Assessment of Chemical Pollution With Routine Pesticides Using PRIMET, a Pesticide Risk Model in the Benoe Stream in the South-West Region of Cameroon

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Abstract
        Widespread extensive and improper application of pesticides may pose risk to aquatic ecosystem and affect non-target organisms. This study aimed at assessing chemical pollution with pesticides using the PRIMET (Pesticides Risks in the tropics to Man, Environment and Trade) model in the Benoe stream. Ecotoxicological data on pesticides, pesticide and water physico-chemistry were used as input parameters. Water parameters were measured monthly for 06 months in 08 sampling points along the stream. Pesticide characteristics were obtained from the Pesticides Properties Data Base (PPDB) and the PRIMET software. The risk assessment was done for 44 active ingredients used in the area and whose ecotoxicological and physico-chemical data were available. Water parameters significantly ($p < 0.05$) varied across seasons. Based on the Exposure Toxicity Ratio (ETR)

and the Predicted Exposure Concentration (PEC), the model predicted 09 pesticides to pose a definite acute risk (ETR>100), seven to pose an acute possible risk (1≤ETR≤100) and 28 to pose no risk (ETR<1). Cadusafos (ETR=5200, PEC=39µg/l) was the most risky pesticide while imazalil (ETR=0.0002, PEC=0.0053µg/l) was the least risky compound. Cypermethrin was predicted to pose both definite acute risk to water and possible chronic risk to fish, water and *Daphnia.* Seven active ingredients were predicted to pose possible chronic risk to *Daphnia.* Pesticide used in plantations near water bodies is a threat to the aquatic ecosystem augmented in case of misuse. Bioaccumulation potential and impact of these compounds on water quality and biota community structure should be examined.

Keywords: *Risk Assessment, PRIMET, Aquatic, ETR*

Introduction

Exposure of organisms to xenobiotics such as pesticides is a serious environmental and toxicological chemistry matter (Olufayo and Alade, 2012). Pesticides have potential effects on organisms in water, in the soil, on plants and pose a threat to human health via dietary exposure when they consume contaminated ground water, macrophytes and fishes found in internal waters (FAO, 2010a). Risk is the chance, within a time frame, of an adverse event occurring with specific consequences (Pollino *et al.,* 2012). Pesticides are carcinogenic and neurotoxic. Those containing chlorine can cause skin irritation known as chloracne (Chevalier *et al.,* 2003). Due to their toxicity and their constant use throughout the world, pesticides are one of the main factors triggering biodiversity decline. Thousands of pesticides are used worldwide but data on contamination for any particular pesticide are usually quite limited (Bhavika and Pragna, 2014). Risk assessment is a process used to collect, organize, integrate, and analyze information for use in a planning environment, where the outcome is the analysis and prioritization of risks or hazards to a stated objective (Pollino *et al.,* 2012).

In recent years, the interest in using ecological population models as a tool for pesticide risk assessment has increased rapidly (Wang and Grimm, 2010). Despite considerable increased pesticide use over the past decades, little research has been done into their fate and effects in surface waters in tropical regions (Daam and Brink , 2010). In poor countries, the lack of resources is the main hindrance in risk assessment. Qualitative, quantitative or a combination of both models play a key role in risk assessment (Pollino *et al.,* 2012). It is still unclear which endpoint (population density, population growth, etc.) is the most sensitive indicator of population-level effects and how risk can be evaluated at the population level (Wang and Grimm, 2010). PRIMET (Pesticides Risks in the tropics to Man,

Environment and Trade) is a simple risk assessment model that requires few inputs and is suitable for use in developing countries (Peteers *et al.,* 2008).This model has been used in two Asian countries (Thailand and Sri Lanka) and in South Africa (Malherbe *et al*., 2013). PRIMET is able to estimate the risk of pesticides application to aquatic and terrestrial life, earthworms, bees, non-target arthropods, the use of groundwater as drinking water and dietary exposure via the consumption of groundwater, vegetables, fish and macrophytes. It has a wide scope for application, needs a limited number of parameters and is cost-effective, thus making it easy to use even by people without specialized training (Peeters *et al.*, 2008).

The risk posed by pesticides in Cameroon remains unclear as there is almost no comprehensive report existing on pesticide risk assessment in the country. The Benoe Stream (South-West Cameroon) takes its sources in Buea and runs through Mutengene, Tiko and makes its estuary around Bwenga; it is surrounded with small scale farms and Cameroon Development Corporation (CDC) plantations, subjecting it to pollution from urban, municipal and agricultural origin. This study aimed at assessing pesticide risk in the Benoe Stream using the PRIMET model, based on a worse-case scenario. This was done through measurement of water parameters (field and laboratory) and pesticide characteristics (physico-chemical characteristics, ecotoxicological data and application scheme) that were all used as input parameters.

Material and methods

PRIMET requires two sets of data as input parameters: pesticide characteristics and water characteristics (Peeters *et al.*, 2008).

Pesticides characteristics

Pesticide characteristics including molecular mass (g/mol), saturated vapour pressure (Pa), solubility (mg/l), half-life in water (days), half-life in sediments (days), organic carbon-water partition coefficient (l/kg) and ecotoxicological data such as LC50-vertebrates (Median Lethal Dose), LC50-invertebrates, LC50-primary producers, NOEC-Fish (No Observable Effect Concentration) and NOEC-*Daphnia* were obtained from the PRIMET software and the PPDB (Pesticide Properties Data Base) (IUPAC, 2017).

