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Relationships between past and present pesticide applications and pollution at a watershed outlet: The case of a horticultural catchment in Martinique, French West Indies



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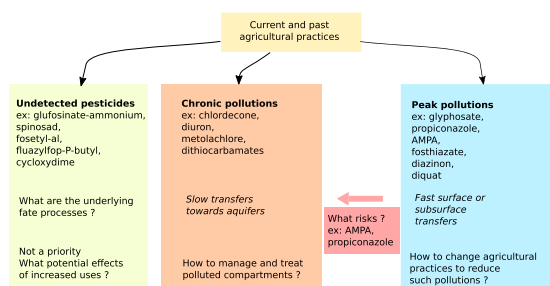
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HIGHLIGHTS

- We monitored pesticides uses with catchment outlet pollution for 67 weeks.
- Outlet polluted by 16 pesticides: 4 forbidden, 2 metabolites and 10 authorized.
- Risk of chronic pollution by AMPA, fosthiazate, propiconazole and dithiocarbamates.
- Several pesticides frequently applied on the catchment remain barely or undetected.
- Requirement to change cropping systems to less dependent on identified pesticides.

GRAPHICAL ABSTRACT



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ABSTRACT

The understanding of factors affecting pesticide transfers to catchment outlet is still at a very early stage in tropical context, and especially on tropical volcanic context. We performed on-farm pesticide use surveys during 87 weeks and monitored pesticides in water weekly during 67 weeks at the outlet of a small catchment in Martinique. We identified three types of pollution. First, we showed long-term chronic pollution by chlordecone, diuron and metolachlor resulting from horticultural practices applied 5–20 years ago (quantification frequency higher than 80%). Second, we showed peak pollution. High amounts of propiconazole and fosthiazate applied at low frequencies caused river pollution peaks for weeks following a single application. Low amounts of diquat and diazinon applied at low frequencies also caused pollution peaks. The high amounts of glyphosate applied at high frequency resulted into pollution peaks by glyphosate and aminomethylphosphonic acid (AMPA) in 6 and 20% of the weeks. Any intensification of their uses will result in higher pollution levels. Third, relatively low amounts of glufosinate-ammonium, difenoconazol, spinosad and metaldehyde were applied at high frequencies. Unexpectedly, such pesticides remained barely detected (<1.5%) or undetected in water samples. We showed that AMPA, fosthiazate and propiconazole have serious leaching potential. They might result in future chronic pollution of shallow aquifers alimenting surface water. We prove that to avoid the past

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errors and decrease the risk of long-term pollution of water resources, it is urgent to reduce or stop the use of pesticides with leaching potential by changing agricultural practices.

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1. Introduction

The increasing population worldwide and especially in tropical countries results in an increase of cultivated areas and in an intensification of cropping systems, especially through intense fertilizer and pesticide uses. Water pollution from agricultural activities affects tropical regions such as Central America, the Caribbean and South-East Asia (Kammerbauer and Moncada, 1998; Rawlins et al., 1998; McDonald et al., 1999; Cabidoche et al., 2009; Charlier et al., 2009; Toan et al., 2013; Crabit et al., 2016). These regions show severe levels of pesticides in water when compared to the European Water Framework (2000/60/CE) and the European Drinking Water Directive (98/83/EC) thresholds that define $0.1 \mu\text{g L}^{-1}$ as the acceptable limit of individual pesticide content in raw water for good ecological status and in drinking water. For instance, Toan et al. (2013) evidenced a mean concentration above $3 \mu\text{g L}^{-1}$ for isopropionate in the Mekong delta (Vietnam). Kammerbauer and Moncada (1998) reported chlordane concentrations as high as $250 \mu\text{g L}^{-1}$ in the Choluteca river basin in Honduras (7000 km²). In the Caribbean, Cabidoche et al. (2009) estimated that streams will be polluted by chlordecone for at least 500 years and Charlier et al. (2009) measured concentrations of cadusafos higher than $1 \mu\text{g L}^{-1}$ in streams and higher than $10 \mu\text{g L}^{-1}$ in aquifers. This is the reason why, the assessment of mid- to long-term persistent pollution of surface water resulting from agricultural practices is highly needed to ensure sustainable water resource management.

Studies were performed at the catchment scale in temperate conditions to better understand the effects of hydrology, pesticide application rates, land uses, and molecular characteristics on the water contamination by pesticides (Blanchard and Lerch, 2000; Guo et al., 2004; Leu et al., 2004; Lewis et al., 2016). Studies focused on water pollution resulting either from pesticides used in agriculture (Palma et al., 2004; Wightwick et al., 2012; Xing et al., 2012) or in urban area (Blanchoud et al., 2004). In the tropical context, several research has been conducted on water contamination by pesticides (Lewis et al., 2016), but few were conducted in tropical context at the catchment scale (Houdart et al., 2009). Tropical studies, that explicitly consider the catchment scale, were focused on one pesticide or one cropping system and did not account for the diversity of horticultural cropping systems of such places (Castillo et al., 2000; Charlier et al., 2009; Varca, 2012; Crabit et al., 2016; Della Rossa et al., 2017). This makes it difficult for water resource managers to select priority measures on such context. Nowadays, there are mitigation options to handle pesticides pollution associated with runoff events such as grassed buffer strips or constructed wetlands (Reichenberger et al., 2007). On the contrary, there is actually no efficient sustainable mitigation option for persistent water contamination resulting from contaminated aquifers discharging in streams. For the drinking water issue, the only costly way is to treat water with several processes to bring water drinkable (Jekel et al., 2015). As a result, the best way to mitigate river pollution is to avoid the appearance of persistent contaminations. Based on a combination of water quality monitoring and farmers' survey, we present and analyze both farmers' practices and water contamination at the outlet of a catchment. We identify and classify present and future risks of river contamination

by pesticides according to pesticide use intensity and transfer pathways. Finally, we propose research priorities to improve the knowledge and control of water contamination by pesticides in tropical contexts.

2. Material and methods

Our research analyses farmers' pesticide use practices and water contamination data acquired on an experimental catchment. Our complete dataset rely on different data acquired over different periods: Fig. 1 summarizes data acquired from 2011 to 2013. We started acquiring farming practices before the water sampling campaign to take into account potential pesticide transfer lags. The 67 weeks period lasting from the 11/10/2011 to the 01/02/2013 is an overlapping period of pesticide practices and water quality samples (Fig. 1). For past farming practices, Houdart provided us with the practices of the Ravine catchment farmers for years 2001–2002 (Houdart, 2005).

2.1. Study site

The experimental horticultural catchment studied is the Ravine catchment (Mottes et al., 2015). It is located on the Northeast side of the Martinique Island, French West Indies ($14^{\circ}49'2''$ N, $61^{\circ}7'14''$ W). This catchment is part of the Capot catchment (57 km²) that provides 20% of the drinking water in Martinique while being chronically contaminated by pesticides. In Martinique, the climate is tropical humid with a maritime influence. Rainfall pattern is characterized by two seasons: a dry season from January to March and a wet season from June to September. The average annual rainfall on the catchment is 3600 mm. The Ravine catchment covers 131 ha with elevation ranges varying from 312 m to 628 m. The mean slope of the catchment is 14% with the upper part slopes comprised between 15 and 30% while the lower part slopes ranges from 0 to 15%. The land use is agriculture, with more than 200 fields which belong to 20 farms (Fig. 2): 18% of agricultural lands are chayote (*Sechium edule*), 13% banana (*Musa* spp.), 6% pineapple (*Ananas comosus*), 17% are covered by other horticultural species, 6.5% by fallow (multiple species), and less than 2% are covered by roads and tracks roads. Forests, meadows and pastures cover the remaining surface (37.5%).

