. All species–pesticide combinations were tested in duplicate to estimate the consistency, i.e. the intra-laboratory variation, in test results. *Daphnia magna* was tested as well to allow the test results to be compared directly with values from the literature. Results indicate that the differences between the EC50s obtained for *D. magna* in this study and those reported in the literature were less than a factor of 2. This indicates that the methodology used is able to provide credible toxicity values. The results of the duplicated tests showed intra-laboratory variation in EC50 values of up to a factor of 3, with one test showing a difference of a factor of 6 at 48h. Comparison with available literature results for arthropod species using species sensitivity distributions (SSDs) indicated that the test results obtained in this study fit well in the log-normal distribution of the literature values. We conclude that the methodology of performing multiple tests to check for consistency of test results and performing tests with *D. magna* for comparison with literature values to check for accuracy is able to provide reliable effect threshold levels and that the tested Ethiopian species did not differ in sensitivity from the arthropod species reported on in the literature.

Keywords single-species toxicity tests; tropics; ecological risk assessment; species sensitivity distribution; Africa

Introduction

The current intensification of agricultural activities in Ethiopia results in a steady increase in both the types and quantities of agrochemicals (Taddese and Asferachew, 2008). Pesticides may, however, cause risks to aquatic ecosystems through contamination by spray drift, run-off, drainage and accidental spills. To prevent environmental harm from the application of these agrochemicals, it is essential to perform a prospective environmental risk assessment before registering a pesticide (Teklu et al., 2015). Estimating the risks of pesticides to the aquatic ecosystem includes an effect assessment which is often based on acute and chronic laboratory tests of the toxicity of these compounds to aquatic species. Brock et al. (2006) noted the importance of acute toxicity tests with fish, algae and invertebrates for the first tier in the risk assessment of pesticides, in order to identify ecosystem components whose sensitivity should be further evaluated in higher-tier risk assessment procedures (Van den Brink, 2013). These tests also help the retrospective chemical risk assessment, by identifying species that are sensitive to pesticide pollution, so that the presence or absence of a sensitive species in an area may be an indication of the pollution status of that particular area (e.g. Wahizatul, et al, 2011), although the absence of a species may have other causes as well.

At present, such an assessment often depends on the results of toxicity tests performed with temperate species, as data on tropical species are scarce (Kwok et al., 2007). Risk assessments performed for tropical ecosystems should be (partially) based on toxicity data for tropical species, since differences in sensitivity might be expected (Daam and Van den Brink, 2010), although empirical data suggest no systematic differences in sensitivity (e.g. Kwok et al., 2007; Rico et al., 2010). Gathering sensitivity data for local species enables further examination of whether European and North American data can be extrapolated to other geographical areas (Hose and Van den Brink 2004; Maltby et al., 2005). Although Ethiopia is located in the tropical region, the risk assessment for pesticide registration is solely dependent on the available temperate acute toxicity data (Teklu et al, 2015). Only a few toxicity tests have been performed with Ethiopian species, one example being a study evaluating the effect of the poisonous extract of the plant *Milletia ferruginea*on Baetidae (mayflies) and Hydropsychididae (caddisflies) (Karunamoorthi et al., 2009).

Besides the laboratory infrastructure needed to perform these tests, one other challenge to conducting such tests in a developing country like Ethiopia is the availability of analytical equipment and the costs of analyses to verify the test concentrations used in the experiments. In this paper we present a simple methodology that circumvents the need for test concentration verification, which might be helpful for future aquatic risk assessment in Ethiopia or elsewhere in the developing world, where the availability of analytical laboratory equipment is limited. The proposed methodology includes performing multiple tests to check for consistency of test results and performing tests with *D. magna* for comparison with literature values to check for accuracy.

The objectives of the current study were (i) to produce toxicity data for local Ethiopian species, (ii) to compare the sensitivity of the Ethiopian species with literature data which relates mainly to temperate species and (iii) to present a simple methodology for conducting tests which reduces the need for analytical verification of the exposure concentrations.

Materials and methods

Test compounds

One organochlorine (endosulfan) and one organophosphate (diazinon) insecticide were chosen as model compounds to evaluate the effects of pesticides on Ethiopian aquatic macroinvertebrates. This choice was based on their frequency of use in Ethiopia, available temperate toxicity data and the results of a previously performed risk assessment for Ethiopian aquatic ecosystems (Teklu et al., 2015). The pesticides, containing 99% active ingredient (endosulfan or diazinon) were obtained from the Adami Tulu Pesticide Processing S.C. in Addis Ababa, Ethiopia.

Test organisms

The sensitivity of two crustaceans (*Daphnia magna* and *Diaphanosoma brachyurum)* and two insect species (*Anopheles pharoensis* and *Culex pipiens*) was assessed for both endosulfan and diazinon. *D. magna* individuals were obtained from the National *Fisheries* and Aquaculture *Research Centre (part of the Ethiopian Institute of Agricultural Research) while D. brachyurum and* A. pharoensis *were collected from the Koka area* and *C. pipiens* from the Entoto natural park located in the periphery of Addis Ababa. Insect larvae were kept for two days for acclimatization in the laboratory in a tray with water from the collection site and introduced to test water. Second and third instar larvae were used in the tests. All collected larvae were maintained in the laboratory until emergence, and the flying adult stage was used for further identification. *D. magna* and *D. brachyurum* were cultured in the laboratory in a culturing dish with water from the collection site, and the tests were started when enough individuals of similar size and age category were available. All arthropods were identified using a standard identification key and in consultation with Addis Ababa University experts (Hopkins 1952; Verrone 1962).*D. magna* was selected because it is the most important international standard test species and could thus be used to validate the test performance against literature data. The other species were selected based on their availability and non-cannibalistic behaviour and to include species from both the insect and the crustacean groups. Second instar individuals were used for the tests with the insect species, while individuals younger than 24h were used for the tests with the crustaceans.

Toxicity tests

All toxicity experiments were performed at the Fisheries and Limnology Laboratory of Addis Ababa University College of Natural Sciences, in accordance with the OECD's *Daphnia* sp. protocol (OECD, 2004). The acute toxicity tests were performed using seven concentrations (including control), with three replications per treatment. The toxicity tests used a static exposure extended for 96 h with a single pesticide spiking at the beginning of the test while establishing treatments.The dissipation from the water phase during the 96h experimental test period was expected to be low for endosulfan ($DT50_{hydrolysis}$ = 20 days, pH = 7, T=20 °C, Lewis et al., 2016) and 50% for diazinon ($DT50_{hydrolysis}$ = 138 days, pH = 7, T=20 °C, Lewis et al., 2016). All tests were done in 1.5 L glass jars filled with 1 or 0.5 L of water for insects and crustaceans, respectively. The crustaceans used were the cultured individuals, while insects were introduced into the test water after two days of acclimatization. Dechlorinated tap water was used for the crustaceans, while insects were tested in filtrated (mesh size 1-1.5 nm) water from the collection site. Stock solutions of 100 mg/L were prepared using demineralised water for both pesticides, using absolute ethanol (0.1%) as a solvent in view of the low and moderate water solubility of the substances (Lewis et al., 2016), leading to an ethanol content of 0.003% at the highest endosulfan concentration and of 0.0004% at the highest diazinon concentration. Test concentrations were prepared following successive serial dilutions stirred thoroughly for 15 seconds for each replication. Concentrations were chosen in such a way that no effects were expected at the lowest concentration and 100% effects at the maximum concentration, using a published EC50 value from a related temperate species as a reference, while the concentrations in between were geometrically spaced (see supplementary information for the concentrations evaluated). In each test, ten individuals were added to each replicate, assuming non cannibalistic behaviour of all test species. During the experiments the average temperature was 20 ± 0.25 °C, dissolved oxygen (DO) averaged 4.57 ± 0.41 mg/L and pH 6.52 ± 0.13. Measurements were performed at the beginning and end of the experiment using a portable dissolved oxygen (Handy Polaris, OxyGuard, USA) and pH meter (WTW multi 340i, USA).

Invertebrate immobility was taken as an endpoint for assessing the effects of endosulfan and diazinon, as described in Rubach et al. (2011). All pesticide–species combinations were tested twice, except for the test with endosulfan and *D. magna*. In most tests, counting was done every 24h until the end of the test (96h), while two tests were only evaluated after 48 and 96h (see supplementary material).

Analytical verification of stock solution

Samples of the stock solutions were taken to Wageningen (The Netherlands) in glass vials for analytical verification of the concentration. Some decrease in the concentration of the stock solutions of diazinon and endosulfan was expected as they were stored for 9 months in a fridge at 5 °C at an Addis Ababa University (AAU) laboratory and for 3 months frozen (in Wageningen). To verify the actual concentration of the stock solutions (100 mg/L) at the time of testing, the expected degradation during the storage period was calculated using the degradation rates available in the literature. It was assumed that no degradation took place while frozen, since both pesticides are moderately volatile given their saturated vapour pressure and associated Henry coefficients of 0.000025 (diazinon) and 0.00043 (endosulfan) (Lewis et al., 2016). The DT50 values of endosulfan and diazinon found in the literature for a pH of 5 were established at 25 and 20 °C, respectively. The effect of the lower temperature in the fridge (5 °C) on the degradation was accounted for using a correction to the rate determined at reference conditions. This was calculated with the Arrhenius equation (Boesten, 1986), using the molar Arrhenius activation energy for hydrolysis of pesticides in water, 75,000 J/mol (Deneer et al., 2010). Since the degradation of diazinon is expected to be mainly driven by hydrolysis and, therefore, pH dependent, we also measured the pH of the solution before analytical verification of the test compound.

After storage of the stock solutions in Addis Ababa and Wageningen, the concentrations in the stock solutions were verified by means of GC-ECD. For this purpose, dilutions of the stock solutions were prepared for both diazinon (50-fold) and endosulfan (10,000-fold). Samples (3 µL) were injected at an inlet temperature of 250 °C with a split ratio of 1:20 on a HP5MS column (15 m x 0.25 mm with 0.25 µm film thickness). The oven was operated under isothermal conditions at a temperature of 180 °C, while the ECD was set at a temperature of 300 °C. The retention times were found to be 8.15 min. (diazinon) and 12.35 min. (endosulfan), respectively. Calculation of the concentrations was based on external standards.

Data analysis

The EC10 and EC50 values and their 95% confidence intervals were estimated after 24, 48, 72, and 96 h by log-logistic regression using the number of immobile individuals per replicate as input (Rubach et al., 2011). The test was considered valid when the immobilisation observed in the controls was 10% or less at 48 h and 20% or less at 96 h. The48 h value is based on the acceptance criteria of the OECD protocols, which is 10% for the 24h *Daphnia* sp. test and 15% for the 48h *Chironomus* sp. test. The test results were considered to be invalid when a control immobilisation higher than 10 % was observed at 48 h or higher than 20% was observed at 96 h. Results from duplicate tests were considered to be different when the 96 h EC50 values differed by a factor of 3 or more (Boxall et al., 2001; Baird et al., 1989). Since some of the 96 h test results were invalid, the comparisons were also made based on 48 h values. The 48 h EC50 and 96 h EC50 values of *D. magna* were compared in the same way with those reported in the in the ECOTOX data base (www.epa.gov/ecotox, assessed on 22-12-2015).

In order to compare our findings with those available in the literature, species sensitivity distributions (SSDs) were constructed for each combination of exposure time (48h and 96h) and pesticide (endosulfan and diazinon) (Posthuma et al. 2002). This was done using the ETX2.0 program (Van Vlaardingen et al. 2004), which fits a log-normal model to the data. For each SSD, the median 50% and 5% hazardous concentration (HC50 and HC5) and its standard deviation (SD) were calculated. The goodness-of-fit was tested using the Anderson–Darling test for normality. The data used for the construction of the SSDs of both pesticides for arthropods were extracted from the valid test results from the current study and the ECOTOX database (www.epa.gov/ecotox, accessed on 22 December 2015). When multiple values were available for the same species, the geometric mean was calculated.

Results and Discussion

Analytical verification of stock solution

According to the analytical results, diazinon had decreased from the nominal concentration of the stock solution of 100 mg/L to a concentration as low as 0.70 mg/L at pH = 4, while endosulfan had decreased to 80 mg/L at pH=5 during the 9 months stay in the fridge at 5 °C (Table 1).

The literature provided DT50 values for both chemicals for a pH of 5 (Table 1). After correction for the temperature, endosulfan was predicted to be very stable at 5°C (DT50 = 806 d), while the half-life of diazinon was much shorter (62 d). The calculated concentrations for both chemicals were in the same range as the measured ones (Table 1). The mismatch between the calculated concentration for diazinon of 4.6 µg/L and the measured concentration of 0.70 µg/L might be explained by the lower pH in the sample (4) than for which the DT50 was determined (5), since it may be expected that the hydrolysis rate of diazinon is higher at a pH of 4 than of 5 (Lewis et al., 2016). This means that it is likely that at the start of the experiments the stock solution was indeed around 100 mg/L for both compounds. We therefore recommend to analytically verify the test concentrations, if this is possible at the test facility, but when this is not possible to at least store some of the stock solution for analytical verification later in a suitable laboratory. It is important to take the properties of the pesticide (e.g. DT50) into account before assuming the validity of this methodology.

Toxicity of endosulfan and diazinon

For diazinon, the first test with *A. pharoensis* (37%), *D. brachyurum* (33%) and *D. magna* (23%) exceeded the 20% threshold level at 96 h, while none exceeded the 10% threshold at 48 h(Table 2). All other tests performed showed a control immobilisation < 20% at 96 h, while all performed tests showed control immobilisations of < 10% at 48 h, which is the duration of the test on which the criterion of 10% is based (OECD, 2004). The tests showed large differences between 48 h and 96 h values. On average the difference was a factor of 13, while the minimum and maximum factor was 1.8 and 65, respectively. This indicates that, when field exposure is expected to be longer than 2 days, the 48 h toxicity values might not be a good predictor for effects and tests with a longer duration are needed.

The test results for endosulfan indicated that, based on the 96h values, *C. pipiens* and *D. brachyurum* proved to be the most sensitive species, followed by *A. pharoensis*, while *D. magna* was the least sensitive species (Table 2). In contrast, *D. magna* proved to be the most sensitive organism for diazinon, followed by the other crustacean species and the two insect species (Table 2).

In order to check the accuracy of our test approach we compared the values obtained for *D. magna* with literature values. The ECOTOX database yielded geometric mean 48 and 96 h endosulfan EC50 values of 356 (n=20) and 54 (n=2) µg/L for *D. magna*, respectively. These values are within a factor of 2 of the corresponding values found by us, which were 181 and 98.4 µg/L, respectively (Tables 2 and 3). For diazinon, only a 48 h EC50 of 1.30 µg/L for *D. magna* could be calculated from the available data in the ECOTOX database. One test result was deleted from the obtained data, since it resulted in an extremely deviating 48 h LC50, which was 162 times higher than the geometric mean of the other values (n=5). The literature value was within a factor of 2 of the 48 h EC50 values obtained in this study (0.875 and 1.11 µg/L) (Tables 2 and 3). Since the variation in threshold levels between laboratories can be substantial due to genetic and environmental variability and their interaction (Baird et al., 1989), the small differences observed here indicate that the lack of analytical verification of the test concentrations did not disqualify the data we found in this study.

In order to check the consistency of our test approach we compared the values obtained in the different tests we performed with the same pesticide–species combinations. Based on the EC50s, only one pesticide–species combination showed a difference larger than a factor of 3 between the test results. The 48 h EC50 values resulting from the two tests performed with *D. brachyurum* and diazinon showed a difference of almost a factor of 6, while no comparison could be made at 96 h because the control immobilisation at 96 h in one of the tests was too high (Tables 2 and 3). None of the other tests showed any systematic differences in sensitivity between the 48h and 96h observations, indicating that the experimental set-up we used resulted in intra-laboratory variations in test results up to a factor of 2 (Table 3), which has also been observed for other laboratories (Boxall et al., 2001).

Comparison of experimental results with literature data

Fig. 1 shows the SSDs for endosulfan and diazinon we found for the different observation periods (see Appendices A-D for the included data). Only the 48h diazinon SSD failed the Anderson-Darling test for normality due to the inclusion of two very insensitive crab species in the SSD. Figure 1 shows that the species tested in this paper were located in the upper (insensitive) part of the endosulfan SSDs, while the same species were located in the middle to lower (sensitive) parts of the diazinon SSDs (Fig. 1). This shows that the toxicity values found in this study are not substantially different from those found in the ECOTOX database and therefore that, at least for these compounds, available data from the literature can be used for an Ethiopian risk assessment, as was done in Teklu et al. (2015).

The endosulfan 48 h HC5 of 0.094 µg/L (0.026-0.26) and the 96 h HC5 of 0.047 µg/L (0.011-0.15) seem lower than the value reported by Hose and Van den Brink (2004) of 0.19 µg/L (0.10-0.59). But this is a result of the use of a different distribution (Reciprocal Weibull) since a similar HC5 of 0.083 µg/L (0.017-0.27) is calculated when the same data are fitted by a log-normal distribution, and also pass the Anderson Darling test. Maltby et al. (2005) reported an HC5 for diazinon of 0.36 µg/L (0.13-0.77), which is only slightly higher than the 48 h HC5 of 0.24 µg/L (0.049-0.76) and the 96 h HC5 of 0.24 µg/L (0.074-0.55) found in our study. This is of course not remarkable, as these values are partly based on the same data.

At the species level, the endosulfan 48 h EC50 value of *D. brachyurum* was in between the other 48 h LC50 values reported for other water fleas, while its 96 h value was a factor of 4 lower than the 96 h LC50 reported for *D. magna*(Appendix A and B), possibly as a result of the use of another endpoint (immobilisation versus mortality). The endosulfan 48 h EC50 values reported for the two tested dipteran species (*A. pharoensis* and *C. pipiens*) were quite similar to the 48 h LC50 reported for two other dipterans (*Chironomus riparius* and *Culex fatigans*). No 96 h EC50 or LC50 data were available for other dipteran species, but our results were in between values for other insect (ephemeropteran, plecopteran and zygopteran) species. The 48 h EC50 value of D. brachyurum for diazinon was higher than the 48 h LC50 value reported for other cladoceran species while its 96 h EC50 value was in between the 96 h LC50 values of two other cladoceran species (Appendix C and D). The 48 h and 96 h EC50 values for the two tested dipteran species (*A. pharoensis* and *C. pipiens*) were in between the 48 h and 96 h LC50 reported for two other dipterans (*C. riparius* and *Chironomus tentans*). So also at the species level there were no systematic differences in sensitivity present between the species tested in this paper and those found in the ECOTOX database.

Table 2. Summary of the results (mean and 95% confidence interval of EC10 and EC50 in µg/L) of the acute toxicity tests performed with endosulfan. Asterisks denote control immobilisation higher than 20%. Values for *D. magna* found in the ECOTOX data base are also shown.

