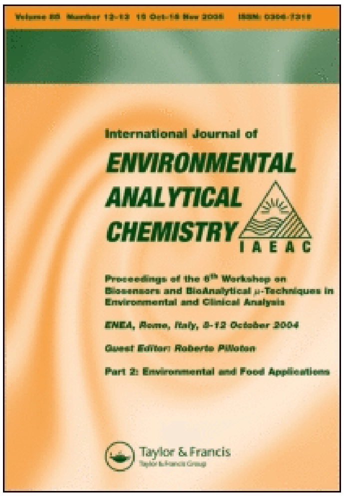

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Use and fate of 17 pesticides applied on a vineyard catchment

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Non point source (NPS) pollution may degrade water quality and is of concern to water quality managers and environmental risk regulators whose responsibility it is to monitor the status of water bodies. There are many methods of evaluating the impact on a water body from NPS pollution, but one of the most important, effective, and unfortunately expensive methods is to monitor the quality of water flowing from a particular catchment. The flux of 17 pesticides from a small (42.7 ha) agricultural (vineyard) catchment in the Alsatian piemont (France) was systematically monitored over 4 years (2003–2006) from June to September. A metrological station is located within the catchment area and run-off of 58 run-off events was monitored throughout. A water sample for pesticide analyses was collected every 8 m^3 of run-off. Detailed information regarding pesticide application was obtained from voluntary surveys submitted annually to active farmers of the studied catchment. There was considerable climatic variation among years. However, variability of the total load of pesticides exported yearly from the catchment was low. Some 78% of the total pesticide applications in the catchment were herbicides and glyphosate was the most used herbicide with annual application ranging from 18 to 61 kg. The run-off coefficient was low (less than 2%), but the frequency of determination was high for some pesticides such as the fungicide dimetomorph (72%) and the herbicides diuron (98%) and glyphosate (100%). The pesticide export coefficients were below 1% of the applied amount, and often below 0.1%. Every water sample exceeded the EU drinking water limit of 0.1 ug L^{-1}.

Keywords: pesticide; fate; catchment; vineyard; NPS pollution; run-off

1. Introduction

Pesticides are of concern to water quality managers and environmental risk regulators to maintain and achieve a good water quality status [1]. Pesticides are continuously introduced in the crop cultivation system throughout the seasons. France is the second largest market for pesticides in the world and the largest user in Europe, with yearly application exceeding 100,000 tons. Ninety-one per cent of the sampling locations in river and more than 50% of groundwater sampling points are contaminated, i.e. with concentrations exceeding the limit for drinkable water defined by the European Union (0.1 $\mu g\,L^{-1}$) [2]. About 400 pesticides are typically analysed in water samples and about

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201 compounds have been identified in surface water and 123 in groundwater [2]. Therefore the assessment of drinkability of water requires determining a priority list of pesticides depending of local applications. Consequently, it appears relevant to more specifically focus on upstream catchment to mitigate the transfer of pesticides to downstream water bodies. One of the objectives of the Water Framework Directive is to obtain a good status for water bodies by 2015 in European countries and to develop water management based on river basin districts [3]. Water quality monitoring must be carried out to define the present chemical status. This directive creates new research needs for its implementation [4,5,6].

As a model agricultural system, our study focuses on vineyard areas. Only a few studies deal with this kind of continuous intensive agriculture [7,8,9] even though poorly managed agricultural operations, e.g. inappropriate compounds, an inappropriate spreading period or defective spreading devices, can lead to contamination of surface and groundwater by nutrients and pesticides [9]. Although vineyard areas only correspond to 3% of the total cultivated area in France, 20% of the pesticide usage is for wine growing. In those areas, a field can receive per year: 10 fungicides, 3 herbicides and 2 insecticides for a total load of 5 kg /year/ha. The estimation of the pesticide use is a necessary step to calculate the input/output pesticide budget at the catchment scale. The methods chosen to obtain these data are closely linked to the scale of studied area. At larger scales, often the assumption is used that actual application rates are equal to the recommended application rates [10,11]. The use of farmer surveys, only possible with a limited number of farmers, may obtain more accurate data in terms of spatial input variability and application dates [12]. Some studies have underscored that pesticide applications in vineyard areas often result in contamination of surface or groundwater [13,14,15,16]. While mitigation strategies to reduce pesticide inputs into surface water and groundwater are currently studied [17], little is known about the behaviour of pesticide in the hydro-systems [18,19].