The soils are andosol (Colmet-Daage and Lagache, 1965; Quantin, 1972), which are young volcanic ash soils with high infiltration rates (Cattan et al., 2007; Charlier et al., 2008). Drillings showed that subsoil is constituted by a 1–12 m pumice layer and multiple layers of pyroclastic block and ash flow deposits (“nuées ardentes”) with different levels of alteration. The total height of block and ash flow deposits exceeds 70 m. Pumices and block and ash flow deposits are porous materials which contain aquifers drained by the volcanic streams (Charlier et al., 2008).

An in-depth analysis of the hydrological functioning of this catchment is presented by Mottes et al. (2015). In particular, they showed that the hydrological functioning of the catchment is dominated by groundwater flows (50–60% of annual flows) and that aquifers are highly connected to surface water.

Year	2011											2012											2013					
Month	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A
Hydrology	Ravine river discharge data																											
Pesticides analyses at outlet												75 molecules analysed (glyphosate and AMPA not analysed)				77 molecules analysed (glyphosate and AMPA analysed)												
Practices from farmers with log notebook	3 farmers (37.2% of cropped area)																											
Practices from farmers without log notebook (follow-up survey)	Incomplete dataset		Complete dataset : 12 farmers (41.9% of cropped area)																									
Farmer general practice survey	19 farmers (95.8% of cropped area)																											

Fig. 1. Data acquired from 2011 to 2013 and associated time periods.

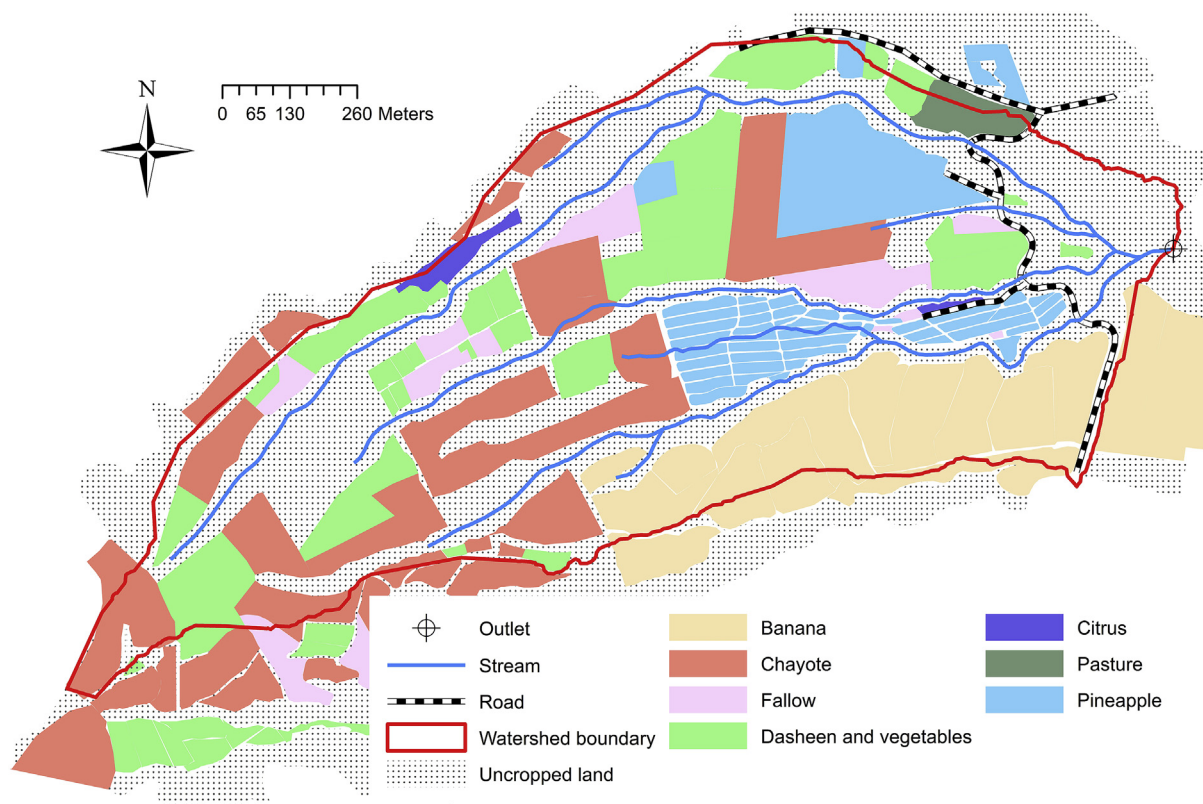


Fig. 2. Land uses of the Ravine catchment.

2.2. Pesticide use survey

We performed two types of survey among farmers. In a first step, we performed a global survey of the current pesticides used on various cropping systems in 2010. From this survey, we built a list of molecules that farmers applied on fields. We completed the list with banned pesticides used in the past, such as chlordecone (banned in 1993), paraquat (banned in 2007), lindane (banned in 1998) or diuron (banned in 2007) and other potential significant pesticides and metabolites that the French water office (ODE) found in water samples at a regional scale. Finally, we consolidated a final list of 77 molecules (Table A1). After we built this consolidated pesticide list, Houdart provided us with a description of the practices of the farmers of the Ravine catchment for years 2001–2002 (Houdart, 2005). We found several molecules applied on the

catchment at that time that we did not identify in our pesticide list: disulfoton, imidacloprid, methomyl, parathion-methyl, simazine, sulfosate, tebuconazole, terbufos and tridemorph (Table 1). As a result, these pesticides were not analyzed in water samples (Table A1).

In a second step, we surveyed all the farmers of the Ravine catchment. First, we asked farmers to describe their cropping systems and their strategies to control pests on the different crops they grow. When it was available, we recorded the log or notebooks of the farmers. Second, we performed practice follow up surveys every month from July 2011 to April 2013. During these surveys and for each field, we asked farmers to detail the field scale practices they performed every week during the previous month. We surveyed plantation, harvest, tillage operation, mowing, pruning as well as pesticide applications and other pest management

Table 1

Characteristics of pesticide used on the catchment. Applications on the different crops in 2001–2002 and 2011–2013, Environmental characteristics (Footprint, 2013): Koc: Soil water – organic carbon coefficient, DT50 soil: pesticide half-life in soil, DT50 water: pesticides half-life in water. Detection and quantification $\geq 0.1 \mu\text{g L}^{-1}$ frequencies at the outlet of the Ravine catchment.