Chemical / Test organism	Test No.	48-hour test results EC10	(conf. int.)	EC50	(conf. int.)	% imm.	96-hour test results EC10	(conf. int.)	EC50	(conf. int.)	% imm.
Endosulfan											
C. pipiens	1	22.2	(11.5-43.0)	132	(91-190)	0	3.02	(1.16-7.84)	20.1	(12.8-31.4)	0
	2	20.1	(10.1-39.7)	131	(90-192)	0	2.39	(0.788-7.25)	17.0	(10.1-28.8)	3
A. pharoensis	1	6.3	(1.96-20.3)	90.7	(52.9-155)	0	5.11	(1.6-16.3)	49.3	(28.7-84.6)	3
	2	8.95	(3.39-23.7)	64.5	(39.4-105)	0	5.00	(1.65-15.2)	25.3	(14.5-44.1)	10
D. brachyurum	1	27.1	(XX-XX)	261	(XX-XX)	0	0.178	(0.009-3.55)	10.8	(3.43-34.1)	7
	2	0.346	(0.055-2.20)	203	(52.1-788)	7	0.013	(0-0.528)	17.6	(4.55-68.3)	17
D. magna	1	16.8	(4.53-62.6)	181	(98.7-332)	10	10.5	(2.94-37.4)	98.4	(53.1-182)	13
	Lit			356					54		
Diazinon											
C. pipiens	1	0.475	(0.101-2.23)	10.6	(5.24-21.4)	7	0.068	(0.009-0.519)	2.38	(1.03-5.51)	7
	2	0.707	(0.22-2.28)	30.1	(11.0-82.4)	0	0.029	(0.005-0.191)	0.943	(0.41-2.17)	10
A. pharoensis	1	1.25	(0.404-3.84)	9.25	(5.35-16.0)	7	0.446*	(0.093-2.15)	2.87*	(1.25-6.57)	37
	2	0.146	(0.016-1.35)	19.0	(6.00-60.2)	10	0.037	(0.004-0.376)	3.00	(1.21-7.45)	13
D. brachyurum	1	0.126	(0.034-0.476)	1.53	(0.83-2.84)	7	0.041*	(0.006-0.26)	0.316*	(0.122-0.819)	33
	2	0.071	(0.002-3.39)	8.92	(0.865-92.1)	3	0.001	(0-0.02)	0.138	(0.044-0.432)	10
D. magna	1	0.037	(0.009-0.154)	0.875	(0.472-1.62)	3	0.003*	(0-0.06)	0.072*	(0.018-0.294)	23
	2	0.007	(0.001-0.07)	1.11	(0.383-3.22)	3	0.001	(0-0.013)	0.089	(0.034-0.236)	10
	Lit			1.3							

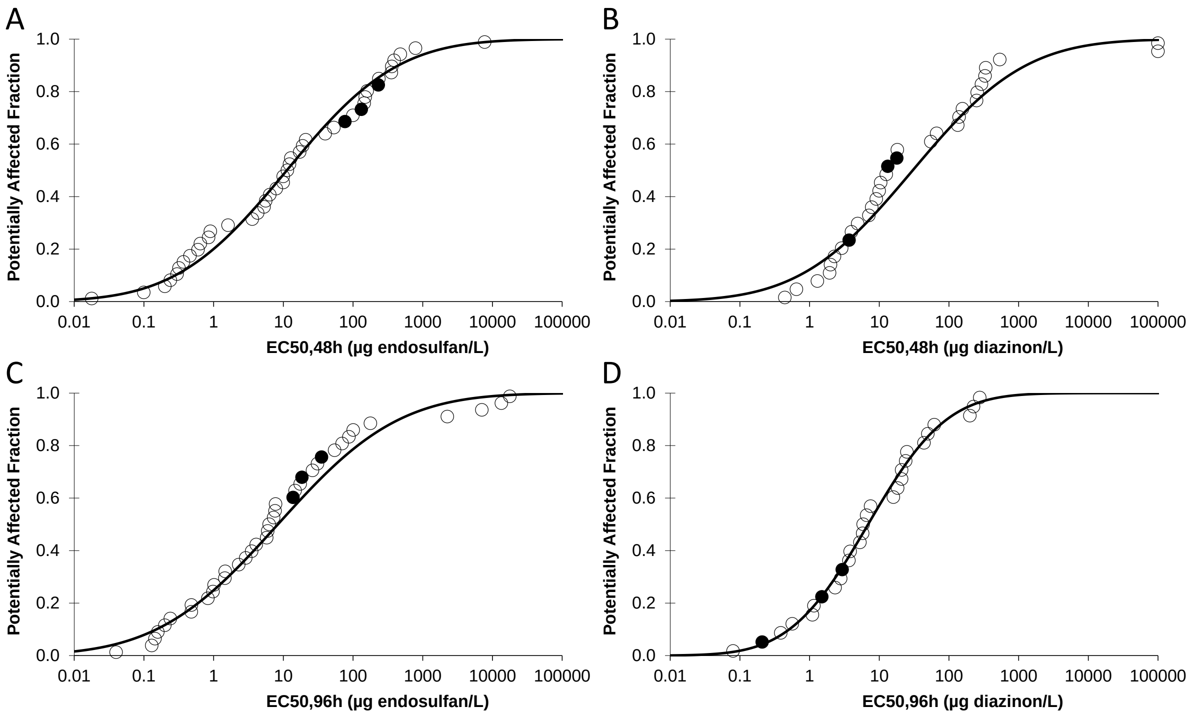

Figure 1. SSD curves for diazinon (A, C) and endosulfan (B, D) for 48h (A, B) and 96h (C, D) toxicity values for arthropods. The filled symbols represent the values found in this study. All curves, except B, passed all tests of normality at the 0.05 significance level (Anderson-Darling test).

Table 3. Ratios between the EC50s of the tests performed with the same species and chemicals. Ratios higher than 3 or lower than 0.33 are indicated by an asterisk. The values for *D. magna* are compared with a value found in the literature for the same species. NA: literature data not available, NV: one of the tests was not valid (see Table 2).

Chemical / Test organism	Test #	Ratio 48 h EC50	Ratio 96 h EC50
Endosulfan			
C. pipiens	1 and 2	1.0	1.2
A. pharoensis	1 and 2	1.4	2.0
D. brachyurum	1 and 2	1.3	1.6
D. magna	Lit and 1	2.0	1.8
Diazinon			
C. pipiens	Lit and 1	1.6	
	1 and 2	2.9	2.5
A. pharoensis	1 and 2	2.0	NV
D. brachyurum	1 and 2	5.9*	NV
D. magna	Lit and 1	1.5	NA/NV
	Lit and 2	1.2	NA
	1 and 2	1.3	NV

Evaluation of methodology and outlook

The results in the present study provide a methodology for performing single-species acute toxicity studies in developing countries with limited resources to verify the concentrations analytically. By performing a test with *D. magna*, the most tested aquatic species in the world, we enabled the results to be calibrated against literature data. Performing duplicate experiments yields the intra-laboratory variation in test results, which includes the errors made in the dosing of the test systems.

The fact that no systematic differences in test results were found between the Ethiopian species and the values obtained from the literature, which mainly relate to temperate species, does not mean that no test protocols should be developed for indigenous species. Since it is important to test indigenous species, e.g. because they are charismatic, economically important or can be used also for in-situ testing, technical protocols should be developed showing how to handle and test indigenous aquatic invertebrates in developing countries.

Compliance with Ethical Standards

- Conflict of Interest: The present study was funded by the Pesticide Risk Reduction Programme – Ethiopia (PRRP-Ethiopia), a collaborative project on pesticide registration and post-registration jointly set up by the Ministry of Agriculture of the Federal Republic of Ethiopia, and the State of the Netherlands represented by the Ministry of Foreign Affairs/Foreign Trade and Development Cooperation, and the Technical Cooperation Programme (TCP) of the Food and Agricultural Organisation of the United Nations.The authors declare that they have no conflict of interest.

- Research involving human participants and/or animals: This article does not contain any studies with human participants or vertebrate animals performed by any of the authors

Informed consent: Informed consent was obtained from all individual participants included in the study.

Appendices for Chapter 3

Appendix A. All toxicity values found in the present study and the ecotox data base for endosulfan with a test duration of 96 h (4d). The results of the present study are in Asterisks

Species Scientific Name	Species Common Name	Species Group	Test Location	Endpoint	Effect	Effect Measurement	Conc. (µg/L)	Number	Rank
Penaeus duorarum	Northern Pink Shrimp	Crustaceans	LAB	LC50	MOR	MORT	0.04	1	0.01
Penaeus indicus	Indian Prawn	Crustaceans	LAB	LC50	MOR	MORT	0.13	2	0.04
Acartia tonsa	Calanoid Copepod	Crustaceans	LAB	LC50	MOR	MORT	0.144417	3	0.06
Paratelphusa jacquemontii	Crab	Crustaceans	LAB	LC50	MOR	MORT	0.159	4	0.09
Crangon septemspinosa	Bay Shrimp, Sand Shrimp	Crustaceans	LAB	LC50	MOR	MORT	0.2	5	0.12
Palaemonetes paludosus	Riverine Grass Shrimp	Crustaceans	LAB	LC50	MOR	MORT	0.24	6	0.14
Macrophthalmus erato	Mangrove Crab	Crustaceans	LAB	LC50	MOR	MORT	0.48	7	0.17
Gammarus palustris	Gammarid Amphipod	Crustaceans	LAB	LC50	MOR	MORT	0.481871	8	0.19
Palaemonetes pugio	Daggerblade Grass Shrimp	Crustaceans	LAB	LC50	MOR	MORT	0.830091	9	0.22
Americamysis bahia	Opossum Shrimp	Crustaceans	LAB	LC50	MOR	MORT	0.98167	10	0.24
Caridina laevis	Smooth Caridina	Crustaceans	LAB	LC50	MOR	MORT	1.02	11	0.27
Macrobrachium rosenbergii	Giant River Prawn	Crustaceans	LAB	LC50	MOR	MORT	1.453554	12	0.29
Jappa kutera	Mayfly	Insects	LAB	LC50	MOR	MORT	1.469694	13	0.32
Pteronarcys californica	Stonefly	Insects	LAB	LC50	MOR	MORT	2.3	14	0.35
Uca pugilator	Fiddler Crab	Crustaceans	LAB	LC50	MOR	MORT	2.897116	15	0.37
Macrobrachium lamarrei	Prawn	Crustaceans	LAB	LC50	MOR	MORT	3.52	16	0.40
Macrobrachium dayanum	Freshwater Prawn	Crustaceans	LAB	LC50	MOR	MORT	4.1	17	0.42
Gammarus lacustris	Scud	Crustaceans	LAB	LC50	MOR	MORT	5.8	18	0.45
Gammarus fasciatus	Scud	Crustaceans	LAB	LC50	MOR	MORT	6	19	0.47
Palaemonetes argentinus	Caridean Shrimp	Crustaceans	LAB	LC50	MOR	MORT	6.28	20	0.50
Hyalella azteca	Scud	Crustaceans	LAB	LC50	MOR	MORT	7.285761	21	0.53
Palaemon macrodactylus	Korean Or Oriental Shrimp	Crustaceans	LAB	LC50	MOR	MORT	7.624959	22	0.55

Species Scientific Name	Species Common Name	Species Group	Test Location	Endpoint	Effect	Effect Measurement	Conc. (µg/L)	Number	Rank
Caridina weberi	Pugnose Caridina	Crustaceans	LAB	LC50	MOR	MORT	7.761294	23	0.58
D. brachyurum	Water Flea	Crustaceans	LAB	EC50	IMM	IMM	13.78695*	24	0.60
Cancer magister	Dungeness Or Edible Crab	Crustaceans	LAB	LC50	MOR	MORT	14.8	25	0.63
Enallagma sp.	Damselfly	Insects	LAB	LC50	MOR	MORT	17.5	26	0.65
C. pipiens	Midge	Insects	LAB	EC50	IMM	IMM	18.48513*	27	0.68
Penaeus monodon	Jumbo Tiger Prawn	Crustaceans	LAB	LC50	MOR	MORT	26.32	28	0.71
Nanosesarma sp.	Crab	Crustaceans	LAB	LC50	MOR	MORT	31	29	0.73
A. pharoensis	Midge	Insects	LAB	EC50	IMM	IMM	35.31699*	30	0.76
Daphnia magna	Water Flea	Crustaceans	LAB	LC50*	MOR	MORT	54.42793	31	0.78
Tigriopus japonicus	Harpacticoid Copepod	Crustaceans	LAB	LC50	MOR	MORT	70	32	0.81
Ischnura sp.	Damselfly	Insects	LAB	LC50*	MOR	MORT	87.65044	33	0.83
Procambarus clarkii	Red Swamp Crayfish	Crustaceans	LAB	LC50	MOR	MORT	100.7571	34	0.86
Scylla serrata	Crab	Crustaceans	LAB	LC50	MOR	MORT	178	35	0.88
Barytelphusa cunicularis	Crab	Crustaceans	LAB	LC50	MOR	MORT	2256.426	36	0.91
Oziotelphusa senex ssp. senex	Crab	Crustaceans	LAB	LC50	MOR	MORT	7060.041	37	0.94
Zilchiopsis collastinensis	Freshwater Crab	Crustaceans	LAB	LC50	MOR	MORT	13469.31	38	0.96
Barytelphusa guerini	Freshwater Crab	Crustaceans	LAB	LC50	MOR	MORT	17780	39	0.99

Appendix B. All toxicity values found in the present study and the ecotox data base for endosulfan with a test duration of 48 h (2d). The results of the present study are in Asterisks

Species Scientific Name	Species Common Name	Species Group	Test Location	Endpoint	Effect	Effect Measurement	Conc.(µg/L)	Number	Rank
Mesocyclops longisetus	Copepod	Crustaceans	LAB	LC50	MOR	MORT	0.017889	1	0.01
Eucyclops sp.	Cyclopoid Copepod	Crustaceans	LAB	LC50	MOR	MORT	0.1	2	0.03
Alonella sp.	Water Flea	Crustaceans	LAB	LC50	MOR	MORT	0.2	3	0.06
Penaeus aztecus	Brown Shrimp	Crustaceans	LAB	LC50	MOR	MORT	0.24	4	0.08
Daphnia longispina	Water Flea	Crustaceans	LAB	LC50	MOR	MORT	0.3	5	0.10
Paratelphusa jacquemontii	Crab	Crustaceans	LAB	LC50	MOR	MORT	0.32	6	0.13
Palaemonetes paludosus	Riverine Grass Shrimp	Crustaceans	LAB	LC50	MOR	MORT	0.37	7	0.15
Penaeus indicus	Indian Prawn	Crustaceans	LAB	LC50	MOR	MORT	0.46	8	0.17
Diaptomus sp.	Calanoid Copepod	Crustaceans	LAB	LC50	MOR	MORT	0.6	9	0.20
Atalophlebia australis	Mayfly	Insects	LAB	LC50	MOR	MORT	0.648074	10	0.22
Cheumatopsyche sp.	Caddisfly	Insects	LAB	LC50	MOR	MORT	0.848528	11	0.24
Cypria sp.	Ostracod	Crustaceans	LAB	LC50	MOR	MORT	0.9	12	0.27
Jappa kutera	Mayfly	Insects	LAB	LC50	MOR	MORT	1.612452	13	0.29
Gammarus palustris	Gammarid Amphipod	Crustaceans	LAB	LC50	MOR	MORT	3.590641	14	0.31
Macrobrachium lamarrei	Prawn	Crustaceans	LAB	LC50	MOR	MORT	4.29	15	0.34
Macrobrachium dayanum	Freshwater Prawn	Crustaceans	LAB	LC50	MOR	MORT	5.3	16	0.36
Pteronarcys californica	Stonefly	Insects	LAB	LC50	MOR	MORT	5.6	17	0.38
Gammarus lacustris	Scud	Crustaceans	LAB	LC50	MOR	MORT	6.4	18	0.41
Macrobrachium rosenbergii	Giant River Prawn	Crustaceans	LAB	LC50	MOR	MORT	7.937254	19	0.43
Crangon crangon	Common Shrimp, Sand Shrimp	Crustaceans	LAB	LC50	MOR	MORT	10	20	0.45
Eretes sticticus	Beetle	Insects	LAB	LC50	MOR	MORT	10	21	0.48
Caridina weberi	Pugnose Caridina	Crustaceans	LAB	LC50	MOR	MORT	11.46606	22	0.50
Sigara alternata	Water Boatman	Insects	LAB	LC50	MOR	MORT	12.3	23	0.52

Species Scientific Name	Species Common Name	Species Group	Test Location	Endpoint	Effect	Effect Measurement	Conc.(μg/L)	Number	Rank
Penaeus monodon	Jumbo Tiger Prawn	Crustaceans	LAB	LC50	MOR	MORT	12.83139	24	0.55
Hyalella curvispina	Scud	Crustaceans	LAB	LC50	MOR	MORT	17.2	25	0.57
Callinectes sapidus	Blue Crab	Crustaceans	LAB	LC50	MOR	MORT	19	26	0.59
Enallagma sp.	Damselfly	Insects	LAB	LC50	MOR	MORT	21	27	0.62
Spicodiaptomus chelospinus	Calanoid Copepod	Crustaceans	LAB	LC50*	MOR	MORT	40	28	0.64
Ceriodaphnia dubia	Water Flea	Crustaceans	LAB	LC50	MOR	MORT	53.3	29	0.66
A. pharoensis	Midge	Insects	LAB	EC50	IMM	IMM	76.48627*	30	0.69
Chironomus riparius	Midge	Insects	LAB	LC50	MOR	MORT	100	31	0.71
C. pipiens	Midge	Insects	LAB	EC50	IMM	IMM	131.499*	32	0.73
Ischnura sp.	Damselfly	Insects	LAB	LC50*	MOR	MORT	144.9138	33	0.76
Culex fatigans	Midge	Insects	LAB	LC50	MOR	MORT	150	34	0.78
Moina macrocopa	Water Flea	Crustaceans	LAB	LC50	MOR	MORT	160	35	0.80
D. brachyurum	Water Flea	Crustaceans	LAB	EC50	IMM	IMM	230.1804*	36	0.83
Litopenaeus stylirostris	Blue Shrimp	Crustaceans	LAB	LC50	MOR	MORT	235	37	0.85
Daphnia magna	Water Flea	Crustaceans	LAB	LC50	MOR	MORT	356.0628	38	0.87
Potamonautes sp.	Crab	Crustaceans	LAB	LC50	MOR	MORT	360	39	0.90
Scylla serrata	Crab	Crustaceans	LAB	LC50	MOR	MORT	389	40	0.92
Daphnia carinata	Water Flea	Crustaceans	LAB	LC50	MOR	MORT	478	41	0.94
Uca pugilator	Fiddler Crab	Crustaceans	LAB	LC50	MOR	MORT	789.5	42	0.97
Oziotelphusa senex ssp. senex	Crab	Crustaceans	LAB	LC50	MOR	MORT	7748.108	43	0.99

Appendix C. All toxicity values found in the present study and the ecotox data base for diazinon with a test duration of 96 h (4d). The results of the present study are in Asterisks

Species Scientific Name	Species Common Name	Species Group	Test Location	Endpoint	Effect	Effect Measurement	Conc. (µg/L)	Number	Rank
Daphnia magna	Water Flea	Crustaceans	LAB	LC50	MOR	MORT	0.08005	1	0.02
D. brachyurum	Water Flea	Crustaceans	LAB	EC50	IMM	IMM	0.138*	2	0.05
Ceriodaphnia dubia	Water Flea	Crustaceans	LAB	LC50	MOR	MORT	0.386573	3	0.09
Chironomus tentans	Midge	Insects	LAB	LC50	MOR	MORT	0.566569	4	0.12
Cyrnus trimaculatus	Caddisfly	Insects	LAB	LC50	MOR	MORT	1.1	5	0.16
Caridina laevis	Smooth Caridina	Crustaceans	LAB	LC50	MOR	MORT	1.157734	6	0.19
C. pipiens	Midge	Insects	LAB	EC50	IMM	IMM	1.498112*	7	0.22
Paratya compressa ssp. improvisa	Freshwater Shrimp	Crustaceans	LAB	LC50	MOR	MORT	2.33	8	0.26
Palaemonetes pugio	Daggerblade Grass Shrimp	Crustaceans	LAB	LC50	MOR	SURV	2.8	9	0.29
A. pharoensis	Midge	Insects	LAB	EC50	IMM	IMM	2.93428*	10	0.33
Hydropsyche angustipennis	Caddisfly	Insects	LAB	LC50	MOR	SURV	3.676303	11	0.36
Ephoron virgo	Mayfly	Insects	LAB	LC50	MOR	MORT	3.828986	12	0.40
Hyalella azteca	Scud	Crustaceans	LAB	LC50	MOR	MORT	5.290841	13	0.43
Gammarus pseudolimnaeus	Scud	Crustaceans	LAB	LC50	MOR	MORT	5.8	14	0.47
Americamysis bahia	Opossum Shrimp	Crustaceans	LAB	LC50	MOR	MORT	5.883507	15	0.50
Ampelisca abdita	Amphipod	Crustaceans	LAB	LC50	MOR	SURV	6.6	16	0.53
Gammarus pulex	Scud	Crustaceans	LAB	LC50	MOR	MORT	7.523696	17	0.57
Attaneuria ruralis	Stonefly	Insects	LAB	LC50	MOR	MORT	16	18	0.60
Gammarus fasciatus	Scud	Crustaceans	LAB	LC50	MOR	MORT	18.43909	19	0.64
Asellus communis	Aquatic Sowbug	Crustaceans	LAB	LC50	MOR	MORT	21	20	0.67
Penaeus duorarum	Northern Pink Shrimp	Crustaceans	LAB	LC50	MOR	MORT	21	21	0.71
Baetis tricaudatus	Mayfly	Insects	LAB	LC50	MOR	MORT	24	22	0.74
Pteronarcys californica	Stonefly	Insects	LAB	LC50	MOR	MORT	25	23	0.78
Paraleptophlebia pallipes	Mayfly	Insects	LAB	LC50	MOR	MORT	44	24	0.81
Lestes congener	Damselfly	Insects	LAB	LC50	MOR	MORT	50	25	0.84

Species Scientific Name	Species Common Name	Species Group	Test Location	Endpoint	Effect	Effect Measurement	Conc. (µg/L)	Number	Rank
Chironomus riparius	Midge	Insects	LAB	LC50	MOR	MORT	61.70575	26	0.88
Amphipoda	Scud Order	Crustaceans	LAB	LC50	MOR	MORT	200	27	0.91
Litopenaeus vannamei	White Shrimp	Crustaceans	LAB	LC50	MOR	MORT	226	28	0.95
Palaemon adspersus	Baltic Prawn	Crustaceans	LAB	LC50	MOR	MORT	277	29	0.98

Appendix D. All toxicity values found in the present study and the ecotox data base for diazinon with a test duration of 48 h (2d). The results of the present study are in Asterisks