The major aim of this study is to assess the contribution of seasonal water contamination originating from a wine-growing agro-system overhanging the Alsatian plain and contributing to its lateral recharge. The specific objectives are (1) the assessment of the agricultural practices over 4 years with respects to pesticides application and (2) to determine the concentration and the export coefficient for each pesticide related to 58 hydrological events. This study represents a first step towards developing knowledge of transferred pesticides loads prior to the development of diffuse pollution management strategies at the catchment scale.

2. Experimental

2.1 *Study site*

The studied Hohrain catchment area is located in the Alsatian vineyard (Eastern part of France, latitude 47°57′9 N; longitude 007°17′3 E; altitude 284 m) (Figure 1). The area of the catchment is 42 hectares. The minimum and maximum annual precipitation for the period of record was 361 mm (1953) and 867 mm (1999), respectively. The average annual rainfall calculated since 1946 is 600 mm. The mean slope of the catchment is 15%. Geologically, Würm loamy loess and Oligocene clayey conglomerates and marls, as well as compact calcareous substrate, largely dominate in the upper and lower parts of the catchment, respectively. The main soil type is mostly calcareous clay loams with medium infiltration capacity. Sixty-eight per cent of the hydraulic catchment is covered by

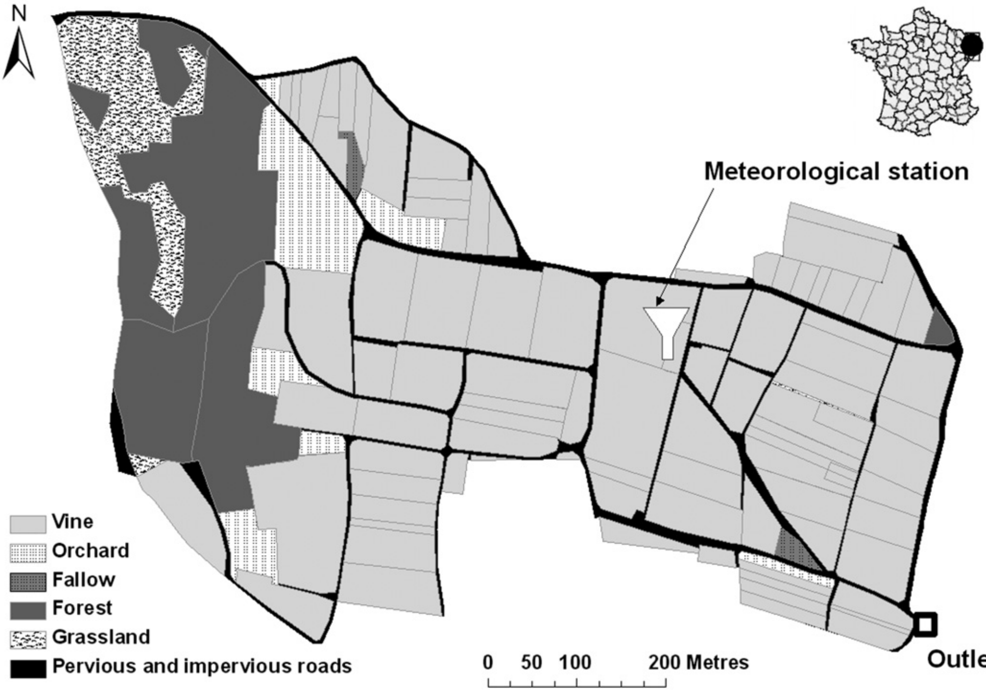

Figure 1. Delimitation of the Hohrain catchment (Haut-Rhin, Alsace, France) and land use.

vineyards (Figure 1). The land use shows a gradient from mostly forested areas and partly orchard at the upstream of the basin to agricultural and vineyard areas nearer to the outlet. With more than 120 farming plots, it should be noted that the road network is dense, mostly impervious and represents about 6% of the area of catchment. The catchment can be qualified as 'dry' catchment with no permanent flow. The hydrological functioning can be summarised in three steps: (1) no discharge occurs without rainfall, (2) then, from >0 to 4 mm of rainfall per event only the road network contributes to the discharge, (3) finally, rainfall greater than 4 mm, the number of fields contributing to the discharge increases with both intensity and total rainfall depth (unpublished results).