Active ingredient	Usage	2011–2013					2001–2002					LQ ($\mu\text{g L}^{-1}$)	Koc (mL g^{-1})	DT50 soil (d)	DT50 water (d)	Detection (%)	>0.1 $\mu\text{g L}^{-1}$ (%)
		B	C	P	D	V	B	C	P	D	V						
Abamectin	I	–	–	–	–	X	X	–	–	–	X	0.05	–	–	–	0	0
Ametryn (banned)	H	–	–	–	–	–	–	–	X	–	–	0.02	316	37	S	0	0
Azoxystrobin	F	–	–	–	–	X	–	–	–	–	–	0.01	589	78	S	0	0
Bacillus thuringiensis	I	–	–	–	–	–	–	–	–	–	X	–	–	–	–	–	–
Benomyl (banned)	F	–	–	–	–	–	X	–	–	–	X	0.08	1900	67	0.8	0	0
Cadusafos (banned)	N	–	–	–	–	–	X	–	X	–	–	0.02	227 (K_{foc})	38	S	0	0
Copper (copper sulfate)	F	–	–	U	U	X	–	–	–	–	X	20	12000	10000	S	4.5	4.5
Cyloxydim	H	–	–	X	–	X	–	–	X	–	–	0.1	59	0.65	172	0	0
Cypermethrin	I	–	–	U	–	X	–	–	–	–	–	0.02	156,250	60	179	0	0
Deltamethrin	I	–	–	–	–	X	–	–	–	–	X	0.02	10,240,000	13	S	0	0
Diazinon	I	–	–	U	–	–	X	–	X	–	–	0.04	609	9.1	138	4.5	1.5
Difenoconazol	F	X	–	–	–	–	X	–	–	–	–	0.05	3760 (K_{foc})	130	S	1.5	0
Diquat	H	–	–	–	X	X	X	–	–	–	–	0.05	2,185,000	2345	S	1.5	1.5
Disulfoton (banned)	I	–	–	–	–	–	–	X	–	–	–	–	1345	30	300	–	–
Diuron (banned)	H	–	–	–	–	–	–	X	–	–	–	0.02	813	75.5	S	81.8	0
Ethoprophos (banned)	N	–	–	–	–	–	–	X	–	–	–	0.04	70	17	S	0	0
Fipronil	I, N	–	–	–	–	–	X	–	–	–	–	0.01	727 (K_{foc})	142	S	1.5	1.5
Fluazifop-p-butyl	H	X	–	–	–	–	X	–	–	–	–	0.05	3394	1	78	0	0
Fosetyl-Al	F	–	–	X	–	–	–	–	–	–	–	0.1	–	0.1	S	0	0
Fosthiazate	N	X	–	U	–	–	–	–	–	–	–	0.02	239	13	104	9.1	1.5
Glufosinate-ammonium	H	X	X	–	X	X	–	–	–	–	–	0.1	600	7.4	300	0	0
Glyphosate	H	X	X	X	–	–	X	–	X	–	–	0.1	1424	15	S	6.4	6.4
Imidacloprid (banned)	I	–	–	–	–	–	–	–	–	–	X	–	225 (K_{foc})	191	S	–	–
Lambda cyhalothrin	I	–	–	–	–	X	X	–	–	–	–	0.02	283,707	175	S	0	0
Mancozeb (Dithiocarbamates)	F	–	–	–	–	X	–	–	–	–	–	0.1	998	0.1	1.3	22.7	22.7
Metalddehyde	M	–	X	–	–	X	–	–	–	–	–	0.05	240	5.1	S	1.5	0
Oxamyl	N	X	–	–	–	–	–	–	–	–	–	0.1	16.6	7	8	0	0
Methomyl	I	–	–	–	–	–	–	–	–	–	X	–	72	7	S	–	–
Paraffinic oil	F, I	X	–	X	–	–	–	–	–	–	–	–	462000	87	–	–	–
Paraquat	H	–	–	–	–	–	X	–	X	X	X	0.05	1,000,000	3000	S	1.5	1
Parathion-methyl	I	–	–	–	–	–	–	–	X	–	X	–	240	12	21	–	–
Propiconazole	F	X	–	–	–	–	X	–	–	–	–	0.05	1086	71.8	53.5	7.6	3
Pirimicarbe	I	–	–	–	–	X	–	–	–	–	–	–	–	86	S	–	–
Simazine	H	–	–	–	–	–	X	–	–	–	–	–	130	60	96	–	–
Spinosad	I	X	–	–	–	–	–	–	–	–	–	0.02	35,838	17.3	–	0	0
Sulfosate	H	–	–	–	–	–	X	–	–	–	–	–	–	–	–	–	–
Tebuconazole	F	–	–	–	–	–	X	–	–	–	–	–	769 (K_{foc})	63	S	–	–
Terbufos	N	–	–	–	–	–	X	–	–	–	–	–	500	8	6.5	–	–
Tridemorph	F	–	–	–	–	–	X	–	–	–	–	–	6250	24	32	–	–
Chlordecone	I	–	–	–	–	–	–	–	–	–	–	0.01	2500	450	S	100	92.5
Metolachlor	H	–	–	–	–	–	–	–	–	–	–	0.02	120	90	S	87.9	3
β -HCH (lindane)	I	–	–	–	–	–	–	–	–	–	–	0.01	1270	980	732	1.5	0
AMPA	Met	–	–	–	–	–	–	–	–	–	–	0.1	2002	121	–	21.3	21.3
Chlordecone 5b hydro	Met	–	–	–	–	–	–	–	–	–	–	0.01	–	–	–	18.2	1.5

B: Banana, C: Chayote, P: Pineapple, V: Dasheen and vegetables.

I: Insecticide, H: herbicide, F: fungicide, N: nematocide, M: molluscicide, Met: Co-product or metabolite.

X: used, U: unofficial use.

LQ: Limit of quantification.

(K_{foc}): K_{foc} (freudlich isotherm) reported.

S: Stable.

practices. We collected the practice application dates as well as the modalities of application (equipment, localization of practices, dose and commercial product).

2.3. Water sampling

We sampled the water at the catchment outlet with an automatic sampler (ISCO 6712, ISCO Incorporation). Throughout each week, that lasted from Tuesday to the next Tuesday unless exception, the sampling frequency of the water in the river was proportional to the stream discharge calculated from the records of a pressure sensor PCDR 1830 (Campbell scientific). Depending on the period, the automatic sampler collected two 100 mL subsamples each time 300–1800 m^3 discharged at the outlet. To avoid pesticides bounding to container, each first subsample was stored in a

plastic container while each second subsample was stored in a glass container (Amalric, 2009). During each week, the automatic sampler progressively built the composites samples by adding each new first subsample into the plastic container, and each new second subsample into the glass container. At the end of each week, we collected the two containers containing the composite samples and filled the bottles provided by the laboratory (3 glass bottles: $2 \times 1 \text{ L} + 100 \text{ mL}$ and 2 plastic bottles: $150 \text{ mL} + 100 \text{ mL}$ totaling 2.35 L) with aliquots from the composite samples stored in the plastic and glass containers. We collected the composite samples every week from 11/10/2011 to 01/02/2013.

2.4. Laboratory analyses

Pesticides concentrations in water samples for the 77 molecules

were analyzed by the “Laboratoire Départemental d’Analyses de la Drôme” (LDA26). The laboratory has been accredited by Cofrac, the French Accreditation Committee for pesticide analyzes providing guarantees for their technical skills and reliability as well as good management practices. LDA26 complies with ISO 17025 standards for testing and calibration. The methods mobilized for pesticides analysis rely on the EPA-methods 507, 508, 610 and 625. Results are given with a 30% confidence interval for the analytical error. Depending on pesticides, extraction and analysis methods, limits of quantification for organic molecules ranged from 0.01 to 0.2 $\mu\text{g L}^{-1}$ (see Table A1 for the details).