The specific pesticide application schemes practiced by the farmers were determined by survey in terms of dosage, number of applications, and interval between applications. These data are found together with ETR values in tables 4, 5 and 6. The default % spray drift in the PRIMET software is 2.77% and is applicable if the distance to the ditch is 1m. That value was used as recommended by Peeters *et al.* (2008) because the stream

was adjacent to farms. These data have been previously collected for 44 active ingredients commonly used in the area (Kenko *et al.,* 2017).

Water characteristics

Water physico-chemical parameters were collected over six months (December 2016 to May 2017) in eight sampling points (S1, S2,…,S8) in the Benoe stream along small scale farms and CDC Ndongo and Holthforth farms. Sampling points were chosen based on land use and the location of farms. Surveys were holistic taking into account seasonal variation in the hydrological regime of the stream.

The ambient temperature was measured *in situ* with a thermometer and values were converted from °C into K (Kelvin) as required by PRIMET. The amount of suspended solids (kg/l) and the mass fraction of organic matter in suspended solids (g/g) were determined using standard methods (Pauwels *et al.,*1992).Water velocity (V) was determined using the float method (Michaud and Wierenga, 2005). The bottom width (B) and the depth of the canal (h) were determined using a measuring tape and results expressed in meters. The length of the canal (l) was calculated from the GPS coordinates. The side slope was determined as recommended by Van den Brink *et al.* (2005) and Peeters *et al.* (2008).

Data processing and analysis

The aquatic risk assessment of pesticides was carried out using pesticides application rate data, physico-chemical properties parameters of the water body. For each active ingredient, PRIMET calculated the Predicted Exposure Concentration (PEC), the Predicted No Effects Concentration (PNEC) and the Exposure Toxicity Ratio (ETR=PEC/PNEC) (Ansara-Ross *et al.,* 2008). Risk assessment for given pesticide active ingredients was done based on the following ETR categories as proposed by Peeters *et al.* (2008):

- ❖ ETR < 1……………….…….No Risk
- ❖ 1 ≤ETR ≤100………………Possible Risk
- ❖ ETR > 100………………...Definite Risk

ANOVA was used to determine if hydrological parameters varied across sampling sites, whereas the t-test was performed to compare the means of these parameters between seasons. Principal Component Analysis (PCA) was used to visualize possibly correlated hydrological variables in a two dimensional plane across sampling points. All statistical analyses were conducted in R 3.4.0 (R Core Team, 2017).

Results
Water Hydrology

The mean values of water parameters (Mean±SEM) are presented in table 1. Table 2 gives the variation of water parameters in space while table 3 presents seasonal variation in water parameters.

Table 1: Hydrological variables of the Benoe stream

Variable	Description	N	Mean±SEM
B(m)	Bottom Width	48	5.28±0.24
H(m)	Depth	48	0.43±0.03
L(m)	Long Profile	1	17284
MOM(g/g)	Mass fraction of organic matter in suspended solids	48	0.07±0.03
S1(/)	Side Slope	48	1.6±0.18
SS(kg/l)	Mass concentration of suspended solids	48	0.001861±0.000485
T(K)	Water temperature	48	299.48±0.21
V(m/d)	Flow velocity	48	31806±2918.2

SEM= Standard Error of Mean   N= Sample Size

Table 2: Variation of hydrological variables means across sampling points

Var.	Sampling Points							
	S1	S2	S3	S4	S5	S6	S7	S8
Sl	1.71±0.93[a]	1.66±1.36[a]	1.77±1.06[a]	2.04±1.57[a]	1.73±1.74[a]	1.51±1.37[a]	1.52±1.26[a]	0.817±0.47[a]
MOM(g/g)	0.17±0.41[a]	0±0[a]	0.007±0.02[a]	0.01±0.024[a]	0.13±0.33[a]	0.11±0.26[a]	0.07±0.171[a]	0.07±0.18[a]
B(m)	7.42±0.80[c]	4.83±1.03[ab]	5.77±1.00[b]	4.47±1.83[ab]	4.6±0.47[ab]	3.53±1.39[a]	5.53±1.77[b]	6.12±1.48[bc]
H (m)	0.27±0.08[a]	0.36±0.15[a]	0.44±0.19[ab]	0.37±0.23[ab]	0.51±0.27[ab]	0.39±0.14[ab]	0.43±0.27[ab]	0.64±0.27[b]
SS(kg/l)	0.001±0.003[a]	0.001±0.003[a]	0.001±0.003[a]	0.003±0.004[a]	0.002±0.003[a]	0.002±0.003[a]	0.001±0.003[a]	0.003±0.005[a]
T (K)	298.11±1.05[a]	298.93±1.21[abc]	299.78±0.68[bc]	298.64±1.67[ab]	300.58±1.42[c]	300.31±1.72[bc]	299.96±1.22[bc]	299.51±0.88[abc]
V (m/d)	31680±17199.2[ab]	37584±5430.2[ab]	21744±12959[a]	23616±11690.1[a]	21600±10694.1[a]	54000±32858.1[b]	39888±25375.2[ab]	24336±16460.6[a]

Var.=variables; On the same line, values bearing the same letter are not significantly different (p≥0.05); Mom= mass fraction of organic matter in suspended solids; SS=amount of suspended solids; Temp= Temperature; B=bottom width

The ANOVA revealed that, for the slope, the mass fraction of organic matter in suspended solids (MOM), the depth, the suspended solids (SS) and the velocity, there was no significant difference in the means of hydrological parameters in the various sampling points (p≥0.05). The bottom width (B) had some significant differences in means between points S1 as compared to S2, S4, S5 and S6. The mean water temperature also varied significantly between S6 and all the other sampling points throughout the study. Seasonal variation of water hydrology was assessed and presented in table 3.