Species Scientific Name	Species Common Name	Species Group	Test Location	Endpoint	Effect	Effect Measurement	Conc.(µg/L)	Number	Rank
Ceriodaphnia dubia	Water Flea	Crustaceans	LAB	LC50	MOR	MORT	0.442442	1	0.02
Daphnia pulex	Water Flea	Crustaceans	LAB	LC50	MOR	MORT	0.65	2	0.05
Daphnia magna	Water Flea	Crustaceans	LAB	LC50	MOR	MORT	1.297053	3	0.08
Procloeon sp.	Mayfly	Insects	LAB	LC50	MOR	MORT	1.94	4	0.11
Simocephalus serrulatus	Water Flea	Crustaceans	LAB	EC50	MOR	MORT	2	5	0.14
Chironomus tentans	Midge	Insects	LAB	LC50	MOR	MORT	2.281885	6	0.17
Hydropsyche angustipennis	Caddisfly	Insects	LAB	LC50	MOR	SURV	2.9	7	0.20
D. brachyurum	Water Flea	Crustaceans	LAB	EC50	IMM	IMM	3.694266*	8	0.23
Gammarus pseudolimnaeus	Scud	Crustaceans	LAB	LC50	MOR	MORT	4	9	0.27
Simulium vittatum	Blackfly	Insects	LAB	LC50	MOR	MORT	4.91	10	0.30
Palaemonetes pugio	Daggerblade Grass Shrimp	Crustaceans	LAB	LC50	MOR	SURV	7.1	11	0.33
Cloeon dipterum	Mayfly	Insects	LAB	LC50*	MOR	MORT	7.8	12	0.36
Americamysis bahia	Opossum Shrimp	Crustaceans	LAB	LC50	MOR	SURV	9.1	13	0.39
Moina macrocopa	Water Flea	Crustaceans	LAB	LC50	MOR	MORT	10	14	0.42
Gammarus pulex	Scud	Crustaceans	LAB	LC50	MOR	MORT	10.49333	15	0.45
Ampelisca abdita	Amphipod	Crustaceans	LAB	LC50	MOR	MORT	12.64911	16	0.48
A. pharoensis	Midge	Insects	LAB	EC50	IMM	IMM	13.25707*	17	0.52
C. pipiens	Midge	Insects	LAB	EC50	IMM	IMM	17.86225*	18	0.55
Hyalella azteca	Scud	Crustaceans	LAB	LC50	MOR	MORT	18.20824	19	0.58
Baetis tricaudatus	Mayfly	Insects	LAB	LC50	MOR	MORT	55	20	0.61
Pteronarcys californica	Stonefly	Insects	LAB	LC50	MOR	MORT	66.63332	21	0.64
Paraleptophlebia pallipes	Mayfly	Insects	LAB	LC50	MOR	MORT	134	22	0.67
Orthetrum albistylum ssp. speciosum	Dragonfly	Insects	LAB	LC50*	MOR	MORT	140	23	0.70
Chironomus riparius	Midge	Insects	LAB	LC50	MOR	MORT	156.8553	24	0.73
Asellus hilgendorfii	Aquatic Sowbug	Crustaceans	LAB	LC50	MOR	MORT	250	25	0.77

Species Scientific Name	Species Common Name	Species Group	Test Location	Endpoint	Effect	Effect Measurement	Conc.(µg/L)	Number	Rank
Litopenaeus vannamei	White Shrimp	Crustaceans	LAB	LC50	MOR	MORT	255	26	0.80
Attaneuria ruralis	Stonefly	Insects	LAB	LC50	MOR	MORT	294	27	0.83
Palaemon adspersus	Baltic Prawn	Crustaceans	LAB	LC50	MOR	MORT	330	28	0.86
Gammarus lacustris	Scud	Crustaceans	LAB	LC50	MOR	MORT	338.3785	29	0.89
Orconectes propinquus	Crayfish	Crustaceans	LAB	LC50	MOR	MORT	537	30	0.92
Carcinus maenas	Green Crab	Crustaceans	LAB	LC50	MOR	MORT	100000	31	0.95
Crangon crangon	Common Shrimp, Sand Shrimp	Crustaceans	LAB	LC50	MOR	MORT	100000	32	0.98

Chapter 4

Impacts of nutrients and pesticides from small- and large-scale agriculture on the water quality of Lake Ziway, Ethiopia

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Abstract:

The area around Lake Ziway in Ethiopia is going through a major agricultural transformation with both small-scale farmers and large horticultural companies using pesticides and fertilisers at an increased rate. To be able to understand how this influences the water quality of Lake Ziway, water quality data was gathered to study the dynamics of pesticide concentrations and physicochemical parameters for the years from 2009 to 2015. Results indicate that for some physicochemical parameters, including pH, potassium and iron, over 50% of the values were above the Maximum Permissible Limit of the Ethiopian standard for drinking water. The insecticide spiroxamine poses a high chronic risk when the water is used for drinking water, while the estimated intake of diazinon was approximately 50% of the acceptable daily intake. Higher-tier risk assessment indicated that the fungicide spiroxamine poses a high acute risk to aquatic organisms, while possible acute risks were indicated for the insecticides deltamethrin and endosulfan. Longer-term monitoring needs to be established to show the water quality changes across time and space, and the current study can be used as a baseline measurement for further research in the area as well as an examplefor other surface water systems in Ethiopia and Africa.

Introduction

The current major agricultural transformation of Africa is increasing the anthropogenic sources of pollution, which are becoming a major concern for the environment (Pretty et al. 2011). One such example is the developments in the Central Rift Valley (CRV) of Ethiopia, where smallholder horticulture farmers and large-scale flower growing companies are located around Lake Ziway. The land-use records of the area for the year 2006 indicate that the area of irrigated agriculture in the Lake Ziway catchment has increased up to 5000 ha since 1973. The total area of small-scale agriculture in the Meki River catchment (situated in the catchment of Lake Ziway) has been recorded to be of the order of 7300 ha, with a sharp increase especially after the year 1999 (Jansen et al. 2007). Farmers and companies in the area use pesticides and chemical fertilisers, which may affect the water quality of the lake and the surrounding surface waters through the release of some trace elements and residues from the agricultural fields into the surface waters (Jansen and Harmsen 2011).Although in most cases, both organic and inorganic pollutants are subjected to biodegradation, biotransformation and abiotic processes that reduce concentrations in the environment, this will not be the case for contaminants like persistent organic pesticides and heavy metals. These compounds may cause damage to aquatic organisms and humans because of their bioaccumulation in the food chain and high toxicity (Van Leeuwen and Vermeire 2007).

Hence, monitoring organic and inorganic pollutants in surface waters is essential to assess their risks to aquatic ecosystems and human health. The increased use of fertilisers by smallholders and enterprises, the increased volumes of (untreated) urban waste water and the reduced outflow from Lake Ziway to the Bulbula River can cause eutrophication, which can result in turbid water, algal blooms, fish mortality, and poor quality of drinking water (Jansen and Harmsen 2011). In general, surface water is used as a source of drinking water in many rural parts of Ethiopia, so the Pesticide Risk Reduction Programme — Ethiopia (PRRP) has declared that priority should be given to the protection of Ethiopian surface waters as a source of drinking water for humans and as an important habitat for aquatic life (Teklu et al. 2015; Adriaanse et al. 2015).

In Ethiopia, this has only sporadically been done for specific water bodies for a longer period of time, mainly due to a lack of finances, skilled professionals and internationally certified laboratories. Moreover, the presence of very few nationally certified laboratories which can provide reliable results of residue analysis is hampering their publication as the societal sensitivity of the results implies that values have to be reliable.

Although a number of studies are being conducted in the Lake Ziway area catchment, most of them focussed on studying the hydro-geochemistry of waters around Lake Ziway by analysing samples from groundwater and surface waters using only a single measurement (Gashaw 1999), and on determining the Low Molecular Mass (LMM) trace element species in the Ethiopian CRV lakes including Lake Ziway (Masresha et al. 2011). Others focus on the heavy metals and organochlorine pesticides present in fish species, sediment and water samples, and the correlations between them (Nigussie et al. 2010; Dsikowitzky et al. 2012; Yohannes et al. 2014).These studies detected e.g. dichlorodiphenyltrichloroethanes (DDTs), hexachlorocyclohexanes (HCHs), chlordanes, heptachlors and heavy metals in organs of fish species in Lake Ziway.

To address the problems identified above, the present research aimed to obtain a better understanding of the water quality changes in Lake Ziway across time and space. To this end, a range of physicochemical parameters were repeatedly measured. In addition, the study monitored pesticide concentrations at several sampling points in Lake Ziway, and compared the results with previously reported pesticide concentrations in the lake. To assess the potential risks of the measured pesticide concentrations to aquatic life, a tiered risk assessment, including Species Sensitivity Distributions (SSD), was conducted. Overall, this study provides a comprehensive analysis of the water quality of Lake Ziway's and its surrounding area, which so far has been described only to a limited extent.

The objectives of this study were (i) to determine the changes in the water quality of Lake Ziway across time and space; (ii) to evaluate whether the physicochemical and nutrient values of the water samples exceed international standards for drinking water. (iii) to show the correlations between the various physicochemical parameters and their levels at the sampling locations, by performing a multivariate analysis; (iv) to examine the changes in the types and concentrations of pesticides recorded in the area and (v) to assess the risks posed by pesticides to aquatic organisms and to the use of the surface water as drinking water.

Materials and methods

Description of the study area

The study was conducted at Lake Ziway, which is located in the CRV zone of Ethiopia (Fig. 1). It is situated in the East Showa zone of the Oromia region at about 160 km from Addis Ababa. Lake Ziway has an open water area of 434 km^2, with an average depth of 4 m, and an elevation of 1636 m above sea level. The Ziway Catchment is situated in between 7°15'N to 8°30'N latitude and 38°E to 39°30'E longitude, covering a total area of about 7300 km^2 (Hughes and Hughes 1992). The lake has flat swampy margins on all sides except the south and south-west, and is fed by many streams. The two main rivers, Meki and Ketar, flow into the lake, while one river, Bulbula, flows out of the lake (Jansen et al. 2007). Horticultural industries are situated between Lake Ziway and the main highway, at altitudes ranging between 1600–1700 m above sea level (Sahle and José 2013).

Sample collection

Under close supervision and facilitation by HoA-REC&N, the sample collection and analysis of physicochemical parameters by the nationally certified laboratory of Horticoop Ethiopia started by mid-2013 and continued until the beginning of 2015, once a month. During this period samples were collected with the assistance of the local research institutions. At first, samples were collected from 13 locations, and this number increased to 18 between October 2014 and February 2015 (Fig. 1). The number of sampling locations was increased to better describe the spatial variability of the water quality parameters. In addition, seven samples were taken for pesticide residue analysis in August 2014 and March 2015, very close to the sampling locations used in previous research by Jansen and Harmsen (2011) (Fig. 1). Pesticide samples were shipped to Altic B.V. (NEN-EN-ISO/IEC 17025 accredited laboratory) in the Netherlands for pesticide residue analysis. Samples were preserved by adding 1 mL of acid, placed in a deepfreeze container and shipped in accordance with the US-EPA protocol for shipping and sample submission procedures for analytical services (US-EPA 2014). The commercial flower farms are expected to be characterised by a year-round nutrient load, whereas on the small-scale irrigated farms, high nutrient loads are expected between February and April and between June and October.

Grab sampling technique was used for all sampling activities (Forrest 2000). The containers were cleaned with distilled water and rinsed two to three times with water at the sampling point before the sample was taken. The collected water was thoroughly mixed and checked to see if all organic matter such as leaves, rags, twigs and other floating materials had been removed. All collected 1 L samples were placed in a labelled sample container and stored in a refrigerator at 4°C.

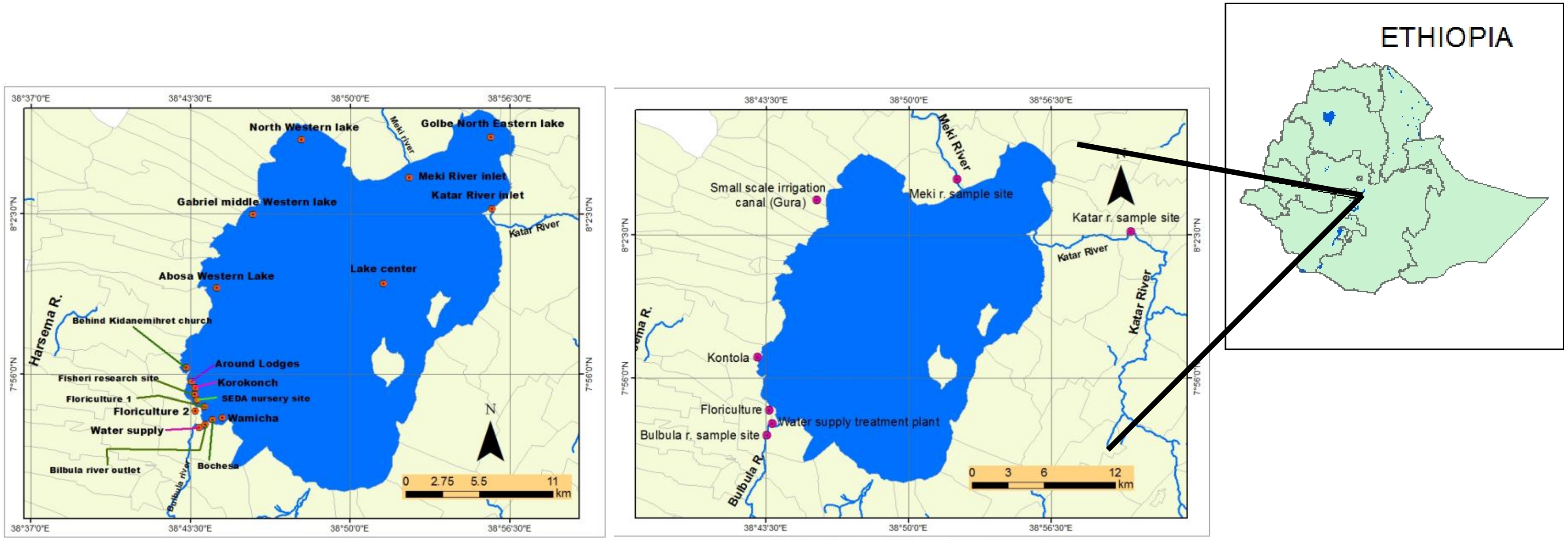

Fig. 1 Physicochemical parameter and pesticide sampling points Lake Ziway.

Physiochemical properties and pesticide residues

At Horticoop Ethiopia, the nutrients N, Ca, Mg, Na, S, P, Si, Cu, B, Fe, K, Mn, Mo and Zn concentrations were measured simultaneously using an optimised and frequently calibrated device for inductively coupled plasma analysis. Chloride was analysed by titration against $AgNO_3$ solution and by weighing the precipitated chloride, bicarbonate was analysed by titration of the sample with HCl solution,ammonium-nitrogen and nitrate-nitrogen (NH4+N, NO_3-N) were analysed by spectrophotometric analysis (Janway 63 UK 2009) and pH and electrical conductivity (EC) were measured by direct reading in the water sample using an electrode pH meter (pH 06, Holland 2006) and an EC Meter (EC 93 Holland 2010). All samples were filtered through a Whitman No 42 filter paper before further analysis was done. Samples sent to the Dutch lab (Altic B.V.) were analysed for more than 300 pesticide residues. Samples were extracted using dichloromethane and petroleum ether, while analysis was performed using standard GC-ECD, GC-MS/MS and LC-MS/MS techniques (Chauhan et al. 2014; Adeyemi et al. 2011; Pitt 2009).

Data analysis

The Ethiopian Maximum Permissible Limits (MPL) as listed by Ministry of Health (MoH, 2011) and the World Health Organisation (WHO, 2010) were used to identify those physicochemical parameters which exceeded the MPL. A multivariate analysis was done to assess the variation in the values of the physicochemical parameters across time and space (Van den Brink et al. 2003a). To this end, a redundancy analysis (RDA) was performed using the measured physicochemical parameters as response variables, while using the sampling locations and sampling dates as explanatory variables. The significance of the explanatory variables was evaluated by a Monte Carlo permutation test following the RDA. More information on the interpretation of RDA-derived biplots can be found in Van den Brink et al. (2003a).

Pesticide concentrations were available for four sampling dates. Data from two sampling dates in 2009 and 2010 was taken from Jansen and Harmsen (2011), while the 2014 and 2015 data was collected for the present study. Pesticide residues detected in each sampling period were first used to determine the acute exposure toxicity ratio (ETR) using predicted no-effect concentrations (PNECs) based on acute values for fish, daphnia, and algae for each detected pesticide, as described in Teklu et al. (2015) and Wipfler et al. (2014), and are given below in (eqs. 1-3). The ETR was computed by dividing the measured concentration by the PNEC, using the maximum value of concentrations and the minimum value of the three PNECs for risk (ETR) calculation. SSDs and HC5 (hazardous concentration protective of 95% of the population) concentrations were determined using acute toxicity data for additional species from the US-EPA database (www.epa.gov/ecotox) and the ETX 2.0. software (Van Vlaardingen et al. 2003). In the second-tier risk assessment the HC5 values were used as PNEC values, following the recommendations by Maltby et al. (2005; 2009) and Van den Brink et al. (2006) for short-term exposure. For insecticides, the 1–7 days EC50 arthropod data was included in the SSD. The SSDs of the fungicides included 2–21 days EC50 data for vertebrates, 1–7 days EC50 data for invertebrates, 2–28 days EC50 data for macrophytes and 1–7 days EC50 data for algae (Maltby et al. 2005 and 2009; Van den Brink et al. 2006). In case more than one value was available for a species, the geometric mean of the available values was used. Human health risk assessment was carried out for pesticides exceeding the EU's threshold level for drinking waters of 0.1 µg/L (Dolan et al. 2013). Risks to humans was determined using the highest detected concentrations. Chronic and acute health risks were calculated using acceptable daily intake (ADI) and acute reference dose (ARfD) values, respectively. Estimated short term intake (ESTI) and the internationally estimated daily intake (IEDI) values were determined to indicate acute and chronic risks to humans from drinking surface water as a source of drinking water. Back ground calculation formulas are given in Teklu et al. (2015), Wipfler et al. (2014) and Adriaanse et al. (2015) and eq. (1). Risks were categorised as ETR < 1: negligible to low risk; 1 < ETR < 10: possible risk and ETR > 10: high risk to aquatic organisms, and as ESTI or IEDI > 100%: high risk and ESTI or IEDI < 100%: low to negligible risk for humans assuming surface water is used as a source of drinking water.

$$\mathrm{IEDI} = \frac{\mathrm{DI} \times P_{concentration}}{\mathrm{ADI} * Fdw \times \mathrm{BW}} \ 100\% \qquad \text{eq.(1)}$$

With: IEDI = internationally estimated daily intake, expressed as % of the total acceptable intake of the pesticide during a lifetime (%); DI = daily intake (L/d); $P_{concentration}$ = measured highest Pesticide concentration in (µg/L); ADI = acceptable daily intake, expressed in µg pesticide per kg BW per day (µg/kg*d); Fdw= fraction of ADI allocated to drinking water (-) and BW = body weight (kg). BW was set at 60 kg, DIat 2 L/d and the fraction of ADI allocated to drinking water at 0.1 for Ethiopia.

Results and discussion

Physicochemical parameters

Table 1 summarises the maximum, minimum and average values of all measured physicochemical parameters. The column headed 'Percentage of values above the MPL' shows that more than 50% of collected samples exceeded the MPL for the following parameters: pH (59%), potassium (87%) and iron 100%); while less than 10% of the observed values exceeded the MPL for the parameters EC, ammonium, nitrate and boron (7%), sodium (6%) and manganese (1%). All observed values for calcium, magnesium and chloride were below the MPL. The amounts of phosphorus, zinc, copper and molybdenum found in this study were either zero or too low to be detected (<0.01 mg/L) so they can be considered to be below the MPL even though no specific value was available. They can therefore be considered as posing no risk to human health (Table 1). The RDA biplot (Fig. 2) displays the temporal and spatial variation of the nutrients and physicochemical parameters. It appears that the sampling point at the Bulbula River had a high correlation with the vertical axis, which explains 20% of the variation among the physicochemical parameters, while the horizontal axis, where floriculture 1, the main liquid waste outlet point of the floriculture area, had a high correlation, explains 34% ($p < 0.01$). These results are in line with recorded changes in land-use, which show that the numbers of both commercial (floriculture, horticulture and viticulture) and irrigated small-scale farming activities are increasing rapidly in the Lake Ziway catchment and its surrounding area. The accompanying contamination of the lake and other water bodies as a result of the use of intensive agriculture inputs like fertilisers may pose risks to human health when the water is used as drinking water (Jansen et al. 2007).