2.5. Data analysis

2.5.1. Pesticide application patterns

In order to determine pesticide application patterns, we calculated two metrics for each pesticide: [1] $I_{frapplied}$, a metric of the temporal intensity of the application dynamics. It is defined by the fraction of weeks with applications of the pesticide on the catchment; [2] I_{amount} , a metric of the weekly average amount of pesticide applied on the catchment when it is applied:

$$I_{amount} = \frac{1}{A_{catch}} \times \frac{\sum_{week}^{Nweeks_{[Q_{pestapplied,week} > 0]}} Q_{pestapplied,week} \times e^{-7 \times \left(\frac{\ln(2)}{DT_{50soil}}\right)}}{Nweeks_{[Q_{pestapplied,week} > 0]}} \quad (1)$$

where $Q_{pestapplied,week}$ is the amount of pesticide applied on the catchment during the week “week” (g). $e^{-7 \times \left(\frac{\ln(2)}{DT_{50soil}}\right)}$ is a degradation factor derived from a first order degradation kinetics that accounts for potential degradation of the pesticide during 1 week (7 d) with half-life DT_{50soil} (d). A_{catch} is the total area of the catchment (ha). $Nweeks_{[Q_{pestapplied,week} > 0]}$ is the number of weeks over the considered period with application of the pesticide. I_{amount} is set to 0 for pesticides that were not applied on the catchment in 2011–2013.

We analyzed pesticides application patterns during the practice-monitored period that last from the 1st of June 2011 to the 1st of February 2013 totaling 87 weeks.

2.5.2. Pesticide water pollution

We calculated two metrics for each pesticide to characterize water pollution by pesticide. First, we calculated the frequency of quantification of each pesticide at concentrations higher than 0.1 $\mu\text{g L}^{-1}$ in water samples. Second, we calculated an average concentration metric by taking into account weeks with concentrations over 0.1 $\mu\text{g L}^{-1}$ only:

$$IConc_{pest} = \frac{\sum_{week}^{Nweeks_{[C_{pest,week} \geq 0.1 \mu\text{g L}^{-1}]}} C_{pest,week}}{Nweeks_{[C_{pest,week} \geq 0.1 \mu\text{g L}^{-1}]}} \quad (2)$$

where $C_{pest,week}$ is the concentration of pesticide “pest” during the week “week” ($\mu\text{g L}^{-1}$). $Nweeks_{[C_{pest,week} \geq 0.1 \mu\text{g L}^{-1}]}$ is the number of weeks over the considered period with concentration of the pesticide “pest” over 0.1 $\mu\text{g L}^{-1}$. We made the comparison with the 0.1 $\mu\text{g L}^{-1}$ threshold for two reasons. First, it is a reference threshold for the European Water Framework (2000/60/CE) good ecological status and for European Drinking Water Directive (98/83/EC) water quality. Second, all molecules analyzed in water samples had limits

of quantification lower or equal to 0.1 $\mu\text{g L}^{-1}$ except 1,3-dichloropropylene (0.2 $\mu\text{g L}^{-1}$) and copper (20 $\mu\text{g L}^{-1}$) (Table A1). Thus, except for these two molecules, the 0.1 $\mu\text{g L}^{-1}$ threshold made it possible to compare water pollution by the different pesticides on a same basis.

3. Results and discussion

3.1. Pesticides applied and pesticides in water samples

Table 1 summarizes pesticides applied on the Ravine catchment in 2001–2002 and in 2011–2013 and pesticides found in water samples in 2011–2013. Farmers applied 27 commercial products corresponding to 17 active ingredients during the 2011–2013 period (Table 1). Table 1 indicates that weekly pesticide samples showed contamination of the water at the Ravine catchment outlet. We found 16 active ingredients at the catchment outlet (Table 1) and provided concentration dynamics for 9 (Fig. 3). Among these, 4 are nowadays prohibited and unreported in the survey (diuron, paraquat, chlordecone and β -HCH), 2 are metabolites or co-products from respectively glyphosate and chlordecone (amino-

methylphosphonic acid (AMPA) and chlordecone-5b-hydro) and 10 are still authorized (propiconazol, difenoconazol, dithiocarbamates, copper sulfate, diquat, fosthiazate, diazinon, glyphosate, metolachlor and metolachlor). Except for banned pesticides, metabolites and metolachlor, farmers of the Ravine catchment declared the use of the measured pesticides in water (Table 1).

We found 5 pesticide application patterns according to our two application metrics calculated from April 2011 to April 2013 (Fig. 4a): [A] high amounts of pesticide applied at high frequency, [B] low amounts of pesticide applied at high frequency, [C] low amounts of pesticide applied at low frequency, [D] high amounts of pesticide applied at low frequency and [E] historical currently unapplied pesticide (removed from Fig. 4a for better readability).

According to Table 1 and Fig. 3 we found three types of pesticide concentration dynamics: [1] undetected pesticides (all pesticides applied on the catchment but never found in water samples), [2] chronic pollution (pesticides showing pollution periods of several weeks such as chlordecone, diuron, metolachlor and dithiocarbamates), and [3] peak pollution (pesticide with isolated pollution peaks such as glyphosate, AMPA, propiconazole, difenoconazol, copper sulfate, diquat, paraquat, chlordecone-5b-hydro, fosthiazate, diazinon, β -HCH and metolachlor). Fig. 4b shows that for the 0.1 $\mu\text{g L}^{-1}$ threshold, chlordecone and dithiocarbamates are the two chronic pollutants. Metolachlor concentrations are barely higher than 0.1 $\mu\text{g L}^{-1}$. Fig. 4b also shows that pollutants over the 0.1 $\mu\text{g L}^{-1}$ threshold belong to all pesticide application patterns except pattern B (low amounts applied at high frequency).

3.2. Historically applied pesticides

Our analysis first showed that water pollution is due to several pesticides which farmers do not use anymore. Indeed, most of them are now prohibited (e-phy, 2010). This shows that even after 5 to more than 20 years after their ban, they still contaminate water at