Table 3: Variation of hydrological variables across seasons

Season	Dry	Rainy	P-value	Statistic
Sl	2.11±1.33	1.08±0.86	0.003	10.19
MOM(g/g)	0.14±0.29	0±0	0.02	5.66
B(m)	5.11±1.74	5.46±1.56	**0.47**	0.54
H(m)	0.35±0.17	0.51±0.24	0.01	6.92
SS (kg/l)	0.0036±0.004	0.00008±0.00009	0.0003	18.56
T(K)	299.93±1.83	299.03±0.64	0.03	5.18
V (m/d)	23436±13607.03	40176±22448.10	0.003	9.76

The t-test revealed that, apart for the bottom width, there was a significant seasonal variation in all the other parameters. The slope was significantly smaller in the rainy season, *idem* the mass fraction of organic matter, the suspended solids and the temperature. The velocity and the depth significantly ($p<0.05$) decreased in the dry season. The linear uncorrelated variables following PCA are shown in figure 1(spatial) and figure 2(temporal).
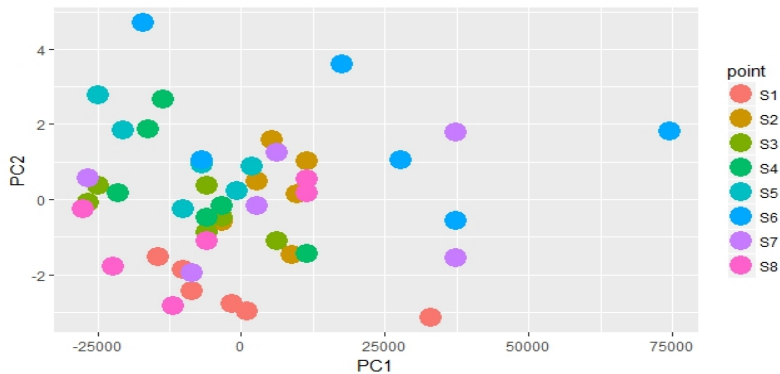

Figure 1: PCA showing linear uncorrelated environmental variables of the Benoe stream across sampling sites

From figure 1, variables of point 6 are a little bit isolated from those in other sampling points. Figure 2 presents linear uncorrelated variables across seasons.
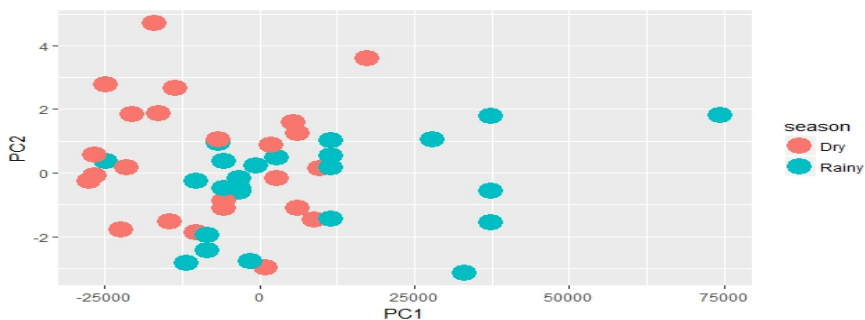

Figure 2: PCA showing linear uncorrelated environmental variables of the Benoe stream across seasons

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It appeared from figure 2 that there was a noticeable seasonal variation on water hydrology. This confirms the necessity to take seasons into account before carrying out risk assessment.

Pesticide risk assessment

PRIMET predicted 28 (63.6% of total active ingredients assessed) pesticides to pose no risk (ETR < 1), 7 (15.9%) pesticides to pose a possible risk (1 ≤ETR ≤100) and 9 (20.5%) pesticides to pose a definite risk (ETR > 100) to water (figure 3). Only cypermethrin was predicted to pose a possible chronic risk to water (ETR_2=1, PEC=0.42µg/l) and fish (ETR_2=5.6, PEC=0.42µg/l). This was the only compound with risks at all the levels (acute, chronic, possible and definite). Seven (15.9%) pesticides were predicted to pose a possible chronic risk to *Daphnia* which was more vulnerable to pesticides than fish.
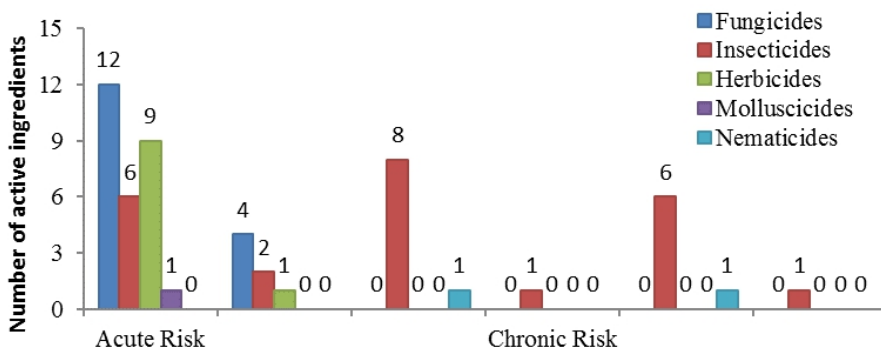

Figure 3: Number of pesticides per families based for each risk category

The pesticide application scheme, PEC and ETR are found in tables 4 (fungicides), 5 (insecticides) and 6 (herbicides-molluscicides-nematicides).