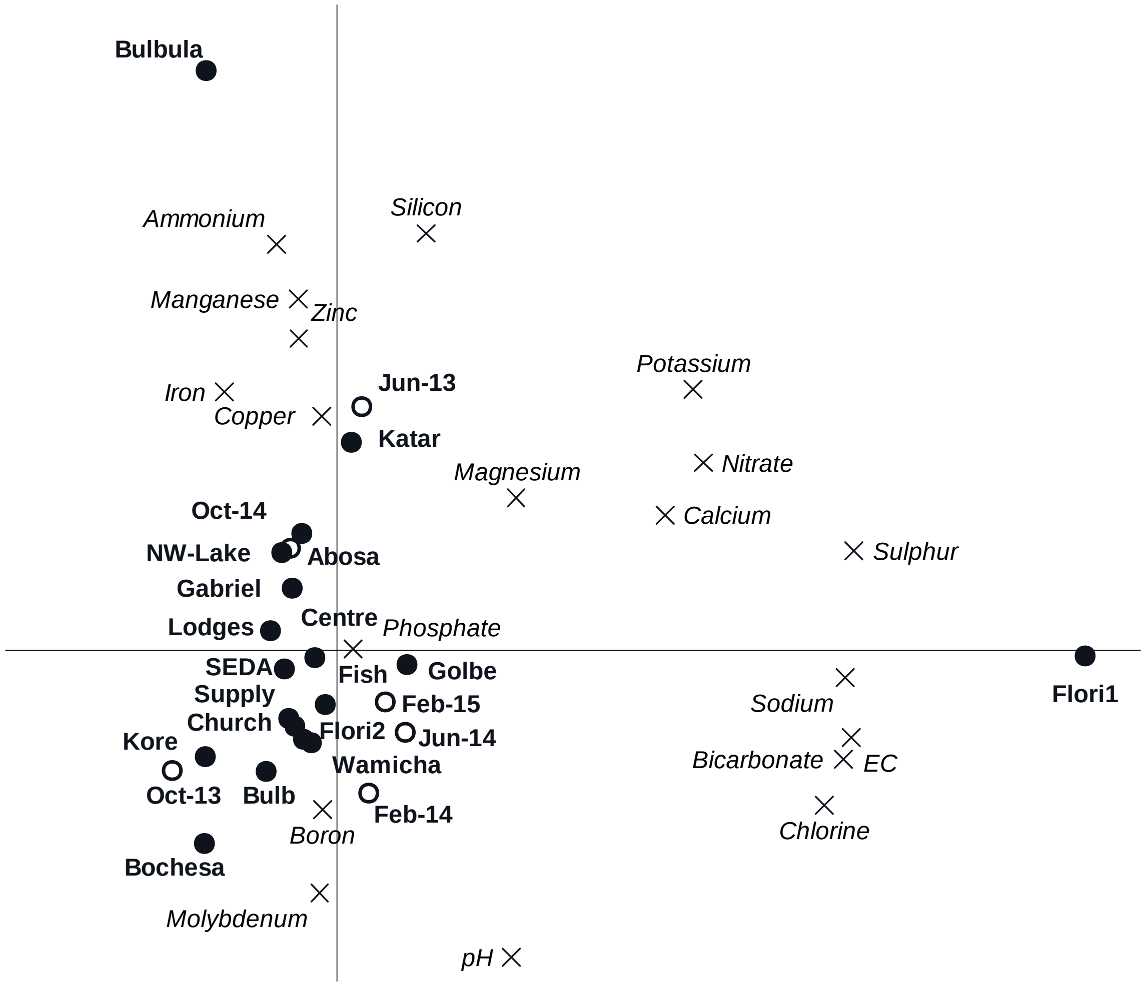

Fig. 2 RDA biplot showing the correlations between sampling date and site and the physicochemical parameters. Sampling date and site explained a significant part of the variation in physicochemical parameter values (44%; p = 0.01) levels. Of this variation, 34% is displayed on the horizontal axis and another 20% on the vertical axis. See Fig. 1 for locations of sampling points.

Previous research results on the Lake Ziway and CRV area indicated that the percentages of measurements exceeding the MPL where 13% for pH and 1% for EC, while 28% of the iron levels were reported to exceed the MPL (Reimann et al. 2003). The single measurement values of pH (8.5) and EC (463 μS/cm) reported in Gashaw (1999) are comparable to the mean results obtained in this study of 8.5 and 474 μS/cm, respectively. Further comparison of these values with a study done in a Kenyan Lake shows that the pH and EC values there were within the WHO (Ethiopian) Maximum Permissible limits for pH (7.5-8.5) and EC (566-601 μS/cm) (Ouma and Mwamburi 2014). In the present study, higher EC values were found for sampling points near the floriculture area (Fig 2). In an aquatic environment, EC is an important and simple indicator to characterise the pollution status of surface waters, as a sudden increase in conductivity can indicate the presence of more dissolved ions, which may have an impact on aquatic life and water quality.

Table 1 Results for physicochemical and nutrient parameters in this study: (n): number of observations, Min: Minimum value, Mean: Mean of all observations, Max: Maximum value, Ethiopian (WHO) MPL: Ethiopian Maximum Permissible Limits for drinking water as listed in MoH (2011) and WHO (2010), which are similar.

Nutrient/physicochemical parameter	(n)	Min.	Mean	Max.	Ethiopian (WHO) MPL	% of values above MPL
pH (-)	87	7.6	8.5	9.0	6.5-8.5	59
EC (µS/cm)	87	140	474	1740	1000	7
Ammonium (NH_4^+; mg/L)	87	0.01	0.64	3.1	1.5	7
Nitrate(NO_3^-; mg/L)	87	0.06	26	296	50	7
Phosphorus (mg/L)	87	<0.01	<0.01	<0.01	NA	<MPL
Potassium (mg/L)	87	0.33	14	53	1.5	87
Calcium (mg/L)	87	0.43	18	39	75	<MPL
Magnesium (mg/L)	87	0.38	8.1	29	50	<MPL
Sodium (mg/L)	87	3.2	72	337	200	6
Sulphur (mg/L)	87	0.09	3.8	20	NA	NA
Chloride (mg/L)	87	0.35	15	38	250	<MPL
Bicarbonate (mg/L)	87	3.9	257	704	NA	NA
Silicon (mg/L)	87	0.53	18	81	NA	NA
Iron (mg/L)	87	0.06	2. 6	29	0.3	100
Manganese (mg/L)	87	<0.01	0.033	0.90	0.5	1
Zinc (mg/L)	87	<0.01	<0.01	<0.01	5	<MPL
Boron (mg/L)	87	<0.01	0.22	5.7	0.3	7
Copper (mg/L)	87	<0.01	<0.01	<0.01	2	<MPL
Molybdenum (mg/L)	87	<0.01	<0.01	<0.01	NA	<MPL

Pesticide detection

The pesticide residue analysis, including the results from the earlier study by Jansen and Harmsen (2011), indicated that overall detections of pesticides showed an increasing trend across the sampling years, but decreased in final year of our study, with lower amounts of pesticides detected in 2015 (Fig. 3). Relatively few different types of pesticides were detected in the Meki and Ketar rivers, Bulula and water supply treatment plant areas, while the floriculture area had the highest total number of detections of pesticides, followed by Kontola and Gura (Fig. 3). High detection results are ascribed to the growing trend towards land-use change on the small- and large-scale farms in the vicinity (Jansen et al. 2007). The environmental impact from the expansion of large-scale flower farms in Ethiopia in general and around Lake Ziway area in particular is of major concern for many environmentalists (Getu 2009). The trend towards increasing use of pesticides in the small-scale irrigated area as the sole pest management technique in the CRV also caused the high residue detections in the Kontola and Gura areas until the year 2014. This was shown by a survey conducted by the Pesticide Action Network- United Kingdom (PAN-UK) on the pesticide use and management by small-scale farmers in the CRV of Ethiopia. The survey found that 97% of respondents reported using pesticides once or twice a year, and about 91% of the farmers who were interviewed prepared their pesticides close to water sources used by local people for drinking, cooking and other household purposes. 61% of the respondents washed their pesticide sprayers and other equipment on the farm field (PAN-UK, 2006). The decreasing number of detections in the floriculture area in the years 2014 and 2015 might be associated with the recent innovations in liquid waste management. Flower farms are increasingly adopting mechanisms to minimise the environmental impacts of pesticides in the surrounding surface water systems, e.g. by constructing soakaway pits and wetlands to meet the standards of fair trade as a sustainable certified flower producer (Teklu et al. 2015).

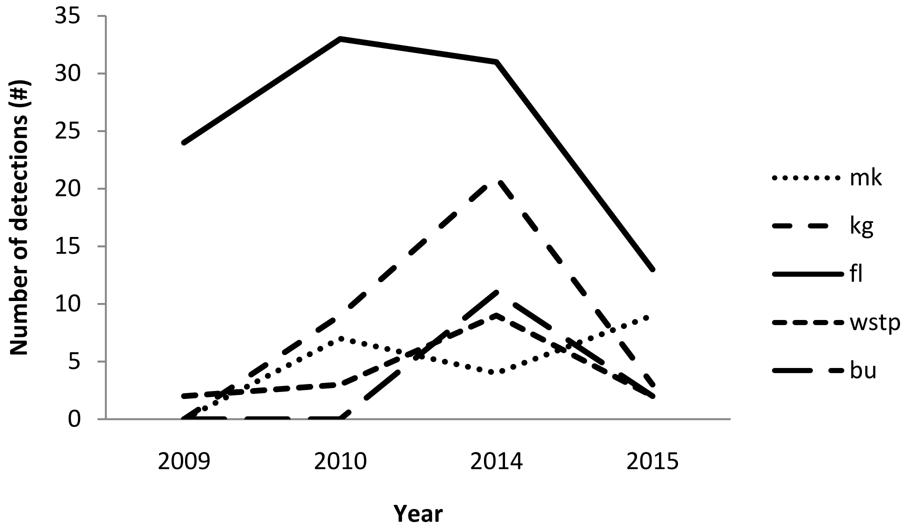

Fig. 3 Numbers of detections over the years of sampling at different sampling locations. Note: mk = Meki and Ketar rivers; kg = Kontola and Gura.; fl = floriculture ; wstp = water supply treatment plant; bu = Bulbula. Note that values for 2009 and 2010 are taken from Jansen and Harmsen (2011).

Detection of DDT was reported by the earlier Jansen and Harmsen (2011) study, though no DDT was detected in the samples taken by HoA-REC&N. Small amounts of other pesticides found in the earlier study may be a result of the dilution and decay of pesticides in oxygen-rich river waters (Jansen and Harmsen 2011).

Acute risks of pesticides to aquatic organisms

The results of the first tier-risk assessment (Table 2) show that chlofentezin,sulphur, spiroxamine and methomyl pose a high acute risk to aquatic organisms, with highest ETR values of 13, 11, 190 and 36, respectively. The table shows that the first-tier risk assessment based on PNEC values indicates higher risk values than the ETR based on HC5 values. This is consistent with the principles of the tiered approach, i.e. greater realism and less conservatism at higher tiers (Brock et al. 2006; Wheeler et al. 2002). There are, however, two exceptions, viz. spiroxamine and endosulfan. The lower and upper limits of HC5 and HC50 and the number of data points on which the SSD was based are provided as (Appendix A)

Model-based risk assessment of pesticides in surface waters in Ethiopia indicates that endosulfan is predicted to pose high risks in lowland ponds in Ethiopia (ETR 32, with a PEC of 0.63 µg/L); while deltamethrin is predicted to pose only a possible risk (ETR = 2.5, with a PEC of 0.0066 µg/L) (Teklu et al. 2015). Although there are many explanations for this difference in concentrations, the most obvious one is the fact that the predicted values represent the 90th percentile of the 33-year predicted environmental concentration (PEC) values just after application (Adriaanse et al. 2015; Teklu et al. 2015), while a measured value is just the outcome of an ordinary measurement not necessarily taken close a pesticide application in space and time. In our study, the highest risk quotient for aquatic organisms for endosulfan was ETR 2.9, with the highest measured concentration (0.14 µg/L) found in the area of the Meki and Ketar rivers, while the highest measured concentration of deltamethrin, with an ETR of 4.1, was found at the water supply treatment plant, with a measured concentration of 0.01 µg/L; both are in the possible risk category (Table 2).

The overall acute risk assessment for aquatic organisms based on HC5 values indicates high risk values for the locations Kontola and Gura (spiroxamine: 317), floriculture (spiroxamine: 22) and Bulbula (spiroxamine: 38), based on a stricter risk category (ETR > 10) (Table 2). Spiroxamine is a fungicide which has been authorised for the control of the powdery mildew infestation that prevails in flowers in Ethiopia, and which is also used in most European countries. Spiroxamine has a short half-life in the water phase (0.8 d). Algae are most sensitive to spiroxamine, followed by invertebrates and fish (Lewis et al. 2016; PHRD 2015). Though no data is available to compare the amounts and frequency of use of this fungicide in small- and large-scale farms, it is probable that a high risk is associated with the frequent use of this pesticide for fungal disease control in the area (Table 2).

Table 2 Risks to aquatic organisms calculated from 1st tier PNEC values (µg/L) and 2nd tier SSD HC5 values (µg/L). Only pesticide – location combinations with a first tier ETR > 1 are included in the table.

Pesticides	Location	year of highest detection	Maximum concentration (µg/L) (n = 4)	PNEC 1st tier	ETR 1st tier	SSD HC5	ETR SSD
Sulphur	mk	2010	7.0	0.63	11	690	0.01
Endosulfan	mk	2014	0.14	0.10	1.4	0.05	2.9
Diazinon	kg	2014	0.28	0.10	2.8	0.51	0.55
Dodemorph	kg	2014	32	22	1.5	NA	NA
Lufenuron	kg	2014	0.080	0.01	6.2	NA	NA
Spiroxamine	kg	2014	57	0.30	190	0.18	317
Sulphur	kg	2010	3.0	0.63	4.8	690	<0.01
Teflubenzuron	kg	2014	0.03	0.03	1.1	0.47	0.07
Methomyl	fl	2009	2.7	0.08	36	11	0.26
Spiroxamine	fl	2009	4.0	0.30	13	0.18	22
Teflubenzuron	fl	2014	0.05	0.03	1.8	0.47	0.10
Trifloxystrobin	fl	2010	0.34	0.15	2.3	1.3	0.27
Carbendazim	fl	2009	9.1	1.5	6.1	19	0.48
Chlofentezin	fl	2010	0.10	0.01	13	NA	NA
Deltamethrin	wtp	2014	0.01	<0.01	3.8	<0.01	4.1
Diazinon	wtp	2014	0.41	0.10	4.1	0.51	0.80
Endosulfan	wtp	2014	0.10	0.10	1.0	0.05	2.1
Lufenuron	wtp	2014	0.02	0.01	1.4	NA	NA
Pyraclostrobin	wtp	2015	0.06	0.06	1.0	0.35	0.18
Sulphur	wtp	2010	10	0.63	16	690	0.01
Teflubenzuron	wtp	2014	0.08	0.03	2.9	0.47	0.17
Spiroxamine	bu	2014	6.9	0.30	23	0.18	38

Note: ETR <1 : negligible/low risk; ETR > 1 : possible risk; ETR > 10 : high risk; mk = Meki and Ketar rivers kg = Kontola and Gura.; fl = floriculture ; wtp = water supply treatment plant; bu = Bulbula.NA: not available.

Human risk assessment

The human risk assessment was performed for values exceeding the European 0.1 µg/L standard (Table 3), and indicated that no acute risk to humans is present when the surface water is used as a source of drinking water (Table 4). This result is in line with Teklu et al. (2015), in which seven registered pesticides were evaluated using model-based risk assessment, and all were found to pose low or negligible acute risks to human health. The fungicide spiroxamine poses a high chronic risk to humans while the insecticide diazinon has the second highest IEDI value (47%), followed by methomyl (36%) and metalaxyl (25%) (Table 4). It is unknown whether pesticides with values above 10% will pose a risk when exposure through other food sources than water are also taken into account. Further investigation is required to assess the presence of high risk in combination with other food sources for the Ethiopian case, in order to get an overall risk estimation for these pesticides (Van den Brink et al. 2003b; Teklu et al. 2015).

Table 3 Measured pesticides concentrations above 0.1 µg/L (data from this paper and from Jansen and Harmsen 2011)

Location	**#>EU 0.1µg/L**	**pesticide with the highest score**	**pesticide with the lowest score**	**max value** (µg/L)	**min value** (µg/L)
Meki and Ketar	7	Metalaxyl	Endosulfan	59	0.095
Kontola and Gura	9	Spiroxamine	Cyprodinil	57	0.11
Floriculture	33	Boscalid	Clofentezine	13	0.17
Water supply treatment plant	4	Sulphur	Endosulfan	10	0.061
Bulbula	4	Spiroxamine	Buprofezin	6.9	0.081

Examination of the number of detections indicates that the locations Kontola and Gura, and floriculture had the highest numbers of pesticide detections (Fig. 3). The fungicides metalaxyland spiroxamine reported the highest concentrations, 59 and 57 µg/L, respectively (Table 3). Metalaxyl is a registered fungicide sold as Folio Gold 537.5 SC for the control of botrytis and downy mildew in flowers in Ethiopia and in some parts of European countries as well (Lewis et al. 2016; PHRD 2015).

Table 4 Acute and chronic human risk assessment results.Data is presented only for pesticide – location combinations with an IEDI values above 10%.

Location	Compound	PEC (µg/L)	ARfD (mg/kgbw/d)	ADI (mg/kgbw/d)	ESTI (%)	IEDI (%)
Meki and Ketar	Metalaxyl	59	0.5	0.08	1.2	25
Kontola and Gura	Diazinon	0.28	0.025	0.0002	0.11	47
	Dodemorph	32	0.33	0.082	0.97	13
	Spiroxamine	57	0.1	0.015	5.7	127
Floriculture	Boscalid	13	NA	0.04	NA	11
	Methomyl	2.7	0.0025	0.0025	11	36
	Carbendazim	9.1	0.02	0.02	4.6	15
Bulbula	Spiroxamine	6.9	0.1	0.015	0.69	15

Conclusion and recommendations

Comparison of our findings with local and international standards indicates that some physicochemical parameters and nutrients exceeded the local and international standards in more than 50% of the cases. The results of our multivariate analysis indicate that the Bulbula outlet and the floriculture outlet are important sources of the variation in some of the physicochemical parameters in this study. These are places reported in an earlier land-use study as undergoing major land-use changes as regards commercial and small-scale irrigated agriculture.

The numbers of pesticide detections in this study and the amounts detected show a decreasing trend relative to the findings reported by Jansen and Harmsen (2011). This result is encouraging for further liquid waste management activities in the small and large scale farming activities in the area. Moreover, only one pesticide was found to pose a high acute risk to aquatic organisms (spiroxamine), while endosulfan and deltamethrin were found to pose a possible risk. All the pesticides pose no or negligible acute risk to humans if surface water is used as a source of drinking water while high chronic risk is expected from spiroxamine.

Some pesticide sampling points are located outside Lake Ziway, but these points are in direct water contact with the lake, so they can contaminate the sampling points at the edge of the lake.

Even though it is believed that the overall dilution factor of the lake will reduce the concentration within the lake, maximum care should be taken in controlling liquid farm wastes on both the small- and large-scale farms. This requires constant interventions in liquid waste management in these areas. Commercial horticultural farms that produce vegetables and cut flowers need to develop or improve the use of mechanical and biological pest management techniques to reduce the use of synthetic chemicals. Together with the relevant authorities, they should extend their best practices for safe ecological pest management and their successful waste water control and treatment experiences to the surrounding small-scale horticulture farms, while waste coming from the commercial farms must also be regularly assessed.

Further investigations should focus on refining the results of this study and further investigating the dynamics of pesticides and physicochemical parameters and their exceedance of the Maximum Permissible Limits of the Ethiopian standard, or the exceedance of the EU 0.1 μg/L standard in the case of pesticides. The chronic risk to humans and aquatic organisms also needs to be assessed, as some of the pesticides may be used regularly. Future studies should also consider studying the ecological risk due to mixtures of pesticides. Planning a continuous monitoring campaign together with all stakeholders concerned, including commercial and small-scale farmers and governmental and non-governmental organisations is important to ensure sustainable water quality in the Ziway Lake catchment.