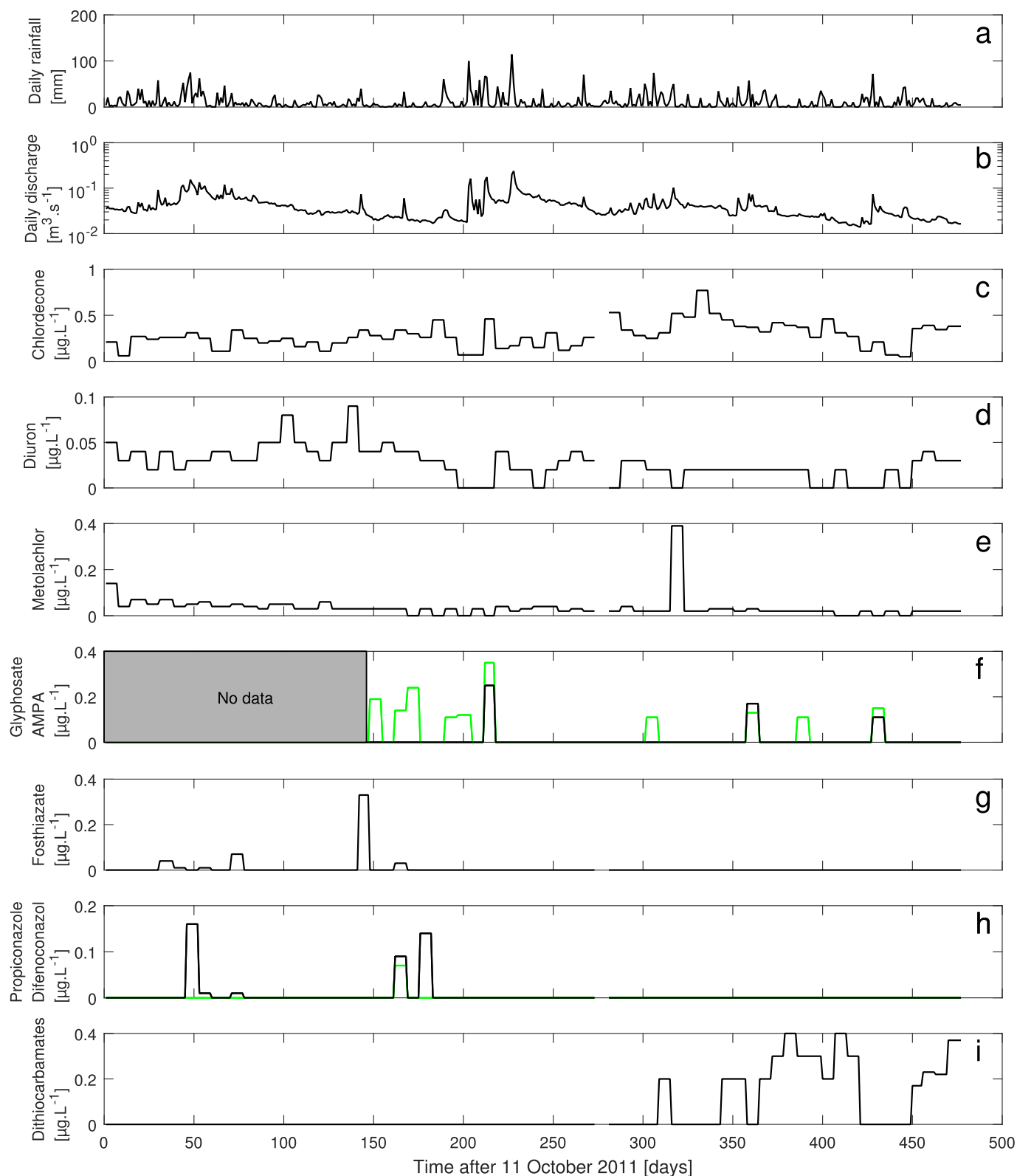


Fig. 3. Meteorological, hydrological and pollution at outlet time series on the Ravine catchment from 11 October 2011 to (a) daily rainfall; (b) discharge at outlet, (c) chlordecone concentrations, (d) diuron concentrations, (e) metolachlor concentrations, (f) glyphosate concentrations (black), AMPA concentrations (green), (g) fosthiazate concentrations, (h) propiconazole concentrations (black), difenoconazol concentrations (green), (i) dithiocarbamates concentrations. For detected but unquantified pesticides, we estimated concentrations to quantification limit divided by 3 as suggested by laboratory guidelines. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

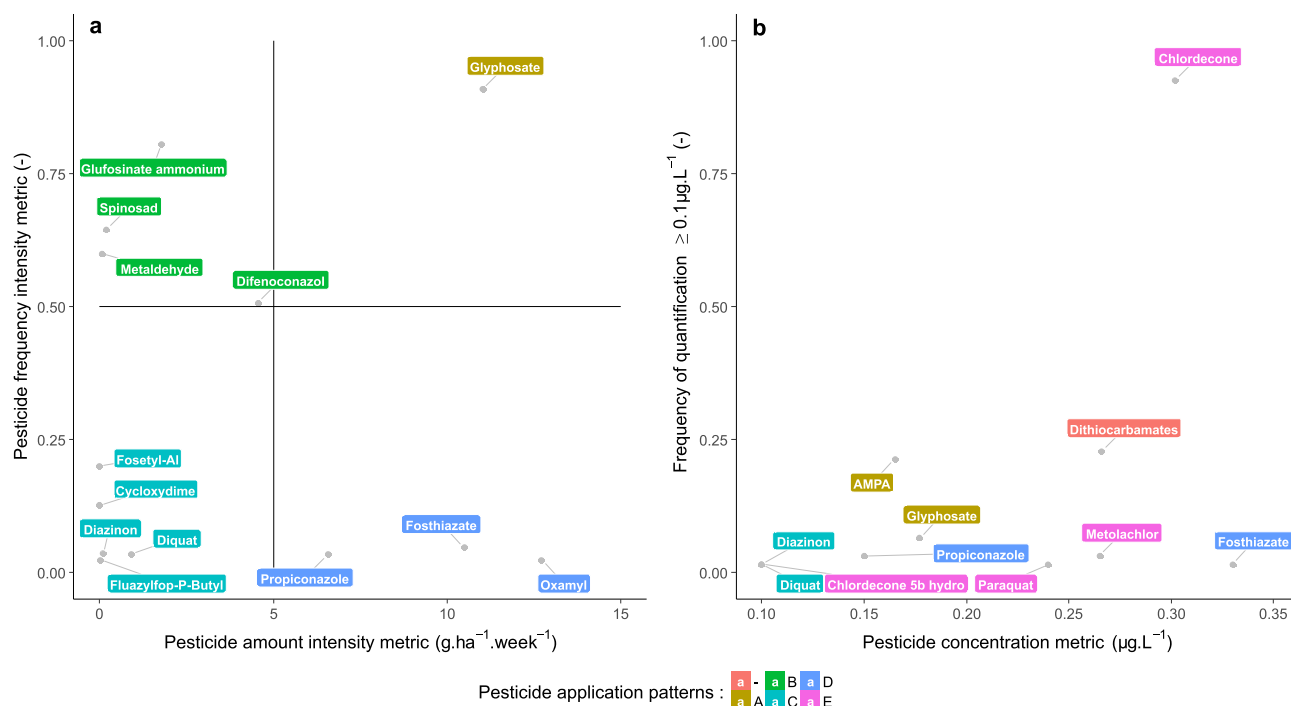


Fig. 4. Pesticide uses and pollution intensities on the Ravine catchment. (a) Pesticide application intensities (see Section 2.5.1 for metric calculations); (b) Pesticide pollution intensities ($\geq 0.1 \mu\text{g L}^{-1}$, see Section 2.5.2 for metric calculations). Pesticides application pattern: [-] Undefined, [A] high amounts applied at high frequency, [B] low amounts applied at high intensities, [C] low amounts applied at low frequency, [D] high amounts applied at low frequency, [E] historical currently unapplied pesticides.

the catchment outlet. The historical pesticides show 3 types of detection patterns at the catchment outlet. First, chlordecone, diuron and metolachlor were detected at a very high frequency throughout the sampling period (Fig. 3, Table 1); second, Paraquat, β -HCH, chlordecone-5b-hydro are detected only anecdotally (Table 1), and finally some are not detected anymore such as ametryn, cadusaphos or ethoprophos. Our hypothesis for the first 2 types is that these pesticides are still stocked in soil ($\text{DT}_{50\text{soil}} > 75 \text{ d}$) so that they slowly leach into groundwater, soil behaving as pollution source.