Table 4: Fungicides application rates as determined from surveys, PEC and ETR values

Active ingredients	Crop	Application interval (days)	Applied or recommended dose (g.a.i/ha)	Number of applications	PEC water (µg/l)	ETR water acute	ETR water chronic	ETR water chronic Daphnia	ETR water chronic Fish
Azoxystrobin	banana	180	100	2	0.69	0.3	0.0005	0.0007	0.0005
Bitertanol	banana	180	300	2	0.02	0.0011	2.00E-05	2.30E-05	2.00E-05
Carbendazim	rubber	36	40	10	0.28	0.11	1.20E-05	1.20E-05	0.0014
Chlorothalonil	banana	180	1000	2	0.5	4.5	0.0019	0.0019	0.0041
Copper hydroxide	cocoa	3	50	40	0.19	0.24	0.0066	0.0066	/
Difenoconazole	banana	180	100	2	0.55	0.071	0.0068	0.013	0.0068
Epoxiconazole	banana	180	100	2	0.64	3.83	0.0002	0.0002	0.0072
Fenpropimorph	banana	180	616	2	4.4	0.11	0.0002	0.0002	0.08
Imazalil	banana	180	1	2	0.0053	0.0002	1.90E-07	1.90E-07	1.20E-05

Active ingredients	Crop	Application interval (days)	Applied or recommended dose (g.a.i/ha)	Number of applications	PEC$_1$ water (µg/l)	ETR water acute	ETR water chronic	ETR water chronic Daphnia	ETR water chronic Fish
Mancozeb	banana	180	2000	2	13	18	0.16	0.16	0.4
Maneb	tomato	2	100	31	0.69	0.49	0.003	0.003	0.17
Metalaxyl	cocoa	20	50	15	0.35	0.0014	4.10E-06	4.10E-06	8.60E-06
Propiconazole	banana	180	100	2	0.66	0.07	9.20E-06	9.20E-06	0.001
Pyraclostrobin	rubber	180	100	2	0.42	7	0.008	0.01	0.008
Tebuconazole	coffee	30	59	4	0.39	0.0093	0.0004	0.0004	0.0036
Thiabendazole	banana	180	500	2	2.2	0.4	0.007	0.007	0.02

Table 5: Insecticides application rates as determined from surveys, PEC and ETR values

Active ingredients	Crop	Application interval (days)	Applied or recommended dose (g.a.i/ha)	Number of applications	PEC$_1$ water (µg/l)	ETR water acute	ETR water chronic	ETR water chronic Daphnia	ETR water chronic Fish
Acetamiprid	cocoa	30	1000	4	7.1	0.014	3.90E-05	0.0002	3.90E-05
Bifenthrin	tomato	21	147	2	0.06	10	0.03	3.3	0.03
Cadusafos	banana	180	5600	2	39	5.20E+03	0.83	25	0.83
Carbofuran	banana	180	5600	2	40	201	0.17	0.71	0.17
Chlorpyrifos	corn	30	73.5	2	0.26	263	0.062	0.062	0.17
Cypermethrin	tomato	7	441	7	0.42	714	1	1	5.6
Deltamethrin	corn	60	73.5	6	0.51	255	0.06	0.06	0.11
Dimethoate	tomato	15	14.7	8	0.088	0.0019	0.0002	0.0008	0.0002
Fipronil	cocoa	60	88	6	0.6	0.32	0.0013	0.0013	0.0045
Imidacloprid	cocoa	56	4412	3	29	0.033	0.0003	0.0024	0.0003
Lambda-cyhalothrin	cocoa	30	1000	4	0.55	3.40E+03	0.12	6.7	0.12
Lindane	cocoa	180	735.3	2	4.8	166	1.30E-05	1.30E-05	0.0002
Malathion	beans	184	441	2	2.8	398	0.0018	3.7	0.0018
Novaluron	tomato	21	147	2	1	0.18	0.03	3.8	0.03
Oxamyl	banana	180	2044	2	15	4.6	0.0014	0.05	0.0014
Thiamethoxam	cocoa	7	2500	9	18	0.02	7.90E-05	7.90E-05	0.0004

Table 6: Herbicides, molluscicides and nematicides application rates as determined from surveys, PEC and ETR values

Active ingredients	Crop	Application interval (days)	Applied or recommended dose (g.a.i/ha)	Number of applications	PEC$_1$ water (µg/l)	ETR water acute	ETR water chronic	ETR water chronic Daphnia	ETR water chronic Fish
2,4-D amine	rubber	60	221	6	1.6	0.0016	2.70E-06	4.90E-06	2.70E-06
Clethodim	corn	120	147	1	1.1	0.0016	2.50E-06	2.50E-06	2.90E-05
Diuron	weeds	365	295	1	2.1	0.94	0.006	0.003	0.0006
Glufosinate ammonium	banana	365	735	1	5.1	0.12	5.40E-06	0.0012	5.40E-06
Glyphosate	coffee	180	588	2	4.2	0.07	1.70E-05	2.70E-05	1.70E-05
Glyphotrimesium	banana	365	588	1	4.2	0.035	9.30E-06	0.0006	9.30E-06
Nicosulfuron	corn	30	147	3	1	0.0016	1.20E-05	3.00E-05	1.20E-05
Oxadiazon	weeds	365	29.5	1	0.18	0.3	0.0005	0.0005	0.022
Paraquat	weeds	90	442	3	0.041	1.8	5.20E-05	5.20E-05	
Triclopyr	weeds	21	551	3	4	0.0034	9.80E-06	9.80E-06	1.50E-05

Metaldehyde	banana	365	12000	1	86	0.11	0.0001	0.0001	0.0002
Ethoprophos	banana	120	54000	3	386	406	0.66	10	0.66

From the above tables (4, 5 and 6), it seems that herbicides, molluscicides and fungicides were generally less risky compounds than insecticides and nematicides.