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Appendices for Chapter 4

Appendix A. HC5/HC50 values and the lower and upper limits of HC5 and HC50 values

Pesticides	#of data points	HC5 (μg/L)	LL HC5 (μg/L)	ULHC5 (μg/L)	HC50 (μg/L)	LLHC50 (μg/L)	ULHC50 (μg/L)
Sulphur	7	6.90E+02	2.91E+00	9.87E+00	2.02E+05	1.83E+04	2.24E+06
Endosulfan	37	4.83E-02	1.15E-02	1.15E-01	6.25E+00	2.77E+00	1.41E+00
Diazinon	34	5.06E-01	1.88E-01	1.07E+00	1.23E+01	7.04E+00	2.15E+01
Spiroxamine	8	1.80E-01	6.97E-04	3.19E+00	1.19E+02	9.50E+00	1.50E+00
Teflubenzuron	6	4.69E-01	1.08E-03	7.10E+00	1.07E+02	8.35E+00	1.38E+03
Methomyl	21	1.06E+01	3.69E+00	2.19E+01	1.29E+02	7.34E+01	2.27E+02
Trifloxystrobin	12	1.27E+00	2.24E+01	3.62E+00	2.12E+01	8.94E+00	5.01E+01
Carbendazim	11	1.91E+01	1.45E+00	8.63E+01	9.52E+02	2.70E+02	3.36E+03
Deltamethrin	12	2.43E-03	2.73E-04	9.07E-03	8.39E-02	2.83E-02	2.48E-01
Pyraclostrobin	14	3.49E-01	2.89E-02	1.67E+00	3.13E+01	8.85E+00	1.11E+02

Chapter 5

Monitoring and risk assessment of pesticides in irrigation systems in Debra Zeit, Ethiopia.

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Abstract

Since Ethiopia is going through a rapid transformation of its agricultural sector, the growing use of pesticides may pose increasing risks to the environment and human health. In order to assess the environmental and human health risks of the current pesticide use as well as the legacy risks due to the past use of organochlorine pesticides (OCPs), a monitoring programme and risk assessment was carried out for the Wedecha-Belbela irrigation system in the Debra Zeit area. The Wedecha and Belbela rivers and adjacent temporary ponds were sampled and examined for the presence of OCPs between August and October 2014, while data on the current pesticide use by small- and large-scale farmers was collected by interviews. The usage patterns were evaluated for risks to adjacent aquatic ecosystems and for the use of these ecosystems as a source of drinking water, using the PRIMET_Registration_Ethiopia_1.1 model. Samples for OCP detection were collected from three pre-identified river sites and temporary ponds representing the upstream, middle and downstream sections of the irrigation system. The samples were collected in five sampling periods, which were chosen to represent different crop development stages as well as seasonal variations in the study area. Results indicate that most of the 18 target OCPs were not detected above the detection limit, while heptachlor epoxide (isomer B) and g-chlordane may pose chronic risks when surface water is used as drinking water. Endosulfan and g-chlordane pose high risks to aquatic organisms at first-tier level. Calculated acute risks to humans for all nine pesticides used by small-scale farmers were low. Current pesticide use data by small-scale farmers in first- and second-tier risk assessment indicated that lambda-cyhalothrin, endosulfan, profenofos, and diazinon may pose a high risk to aquatic organisms.

Introduction

Due to the ongoing agricultural transformation in Ethiopia, the impact of pesticides on human health and the environment has recently become a major concern (Teklu et al., 2015). In such a dynamic era, it is important to evaluate the risks caused by the legacy use of hazardous substances like organochlorine pesticides (OCPs), as well as assessing the risks of current pesticide use to human health and the environment in locations with past and current use of pesticides, like the Wedecha-Belbela irrigation system in Ethiopia. The use of OCPs has been banned or partially restricted in developed nations, but they are still being used for agricultural and public health purposes in developing countries, including for the control of agricultural pests as well as mosquitoes (Westbrom et al. 2008; Safford and Jones 1997; Wei et al. 2007). Although most OCPs are banned from Ethiopian agriculture following the enforcement of the Stockholm convention in 2004 (Fiedler et al. 2013), DDT has been used for indoor spraying purposes in malaria control. Illegal use to control agricultural pest controls has, however, been reported on various occasions, and endosulfan is widely used for insect pest control in vegetables, even though it is registered only for controlling pests in cotton (Mengistie et al. 2015).

It is therefore important to evaluate the risks of current environmental concentrations of OCPs, as they are among the serious pollutants of global concern (Tenabe et al. 1994). They are known for their environmental persistence, their ability to bioaccumulate and biomagnify in the food chain, and their chronic toxicity to wildlife and humans. Hence, OCPs are categorized among the POPs (persistent organic pollutants), an example of which is DDT, which stays in the environment for a long time (4-30 years). Other chlorinated pesticides share this persistence due to their resistance to biochemical degradation once released into the environment (Elvira et al. 2011; Jones and De Voogt 1999). The impacts of OCPs on human and animal health include failure of the reproductive system and increased cancer risk (Perry et al. 2015; Bouman 2004), immune system malfunction (Repetto and Baliga 1996), endocrine disruption (Mnif et al. 2011), pancreatic cancers (Andreotti et al. 2009) and breast cancers (Olaya - Contrras et al. 1998).

Monitoring the amounts of OCPs in different environmental matrices including water is important, since the assessment of the risks posed by these highly controversial pesticides to the environment and human health has to be based on scientific research. According to the EU guidelines the allowable residual limit concentration of OCPs in drinking water is 0.1µg/L (Jansen and Harmsen 2011). Little work has been done on monitoring the residues of OCPs in surface waters in Ethiopia, and most of the studies have concentrated on evaluating the OCP and heavy metals residue levels in big Rift valley lakes like Ziway and Hawasa, focusing on quantifying the residue levels in fish (Abayneh et al. 2003; Dsikowitzkyet al. 2012; Yohannes et al. 2013). Some other studies in Africa examined the status of organochlorine pesticides in freshwater systems, and detected a number of OCPs in water samples (Awofolu and Fatoki 2003; Adeyemi et al. 2011).

The current use of pesticides in Ethiopia has been surveyed at local and national level. National level (2000- 2010) data showed that the average import of pesticides has now grown to over 2400 tonnes per annum, with an overall increasing trend and with herbicides making up the lion's share (www.prrp-ethiopia.org). At local level, a survey of pesticide use conducted by FAO in the Dugda and Ada districts found that small-scale farmers were using higher application frequencies than commercial farmers in the same area. In addition, mismanagement in handling, transporting, storing and applying pesticides has been reported (FAO, 2012 unpublished). In a similar survey undertaken by the Pesticide Action Network-United Kingdom (PAN-UK) on pesticide use and management by small-scale farmers around the Central Rift Valley, Ethiopia, 97% of the respondents reported using pesticides once or twice a year, and about 91% of them prepared their pesticides close to water sources used by local people for drinking, cooking and other household purposes, while 61% washed their pesticides sprayers and other equipment on the farm field (PAN-UK, 2006). A similar study indicated that farmers applied pesticides in violation of standard recommendations, used unsafe storage facilities, ignored risks and safety instructions, did not use protective devices when applying pesticides and disposed of containers unsafely. The same study found that 74% of the farmers mixed their pesticides close to a river and that 96% did not know that pesticides can cause damage to water bodies, while 88% indicated an increase in their pesticide use in the past 5 years (Mengistie et al., 2016).

Objectives of the present study were to (i) assess the current OCP residue levels in the Wedecha-Belbela irrigation system, (ii) quantify the risk posed by the OCPs to humans and aquatic organisms, (iii) determine the risks from actual pesticide use by small-scale farmers at the Wedecha-Belbela irrigation system using the PRIMET-Registration_Ethiopia_1.1 model (Wipfler et al. 2014), and (iv) compare actually measured concentrations of endosulfan with predicted environmental concentration (PEC) values obtained with the PRIMET-Registration_Ethiopia_1.1 model.

Materials and Methods

The study area

The study area is located in the Oromia region, Debra Zeit, some 55 km south of Addis Ababa. The Wedecha-Belbela irrigation system is situated in this area, where elevation ranges from 1,895 m at the downstream end of the irrigation system to 2,437 m in the upstream highlands. It has an average annual rainfall of 815 mm, and annual average minimum and maximum temperatures of

10.5 °C and 25.4 °C, respectively. The irrigation system is dominated by small-scale farmers in the upstream and middle sections, while small-scale and afew medium-scale vegetable farms and commercial flower greenhouses concentrate in the downstream part of the system (Michael and Seleshi 2007)(Fig 1). Farms in the area are mostly 1 to 3 ha in size. The main production period is between June and December, during which the crops receive both rainfall and irrigation water. Major crops in the area include vegetables (cabbage, tomato and onion) while only a few farmers grow cereals.

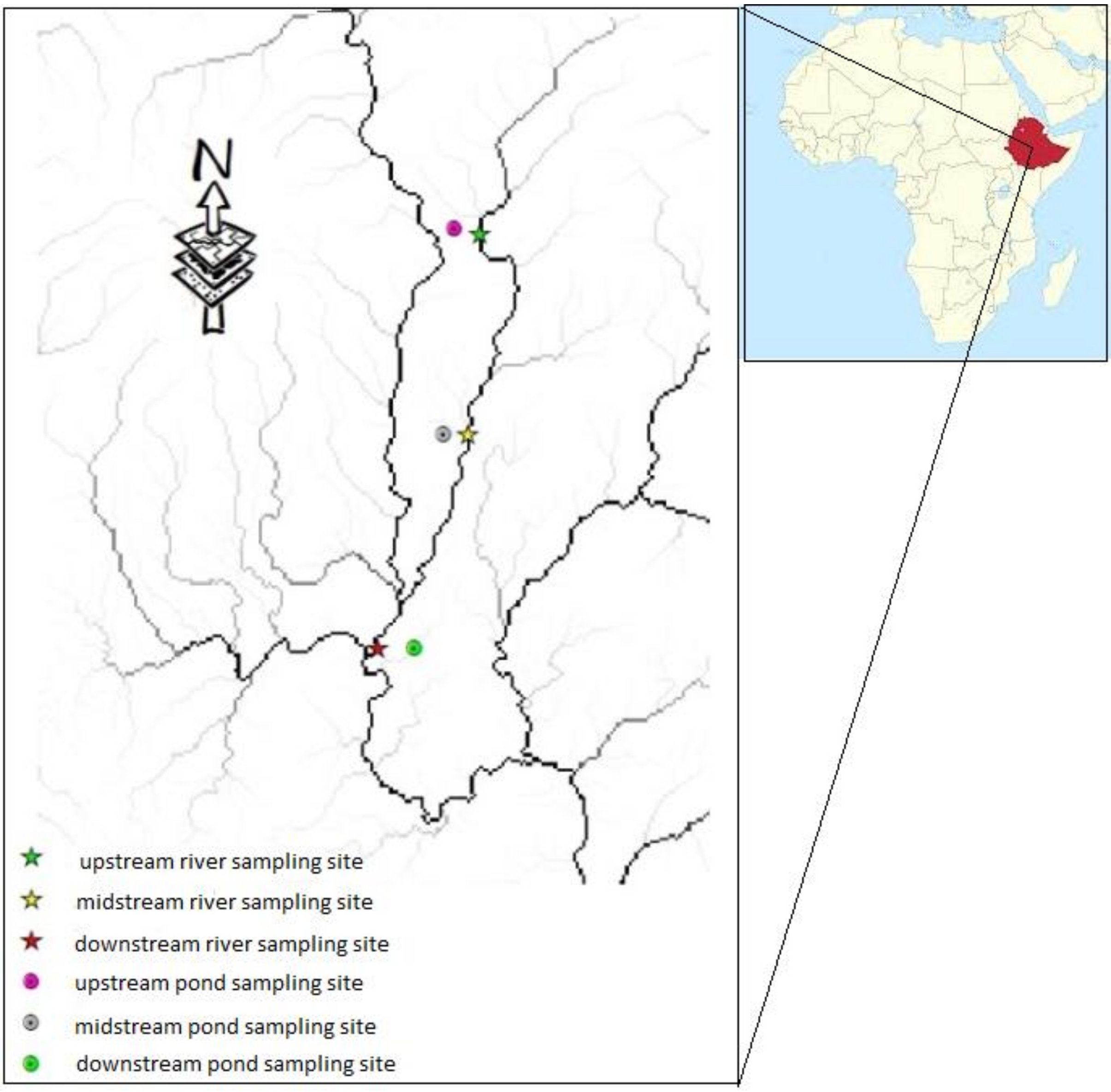

Fig 1 Map of the study area

Sample and data collection and laboratory analysis of OCPs

Samples were collected from three river sampling sites in the Wedecha and Belbela rivers, and three temporary ponds, representing the upstream, midstream and downstream parts of the irrigation system. The river sampling sites were at elevations of 2190, 1935 and 1879 m, while the pond sampling sites were situated at 2228, 1943 and 1882 m (Appendix A). Locations were chosen based on the presence of a small- or large-scale farming activity by the side of the river/canal or pond sampling sites.

Samples were collected during five sampling periods, encompassing the crop development stages as well as seasonal variations in the study area. A total of 15 samples were taken by sampling three river sites four times and one sample from each of the three additional temporary ponds, which were only formed at the end of rainy season.

A hand grab method was used to collect the water samples in 4 L amber glass bottles. Collected water was thoroughly mixed in a bucket and transferred to the 4 L amber bottles, supplemented with some drops of sodium thiosulfate as a preservative and filled up to the seal, leaving no space for air bubbles to be included. Properly sealed samples were taken to the quality monitoring and pesticide testing laboratory of the Ethiopian Ministry of Agriculture and stored at 4 °C (Forrest 2000). Together with the water sample collection, the physiological parameters of the water, including pH, temperature, dissolved oxygen (DO) and electrical conductivity (EC) were measured using a Handy Polaris (OxyGuard, USA) and a WTW multi 340i (WTW, USA) meter. The total dissolved solids (TDS) and total suspended solids (TSS) of the water were measured at a laboratory (JIJE laboglass plc; http://jijelaboglassplc.com/), which is ISO/IEC 17025:2005 accredited by the Ethiopian National Accreditation Office. TSS was measured by filtering (mesh size 1.12µm) and drying in an oven at 103–105 °C (Clesceri et al. 1999), while TDS was measured using a TDS meter (TDS_EZ water quality tester HM-Digital USA).

Samples were analysed at the laboratory of the Plant Health Regulatory Directorate (PHRD) (accredited by the Ethiopian National Accreditation Office) for pesticide residues. For all 15 samples, quality control was implemented, to keep the laboratory assessment free from unnecessary interference and cross-contamination (Adeyemi et al. 2011; Kashyap et al. 2005). A simple liquid/liquid extraction method followed by a solid phase extraction florisil clean-up was used (Żwir-Ferenc and Biziuk 2006; De Koning et al. 2009; Awofolu and Fatoki 2003). Analysis was performed by screening for the 18 OCPs using a gas chromatograph (GC) with an electron capture detector (ECD) (Agilent Technologies Inc., Palo Alto, CA, USA). OCP standards (99.95%) for 18 target chemicals were purchased from Restek Ltd, New Haven, CT, USA. A column (Stx-clpesticides 30 m x 250 µm x 0.25

µm) was used to separate and analyse extracted samples, with 1 µL volume being injected automatically. GC temperature was programmed at 120 °C; 225 °C and 280 °C, at an injector and detector temperature of 230 °C . Helium was used as a carrier gas at a flow rate of 1 mL/min, while nitrogen was used as a makeup gas at a flow rate of 60 mL/min (Chauhan et al. 2014; Adeyemi et al. 2011; Pitt 2009).

Calculation of PECs for nine pesticides used by small scale farmers using PRIMET_Ethiopia_1.1

Data on current pesticide use was collected by interviewing 15 representative small-scale farmers from the upstream, midstream and downstream parts of the river; in addition, seven large-scale farms located along the downstream part of the river were also surveyed. Farmers were considered to be representative when farming close to the river or a large irrigation canal. Data for the small-scale farmers was verified by the district agricultural experts in the area. In addition, some basic information about resource ownership and use and awareness of pesticide application was collected using a simple questionnaire. Since the entry routes of pesticides into surface water fromgreenhouse production systems are very different from those from crops grown in fields outside, a greenhouse scenario is not included in the PRIMET_Registration_Ethiopia_1.1 model, so it was not possible to calculate the PEC values for the surrounding surface waters regarding the usage data of the large-scale greenhouse farmers.

The physicochemical data for the reported pesticides was obtained from the Footprint pesticides properties database (Lewis et al. 2016). When multiple application schemes were recorded for an active ingredient, the one with the highest application rate was evaluated. The actual application rate and frequency of use were used in the risk calculations (Appendix B). The two scenarios for (i) small streams in areas above 1500 m (grid 191, see Teklu et al., 2015 for explanation) and (ii) temporary ponds in areas between 1500-2000 m (grid 217) as incorporated in PRIMET_Registration_Ethiopia_1.1. correspond well to the situation in our study area, considering the altitude and the presence of intensive agricultural activity adjacent to the river and the temporary ponds in the Debra Zeit area. However, the long-term annual rainfall in the two scenarios (2581 and 2779 mm) is clearly higher than the reported rainfall for the Wedecha-Belbela irrigation system with its supplementary irrigation. Two dominant crops (cabbage crop cycle 1 and tomato crop cycle 1, i.e. non-irrigated crop cycles grown during the rainy season) were selected as representative crops grown in the area, based on observations and after discussions with the farmers. Pesticide data including their molar mass, saturated vapour pressure at 20 °C, water solubility, half-life of transformation in soil (DT_{50soil}), half-life of transformation in water ($DT_{50water}$), dissociation constant (pKa), and coefficient of sorption to soil based on organic carbon content (K_{oc}), were obtained from the Footprint pesticide properties database (Lewis et al. 2016) (Appendices C and D).

Risk assessment

Acute and chronic risks to humans and aquatic organisms from detected OCPs

For the OCPs we detected, the risks to humans were determined using the highest detected concentrations. Chronic and acute health risks were calculated using acceptable daily intake (ADI) and acute reference dose (ARfD) values, respectively. Estimated short-term intake (ESTI) and the internationally estimated daily intake (IEDI) values were determined to indicate acute and chronic risks to humans from using surface water as a source of drinking water. Background calculation formulas are given below and in other publications (Teklu et al. 2015; Wipfler et al. 2014; Adriaanse et al. 2015; Deneer et al. 2014). The ESTI was determined using a body weight of 60 kg and assuming a large portion of drinking water (LP_dw) of 6 L per day. The value of 6 L is triple the amount used by the WHO (WHO, 2011) as daily intake. We nevertheless chose this high value in assessing the acute risks to humans, as 6 L represents a worst-case scenario accounting for incidental high intakes, e.g. during hard labour on the land on hot days (eqs. 1 and 2).

Similarly, both acute and chronic risks to aquatic organisms were determined using the measured OCP concentrations. A first-tier risk assessment was performed for aquatic organisms by calculating the exposure-to-toxicity ratio (ETR) by estimating acute and chronic no-effect concentrations (NECs) from the corresponding EC50, LC50 or NOEC values for three representative aquatic organisms (fish, Daphnia, and algae) (eqs. 3-8)(Lewis et al. 2016) (Appendix E). A second-tier risk assessment was performed for ETR values >1 using HC5 (hazardous concentration protective of 95% of the population) values from chronic species sensitivity distributions (SSDs). SSDs were calculated and HC5 concentrations determined using data from the US-EPA database (www.epa.gov/ecotox). Using the ETX 2.0.software (Van Vlaardingen et al. 2003) to calculate the HC5, data was selected as discussed by Maltby et al. (2005). In the second tier the HC5 values were used as NEC values (Teklu et al. 2015). Risk category intervals were as follows; 0–1 equals low risk for algae, Daphnia and fish; 1–100 medium risk for algae and Daphnia; 1–10, medium risk for fish; >100 high risk for Daphnia and algae and >10 high risk for fish (Teklu et al 2015). All risk calculations for the detected OCPs were performed by hand, using the highest concentration detected.

$$\mathrm{ESTI} = \frac{\mathrm{LP\_dw} \times \mathrm{OCP}_{\mathrm{concentration}}}{\mathrm{ARfD} \times \mathrm{BW}} 100\% \qquad \text{eq. (1)}$$

With: ESTI = estimated short-term intake (%); LP_dw = Large portion of drinking water (L/day); $\mathrm{OCP}_{\mathrm{concentration}}$ = measured OCP concentrations (µg/L); ADI = acceptable daily intake (µg/Kg BW*d); ARfD = acute reference dose (µg/Kg BW*d) and BW = body weight (kg).

$$\mathrm{IEDI} = \frac{\mathrm{DI} \times OCP_{concentration}}{\mathrm{ADI} * Fdw \times \mathrm{BW}} \; 100\% \qquad \text{eq.(2)}$$

With: IEDI = internationally estimated daily intake, expressed as % of the total acceptable intake of the pesticide during a lifetime (%); DI = daily intake (L/d); $ECP_{concentration}$ = measured OCP concentration in (µg/L); ADI = acceptable daily intake, expressed in µg pesticide per kg BW per day (µg/kg*d); Fdw= fraction of ADI allocated to drinking water (-) and BW = body weight (kg). BW was set at 60 kg, DIat 2 L/d and the fraction of ADI allocated to drinking water at 0.1 for Ethiopia.

$$\mathrm{ETRwater\_org} = \frac{OCP_{concentration}}{NEC_{\mathrm{org\ (acute\ \ or\ chronic\ )}}} \qquad \text{eq.(3).}$$

With:

$OCP_{concentration}$ = measured OCP concentrations (µg/L)and

$NEC_{org(acute/chronic)}$ = acute or chronic no-effect concentration for the respective aquatic organism (fish, Daphnia or algae) (µg/L).