2.2 *Sampling and sample collection*

The catchment area is equipped with a meteorological station (Figure 1) and the outlet of the catchment has been instrumented for 4 years to monitor water, only observed during rainfall-run-off events, and pesticide concentrations. The measurement of the water level was carried out with a Venturi channel (ENDRESS and HAUSER, Huninge, France) and was performed with a surface water level sensor. Flow proportional water samples of 0.9 L were systematically collected every 8 m^3 for measurement of pesticide concentrations by a cooled automatic sampler (Hydrologic, Sainte-Foy, Québec, Canada). Samples were transferred via a polyethylene pipe to glass bottles and stored in the dark at 4°C. Twice a week, samples were collected and subsampled into plastic and glass bottles and analysed for glyphosate and aminomethyl phosponic acid (AMPA) and for the other pesticides.

Then, the samples were frozen until their analysis. According to the quality assurance procedures performed during this work [20], volatilisation, degradation and adsorption between the sampling and the analysis of the samples is negligible. Water sampling was conducted from 2003 to 2006, during the active wine growing season that corresponds to the major period of pesticide application and where the risk of offsite movement is large, i.e. March to October. Fifty-eight storm events were measured, which include a total of 280 collected water samples for pesticide concentration analyses and transfer quantification.

The variability of pesticide concentration was analysed over the targeted run-off events. Hydrograms and chemograms were available for each storm event from April 2003 to September 2006. Corresponding hyetograms were provided by the Meteo France station.

2.3 *Estimation of applied pesticides and selection of monitored pesticides*

Surveys were sent annually to the 28 farmers active in the Hohrain catchment in order to record the type and amount of pesticides applied. The survey includes the chemical species, their quantities, and their application date. No farmyard or urban area is located within the Hohrain catchment, which minimises the potential for pesticide point source pollution.

The goal of this study is to assess a broad spectrum of pesticides that display various physico-chemical characteristics in order to allow a thorough estimation of contaminant transfer at the catchment scale. The selection of compounds analysed at each sample series was based on preliminary knowledge regarding annual pesticide applications on the Hohrain catchment and on the physico-chemical properties of compounds most likely to move from their application site. According to the monitoring studies of the pesticide fate at the catchment scale [11], the sorption coefficient normalised to soil organic carbon content (K_{oc}) and the time for 50% decline of the initial pesticide concentration in soil, i.e. dissipation half-time (DT_{50soil}) are the important physico-chemical properties to explain pesticide fate.

The full list includes 17 molecules (8 herbicides, 8 fungicides and 1 insecticide) and 3 degradation products. The K_{oc} and DT_{50soil} values of the 17 molecules and the three metabolites are summarised in Table 1.

Pesticides such as diuron [22,23], the triazines, e.g. atrazine, simazine and terbuthylazine [24,25], have had their environmental behaviour studied for years; oryzalin and others such as glyphosate and glufosinate [26] (Table 1) have been studied fewer times. Carbendazim and norflurazon belong to the priority list for groundwater survey in the Alsace area (France) and were included in the list of analyses because of their persistence, even if they are no longer applied (Table 1). The three degradation products investigated are AMPA (amino-methyl phosphonic acid), glyphosate's degradation product, DCPMU (3,4-Dichlorophenyl-N-methyl urea) and DCPU (3,4-Dichlorophenyl urea), both degrades of diuron.

The application method, i.e. directly onto the soil for herbicides or on the leaves for fungicides and insecticides, represent a key-information to assess the fate of pesticides at the catchment scale. The herbicides, applied directly onto the soil, were *a priori* more available during the run-off process whereas the fungicides and insecticides can be also mobilised by foliar wash-off during rainfall event.