Discussion
Seasonal variation in water parameters

Due to seasonal variation and the contribution of tributaries and points sources, water hydrology may be subjected to some changes. Variations may also be related to anthropologic pressure on the stream. According to Zhang *et al.* (2012), environmental degradation and rapid socioeconomic growth drastically changed the patterns of flow discharge in China's river basins. In the dry season, almost half of the stream is diverted into the CDC farm for irrigation, pesticide application and banana processing purposes. This may account for the seasonal variation in the water parameters of the stream. Hydro-meteorological factors such as water flow, rainfall and temperature change significantly relate to the temporal and spatial dynamics of phytoplankton (Li *et al.,* 2013).

Risk Assessment
The "no risk" category

Most of the active ingredients (63.6%) were predicted to pose minor risk. The toxicity of pollutants to aquatic organisms is influenced by water physico-chemistry, concentration of the chemical and the physiological state of the organism (Mischke and Avery, 2013). Pesticide ability to persist may also determine its potential to pose risk. The persistence, measured as half-life is determined by degradation processes such as biodegradation, metabolisms, hydrolysis, photolysis and oxidation (FAO, 2010b). If degradation is rapid, then the compound may be unlikely to pose a serious risk especially a chronic one. The faster a given pesticide breaks down in the environment, the less threat it poses to aquatic life (Sarwar, 2012). In addition, on the population level, effects of pesticides depend not only on exposure and toxicity, but also on factors such as life history characteristics, population structure, timing of application, presence of refuges in time and space, and landscape structure (Schmolke et al. 2010).

Herbicides

Ten herbicides were assessed and nine were predicted to pose no risk. It has been reported that, many herbicides are found in surface and groundwater worldwide in varying concentration (Leblanc, 2004), but they

are usually more toxic to plants since animals lack their target enzyme. Herbicides are generally less toxic to aquatic organisms than insecticides (Helfrich, 2009).

The ability of diuron to pose no risk may be related to the long application interval at relatively low dosage. Also, this pesticide has been reported to show moderate toxicity to aquatic invertebrates (Giacomazzi and Cochet, 2004) and it is less hazardous to fish (Mhadhbi and Beiras, 2012) despite its detection in water above its lowest benchmark (Ensminger *et al.,* 2013).

Oxadiazon, a pre-emergence selective herbicide that inhibits protoporphyrinogen oxidase was predicted to pose no risk probably because of its low application rate and moderate toxicity to fish and *Daphnia* (IUPAC, 2017). In addition to this oxadiazon was reported by Fourie (1992) to exhibit less persistence as compared to other pre-emergence herbicides.

Glufosinate ammonium is a herbicide which is highly soluble in water. Applied on banana, its low application rate may justify its classification in the no risk category even though the dosage was relatively high. This pesticide shows a moderate to low toxicity to most aquatic organisms (IUPAC, 2017). Its persistence is also relatively low (Syan *et al.,* 2014) making it less risky.

Glyphosate is a non-selective herbicide, the world's most widely used herbicide (Evan *et al.,* 2007). Kenko *et al.* (2017) also reported that glyphosate was the most used herbicide in the Fako Division, South West Cameroon. It is moderately toxic to most aquatic organisms (IUPAC, 2017) and low application rate and dosage might have accounted for its capacity to pose no risk. In a previous study, this pesticide had an ETR=0.2 putting it in the no risk category (Malherbe *et al.,* 2013). This value is larger than the 0.07 ETR value found in this study but both values are lower than 1. In water glyphosate bound to suspended particles and bottom sediments and is rapidly inactivated (Helfrich, 2009).

Glyphosate trimesium is a non-selective herbicide used in banana farms at CDC once a year, it has a high degradability; this low persistence and long application interval may explain its ability to pose no risk. Also, IUPAC (2017) reported it to be moderately toxic to most aquatic organisms. This compound has even been recommended for combination with biocontrol in IPM, a sustainable and eco-friendly technique because of its low toxicity to aquatic vertebrates (Mohan, 2011).

Triclopyr is a herbicide for perennial broad-leaved and woody weed control. Despite its detection in water and sediments around urban areas in California (Ensminger *et al.,* 2013), it was predicted to pose no risk. This may be related to its low application frequency and moderate persistence

(DT50-water=24.8days). So its presence in water or sediments samples may be punctual.

Nicosulfuron is a post-emergence selective herbicide. This compound was reported to have a relatively higher persistence in water (DT-50=75d) as compared to other sulfonylurea herbicides (Cessna *et al.,* 2015. Nevertheless, it was predicted to pose no risk probably because of its use in relatively low dosage.