Where:

$NEC_{fish\ acute}$= 0.01 * LC50 of fish (µg/L) eq. (4)

$NEC_{daphniaacute}$= 0.01 * EC50 of Daphnia (µg/L) eq. (5)

$NEC_{algaeacute}$= 0.1 * EC50 of algae (µg/L) eq. (6)

$NEC_{fish\ chronic}$ = 0.1 * NOEC of fish (µg/L) eq. (7)

$NEC_{daphnia\ chronic}$ = 0.1 * NOEC of Daphnia (µg/L) eq. (8)

Acute risks to humans and aquatic organisms for nine pesticides used by small-scale farmers

Nine pesticides in current use by the small-scale farmers were evaluated for the risks they may pose to aquatic organisms and humans, using the PRIMET_Registration_Ethiopia_1.1. model (Wipfler et al 2014). A lower-tier risk assessment was performed to calculate exposure concentrations based on the incorporated exposure scenarios and threshold levels of effects, using the NEC calculations as provided above (Teklu et al. 2015). Risks were calculated using the cabbage crop cycle 1 and tomato crop cycle 1, which are non-irrigated crops grown during the rainy season, as this is the main production time in the area.

Second-tier risks were calculated using acute SSD and HC5 values. Data from the US-EPA database (www.epa.gov/ecotox) were included and the ETX 2.0. software (Van Vlaardingen et al. 2003) was used to calculate the HC5s. Data was selected as discussed by Maltby et al. (2005). The calculated HC5s were used as NEC values (Teklu et al. 2015).

Results and discussion

Measured water physical properties

Values of physicochemical parameters measured in this study are given in Annex 1. No correlation was found between the physicochemical parameters and the residues detected in this study. EC and pH were found to be within the maximum permissible limits set by the WHO (WHO 2010; Teklu et al. 2016) while the value for the total suspended solids in the samples was at a maximum during the period of land preparation and sowing, indicating high erosion at the onset of the rainy season in the area. Average pH and temperature of the river and pond sites sampled in this study were 7.62 and 20.4 °C, respectively. This justified the use of the DT50 aqueous hydrolysis at pH 7 for the PRIMET_Registration_Ethiopia_1.1 model calculations (Appendix F).

Pesticide use and PEC values for the nine pesticides used by small scale farmers

The results of the survey on pesticide use and handling by small-scale farmers show that 69% of the respondents did not know that spray drift and run-off can be a possible source of pesticide pollution to the surrounding surface waters. The majority (91%) did not maintain a safe distance from the river (or canal) while spraying pesticides, and 71% of the farmers mixed pesticides and washed pesticide containers near the river/canal. Eighty-two percent of all farmers had increased the frequency and dosage of pesticide applications in the past five years, and 67% of them mentioned pest resistance as the major reason for the increment, while 67% indicated they had recently been trained in pesticide application methods (n=45) (Table 1). Almost all pesticide types were used by the small-scale farmers with increasing amounts and frequencies of application, except for the herbicides pyroxsulam and glyphosate, for which no change was found. Flower farms data showed that they all followed the prescribed dosage and frequency of application. These results are in line with Mengistie et al. (2016) and FAO (2012 unpublished) who found that small-scale farmers use higher application rates and frequencies than recommended. A similar increase of 47% in pesticide application rate per hectare and per season was reported by small-scale vegetable producers in Kenya (Macharia 2015). Although pest resistance has been reported as the main reason for the increment by small-scale farmers, the lack of awareness regarding pesticide handling issues could also explain the difference in pesticide misuse between small-scale and large-scale farmers (Mengistie et al. 2016). The general description on the current status of the liquid waste management by these farms are provided in Table 2.

Table 1 Training and knowledge on pesticide handling and application trends

Question	Response (%) (n=45)
Trained on pesticide application methods	
yes	66.6
no	33.4
Understand pesticide labelling	
yes	64.4
no	35.6
Fate of used pesticide containers:	
throw it to the river,	0
used as drinking water container	8.9
burn them,	60
sell them	11.1
use them as kerosene container	20
Know drift and runoffs can be case for surface water	
pollution	31.1
yes	68.9
no	
Keep safety distance from canal/river while spraying	
Yes	8.9
No	91.1
Place of pesticide mixing and container washing	
near river/cannel,	71.1
at home,	8.9
in the field (farm)	20
Increment of pesticide amount and frequency used	
before five years	82.2
increase	0
decreased	17.8
no change	
Reason for increment	
everyone increase,	22.2
pest resistance,	66.7
pesticide sellers said so,	0
for trial	11.1

Table 2 The status of liquid waste management by the seven commercial farms downs stream with irrigated flower crops in green houses

#Farm	Major source of liquid waste(1= greenhouses 2= pack houses and cleaning rooms 3= pesticide mixing rooms 4= any other)	Availability of liquid waste accumulation and detoxification (recycling) (1= yes 2= No)	Type of liquid waste management(1= wet land plates 2= soak away pits 3 = recycling through silo 4= any other)
1	1,2,3	1	2,3
2	2,3,4(fertigation)	1	2,3
3	2	2	None
4	1	1(under construction)	1(under construction)2,3
5	1,2,3	1	2,3(under construction)
6	1,2,3	1	1,2,3
7	1,2,3	1	2

Acute and chronic risks to humans and aquatic organisms from detected OCPs

Our risk assessment results for humans indicate that all the OCPs we detected pose a low chronic risk to humans, except g-chlordane, which poses a high risk when surface water is used as drinking water. Similarly, low acute risks for humans were found for the two pesticides dieldrin and endosulfan (Table 3). This result is in line with those of Teklu et al. (2015) who found a low acute risk to humans for all evaluated pesticides when surface water is used as drinking water. Although beta-hexachlorocyclohexane (b-BHC) detected at 2.27 and 2.72 µg/L and g-chlordane detected at 5.02 and 10.0 µg/L (Table 2) exceed by a factor 22 to 100 the acceptable concentration of 0.1 µg/L in the EU (EC 1998), this is not in contradiction with the conclusion of low human risks, as the EU standards have no toxicological basis.Also, the three detected concentrations heptachlor epoxide B of 0.094 to 0.115 µg/L are up to a factor of nearly 4 higher than the acceptable concentration of 0.03µg/L in the EU and for a-chlordane the detected concentration of 0.192 µg/L is a factor 2 higher than the acceptable concentration of 0.1 µg/L in the EU (EC 1998). The first-tier risk assessment results indicate many medium and two high risks that pesticides may pose to fish (Table 7). A high chronic ETR of 3086 was calculated for endosulfan for one river sampling site, as well as a high acute ETR for g-chlordane (11) at a temporary pond. Two medium acute risks were calculated for beta-hexachlorocyclohexane (b-BHC) for algae (2.3 and 2.7) in ponds, as well as two medium risks (chronic, ETR = 1.44 and acute, ETR = 1.71) for Daphnia, alsoin ponds (Table 4). The second-tier assessment, which is based on chronic SSDs, revealed no risks to aquatic organisms (Table 5).

Table 3.IEDI/ESTI (%) indicating chronic/acute toxic effects to humans for the detected OCPs (Calculated according to eq. 1).When only one value is present, it represents the IEDI.

OCPs detected	**Human risk (IEDI/ESTI%)**					
	upstream	**Middle part**	**Downstream**	**Upstream***	**Middle part***	**Downstream***
a-Chlordane	13	-	-	-	-	-
g-Chlordane	-	-	-	334	-	673
Dieldrin	-	8.9/0.089	-	-	-	-
Endosulfan	-	-	0.17/0.02	-	-	-
Heptachlor-Epoxide B	38	33	33	-	-	-
Heptachlor	-	31	-	-	-	-

Note: - = no risk quotient since the concentration is below the detection limit; * = results for pond sites

Table 4.ETRs first tier indicating acute/chronic toxic effects to aquatic ecosystems for the for the detected OCPs (Calculated according to eq. 2-7)

OCPs detected	Risk to aquatic organisms (ETR)								
	upstream river or pond			midstream river or pond			downstream river or pond		
	algae	Daphnia	Fish	algae	Daphnia	Fish	algae	Daphnia	fish
a-Chlordane	-	0.027^{+}	0.213	-	-	-	-	-	-
Dieldrin	-	-	-	0.003	0.01	2.22	-	-	-
Endosulfan	-	-	-	-	-	-	<0.01	<0.01	3085.6^{+}
Heptachlor-Epoxide B	0.043	0.274	1.643	0.037	0.239	1.435	0.037	0.239	1.435
Heptachlor	-	-	-	0.035	0.223	1.341	-	-	-
g-Chlordane		1.44*$^{+}$	5.58*	-	-	-	-	1.71*	11.21*
b-BHC	2.27*	0.45*	7.57*	-	-	-	2.72*	0.54*	9.07*

Note: - = no risk quotient since the concentration is below the detection limit;; * = risk values for temporary pond; $^{+}$ chronic risks

The results on OCP residues in the river samples indicated that the highest concentrations detected were those of heptachlor epoxide B (0.115 µg/L) and a-chlordane (0.192 µg/L). The level of heptachlor epoxide B was slightly below the chronic threshold value (HC5 = 0.579) while no threshold level was available for a-chlordane (Table 6). High concentrations of g-chlordane (10.1 µg/l) and b-BHC (2.72µg/l) were detected in the downstream temporary pond samples. These results are in line with the model predictions (Teklu et al. 2015), which indicated higher PEC values for temporary ponds than for rivers. A similar study done in Tanzania detected no heptachlor epoxide (Hellar 2011). In our study, we detected no DDT or breakdown products of DDT, whereas DDT and its breakdown products were detected in more than 90% of the samples in water from the four rivers investigated in Tanzania (Hellar 2011). In a study from Nigeria, most of the target OCPs analysed were reported not to be detected above the detection limits in the majority of the river water samples, as was also found in the present study (Okoya et al. 2013) but with higher reported concentrations of 1.51, 0.11, 0.13 and 0.13 μg/L for dieldrin, p,p'-DDE, cis-chlordane and α-endosulfan, respectively (Okoya et al. 2013). No data are available from studies done elsewhere in Africa to indicate the risk level to aquatic organisms from OCPs, but the number and type of detections suggest that there are similarities in the OCP detections in different areas in Africa.

Table 5ETRs second tier indicating chronic toxic effects to aquatic ecosystems for the for the detected OCPs

a.i	PEC	NEC_{ssd}	ETR
Dieldrin	0.027	7.53E-02	0.35
Endosulfan	0.031	4.13E-02	0.75
Heptachlor- Epoxide B	0.12	5.79E-01	0.19
Heptachlor	0.0948	5.79E-01	0.16
g-Chlordane	10.09	NA	NA
b-BHC	2.27	NA	NA

Table 6. Concentration of OCPs measured (μg/L) in river and temporary ponds in 2014

	Up-stream river				Mid-stream river				Down-stream river				USP	MSP	DSP
OCP	11-07	11-08	11-09	11-10	11-07	11-08	11-09	11-10	11-07	11-08	11-09	11-10	20-10	20-10	20-10
Dieldrin	ND	ND	ND	0.010	0.027	ND	ND	0.012	ND	ND	ND	ND	ND	0.012	ND
Heptachlor Epoxide B	ND	0.115	ND	ND	ND	0.100	0.094	ND	0.015	0.100	ND	ND	ND	ND	ND
Endosulfan	ND	ND	ND	0.023	ND	ND	ND	ND	0.031	ND	ND	ND	ND	ND	ND
a-Chlordane	ND	0.192	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.004	ND
Heptachlor	ND	ND	0.009	ND	ND	0.007	0.007	0.024	ND	ND	ND	ND	ND	ND	ND
b-BHC	ND	ND	ND	0.029	ND	ND	ND	ND	ND	ND	ND	ND	2.27	ND	2.72
Aldrin	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.001	ND
g-chlordane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	5.02	ND	10.1

Note: USP = Up-stream pond; MSP = Mid-stream Pond: DSP = Down-stream Pond.

Acute risks to humans and aquatic organisms from nine pesticides used by small-scale farmers

All nine pesticides used by the small-scale farmers pose a low risk when the surface water is used as drinking water, which is in line with earlier model-based risk assessments by Teklu et al. (2015) (Table 7). Their detected concentrations range up to 30.79 (diazinon in pond) and thus exceed the acceptable concentration of 0.1 µg/L in the EU (EC 1998). First-tier risk assessment results from the data on pesticide use predicted by PRIMET_Registration_Ethiopia_1.1 indicate that lambda-cyhalothrin, endosulfan, and profenofos are associated with high risk for fish, and diazinon for Daphnia, in both the river and pond sites in the area. Malathion and pyroxsulam were found to pose a medium risk to fish and Daphnia, while only propiconazole posed a medium risk to algae (Table 8). Similar work done using model-based first-tier risk assessment in South Africa found that analysis of the application patterns of aldicarb, methomyl, linuron, bromoxynil, carbaryl, dichlorvos, parathion, and two pyrethroids, cypermethrinand deltamethrin, indicated a possible risk at their respective predicted environmental concentrations (Ansara-Ross et al. 2008). These results are not in line with those of the present study, which identified four pesticides with high risks at the first-tier level.

Table 7 ESTI (%) indicating acute toxic effects to humans for the nine pesticides used by the small-scale farmers (Calculated by PRIMET_Ethiopia_1.1.)

Active ingredient		PEC (µg/L)		ESTI	
	ARfD(mg/kgBW/d)	River	Pond	River	Pond
Lambda-cyhalothrin	0.005	0.0251	0.053	<0.1	<0.1
Profenofos	1	16.47	14.91	<0.1	<0.1
Malathion	0.3	0.32	0.33	<0.1	<0.1
Endosulfan	0.02	3.54	6.49	0.018	0.032
Deltamethrin	0.01	0.00014	0.00091	<0.1	<0.1
Pyroxsulam	0.9*	3.37	1.32	<0.1	<0.1
Propiconazole	0.3	13.53	20.64	<0.1	<0.1
Glyphosate	0.3*	17.68	21.59	<0.1	<0.1
Diazinon	0.025	25.07	30.79	0.10	0.12

*ADI (no ARfD available)

Second-tier risk assessment for aquatic organisms indicated that lambda-cyhalothrin, profenofos, endosulfan, anddiazinon posed high risks for both the river and pond sites, while propiconazole and malathion were found to pose a low risk (Table 9). Slightly higher second-tier risks were observed in this study for lambda-cyhalothrin and profenofos, compared to their first-tier estimates, while risks of endosulfan and diazinon were considerably lower in the second-tier assessment (Table 9). This is in line with what was found by Teklu et al. (2016), who observed greater realism and less conservatism at higher tiers (Brock et al. 2006; Wheeler et al. 2002).

Table 8 First tier ETRs (-) indicating acute toxic effects to aquatic ecosystems for the nine pesticides used by small-scale farmers (calculated by PRIMET_Registration_Ethiopia_1.1.).

	PEC(μg/L)		NEC(μg/L)			ETR fish		ETR daphnia		ETR algae	
Active ingredient	River	Pond	Fish	Daphnia	Algae	River	Pond	River	Pond	River	Pond
Lambda-cyhalothrin	0.024	0.050	0.0021	0.0036	30	11.61	24.01	6.77	14.01	<0.01	<0.01
Profenofos	15.95	11.45	0.8	5	10000	19.94	14.31	3.19	2.29	-	-
Malathion	0.19	0.26	0.18	0.007	1300	1.037	1.448	26.67	37.24	<0.01	<0.01
Endosulfan	3.414	4.93	0.02	44	215	170.7	246.5	0.078	0.11	0.016	0.023
Deltamethrin	0.00014	0.00086	0.0026	0.0056	910	0.054	0.33	0.025	0.15	<0.01	<0.01
Pyroxsulam	2.78	0.71	870	1000	92.4	<0.01	<0.01	<0.01	<0.01	0.03	<0.01
Propiconazole	11.68	15.47	26	102	9.3	0.449	0.60	0.11	0.15	1.26	1.66
Glyphosate	16.5	12.42	380	400	440	0.043	0.033	0.041	0.031	0.038	0.028
Diazinon	23.98	28.02	31	0.01	640	0.774	0.904	2398	2802	0.037	0.044

- No output for algae since no EC50 value is available for algae for profenofos in the toxicity data base.

Table 9 Second-tier ETRs indicating acute toxic effects to aquatic ecosystems for the nine pesticides used by small-scale farmers (calculated by PRIMET_Registration_Ethiopia_1.1). NEC based on acute SSDs.

	PEC(μg/L)				
Active ingredient	River	Pond	NEC(μg/L)	$ETR_{ssd\ river}$	$ETR_{ssd\ pond}$
Lambda-cyhalothrin	0.024	0.05	1.75E-03	13.7	28.6
Profenofos	15.95	11.45	2.09E-01	76.3	54.8
Malathion	0.19	0.26	5.50E-01	0.35	0.472
Endosulfan	3.414	4.93	4.83E-02	70.7	102.2
Propiconazole	11.68	15.47	4.26E+02	0.027	0.036
Diazinon	23.98	28.02	5.06E-01	47.4	55.4

Comparison of endosulfan as a detected OCP and as model prediction PEC value

We expected higher concentrations of endosulfan than of other OCPs in river and/or pond samples, since this pesticide is currently used by farmers (see results of interviews). The residue levels found in our study were, however, quite low, with a highest detected concentration of 0.03µg/L. This is lower than the levels predicted in a recent model-based study (Teklu et al. 2015), with the model predicted PEC values of 1.3 µg/L and 0.6 µg/L for the grids 191 and 217, respectively, for Maize.These values are even much lower than those obtained by the PRIMET_Registration_Ethiopia_1.1, with PECs of 3.14 and 4.93 µg/L for the cabbage and tomato crops in the river and pond scenarios respectively in the present study (Table 8). There are many explanations for this difference, the most obvious of which is that the predicted values represent the 90th percentile of the 33-year PEC values just after application (Adriaanse et al. 2015; Teklu et al. 2015), while a measured value just results from one ordinary measurement. Other possible reasons include a difference in the amounts and frequency of applications of endosulfan as actually used by the farmers and the values used for the PEC calculations (Baveye et al. 2007). The difference in the annual rainfall between the DebreZeit area (815 mm) and the scenario locations, i.e. grids 191 (2581 mm) and 217 (2779 mm), is considerable, which will result inhigher incidences of runoff with higher PECs in the scenarios than in the Wedecha-Belbela irrigation system (Adriaanse et al. 2015). Moreover, the measurements were not made when endosulfan was being applied adjacent to fields or just after a run-off event, while PRIMET_Registration_Ethiopia_1.1 calculates peak concentrations immediately after application or run-off, which might also explain the difference.

Generally, higher PEC values were calculated for the river and pond scenarios by PRIMET_Registration_Ethiopia_1.1 when actual use patterns were used as input (Table 8) than when using usage patterns based on good agricultural practices (GAP) (Teklu et al. 2015). Endosulfan PEC values found by Teklu et al. (2015) are based on a worst-case scenario when GAP is followed, while the present study used the actual application rate and frequency to predict the values, which explains the higher concentrations.

To conclude, the calculated concentrations are expected to be protective against risks in the Wedecha-Belbela irrigation system, as the long-term annual average rainfall in the two scenarios is higher than those in the irrigation system. Grid 191 is the worst-case scenario for all rivers above 1500 m in Ethiopia and was considered to provide a protective PEC value for the river sites in the present study (Appendix F). Grid 217 represents a worst-case scenario for temporary ponds with an altitude of 1500-2000 m (Adriaanse et al 2015) and was considered to provide a protective PEC value for the midstream and downstream pond sampling sites in the present study (Appendix F).

Our study was unable to quantify the risks of pesticide use for aquatic ecosystems near greenhouses. The scenario for such systems is different from those included in the PRIMET_Registration_Ethiopia_1.1 model, for instance in that all spray activity takes place indoors. Most large-scale farmers reported possessing a mechanism for recycling liquid waste from their greenhouses, besides the use of soakaway pits and wetlands for further detoxification of liquid wastes to protect the surrounding soil and surface waters. Future studies need to concentrate on the applicability of these systems and the generation of plausible scenarios for surface water risk assessment of pesticides for Ethiopian greenhouse systems. Moreover, the two grids (191 and 217) from the PRIMET_Registration_Ethiopia_1.1 represent vulnerable exposure situations in Ethiopia (and thus not average situations), i.e. the 99th-percentile worst case for drinking water and the 90th-percentile worst case for aquatic organisms, of all possible situations in time and space in Ethiopia. Comparison of the elevation, rainfall pattern (i.e. total annual average, period, and if possible number of events >20 mm/d per year) and agricultural crops between the small stream scenario (grid 191) and the pond scenario (grid 217) with those of the Wedecha-Belbela irrigation system showed that the grid scenarios provided a worst case scenario for the irrigation system.