Chlordecone, diuron and metolachlor were applied for a long time and on large areas of the catchment. These three pesticides still chronically contaminate water at the outlet. Their detection frequency is higher than 80% at the catchment outlet and reaches 100% for chlordecone. Such pollution are characterized by a weekly concentration varying within a narrow range (from 0.05 to $0.77 \mu\text{g L}^{-1}$ for chlordecone; from <0.02 to $0.09 \mu\text{g L}^{-1}$ for diuron and from <0.02 to $0.14 \mu\text{g L}^{-1}$ for metolachlor (pollution peak removed)). We did not observe a strong relationship between water concentrations and rainfall. According to Dores et al. (2009), we found metolachlor and diuron to leach in tropical conditions. The three historical pollutants are characterized by long soil half-lives ($>75 \text{ d}$). Because persistent and long-term pollution involve the contamination of soils and aquifers, such soil persistence favor permanent pollution of rivers (Cabidoche et al., 2009; Mottes et al., 2016). We measured a persistent pollution of the stream by metolachlor with water concentrations under $0.1 \mu\text{g L}^{-1}$ most of the time. We could expect the ending of a chronic pollution as with diuron. Nevertheless, its use is still authorized on pineapple crop (S-metolachlor compound). We suspect an application on the catchment even if no surveyed farmer reported S-metolachlor application. Indeed, we observed a pollution peak ($0.39 \mu\text{g L}^{-1}$) in water samples (Fig. 3e). This pollution peak is consistent with the high transfer rate with runoff found by Dores et al. (2009) that

could follow applications. This is the reason why this specific use could maintain the long-term pollution of the river. The use of such persistent contaminant of the environment should therefore be stopped in tropical context to avoid any increase of the pollution.

Paraquat and β -HCH were used in a less intensive manner or during shorter periods of time than chlordecone, diuron and metolachlor. **Chlordecone-5b-hydro** is a co-product of chlordecone production that corresponds to a very small fraction of the chlordecone amount applied. Chlordecone-5b-hydro and paraquat were unfrequently quantified at concentrations higher than $0.1 \mu\text{g L}^{-1}$ (Fig. 4b) while β -HCH did not exceed this threshold. The low detection frequencies of these pesticides could be explained by the lower amounts of residues remaining in soil because smaller amounts of these pesticides or co-products were applied on the catchment. It is likely that specific environmental characteristics such as tillage, high water flows, or both led to their remobilization from soil to the catchment outlet. Nevertheless, the small number of detections and the lack of knowledge on the behavior or the spatial and temporal application patterns of these pesticides in the past harms the robustness of this conclusion.

Ametryn, cadusaphos or ethoprophos are pesticides with high dissipation potentials. Charlier et al. (2009) clearly demonstrated that cadusaphos quickly contaminated surface water during both high and low flows. Farmers used cadusaphos and ethoprophos as nematocides, they applied both onto the soil. Although these pesticides may have contaminated the environment when they were applied, they were apparently quickly transferred, diluted and/or degraded in the environment leading to no more detection nowadays. At the molecular composition level, we observed that chlordecone, diuron and metolachlor carry at least one chlorine radical, while ametryn, cadusaphos and ethoprophos do not. According to our results, we are in the opinion that chlorine radicals could favor the stability and the persistence of molecules in the environment. This is confirmed by Calvet et al. (2005) who indicated that chlorine

radical decreases the speed of the breaking of aromatic cycles in organic compounds. Henschler (1994) also support this hypothesis by indicating a frequently increased chemical stability of chlorinated organic compounds along with an easier enzymatic conversion. Consequently, the presence of chlorine radical in the molecule could favor the long-term potential pollution of the environment even if the molecule is classified under another organic compound family than organochlorine such as phenylurea, carbamate or triazole.

3.3. Pesticides used on the catchment during the sampling period

3.3.1. Pesticides regularly applied on the catchment

The survey showed that 5 pesticides were regularly applied on the catchment: glyphosate, glufosinate ammonium, difenoconazol,

spinosad and metaldehyde (Fig. 4a). These pesticides were applied on more than 50% of the weeks during the sampling period. Glyphosate was applied on 90% of the weeks at very high rates (Figs. 4a and 5). Glufosinate ammonium was applied 75% of the weeks at lower rates (Figs. 4a and 5). Difenoconazol was applied during half of the weeks of the sampling period at intermediate application rates while spinosad and metaldehyde were applied during more than half of the weeks but at low rates (Figs. 4a and 5). In the water samples, Glyphosate and its metabolite AMPA were quantified over $0.1 \mu\text{g L}^{-1}$ (Figs. 3 and 4b) which is consistent with its very intensive use at the catchment scale. In spite of their frequent uses, glufosinate ammonium and spinosad were never detected in water samples while difenoconazol and metaldehyde were both quantified only once at concentrations lower than $0.1 \mu\text{g L}^{-1}$.

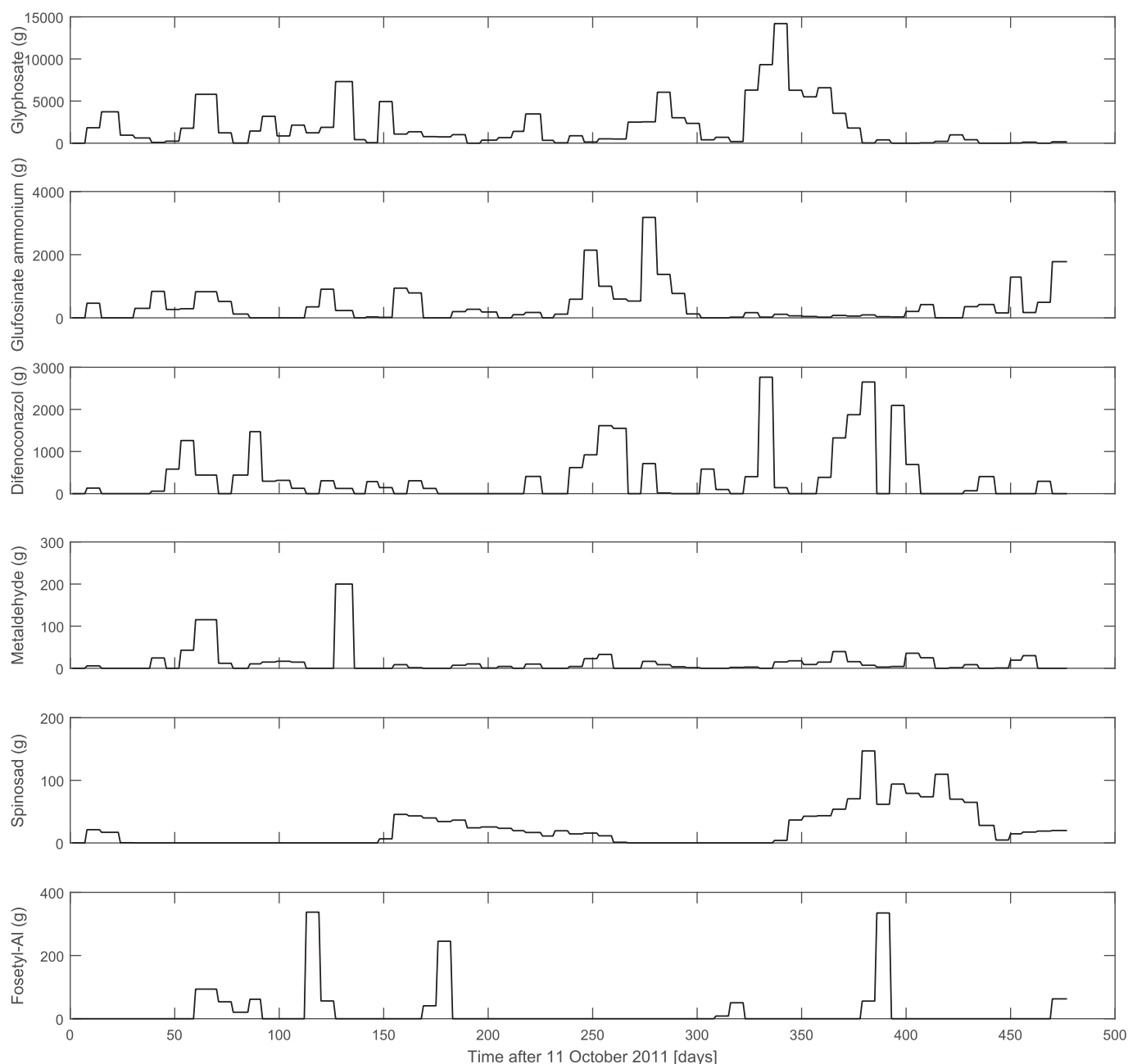


Fig. 5. Weekly amounts of pesticides applied on the Ravine catchment (g) for glyphosate, glufosinate-ammonium, difenoconazol, metaldehyde, spinosad and fosetyl-al.