2,4-D is a selective systemic herbicide highly soluble in water and slightly toxic to fish and aquatic invertebrates (IUPAC, 2017). It was used at moderate dosage (221ga.i/ha), hence its capacity to pose no risk. This compound has been detected in water and sediment samples (Ensminger *et al.,* 2013) but it rapidly and completely decomposes in about 3 weeks (Helfrich, 2009).

Clethodim is a systemic herbicide used to control annual and perennial grasses. It was predicted to pose no risk probably because of the low application rate and high degradability. In addition, new families of herbicides have low toxicity to animals (Leblanc, 2004).

Fungicides

Of the 16 fungicides assessed, 12 were predicted to pose no risk. This goes along with the findings of Leblanc (2004) for whom fungicides may be relatively non-toxic even though their hydrolysis yields carcinogens such as ethylthiourea. Helfrich (2009) also found that fungicides are not as highly toxic to fish and aquatic animals as insecticides.

Thiabendazole is post-harvest fungicide with systemic action;it compromises the cytoskeleton (IUPAC, 2017). It is used on banana by the CDC at 500g.a.i/ha twice a year; this application interval may explain its ability to pose no risk. Idem like Maneb, a fungicide that has a multi-site activity and a non-specific mode of action. It did not pose risk because of high degradability ($DT_{50-water}$=0.35days) and low dosage (100g.a.i/ha).

Copper hydroxide is a fungicide used on cocoa. With a very long $DT_{50-water}$ (1.0E+6days), it was used for cocoa at 50g.a.i/ha, this low dosage may justify its ability to pose no risk. Also, its long DT50-water is due to its heavy metal component (Cu). Copper is among the most hazardous heavy metals for health (Chevalier *et al.,* 2003) and it accumulates in fish liver and kidneys but its concentration is expected to be metabolically regulated in vertebrates since it is an essential element (Metcheva *et al.,* 2010). Rauf and Javed (2007) showed a significant relationship between accumulation of plankton and water physico-chemistry but PRIMET predicted it to pose no risk; in fact environmental conditions (oxygen, temperature, hardness, salinity, other metals) may also affect metal toxicity.

Azoxystrobin is a post-emergence broad-spectrum fungicide that was used on banana by the CDC. It is moderately toxic to most aquatic life (IUPAC, 2017) hence its potential to pose no risk. It was also applied at relatively low dosage. Azoxystrobin residues have been detected in water bodies (Telo *et al.,* 2015) but its degradation is faster in alkaline pH (Singh *et al.* 2010).

Fenpropimorph is a fungicide having a systemic action. It was used on banana at 616g.a.i/ha twice a year and because of its high degradation rate ($DT_{50\text{-water}}$ is 2.65days), it could not pose a risk.

Carbendazim is a fungicide with a low aqueous solubility. It can be very persistent in water systems (Grogan and Jukes, 2003), but it was used at low dosage (40g.a.i/ha). Its moderately toxicity to most aquatic organisms may explain why PRIMET predicted it to pose no risk. This result corroborates those of Malherbe *et al.* (2013) who also predicted this active ingredient to pose no risk to water (ETR=0.2); the ETR value (0.11) of this study is even smaller.

Difenoconazole is a broad-spectrum fungicide. It was used on banana twice a year at 100g.a.i/ha. Having it in the no risk group goes along with its moderate toxicity to most aquatic organisms (IUPAC, 2017), low dosage and low application rate. It may be detected in water bodies (Telo *et al.,* 2015) but the quantity and the persistence may be at acceptable levels.

Propiconazole is systemic fungicide acting via the demethylation of C-14 during ergosterol biosynthesis (IUPAC, 2017). It was predicted to pose no risk because of its high degradability ($DT_{50\text{-water}}$=6days), low application rate and dosage on CDC banana (twice a year at 100g.a.i/ha).

Bitertanol is a fungicide with moderate toxicity and low solubility (IUPAC, 2017). With 20 days for $DT_{50\text{-water}}$, it was used in CDC banana farm at 300g.a.i/ha twice a year. This application scheme justifies its classification in the no risk category.

Tebuconazole is a systemic fungicide that inhibits sterol biosynthesis disrupting membrane function (IUPAC, 2017). The low application dose (59g.a.i /ha) may explain its prediction to pose no risk. This result corroborates the findings of Malherbe *et al.* (2013) who had an ETR=0.04; the value of this study is smaller (ETR=0.0093).

Metalaxyl is a systemic fungicide. It was used for cocoa in this study at 50g.a.i/ha. This low dosage may justify its ability to pose no risk together with its moderate degradability.

Imazalil is a systemic fungicide which disrupts membrane function (IUPAC, 2017). This is the less risky compound of this survey. It was used for banana cultivation at CDC with 2 applications per year; this may justify its low ETR.

Insecticides

Fripronil is a broad-spectrum insecticide. It may occurs in relatively high dose in water samples (Ensminger *et al.,* 2013) but its use on cocoa at low dosage may account for its ability to pose no risk. *Idem* like novaluron, a growth regulator (chitin synthesis inhibitor) used to control a range of pests. It was predicted to pose no risk because of its low persistence (DT50-water=0.95days) and its relatively low dosage and application rate.

Imidacloprid is a neonicotinoid insecticide, highly soluble and non-toxic to fish (IUPAC, 2017); this may be why it was predicted to pose no risk even though according to laboratory work, this pesticide caused an increase in the mortality of fish with the duration of exposure (Bhavika and Pragna, 2014). Its classification in the no risk group here may assume that the toxicity depends on other environmental variables.