Acknowledgements

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Appendices for Chapter 5

Appendix A. Measured physico-chemical parameters at the different sampled locations and sampling times.

Sampling location and (elevation (m))	Sampling time in 2014	EC µS/cm	pH	DO(mg/L)	T (^{o}C)	TDS (mg/L)	TSS (mg/L)	TS(mg/L)	Crop development stage
Upstream river (2190 m)	11-07	670	7.82	7.45	18.9	420	1180	1600	land preparation
	11-08	420	6.96	5.46	19.3	260	1060	1320	seedling
	11-09	560	7.65	6.45	20.1	370	700	1070	flowering
	11-10	545	7.45	7.45	22.1	320	240	560	maturity
Midstream river(1935 m)	11-07	490	8.17	6.34	22.2	310	750	1060	land preparation
	11-08	570	7.45	6.34	20.1	360	1190	1550	seedling
	11-09	520	8.12	4.34	20.4	330	440	770	flowering
	11-10	598	6.97	7.45	22.2	380	260	640	maturity
Downstream river(1879m)	11-07	320	7.52	6.22	19.5	200	1460	1660	land preparation
	11-08	616	7.98	7.22	19.8	390	810	1200	seedling
	11-09	440	7.34	6.34	21.4	280	670	950	flowering
	11-10	470	8.21	8.98	21.4	300	500	800	maturity
USP (2228 m)	20-10	360	7.34	7.56	22.5	220	320	540	maturity
MSP (1943 m)	20-10	510	7.98	5.45	21.3	320	180	500	maturity
DSP (1882 m)	20-10	540	7.34	7.34	22.1	340	1260	1600	maturity

Note: Note: USP = Upstream Pond; MSP = Midstream Pond: DSP = Downstream; EC = Electrical Conductivity; DO = Dissolved Oxygen; T = Temperature; TDS = Total Dissolved Solids; TSS = Total Suspended Solids; TS = Total Solids (Dissolved + Suspended).

Appendix B. Pesticide use by small-scale farmers, according to GAP and applied according to farmers

Active ingredient	Type	Substance group	Conc. a.i. in product g/kg or g/L	Method of application	Dose of formulated product According to GAP (kg/ha or L/ha)	Actual dose of formulated product (kg/ha or L/ha)	Appl. rate according to GAP (g a.i./ha)	Actual Appl. rate (g a.i./ha) actual	Prescribed # of application/ cropping season	Actual number of application	Application intervals (According to GAP as well as actual) (d)	Crop type in PRIMET_Ethiopia	Application start
Lambda-cyhalothrin	IN	Pyrethroid	80	spray	0.4	1.2	32	96	3	6	7	C1st	July 15
Profenofos	IN	Organophosphate	720	spray	1.5	3.5	1080	2520	2	4	20	T1st	July 15
Malathion	IN	Organophosphate	500	spray	1.5	3.5	750	1750	2	4	25	T1st	July 15
Endosulfan	IN	Organochlorine	350	spray	2.5	3.5	875	1225	2	4	20	T1st	July 15
Deltamethrin	IN	Pyrethroid	60	spray	1	1.5	60	90	2	4	15	C1st	July 15
Pyroxsulam	HB	Triazolopyrimidine	450	spray	0.4	0.4	180	180	1	1		T1st	June 15
Propiconazole	FU	Triazole	250	spray	1	2.5	250	625	2	4	7	T1st	July 15
Glyphosate	HB	Phosphonoglycine	480	spray	4	4	1920	1920	1	1		C1st	June 15
Diazinon	IN	Organophosphate	600	spray	2	2.5	1200	1500	2	3	15	C1st	July 15

Note : C1st = Cabbage first cycle; T1st = Tomato first cycle

Appendix C. Toxicity data for nine pesticides used by small scale farmers (Source: Lewis et al. 2016)

	Aquatic ecosystem				Human Health
	Acute		Acute		Acute
a.i.	fish LC50 (mg/L)	daphnia EC50(mg/L)	algae EC50(mg/L)	macrophyts EC50(mg/L)	ARfD (mg/kgbw/d)
Lambda-cyhalothrin	0.00021	0.00036	>0.3	NA	0.005
Profenofos	0.08	0.5	NA	NA	1.0
Malathion	0.018	0.0007	13	NA	0.3
Endosulfan	0.002	0.44	2.15	NA	0.02
Deltamethrin	0.00026	0.00056	9.1	NA	0.01
Pyroxsulam	>87	100	0.924	0.0026	0.9*
Propiconazole	2.6	10.2	0.093	4.9	0.3
Glyphosate	38	40	4.4	12	0.3*
Diazinon	3.1	0.001	6.4	NA	0.025

*= values are ADI no AfRD values available

Appendix D. Physico-chemical properties for nine pesticides used by small scale farmers (Source: Lewis et al. 2016)

a.i.	Type	Substance group	DT50_Soil (lab at 20°C)(d)	DT50 r Aqueous hydrolysis at 20°C and pH 7(d)	DT50_water sediment(d)	Molar mass pesticide (g)	Water solubility at 20°C (mg/L)	Vapour pressure at 25°C (mPa)	K_{OC} (mL/kg)
Lambda-cyhalothrin	IN	Pyrethroid	175	1000	15.1	449.85	0.005	2.00E-04	283707
Profenofos	IN	Organophosphate	7	1000	-	373.63	28	2.53	2016
Malathion	IN	Organophosphate	0.17	6.2	0.4	330.36	148	3.1	1800
Endosulfan	IN	Organochlorine	39	20	-	406.93	0.32	0.83	11500
Deltamethrin	IN	Pyrethroid	26	1000	65	505.2	0.002*	1.24E-05	10240000
Pyroxsulam	HB	Triazolopyrimidine	3.3	1000	-	434.35	3200	1.00E-04	33.22
Propiconazole	FU	Triazole	90	53.5	636	342.22	150	0.056	1086
Glyphosate	HB	Phosphonoglycine	15.3	1000	74.5	169.1	10500	0.0131	1424
Diazinon	IN	Organophosphate	9.1	138	10.4	304.35	60	11.97	609

*Value multiplied with a factor of 10 (for software reasons, having a negligible effect on PEC in pond)

- = no value available in Lewis et al. (2016), a value of 1000 d is used in the PRIMET_Registration_Ethiopia_1.1. calculations, resulting in conservative, i.e. protective, exposure concentrations)

IN = Insecticide; FU = Fungicide; HB = Herbicide

Appendix E. The ADI,ARfD and aquatic toxicity data for detected OCPs (Source: Lewis et al. 2016)

			Algae		Daphnia		Fish					
OCP detected	ARfD (mg/kgBW/d)	ADI (mg/kgBW/d)	EC50 (mg/L)	NOEC (mg/L)	EC50 (mg/L)	NOEC (mg/L)	LC50 (mg/L)	NOEC (mg/L)	NECchronic fish	NECchronic daphnia	NECacute fish	NECacute daphnia
a-Chlordane	NA	0.0005	NA	NA	5.9	0.07	0.9	NA	NA	7	0.9	5.9
g-Chlordane	NA	0.0005	NA	NA	5.9	0.07	0.9	NA	NA	7	0.9	5.9
b-BHC	NA	NA	1	NA	5	NA	0.3	NA	NA	NA	0.3	5
Dieldrin	0.003	0.0001	10	NA	0.025	NA	0.012	NA	NA	NA	0.012	2.5
Endosulfan	0.02	0.006	215	NA	0.44	NA	0.002	0.0000001	0.00001	NA	0.02	4.4
Heptachlor Epoxide B	NA	0.0001	2.7	NA	0.042	NA	0.007	3.29	329	NA	0.07	0.42
Heptachlor	NA	0.0001	2.7	NA	0.42	NA	0.07	3.29	329	NA	0.07	0.42

Note: NA = Not Available; ADI = Acceptable Daily Intake; ARfD = Acute reference dose; EC/LC50 = Effect/Lethal concentrations

Appendix F. Measured physico-chemical parameters at the different sampled locations and sampling times.

Sampling location and (elevation (m))	Sampling time in 2014	EC µS/cm	pH	DO(mg/L)	T (^oC)	TDS (mg/L)	TSS (mg/L)	TS(mg/L)	Crop development stage
Upstream river (2190 m)	11-07	670	7.82	7.45	18.9	420	1180	1600	land preparation
	11-08	420	6.96	5.46	19.3	260	1060	1320	seedling
	11-09	560	7.65	6.45	20.1	370	700	1070	flowering
	11-10	545	7.45	7.45	22.1	320	240	560	maturity
Midstream river(1935 m)	11-07	490	8.17	6.34	22.2	310	750	1060	land preparation
	11-08	570	7.45	6.34	20.1	360	1190	1550	seedling
	11-09	520	8.12	4.34	20.4	330	440	770	flowering
	11-10	598	6.97	7.45	22.2	380	260	640	maturity
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	11-09	440	7.34	6.34	21.4	280	670	950	flowering
	11-10	470	8.21	8.98	21.4	300	500	800	maturity
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Note: Note: USP = Upstream Pond; MSP = Midstream Pond: DSP = Downstream; EC = Electrical Conductivity; DO = Dissolved Oxygen; T = Temperature; TDS = Total Dissolved Solids; TSS = Total Suspended Solids; TS = Total Solids (Dissolved + Suspended).

Chapter 6

General discussion and concluding remarks

Agricultural productivity in sub-Saharan African countries has increased through the use of high-tech production systems and increased amounts of inputs, to meet the ever increasing demand for food due to disproportionate population growth (Berhanu, 2012; Pretty et al. 2011). The rapid transformation from subsistence, low-input agriculture to commercial, large-scale, high-input and high-tech agriculture is essential and has been going on in the past few decades in Ethiopia. This has turned the country into one of the few in the region with a rapid economic growth, and seeking to grow even faster to ensure food self-sufficiency and become one of the middle-income countries in the decade to come (Brixiova and Ncube, 2013; Berhanu, 2012).

Since such ambitious goals can only be achieved by increasing the use of inputs like fertilisers and agrochemicals, their intensive application is now commonly observed in Ethiopia. However, pesticide use practices by small-scale farmers in Ethiopia often violate recommendations like the use of safe storage facilities, complying with health and safety instructions, using protective devices when applying pesticides, and safe disposal of pesticide containers (Negatu et al., 2016; Mengistie et al., 2016). Similarly, large-scale production agriculture, including the horticultural and flower farms, also fails to adhere to international safety standards for the environmental and for workers (Mengistie et al., 2014).

The problem of irrational use of inputs has been aggravated by the lack of a scientifically and logistically up-to-date registration and post-registration systems in Ethiopia. According to Mengistie et al. (2015), the organisation of the pesticide supply chain in Ethiopia is fragmented. The environment and human health hardly played a role in pesticides handling by the different supply chain actors, which has been dominated by immediate profit motives.Although Ethiopia has long ago developed a legal framework for pesticide registration and control, pesticides are still registered, traded and used inappropriately (Mengistie et al., 2014). Under such circumstances, negative impacts of uncontrolled pesticide use on the environment and human health are inevitable.

In order to address the above problems, the Pesticide Risk Reduction Programme (PRRP) was introduced. In addition to the present PhD project, two more PhD projects have been initiated under this programme. One focusses on environmental policy and governance issues associated with pesticides in Ethiopia (Mengistie et al., 2014; 2015; 2016) while the other focuses on the overall health impacts of pesticides in Ethiopia (Negatu et al., 2016). A general description of the PRRP programme is provided in the Introduction to this thesis, and on (http://www.prrp-ethiopia.org/).

The research reported on in the present thesis aimed to perform risk assessments of pesticide use for surface waters in Ethiopia, and to develop new tools and approaches to better protect these surface waters. Ethiopia has been called the water tower of Africa, which implies there is an urgent need for action to change the current state of pesticide registration by increasing its level of protection for major environmental concerns including the country's surface water systems **(Chapter 1).**

Although ideally, environmental risk assessment should be performed using the best available methods, data availability, costs and efficiency need to be considered whenever making an assessment (Posthuma et al., 2008). In order to achieve this goal, tiered approaches can be used in environmental risk assessment schemes to support the registration of plant protection products (Campbell et al., 1999; Boesten et al., 2007). The overall idea of the tiered approach is to start with a conservative, simple approach and to only do additional, more complex work if necessary, that is, when the first assessment suggests the presence of risks (Brock et al., 2011;VanLeeuwen and Vermeire, 2007) (Figure 1).

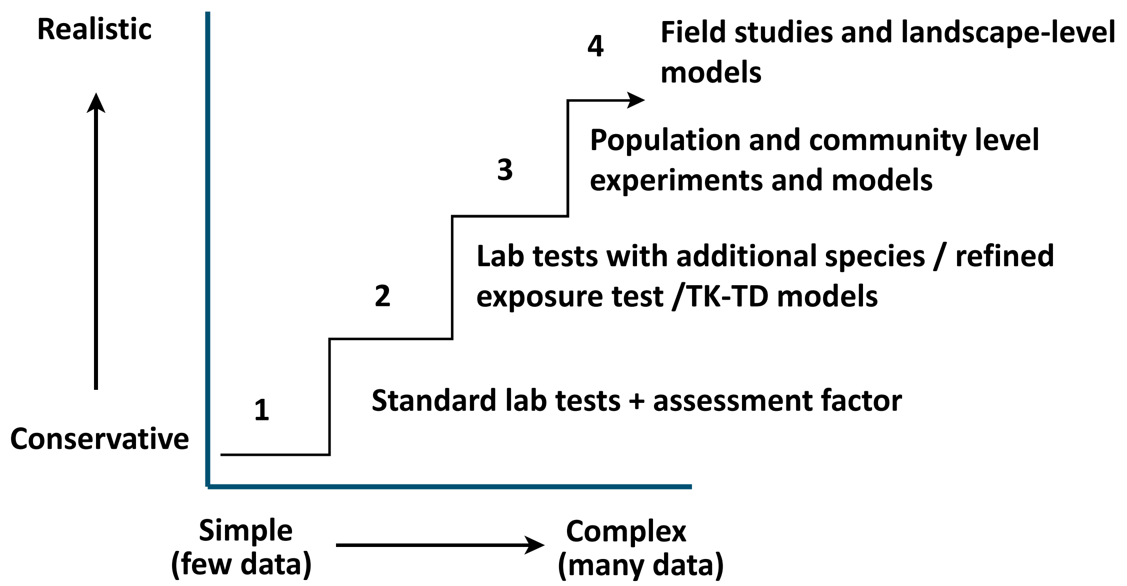

Fig. 1. Tiers in the risk-assessment process (Brock et al. 2011).

Performing higher-tier risk assessments requires more advanced studies to provide more realistic input, with greater complexity and data requirement, while lower tiers require less effort and are less costly (Boesten et al., 2007; Solomon et al., 2008). Therefore it is very important to evaluate the different options available for such an assessment in a developing country like Ethiopia. In this thesis I evaluated which tools can be used to perform risk assessments to protect surface waters both as a source of drinking water and as a habitat for non-target organisms, including algae, Daphnia, and fish. In this synthesis I focus on the way risk assessment was performed in the studies reported on in the different chapters, following the principles of the tiered approach, to arrive at different results when using data from monitoring and laboratory studies. I also discuss its feasibility in the Ethiopian situation, pointing out constraints and ideas that need future attention (**Chapters2, 3, 4 and 5).**

Risk assessment for registration of pesticides in the Ethiopian and European contexts

European regulations on pesticides include the use of a first-tier risk assessment which requires a minimum of data, followed by higher-tier risk assessments. Following this hierarchical procedure implies an increasing need for data for the assessment and increasing complexity (Brock et al. 2011; Campbell et al. 1999). The European Plant Protection Products directive describes the procedures which every pesticide is obliged to pass through in a risk assessment process before they can be admitted on the European market (European Commission, 2002).

In Ethiopia, pesticide registration has so far been based on the simple first-tier assessment, by evaluating to which WHO pesticide category the pesticide belongs and performing a simple test to evaluate the pesticide's effectiveness. This evaluation does not include the assessment of the negative impacts that the pesticide may have on non-target organisms, humans or the environment in general. This is why many pesticides that are banned in Europe are still in use in Ethiopia (Lewis et al. 2016). It is therefore important to evaluate the currently registered pesticides for their effects on human health and non-target organisms at risk **(Chapter 1)**.

This evaluation requires revising the registration system currently in use in Ethiopia for registering pesticides, and developing a new system that is adapted to the Ethiopian situation, a system that can also be used as a prototype for similar countries elsewhere in Africa. It was for this purpose that the PRIMET_Ethiopia_registration_1.1 model was developed by the Alterra ERA (Environmental Risk Assessment) group in the context of the PRRP project (Wipfler et al. 2014). This tool is suitable for registration purposes and is currently ready to be implemented by the Plant Health Regulatory Directorate (PHRD) in Ethiopia. The first chapter of this thesis reports on a study evaluating seven pesticides, selected on the basis of volume of use and toxicity, for their acute risks to humans and surface water aquatic organisms, using this newly developed model. The protection goal was defined as surface water as a source of drinking water and as a habitat for surface water organisms, as was decided at a consultative workshop by PRRP-Ethiopia (Adriaanse et al. 2015).

Model-based risk assessment for regulatory purposes in developing countries

The use of model-based risk assessment for developing countries like Ethiopia is a new approach, which therefore needs careful consideration before it is applied. Difficulties have to be overcome to arrive at the point which more advanced countries have reached at present. Model-based risk assessment has its own general limitations and strengths, and is widely applied for assessing the fate and increasingly also to assess the effects of pesticides for registration purposes in Europe (FOCUS, 2001; Forbes et al., 2009; Galic et al., 2010; Dohmen et al., 2015; De Laender et al., 2014). The development of the integrated fate, effects, and risk assessment model called PRIMET_Registration_Ethiopia_1.1 is believed to take the current registration system in Ethiopia a big step forward. In order to test and evaluate the model, the risks to surface water systems posed by seven selected pesticides used in Ethiopia were assessed, and the results are described in **Chapter 2**.

The main constraints on the introduction of such models in Ethiopia include bringing the model to the attention of all stakeholders, including the government, who are believed to be affected by the adoption of this tool, and convincing them that the risk assessments represent realistic worst-case outcomes. Since the model needs a minimum of input data, it is believed that all the data needed to run the model can be gathered easily by the registrants. Therefore, the implementation of this modelling framework will give a better estimate of the risk posed by the pesticides currently in use and those to be registered in the future, than using the old registration system, which only included a hazard assessment. The new tool is expected to support decision-making on registration of new pesticides and banning risky ones that are already on the shelf.

Comparing monitoring results with predicted environmental concentrations, and the applicability of single-species toxicity tests

Despite the above constraints, this PhD project tried to investigate the use of model-based prediction for risk quantification, using Ethiopian surface water systems as a target protection goal. Model prediction values obtained in this study were compared with concentrations measured in a monitoring scheme implemented in a river, temporary ponds and effluent entry points of a lake in Ethiopia.

Some of the predicted environmental concentration (PEC) values for Ethiopian surface water resulting from the PRIMET_Registration_Ethiopia_1.1 model **(Chapter 2)** can be compared with concentration measurements from monitoring studies **(Chapters 4 and 5)**. Taking the case of endosulfan as an example, we found higher $90^{th}/99^{th}$ percentile PEC values for endosulfan calculated by the model **(Chapter 2)** than were measured in Lake Ziway and the Wedecha and Belbela irrigation system **(Chapters 4 and 5)** (Table 1). This difference was expected, as PRIMET_Registration_Ethiopia_1.1 presents the worst-case concentrations ($90^{th}/99^{th}$ percentile), while our measurements represent average concentrations. Furthermore, the model-based PEC is expected to occur next to an agricultural field to which a pesticide has recently been applied, located next to a watercourse and where the watercourse can be reached by spray drift or a run-off event. By contrast, the samples used for pesticide identification were taken at a chosen time and place in a region where pesticides are applied. Hence, the model can be considered valid to be used for registration purposes, but further model validation studies need to be conducted in parallel.

On the other hand, lower PEC values for endosulfan have been reported in similar studies in South Africa (Ansara-Ross et al. 2008) (Table 1). The discrepancy might result from a difference in the scenario parameters considered in South Africa and Ethiopia. The actual endosulfan concentrations measured in our studies were lower than literature values reported from Nigeria, but slightly higher than those reported from Brazil. Such differences are expected, as the actual usage pattern of endosulfan in these different locations varies, and as differences may be expected in the efficiency of the analytical verifications used in these different studies (Adeyemi et al.2015; Nwakwoala et al., 1991; Raposo Junior et al., 2007) (Table 1).