Table 1. Half-life of pesticide in soil (DT_{50soil}) and sorption coefficient normalised to soil organic carbon content (K_{oc}) [21] for 17 pesticides and 3 degradation products (AMPA: amino-methyl phosphonic acid; DCPMU: 3,4-Dichlorophenyl-N-methyl urea and DCPU: 3,4-Dichlorophenyl urea).

	DT_{50soil} (Field)	K_{oc}
Substances	Day	$L\,kg^{-1}$
Fungicides applied		
Azoxystrobin	21	423
Cymoxanil	3.5	44
Dimetomorph	44	348
Kresoxim methyl	16	308
Penconazole	86	2205
Pyrimethanil	30	301
Tetraconazole	61	1039
Herbicides applied		
Diuron	89	1067
Glufosinate	7	755
Glyphosate	12	21699
Isoxaben	123	601
Oryzalin	50	949
Terbuthylazine	46	220
Simazine	90	130
Insecticides applied		
Thiodicarb	18	418
Pesticides not applied		
Carbendazim (*Fungicide*)	18	223
Norflurazon (*Herbicide*)	225	700
Degradation products		
AMPA (from Glyphosate)	151	8027
DCPMU (from Diuron)	–	928
DCPU (from Diuron)	–	694

2.4 *Pesticide analyses*

Suspended sediment was separated from the water phase by filtration through 1 µm glass fibre filters. Aqueous samples were solid-liquid extracted and extracts were analysed. The fungicides azoxystrobin, cymoxanil, dimethomorph, kresoxim methyl, penconazole, pyrimethanil, tetraconazole, carbendazim, the herbicides diuron and its degradation products DCPMU and DCPU, as well as isoxaben, oryzalin, simazine, terbuthylazine, norflurazon, and the insecticide thiodicarb were analysed by liquid chromatography coupled to tandem mass spectrometry (LC-MS-MS), according to the French standard [27]. For glyphosate, AMPA, its degradation product and glufosinate-ammonium, the method of analysis consists of a derivatisation with 9-fluorenylmethyl chloroformate (FMOC-Cl) [28] and detection by LC-MS-MS. The recovery rates ranged between 70% and 88% depending on the compound. All the analyses were carried out by the Pasteur Institute of Lille (France) certified by the French Ministries of Health and Environment. Due to this externalisation, no replicates were managed during the study. Therefore, duplicate frozen samples were stored in case of analytical problems with the original sample.

2.5 *Pesticide use and fate metrics*

Various pesticide metrics have been developed to evaluate the transfer of pesticides at the catchment scale [10,29,30]. Metrics defined in the following equations (1 to 5), have been calculated and include the estimated values of pesticide use, as well as rainfall, run-off and the concentration of pesticides in water samples collected during each storm event. The selection of these metrics has been based on the balance between the required and available data, the environmental relevance of the information provided by these metrics and the possibility of performing a mass balance between the annual pesticide inputs applied to the fields and the loads detected at the outlet of the catchment.

The run-off coefficient (%) provides essential information about the hydrological behaviour during a rainfall event. Knowledge on the run-off to infiltration ratio is required to assess the potential vulnerability of surface water and groundwater [25,31,12]. The run-off coefficient RC is calculated for each event by normalising the total run-off generated during a rainfall event (V_{run}, m^3) by the total rainfall amount over a rainfall event (V_{rain}, m^3) (Equation (1)).

$$\mathrm{RC} = \frac{V_{\mathrm{run}}}{V_{\mathrm{rain}}} \tag{1}$$

To assess the occurrence of pesticides in the various environment compartments, a widely used metric is the detection rate [29,32,11]. This metric is usually performed with the limit of detection (LOD), but it can also be performed with the limit of quantification (LOQ). A frequency of determination (FOD) is calculated by Equation (2):

$$\mathrm{FOD} = \frac{n_{\mathrm{sloq}}}{n_i} \tag{2}$$

where n_{sloq} is the number of samples during an event i for which the pesticides were detected at a concentration higher than the limit of quantification (LOQ) and n_i is the total number of samples collected during an event i. The frequency of determination (FOD) is mathematically lower or equal to the limit of detection.