Thiamethoxam is an insecticide that shows a broad spectrum systemic action. It was used on cocoa at 2500g.a.i/ha. Despite this high dosage, its ability to pose no risk is due to its low toxicity (IUPAC, 2017) and low persistence even though thiamethoxan residues have been detected in irrigation water in rice farms (Telo *et al.,* 2015). The amount detected might be either negligible or its presence might be punctual in water.

Acetamiprid is an insecticide highly soluble in water that may be very persistent in aquatic systems. It was predicted to pose no risk because of its moderate toxicity to most aquatic organisms and relatively low application rate.

Dimethoate is an organophosphate insecticide highly soluble in water. Illegally used in Cameroon (Kenko *et al.,* 2017), it does not normally persist in aerobic aquatic systems and its moderate toxicity to most aquatic species (IUPAC, 2017) accounted for its ability to pose no risk. In this study it was used on tomato at relatively low dosage. These results corroborate the findings of Malherbe *et al. (*2013) who predicted dimethoate to pose no risk (ETR=0.01).

Molluscicides

Metaldehyde is a contact and systemic molluscicide used to control slugs and snails. Hundreds of snails are caught daily by villagers to prepare a meal locally known as "congo meat"; this may contribute to a reduction of molluscicide-dependence, hence its one year application frequency and its inability to pose aquatic risk even in high dosage (12000g.a.i/ha). In addition, it has a low persistence based on its half-life in water.

The "possible risk" category

Seven active ingredients (15.9%) were predicted to pose a possible risk. The environmental fate of a pesticide depends on factors such as the soil

sorption coefficient, the solubility, the saturated vapour pressure and molar mass. These parameters can be used to predict the environmental fate of a pesticide (FAO, 2010b). Aquatic organisms in streams flowing through croplands are likely to receive repeated low doses of pesticides from runoff (Helfrich, 2009).

Mancozeb is a broad-spectrum fungicide having low aqueous solubility but it may be persistent in water. Its ability to pose a possible risk may be related to its high toxicity to fish and aquatic invertebrates (IUPAC, 2017). Also, it was applied in a relatively high dosage (2000g.a.i/ha).

Bifenthrin is a parathyroid insecticide having low aqueous solubility. Used twice a season on tomato 147g.a.i/ha, this sodium channel modulator has been reported to be toxic to most aquatic organisms (IUPAC, 2017), hence its ability to pose a possible risk. Bifenthrin was reported by Ensminger *et al.* (2013) to be a serious contaminant in water samples in a study carried out in California; it was found above the lowest USEPA aquatic benchmark.

Pyraclostrobin is a fungicide that inhibits respiration. This compound is highly toxic to fish and aquatic invertebrates ($LC_{50\text{-fish}}$=0.006mg/l, $LC_{50\text{-Daphnia}}$ =0.016mg/l) hence the prediction to pose a possible risk despite the low application rate.

Oxamyl is a soil-applied insecticide. With a systemic action, it acts as acetyl cholinesterase inhibitor (IUPAC, 2017). The application dose was 2044g.a.i/ha on banana 2 times a year. Its ETR value may be related to this use in relatively high dose.

Chlorothalonil has a low aqueous solubility and it may be persistent in water. With a great bioaccumulation potential, Chlorothalonil is toxic to aquatic organisms (IUPAC, 2017) and the application rate was 1000g.a.i/ha on banana two times a year, making it risky for the aquatic milieu.

Epoxiconazole is a broad-spectrum fungicide that may persist in water systems. It was used in relative low dose and it has a low bioaccumulation capacity (IUPAC, 2017). So its presence in the possible risk category may be related to its DT50-water (65.8days) and its moderate toxicity to most aquatic organisms.

Paraquat is an herbicide with a broad-spectrum action. It has high degradability, stable in sediments and was used in moderate rate (442g.a.i/ha, three times a season). This application rate may justify its ability to pose a possible risk. In the same line, Malherbe *et al*. (2013) reported Paraquat (ETR=73) to pose a possible risk to water in South Africa. In the study, a lower ETR=1.8 was obtained but both values are in the possible risk category.

The "definite" risk category

Nine pesticides (20.5%), including 8 insecticides were predicted by PRIMET to pose a definite risk. Insecticides are extremely hazardous to fish and wildlife and their capacity to harm fish and aquatic animals is largely a function of their toxicity, exposure time, dose rate and persistence in the environment (Helfrich, 2009). Insecticide contamination is a major risk for biodiversity in water bodies (Sarwar, 2012). The impact of pesticides on water is tributary to many pesticide related factors such as active ingredient formulation, impurities, additives, depredates (FAO, 2010). Factors accounting for frequent water pollution by pesticides include spray drift, runoff, leaching or direct application of pesticides onto surface water (PAN, 2010).

Cadusafos is an organophosphate insecticide having a moderate aquatic solubility and can be persistent in water systems (IUPAC, 2017). The $LC_{50\text{-Daphnia}} = 0.75\mu g/l < PEC = 39\mu g/l$, therefore, it can be toxic even at low dosage. It is highly toxic to most aquatic organisms and since it was used in high rate (5600g.a.i/ha of banana two times a year),it is not surprising to have it as the most risky compound in this study with the highest ETR (5200).