The toxicity studies we performed with endosulfan and diazinon, using three Ethiopian arthropod species and *Daphnia magna*, showed that the results of the *D. magna* tests were very comparable to literature values. This implies that performing tests in duplicate to check the consistency of the results and at the same time testing *D. magna* as a benchmark, that is, checking the accuracy of the method in the local circumstances, might be a suitable protocol for performing toxicity studies in developing countries where resources to analytically verify the test concentrations are limited **(Chapter 3).** A similar study conducted on Amazonian freshwater organisms came to a similar conclusion, namely that the use of water quality criteria derived from laboratory toxicity data for temperate species will result in a sufficient protection level for Amazonian freshwater organisms (Rico et al., 2011). The results reported in the present thesis and results of studies in some other parts of the tropical world support the use of temperate species data for risk assessments in developing countries, until more data has been compiled. Nevertheless, there are opportunities for the establishment of tropical standard test species in the future if more emphasis is put on further toxicity studies with more local macroinvertebrate species.

Table 1: PECs calculated and residues determined for endosulfan as reported in this thesis and in studies elsewhere in Africa and Brazil. Note: maximum PECs and residue levels are given.

PEC this thesis (µg/L)	PEC literature (µg/L)	Residue this thesis (µg/L)	Residue literature (µg/L)
1.3 (Chapter 4) 4.93 (Chapter 2)	0.0026 (Ansara-Ross et al. 2008) South Africa	0.03 (Chapter 5) 0.10 (Chapter 3)	0.355 (Adeyemi et al. 2015) Nigeria 0.43 (Nwakwoala and Osibanjo et al., 1992) Nigeria 0.003 **(**Raposo and Nilva, 2007) Brazil

Overview of ETR/ESTI/IEDI results

This thesis starts with a model-based risk assessment for seven selected pesticides. The selection was based on volume of use and acute toxicity to humans, with exposure toxicity ratio / estimated short-term intake (ETR/ESTI) outputs based on PRZM/TOXWA predictions **(Chapter 2)**. The next risk assessment produced ETR values based on concentrations measured in a monitoring study in Lake Ziway **(Chapter 4)**.Risks were further calculated in a higher-tier assessment using hazardous concentration 5% (HC5) values derived from species sensitivity distribution (SSD) analyses. The assessment included monitoring results obtained previously by Jansen and Harmsen (2011). Chronic risks to humans using internationally estimated daily intake (IEDI) values were also introduced (**Chapters 4 and 5)**. Results of analysing organo-chlorine pesticide (OCP) residues at sampling sites in rivers and temporary ponds were evaluated in terms of their risks to the environment and human health, using the framework proposed by Teklu et al. (2015). Current usage data obtained from interviews with small-scale farmers in the Debra Zeit area were also evaluated in terms of risks, using the PRIMET_Registration_Ethiopia_1.1 model. Chronic risks to aquatic organisms and SSDs using NOEC values were also introduced in this chapter. Both acute and chronic risks were also determined for the identified OCPs. Only in a few cases were aquatic organisms found to be at high to moderate risk from some pesticides, while the overall risk assessment for humans using surface water as a source of drinking water predicted low to negligible acute risks **(Chapter 5)**. On the other hand, the pesticides spiroxamine and g-chlordane were found to present high chronic risk to humans **(Chapters 4 and 5, respectively)**. In all cases, lower-tier risk assessments were characterised by greater conservatism, and required less effort and data **(Chapter 2)**, while higher-tier assessments were characterised by greater realism but also by greater effort and data requirements **(Chapters 4 and 5)**. All results were in line with the principles of the tiered approach mentioned above. These findings support the use of model-based risk assessment procedures in the Ethiopian pesticide registration system, although further model validation studies need to be undertaken for the introduction of this modern approach in Ethiopia. Similar risk assessment projects elsewhere in Africa found some high risks to humans and aquatic organisms from pesticide use by small-scale farmers(Ahouangninou et al. 2012; Ansara-Ross et al. 2008; Malherbe et al. 2013; Jepson et al. 2014).

In the present project, ETRs, ESTIs, and IEDIs were determined in different studies using different approaches, providing an example of using a tiered approach to risk estimations. **Chapter 2** presents a first-tier assessment, which can be used when little input and data is available. The resulting risk assessment can be referred as more conservative (Boesten et al. 2007; Solomon et al. 2008). In other chapters, more detailed primary (monitoring studies) and secondary (www.epa.gov/ecotox) data was gathered to enable a second- and third-tier risk assessment. This assessment also used SSDs to construct HC5 values and also considered chronic risks **(Chapters 4 and 5)** (Brock et al. 2011;van Leeuwen and Vermeire 2007). An overview of the risk assessments and tier categories in this study is provided in Figure 2.

Chapter 2	Chapter 3	Chapter 4	Chapter 5
• Scenario development • Risk assessment of registered compounds • Humans and environment	• Simple test methodology with local aquatic species • Validation of use of temperate data in risk assessment	• Risk assessment of measured concentrations • Area with large- and small-scale farmers • Humans and environment	• Risk assessment of legacy compounds • Risk assessment of actual usage patterns • Human health and environment

Lower tier → Higher tier

Fig. 2. The tiered risk assessment in the different chapters

Concluding remarks and outlook

The model-based risk assessment of selected pesticides for surface water reported on in **Chapters 2 and 5** ofthis thesis shows that such an assessment can serve as the first tier in the Ethiopian registration procedure. This method can also be used to evaluate the pesticides already registered in Ethiopia. However, adoption of the model requires future commitment from all stakeholders participating in the import, distribution and sales of pesticides in the country. Further model validation studies need to be conducted to further strengthen the reliability of using this model for the Ethiopian context.

The results of the monitoring studies reported on in **Chapters 4 and 5** of this thesis indicate that some pesticides pose a risk to surface water aquatic organisms; this was found for e.g. spiroxamine, lambda-cyhalothrin, profenofos, endosulfan and diazinone in the Debra Zeit and Lake Ziway areas. Follow-up studies need to concentrate on these pesticides to decide on their registration status. This calls for a better monitoring of the pesticide use and liquid waste management at commercial and small-scale farms in close proximity to lakes like Ziway and rivers like Wedecha and Belbela. More effort should also be invested in developing a scenario for large-scale agriculture in greenhouses, since the present tool, which was developed to conduct risk assessments for surface waters, cannot address greenhouse farming. The assessment results show that, overall, acute human health risks posed by using surface water as a source of drinking water can be described as low or negligible.

The single-species toxicity tests we performed with three Ethiopian macroinvertebrate species showed that data relating to temperate species can be used to perform risk assessment for registration purposes until better local data is obtained (**Chapter 3)**. There is, however, a need for a refined technical protocol for standardised toxicity tests with minimum requirements in terms of funding and laboratory facilities in developing countries like Ethiopia.

The overall conclusion of this thesis implies that there is a need to adopt a more structured and scientific method of risk assessment before registration. The political decision to adopt the tool developed by PRRP Ethiopia needs careful consideration. Already registered pesticides should be screened using PRIMET_Registration_Ethiopia_1.1 model, followed by screening pesticides to be registered in the country in the future. Further experimental and monitoring studies, model validation studies and nationwide monitoring also need to be considered. If such measures are implemented successfully, other African countries can use the experience gained by PRRP Ethiopia as a baseline for future activities related to the safe handling of pesticides, by quantifying risks to non-target aquatic organisms and humans before considering these products for registration. Future monitoring should take place at a national level, and a standardised laboratory for pesticide residue analysis should be established in the country so that analytical verification and all kinds of toxicity studies can easily be done for all matrices, and results can be used for regulatory purposes (Fig. 3).

Fig. 3. Future measures for better implementation of pesticide registration system in Ethiopia.

Summary

The current increase in application rate and usage frequency of application of pesticides in Ethiopia pose direct risks to surface water aquatic organisms and humans using surface water as a source of drinking water in rural parts of the country. Therefore it is important to quantify the risks and show the current status of the surface water systems in Ethiopia as regards exposure from pesticide applications. An important tool for the regulation of pesticide-related issues is that of model-based risk assessment, which is currently being used in Europe and elsewhere in the world. Checking the suitability of input data like EC50 values is also important, as this data is currently only available from tests done on temperate species. Subsequent monitoring activities to check the actual residue levels of pesticides in rivers and temporary ponds adjacent to extensive farming activities also provide some idea of the current status of the surface water systems. Combining all this knowledge is believed to bring the current pesticide registration system in Ethiopia one step closer to a more reliable approach, protecting non-target organisms as well as the health of humans at risk.

Chapter 1 of this thesis introduces the current status of pesticide use in Ethiopia compared with global trends and statistics. It describes the urgent need to protect the Ethiopian surface water systems, as the country is endowed with a great many of them and pesticide use is increasing rapidly. This requires an improved registration system for pesticides, which includes tools specifically applicable in the local situation.The present PhD project therefore aimed to assess the environmental risks posed by the extensive use of pesticides in the surface water systems in Ethiopia.The research objectives of the studies reported on in this thesis were to investigate the applicability of model-based risk assessment to predict environmental concentrations in the Ethiopian surface water systems using the PRIMET_Registration_Ethiopia1.1 model, as well as to perform simple chemical monitoring programmes to show the status of residues in Ethiopian surface waters and undertake single-species toxicity tests to compare sensitivities with those of European species.

Chapter 2 addresses the applicability of the model-based risk assessment used currently in the European system, after adjustment to the Ethiopian situation. Seven pesticides, selected on the basis of their toxicity and volume of import, were evaluated. Results of this study indicated that some crop–pesticide combinations posed a risk to aquatic organisms (fish, Daphnia), even when good agricultural practices were implemented in pesticide application. No acute health risks were found for humans using surface water as a source of drinking water for any of the pesticides evaluated.

Toxicity values for risk assessment based on results of tests done only on temperate species need to be verified, by evaluating whether the sensitivity of tropical species is different from temperate ones. We did an experiment to verify this, which is reported on in **Chapter 3.** The test strategy was such that the results obtained for *Daphnia magna* could be compared with literature values to evaluate the accuracy of the strategy. All local species were evaluated in duplicate tests to assess the consistency of the results. We believe that these checks on accuracy and consistency make it possible to (partially) circumvent the need for analytical verification of the test concentrations. The results of this study indicated no systematic differences in sensitivity between the temperate and Ethiopian species as regards the effects of the pesticides endosulfan and diazinon on three arthropods. Future research is needed to confirm these results by developing a suitable protocol for such studies in developing countries with local tropical species.

A monitoring project in Lake Ziway **(Chapter 4)** was performed by screening water samples for more than 300 pesticides. The findings indicated that some of the pesticides posed risks to aquatic organisms, while only one pesticide (spiroxamine) posed a high chronic risk to humans using surface water as a source of drinking water. Long-term monitoring taking account of spatial and temporal variations by determining pesticide residue levels at major entry points to big impoundments like Lake Ziway provides an overview of their current pollution status. The findings of **Chapter 4** indicated that it is not only the commercial farms but also the small-scale farms in the Meki Ziway area which need careful monitoring, as several pesticide residues exceeded the European drinking water standard of 0.1 µg/L in these areas. Careful liquid waste management to protect entry points to Lake Ziway is also important for both small- and large-scale farming activities in the area.

In developing countries like Ethiopia, organochlorine pesticides (OCPs) like endosulfan are still on the list of registered pesticides, even though they have long since been banned from the European system. **Chapter 5** presents the results of a monitoring project in the Wedecha and Belbela irrigation system. The study was mainly done to check the residue levels of OCPs in the river and temporary ponds in the area, and also tried to assess the risks posed by the current use of pesticides by small-scale farmers, by taking the actual application rate and frequency and assuming that the worst-case scenario for surface waters of PRIMET_Registration_Ethiopia_1.1 model is applicable in the area. Results of this study revealed that some OCPs were detected at some sampling sites in rivers and temporary ponds, even though no residues were detected in most of the samples and any residues detected were found in low concentrations. The risk assessment for the current usage data using the PRIMET_Registration_Ethiopia_1.1 model indicated that some pesticides pose high risks to aquatic organisms. The model predicted no acute risk to humans using surface water as a source of drinking water, although a high chronic risk was predicted from the OCP g-chlordane that was detected.

The major findings of this thesis are discussed in **Chapter 6**, like the results for endosulfan as a model output are compared with the residue levels found in the monitoring activities undertaken as part of the PhD project. I also discussed the differences and similarities in the ETR/ESTI values reported throughout the project and the status of model-based risk assessment in the Ethiopian and European contexts, as well as the need for further action to put the results presented in this thesis in particular, and of the PRRP in general, into practice.

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Abbreviations

%	:	percent
<	:	Less than
>	:	Greater than
°C	:	degree celsius
µm	:	micro meter
µS/cm	:	micro Siemens per centimetre
1/n	:	Freundlich exponent
a.i.	:	Active ingredient
AA	:	Addis Ababa
AAU	:	Addis Ababa University
ADI	:	Acceptable Daily Intake
APHRD	:	Animal and Plant Health Directorate
ARfD	:	Acute Reference Dose
B	:	Boron
BW	:	Body Weight
Ca	:	Calcium
Cm	:	Centimetres
CRV	:	Central Rift Valley
Cu	:	Copper
d	:	days
DDT	:	dichlorodiphenyltrichloroethane
DO	:	Dissolved Oxygen
DT_{50soil}	:	Half-life of transformation in soil
$DT_{50water}$,	:	half-life of transformation in water
EC	:	Electrical Conductivity
EC50	:	Median Effect Concentration
ECMWF	:	European Centre for Medium-Range Weather Forecasts

EIAR	:	Ethiopian Institute of Agricultural Research
ERA	:	Environmental Risk Assessment
ESTI	:	Estimated Short Term Intake
ETR	:	Exposure Toxicity Ratio
EU	:	European Union
FAO	:	Food and Agriculture Organization
Fe	:	Iron
FOCUS	:	Forum for the Coordination of Pesticide Fate Models
g a.i./ha	:	gram active ingredient per hectare
g/Kg	:	gram per kilogram
g/L	:	gram per litter
GC_ECD	:	Gas Chromatography with Electron Capture Detector
GC_MS	:	Gas Chromatography_ Mass Spectrometry
h	:	Hour
ha	:	hectare
HC5	:	Hazard Concentration for 5% of the population predicted from ssd curve
HC50	:	Hazard Concentration for 50% of the population predicted from ssd curve
HCH	:	hexachlorocyclohexane
HCl	:	Hydrochloric Acid
HoA REC&N	:	Horn of Africa Regional Environment Centre and Network
IBC	:	Institute of Biodiversity Conservation
IEDI	:	Internationally Estimated Daily Intake
J/mol	:	joules per mole
K	:	Potassium
Kg	:	Kilogram
Kg/ha	:	kilogram per hectare
Km^2	:	Square Kilometres

K_{oc}	:	Coefficient for sorption on soil based on organic carbon content
L	:	Litter
L/ha	:	Litter per hectare :
LC/MS	:	Liquid Chromatography / Mass Spectrometry
LC50	:	Median Lethal Concentration
LL HC5	:	Lower Limit Hazard Concentration for 5% of the population
LLHC50	:	Lower Limit Hazard Concentration for 50% of the population
LMM	:	Low Molecular Mass
LP_dw	:	Large Portion of drinking water
m	:	Meter
mg	:	milligram
Mg	:	Magnesium
mg/kgbw/d	:	milligram per kilogram body weight per day
mg/L	:	milligram per litter
mL/Kg	:	milliliter per killogram
ml/min	:	millilitre per minute
mm	:	millimetre
Mn	:	Manganese
Mo	:	Molybdenum
MoA	:	Ministry of Agriculture
MOARD	:	Ministry of Agriculture and Rural Development
MoH	:	Ministry of health
mPa	:	Vapour pressure
MPL	:	Maximum Permissible Limits
MRLs	:	Maximum Residue Levels
NA	:	Not Available
Na	:	Sodium

NEC	:	No Effect Concentrations
NH4+N	:	Ammonium- Nitrogen
nm	:	Nano Meter
No_3-N	:	Nitrate-Nitrogen
OCPs	:	Organo Chlorine Pesticides
OECD	:	Organization for Economic Co-operation and Development
OPs	:	Organophosphates
P	:	Phosphorus
PAN-UK	:	Pesticide Action Network- United Kingdom
PEC	:	Predicted Environmental Concentration
PEC_{90th}	:	90^{th} percentile concentration in the selected surface water
PEC_{99th}	:	99^{th} percentile concentration in the selected surface water
PHRD	:	Plant Health Regulatory Directorate
pKa	:	Dissociation constant
PNEC	:	Predicted No Effect Concentrations
POPs	:	Persistent Organic Pollutants
PPDB	:	Pesticide Properties Database
PRIMET	:	Pesticide Risks in the tropics to Man Environment and Trade
PRRP	:	Pesticide Risk Reduction Programme
PRZM	:	Pesticides in Root Zone Model
PSMS	:	Pesticide Stock Management System of
RDA	:	Redundancy Analysis
S	:	South
S	:	Sulphur
SE	:	South East
Si	:	Silicon
SPE	:	Solid Phase Extraction

SSD	:	Species Sensitivity Distribution
T	:	Temperature
TCP	:	Technical Cooperation Programme
TDS	:	The Total Dissolved Solids
TOXSWA	:	**TOX**ic substances in **S**urface **WA**ters
TSS	:	Total Soluble Solids
ULHC5	:	Upper Limit Hazard Concentration for 5% of the population
ULHC50	:	Upper Limit Hazard Concentration for 50% of the population
UN	:	United Nations
US-EPA	:	Unites States Environmental Protection Agency
W	:	West
WHO	:	World Health Organization
WHO GEMS	:	World Health Organization Global Environmental Monitoring System
ZFRRC	:	Ziway Fisheries Resources Research Centre
Zn	:	Zink
ZSRC	:	Ziway Soil Research Centre
µg/L	:	micro gram per litter

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Berhan Mellese Teklu

Wageningen University

June 2016

Short Biography

''Our lives are a sum total of the choices we have made''

(Wayne Dyer)

Berhan Mellese Teklu (1976) was born in Ethiopa in a place called Sefere Selam (meaning a village for peace) found in a commercial area called Mesalemia in the capital city Addis Ababa. He is the seventh son of Mellese Teklu (late, 1990) and Fana Kidane. His late father was a surveyor at the then Ethiopian Roads Authority, while his mother is a house wife. His mom took the responsibility of raising him as a single mom struggling through an utter poverty faced because of the reality created by the dictatorial and absolute command economy of the time.

Berhan when getting through the high school education had the chance to join Haromaya University known for specializing in Agricultural Sciences and had a BSc. degree in Plant Sciences (2000). Right after graduation he had the chance to get hired as a junior instructor at Alage Agricultural Vocational and Technical College found some 220 kms away from Addis Ababa. He then joined the Addis Ababa University to study entomology at the department biology and had his MSc degree in the year 2008. Right after having his MSc he worked for a short time in a private company and joined the Ministry of Agriculture of the Extension Directorate.

In the year 2011 he was awarded a scholarship through project called PRRP_Ethiopia funded by the Dutch government to peruse his doctoral degree in the University of Wageningen, The Netherlands, in what is called ‘a sandwich setting’. He then started his PhD in the Aquatic Ecology and Water Quality Management Group of the Wageningen University supervised by Prof. Dr. Paul van den Brink and locally co supervised by Prof. Nigussie Retta of the Addis Ababa University. In his doctoral thesis he tried to put forward the Environmental risk assessment of pesticides in Ethiopia especially considering surface waters as the main protection goals which is quite a new science and a different approach for the country Ethiopia.

During his PhD Berhan has participated in several workshops organized by the PRRP_Ethiopia and also attended one SETAC conference held in Barcelona. He also took several courses and participated in document preparation in connection with PRRP project. In his spare time Berhan likes playing football and watching movies. After his dissertation, Berhan Plans to investigate the possibilities of implementing the model based risk assessment of pesticides for improving the pesticide registration system of Ethiopia or elsewhere in Africa, he is also looking forward to work in future projects related to pesticide fate and effect studies in Africa or elsewhere in the world.

Publications

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A K A D E M I E V A N W E T E N S C H A P P E N

The SENSE Research School declares that **Mr Berhan Teklu** has successfully fulfilled all requirements of the Educational PhD Programme of SENSE with a work load of 39.9 EC, including the following activities:

SENSE PhD Courses

- Introduction to R (2011)
- iGIS: A practical post-graduate GIS course (2011)
- Environmental Risk Assessment of Chemicals (2012)
- Multivariate analysis (2015)
- Environmental Research in Context (2015)
- Research in Context Activity: 'Writing Facebook blog: Be aware of pesticides impacting health and environment in Ethiopia and the World' (2016)

Other PhD and Advanced MSc Courses

- Scientific Publishing, Wageningen University (2011)
- Ecology: Classics and Trends, Wageningen University (2011)
- Information Literacy PhD including End Note introduction, Wageningen University (2012)
- The Use of Biological Traits in Ecology, University of Coimbra (2011)

Oral Presentations

- *Surface water risk assessment of pesticides in Ethiopia.* SETAC Europe 25th Annual Meeting, 3-7 May 2015, Barcelona, Spain

SENSE Coordinator PhD Education

Dr. ing. Monique Gulickx