Glyphosate is widely used as a general systemic herbicide. Glyphosate and its major metabolite **Aminomethylphosphonic acid (AMPA)** were frequently quantified at concentrations higher than $0.1 \mu\text{g L}^{-1}$ in our water samples at the catchment outlet. AMPA is a major pollutant detected in 21.3% samples. Glyphosate was found to have concentrations higher than $0.1 \mu\text{g L}^{-1}$ in 6.4% samples. For glyphosate pollution peaks, the pollution corresponded to a stormflow event occurring right after the application of glyphosate (Figs. 3f and 5a). It indicates that glyphosate was quickly degraded or highly adsorbed onto soil particles forming irreversible bounding in agreement with the conclusions drawn by Vereecken (2005) and Borggaard and Gimsing (2008). The surveyed farmers applied glyphosate all year round because weeds are one of the strongest constraints in the humid tropics. Because of this constant application pattern, it is likely that rainfall generating pollution peaks occurred after applications, especially in our tropical climate characterized by heavy and intense rains. AMPA, one of the major glyphosate metabolites, was always present in water samples when we found glyphosate. Nevertheless, we found AMPA with no companion glyphosate during eight weeks over the sampled period. AMPA was found during weeks that are not characterized by significant runoff events. Similarly to chlordecone and diuron, two pesticides which led to permanent contamination at the outlet, AMPA shows a long half-life and a high Koc (Table 1). In the literature, results from different studies do not agree on the leaching potential of AMPA but some studies showed that AMPA potentially leaches in structured soil conditions (Kjaer et al., 2005; Landry et al., 2005; Bergstrom et al., 2011). In tropical volcanic catchment conditions, soils are structured with very high infiltration rates (Cattan et al., 2007; Charlier et al., 2008). Because of the quantification of AMPA outside runoff periods, it is likely that AMPA contaminates at least shallow aquifers on a regular basis. It is likely that glyphosate quickly degrades into AMPA, which is stored in high organic soils, and is leaching to aquifers along with rainfalls. As a result, we can conclude that the widespread and quasi-permanent use of glyphosate on tropical volcanic catchments, such as the Ravine catchment, is likely to result in persistent stream pollution by AMPA within mid-to-long-terms.

Glufosinate-ammonium is the second most used herbicide on the catchment. We never detected this pesticide during our weekly analyses, even when runoff events occurred during the same week when farmers applied glufosinate-ammonium. In the literature, glufosinate transfers have been found with that for glyphosate and other herbicides (Screpanti et al., 2005; Shipitalo et al., 2008). Anionic retention capacity of andosol (Sansoulet et al., 2007) may cause glufosinate ammonium retention in the soils of the catchment. In spite of a high application frequency, the amount of glufosinate-ammonium applied at the catchment scale is lower than glyphosate (Fig. 5) and even lower when considering the degradation rate (Fig. 4a). It might be that pollution is not yet measurable now but could appear in the case of an increase of the amount of glufosinate-ammonium applied at the catchment scale. Glufosinate-ammonium has two identified metabolites that could contaminate the river (3-methyl-phosphinico-propionic acid and 2-methyl-phosphinico-acetic acid) (Footprint, 2013). Unfortunately, their quantifications were outside of the analytic capacity of the laboratory. In the light of this discussion, we therefore recommend further investigation on the fate of this pesticide and its metabolites in andosol. We also recommend not to substitute glyphosate by glufosinate-ammonium but rather to find alternatives to exclusive chemical weeding with reduced uses of herbicides.

Difenoconazol has been detected only once in water samples at a concentration below $0.1 \mu\text{g L}^{-1}$ (Fig. 3h). Difenoconazol has an intermediate application pattern at catchment scale in term of

frequency and amounts: it is applied on a relatively frequent manner (~50% of the weeks) at intermediate levels (Fig. 4a). Because of its long soil half-life (85–130 d) reported in the Footprint database (Footprint, 2013) we expected to detect more frequently difenoconazol in water samples. The only detection occurred on a week characterized by a runoff event the same day that application was performed. That event may have transported the pesticide directly to the outlet during application or right after its application bypassing the soil compartment. This is the reason why we are in the opinion that the half-lives of difenoconazol may be lower than the one reported in the Footprint database. This hypothesis is supported by Wang et al. (2012) who found short half-life of difenoconazol in water (0.30–2.71 d) and by Mukhopadhyay et al. (2011) and Wang et al. (2012) who found soil half-life ranging between 4 and 23 d. In the light of this discussion, it is very likely that difenoconazol degraded faster than expected and that such high degradation rates in water explain the single quantification of difenoconazol at the outlet of the Ravine catchment.

Spinosad was frequently used on the banana fields of the catchment. According to Fig. 4a, the amount intensity metric of spinosad is low. The pesticide is applied on banana bunches which are protected by a plastic bag thus limiting washoff and environmental diffusion of that pesticide. We are in the opinion that such low application rates under protected conditions limited spinosad transfers to the environment.

Metaldehyde was frequently applied on the catchment but according to Fig. 4a, the amount intensity metric of metaldehyde is very low. Because of such very low amount intensity metric metaldehyde was not expected to be detected in water samples. Nevertheless, it was quantified once below $0.1 \mu\text{g L}^{-1}$. As for other frequently applied pesticides, we are in the opinion that the high application frequency of the pesticide increases the probability of incorrect application conditions on a rainy day that transferred pesticides directly to outlet towards runoff.