Lambda-cyhalothrin is a pyrethroid insecticide with a low aqueous solubility. Acting as sodium channel modulator, it is highly toxic to fish and aquatic invertebrates. It definitely posed a risk because of the high rate of application (4 times a season) in addition to its high toxicity to *Daphnia* ($LC_{50} = 0.36\mu g/l < PEC = 0.55\mu g/l$).

Cypermethrin is a pyrethroid insecticide with a low aqueous solubility. Its high toxicity to *Daphnia* ($LC_{50} = 0.36\mu g/l < PEC = 0.42\mu g/l$) and the number of applications (441g.a.i/ha 7 times per season) account for its ability to pose a risk. IUPAC (2017) reported it to be a serious marine pollutant. PRIMET predicted this insecticide to pose a possible risk to water (ETR=55) in a study led by Ansara-Ross *et al.* (2008) in South Africa. The ETR value for this study is quite higher (ETR=714).

Ethoprophos is abroad-spectrum nematicides. This chemical is highly toxic to fish ($LC_{50} = 320\mu g/l < PEC = 386\mu g/l$) and *Daphnia* ($LC_{50} = 200\mu g/l < PEC = 386\mu g/l$). In addition, it was used in high dose (54000g.a.i/ha in CDC banana farms). Its toxicity and application dose are closely linked to its ability to be risky in aquatic systems.

Malathion is an insecticide that is moderately soluble in water. It has been detected above the lowest US EPA aquatic benchmark (Ensminger *et al.,* 2013) but it is not usually persistent in water systems (IUPAC, 2017).However it is highly toxic to aquatic species ($LC_{50\text{-Daphnia}} = 0.7\mu g/l < PEC = 2.8\mu g/l$) with the exception of algae, hence its ability to

pose a definite risk. In a previous study, this compound was reported by Kenko *et al.* (2017) to be used in an unorthodox manner.

Chlorpyrifos is an organophosphate (acetyl cholinesterase inhibitor) that is not usually persistent in water systems (IUPAC, 2017). It is extremely hazardous to fish (Mhadhbi and Beiras, 2012) and aquatic invertebrates ($LC_{50\text{-Daphnia}}$=0.10µg/l< PEC=0.26µg/l), this may explain its ability to pose a definite risk even at low dosage (73.5g.a.i/ha).

Deltamethrin (ETR= 255, PEC=0.51µg/l) is a fast-acting pyrethroid insecticide with low aqueous solubility. It presents a high risk to most aquatic organisms ($LC_{50\text{-Fish}}$=0.56µg/l<PEC=0.51µg/l) and was used 6 times a season on corn hence the ability to pose a risk even at low dose (73.5g.a.i/ha). This pesticide was classified into two categories by Malherbe *et al.* (2013) since it posed a possible risk (ETR=49.9) when used on maize and a definite risk (ETR=208) when used on cotton because of different dosage and application intervals. Ansara-Ross *et al.* (2008) also grouped it in the possible risk category (ETR=75) in the Crocodile Marico catchment in South Africa.

Carbofuran is an insecticide with moderate solubility in water. Its presence in the definite risk category may be related to its ability to persist in water, its moderate to high toxicity to most aquatic organisms ($LC_{50\text{-Daphnia}}$=9.4µg/l< PEC=40µg/l) and high application dose (5600g.a.i/ha on banana).

Lindane is an insecticide having low aqueous solubility; this illegally used compound in Cameroon (Kenko *et al.,* 2017) is a GABA-gated chloride channel antagonist. It was used on cocoa at 735.3g.a.i/ha two times a season. Its potential to pose a definite risk in water may be related to its high persistence and high toxicity to fish ($LC_{50\text{-Fish}}$=2.9µg/l< PEC=4.8µg/l). Lindane was earlier identified as an obsolete pesticide in Cameroon, present in form of Gammophele 320® and Callindim Fc320® for a total of 35,605 litres (Souop, 2000).

Chronic risk

Cypermethrin was the only active ingredient able to pose a possible chronic risk to water and fish (ETR_2=1, PEC=0.42µg/l). From a study led by Olufayo and Alade (2012), this compound is known to bring about pathological changes and alterations in fish. Exposure of fish to pesticides depends on its bioavailability, bioconcentration, biomagnification and persistence in the environment (Helfrich, 2009). Literature says cypermethrin is highly toxic to fish and is a serious aquatic pollutant (IUPAC, 2017). *Daphnia* was more sensitive to fish to pesticides than fish; in fact, pesticide used is responsible for the absence of zooplankton in water around agricultural areas with the proliferation phytoplankton (Rissik *et al.,* 2009).

Conclusion

This study aimed at assessing chemical pollution with pesticide in the Benoe Stream using the PRIMET model. A significant seasonal variation in water parameters was noticed. Out of the 44 active ingredients tested, 28 were predicted to pose minor risk; seven indicated a possible acute risk and nine presented a definite acute risk to the aquatic ecosystem. For chronic risk, two compounds, showed a possible risk to water and fish while seven presented a risk to *Daphnia.* Cypermethrin is the most hazardous compound since it indicated both acute and chronic risk; also, *Daphnia* appeared to be more sensitive to pesticides than fish. Cadusafos had the highest ETR value while imazalil was the less risky compound in the study. The PRIMET model is a tremendous tool for developing countries like Cameroon where no record in literature makes mention of pesticide risk assessment. Pesticide use in plantations near water bodies can pose a risk to non-target organisms. These compounds should then be used with care as part of IPM. The impact of pesticides on water quality, their bioaccumulation potential and their impact on aquatic biota community structure is necessary.

Acknowledgements

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