3.3.2. The uncertainty surrounding the dithiocarbamates

Dithiocarbamates represent a family of molecules they are mainly used for their fungicide effects. The analytical procedure of the laboratory did not make it possible to identify the specific dithiocarbamate molecules among them. We started quantifying frequently dithiocarbamates in the stream from day 309 at concentrations higher than $0.1 \mu\text{g L}^{-1}$ (Fig. 3i). The pollution by dithiocarbamates is the second most intensive after chlordecone (Fig. 4b). Farmers highlighted the intensive use of fungicides on horticultural crops such as tomato, cucumber or pepper but we did not have confident enough application dynamics on the catchment to classify the dithiocarbamates application pattern (Fig. 4). Dithiocarbamates were not found any more during high flow periods (Fig. 3). Different hypotheses can be drawn to explain this situation: (1) the molecules contaminate aquifers but the pollution is diluted below detection limits during high flow periods. However, according to data from the Footprint database (Footprint, 2013), this is unlikely because of the very short reported half-lives of dithiocarbamates (Table 1). On the contrary, Wilmington (1983), the first manufacturer of mancozeb, the dithiocarbamate used on the catchment, reported soil half-life to range from 4 to 8 weeks. Such values seem to be more realistic and consistent when compared with degradation rates of other pesticides (e.g. Table 1). (2) The contamination comes from a point source due to inappropriate handling of the unsprayed pesticides fraction. (3) Applications are regularly performed on vegetable crops but no pesticide is sprayed during rainy weeks. (4) Dithiocarbamates were used to produce photodegradable plastic mulches that can be ploughed directly into the soil (Wolfe et al., 1990; Scott, 1997). Degradable plastic mulches are used under pineapple crops but farmers could not attest

whether they used photodegradable or biodegradable mulches. In spite of the difficulty to interpret our results, this pollution that appeared at the end of our sampling period is alarming because the stream is polluted in a quasi-persistent manner at high levels. The verification of these different hypotheses would require specific studies on cropping systems using dithiocarbamates and associated transfers to water. In the meantime, improvements of the analysis methodologies are required. Nevertheless, according to the long soil half-life reported by Wilmington (1983) and the Koc of mancozeb (998 mL g^{-1} - Table 1), we are in the opinion that mancozeb may have contaminated shallow aquifers in our conditions.

3.3.3. Pesticides barely applied on the catchment that generated pollution

Propiconazole and **fosthiazate** were barely used on the catchment but at high application rates (Fig. 4a). Our practice survey showed that both pesticides were applied before the sampling period in response to specific problems such as high sigatoka (*Mycosphaerella fijiensis*, *Mycosphaerella musicola*) pressures or high infestation by nematodes (*Radopholus similis*, *Pratylenchus coffeae*) on banana fields. **Diquat** and **diazinon** were also barely applied but at low rates (Fig. 4a). The four pesticides were detected in water samples at concentrations higher than $0.1 \mu\text{g L}^{-1}$ (Figs. 3 and 4b) meaning that any intensification of the use of these pesticides will result in pollution at levels higher than the one already observed.

Fosthiazate is an organophosphate nematicide applied onto banana fields. We detected the pesticide during two periods. During the first period (days 30–77), fosthiazate was detected at concentrations lower than $0.1 \mu\text{g L}^{-1}$ (Fig. 3g). During this high flow period we did not observe the highest concentrations at the peak flow in spite of a high solubility and a low Koc of the pesticide. This result supports the hypothesis of a fast transfer toward a shallow aquifer diluted by surface runoff barely occurring in tropical volcanic conditions (Charlier et al., 2008; Mottes et al., 2015). Later, fosthiazate was detected twice when high rainfall events occurred during a dry period (low average stream discharge). It is likely that the peaks observed during the second period resulted from an unofficial use of the pesticide on pineapple fields before high rainfall events occurred during the dry period (field observations). In the literature, fosthiazate persistence in soil is reported to increase under low pH (Qin et al., 2004; Pantelelis et al., 2006). Thus, in spite of a short reported soil half-life of 13 d (Footprint, 2013), its persistence in tropical andosols with low pH (Clermont-Dauphin et al., 2004) may reach the 47 d values obtained by Pantelelis et al. (2006). Its increased stability in tropical volcanic condition can enhance its leaching potential. The contamination of both overland flows and shallow aquifer flows has been observed in similar pedoclimatic conditions by Charlier et al. (2009) who studied the transfers of cadusaphos, a nematicide with close molecular characteristics. On the basis of the pollution observed with moderate high flows on the Ravine catchment and results from Charlier et al. (2009), there is every likelihood that fosthiazate transfers to catchment outlet toward both overland flows and shallow aquifers.

Propiconazole was detected during a peak flow that took place during the first high rainy event after the beginning of the sampling period (Fig. 3h). The only reported use for propiconazole occurred 82 d before the beginning of the sampling period. We believe that the pollution peaks resulted from that particular pesticide application because a large proportion of the catchment (13%) was treated on that day by helicopter and because the reported half-life of propiconazole in soil is high 70–200 d (Bromilow et al., 1999; Footprint, 2013). Although, propiconazole was reported by several authors to have low leaching potentialities (Bromilow et al., 1999;

Kim et al., 2002), Oliver et al. (2012) found that propiconazole was transported in a persistent manner from horticultural cropping systems in Australia. Battaglin et al. (2011) also observed its presence in United States streams and Toan et al. (2013) found that propiconazole significantly contaminated surface water in Vietnam. Propiconazole was frequently found (in 43% of samples) in a banana oriented catchment in Costa Rica where it was intensively applied (Castillo et al., 2000). Propiconazole pollution dynamics is difficult to interpret because it did not appear systematically during all runoff events; it showed contamination tail during high flow period and a high concentration on weeks without high flow (Fig. 3h). The high soil half-life of the pesticide reminds the ones from historical permanent pollutants (chlordecone, diuron and metolachlor). Propiconazole polluted surface waters in many places but on the Ravine catchment, it did not show clear transfers pathways. We suspect however propiconazole to have punctually reached shallow aquifers. Further research on the fate of this pesticide in our specific conditions is warranted, as well as reduction measures to avoid further contaminations of streams. In the French West Indies, application of propiconazole is authorized only once a year. In spite of this restriction, it keeps contaminating water for a long time after being applied. Because this pesticide was found to be a significant water contaminant over the world (Castillo et al., 2000; Battaglin et al., 2011; Oliver et al., 2012; Toan et al., 2013) and in the Ravine catchment, we recommend restricting the usage of propiconazole in cases where farmers cannot use alternative techniques, or at least on very small areas of catchments.

4. Conclusions

We have shown that the current and past uses of pesticide in a tropical volcanic catchment resulted in pesticide pollution at catchment outlet and that our approach was relevant to identify potential sources of water pollution at different time scales. We showed that pesticide pollution was not only dependent on the intrinsic characteristics of pesticides but also on the combination of application intensities in terms of frequencies and amounts and on the hydrological functioning of the catchment. We showed that historical pesticides used in horticulture 10–20 years ago resulted in persistent pollution at catchment outlet due to soil and aquifer contaminations. **This type of pollution raises the question of the management of the contaminated compartments (such as soils and aquifers) and of the potential implication of such long-term local conditions on larger scale pollution.** We also showed that pesticides still in use in tropical conditions present serious risk of aquifers contamination. Metolachlor is still authorized while it chronically polluted the catchment outlet. We think that the use of glyphosate, fosthiazate and propiconazole could result in mid-to long term persistent contamination of the stream, as some historical pesticides. In order to avoid the past errors and decrease the risk of long-term pollution of water resources, the only mean to protect them is to reduce or ban the use of these pesticides in horticultural systems. **This conclusion raises the question of the design of cropping systems less dependent on pesticides and their appropriation by farmers.** Our classification also showed that several pesticides remain undetected in rivers in spite of intensive application patterns. **These undetected pollution raise the questions of the underlying processes of the fate of such pesticides.** First, the understanding of their fate will make it possible to better anticipate and avoid forthcoming pollution. Second, this will make it possible to assess the potential effect of their increased use in case of farmers shifting of pesticides (cropping system change or regulation evolutions). To assess the three questions raised in our conclusion, we recommend further research combining modeling and monitoring to assess the current and

future effects of pesticides in tropical horticultural cropping systems on water resources. The combined approach of modeling and monitoring appears to be an interesting approach for co-designing and adjusting cropping systems with farmers.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.chemosphere.2017.06.061>.

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