Assuming that the water sample is flow proportional, the calculation of the mean concentration for an event is Equation (3):

$$\mathrm{C}_{\mathrm{mean}\,j} = \frac{\sum_{s=1}^{n_j} \mathrm{C}_{js}}{n_j} \tag{3}$$

where n_j is the total number of instantaneous concentrations available for a pesticide j, C_{js} is the instantaneous concentration of the pesticide j.

Because of analytical difficulties in analysing the fraction of pesticides sorbed on sediments, several studies [33,34,29] on the fate and transport of pesticide only examine pesticides in the dissolved phase. Unless the pesticide has a very high partitioning coefficient most of the flux of pesticide will be the dissolved phase [26]. The sampling devices in the Hohrain catchment allow only monitoring pesticide in the dissolved phase.

Furthermore, the pesticide loads in the dissolved phase were calculated with the run-off and the pesticide concentration data. We have assumed a linear change between two successive analysed concentrations and monitored run-off data. We assumed a linear concentration between a null value of concentration at the beginning of discharge and the concentration of the first sample and between the concentration of the last sample and a null value at the end of the discharge. The exported quantities LPj out are calculated with one minute time step according to Equation (4):

$$\mathrm{LP}_{j\,\mathrm{out}} = \sum_{t=1}^{n} \mathrm{C}_{jt} \times \mathrm{Q}_t \tag{4}$$

where C_{jt} is the instantaneous concentration of the pesticide j, n the duration of run-off event expressed in minutes and Q_t is the instantaneous run-off. To perform a mass balance between applied pesticide amount and pesticide loads, the estimation of the pesticide sorbed both in bedload and suspended matter would be also required. This pesticide amount can either be directly monitored [35] or derived from the pesticide amount in the dissolved phase according to empirical equations [29]. In the Hohrain catchment, the sampling device does not allow to collect enough suspended matter to perform pesticide analyses on the sorbed phase. The empirical equations [29] cannot be applied without calibration in the Hohrain catchment. Therefore, the exported pesticide load (Equation (4)) should be considered lower than the total pesticide loads at the catchment outlet.

A yearly overall export coefficient Ec (%) for each compound by Equation (5) based on the estimates of pesticide application and the pesticides outputs calculated according to the Equation (4). Ec is calculated by comparing $\mathrm{LP}_{j\,\mathrm{out}}$ (g) the load of the pesticide j exported at the outlet of the catchment with $\mathrm{LP}_{j\,\mathrm{in}}$ (g), the cumulated load of each pesticide applied each year:

$$\mathrm{Ec} = \frac{\mathrm{LP}_{j\,\mathrm{out}}}{\mathrm{LP}_{j\,\mathrm{in}}} \tag{5}$$

Focusing on the removal rates calculated by comparing the pesticide inputs and the loads detected at the outlet of a hydro-system, this metric seems to be the most relevant to assess the export of active substances [36,11].

These 5 metrics were calculated for the 58 monitored run-off events to analyse the pesticide fate on vineyards in the Hohrain catchment.

3. Results and discussion

3.1 *Hydrology*

Over the study period of 4 years, there was a large variability in rainfall amounts ranging between 359 and 730 mm per year (Table 2). There is no correlation between annual rainfall and the number of events analysed. All the rainfall events which generated a run-off volume higher than 8 m^3 were monitored and the associated pesticide concentrations were analysed according to the sampling method (Section 2.2). The main run-off events, i.e. with more than 8 m^3, represented each year only 29% of the total rainfall amount between March and October (Table 2). No samples were collected for the run-off events generating less than 8 m^3. The threshold of 8 m^3 had the advantage to focus on the main run-off events with a contribution of vineyard fields on which the pesticides were applied but introduced a bias in the total annual pesticide loads. The mean run-off per event is stable (mean: 4 L s^{-1}; standard deviation: 0.9 L s^{-1}). The maximum run-off value observed each year is quite variable between 19 and 127 L s^{-1}. The run-off coefficients calculated (Equation (1)) are less than 2% for the 4 years. This low value from an agricultural area can be explained by (1) the medium infiltration capacity of the soil, (2) the vineyard

Table 2. Hydrological metrics: Number of monitored events; total yearly rainfall; rainfall from March to October; rainfall of monitored events; proportion of monitored rainfall/rainfall from March to October; mean and maximum discharge observed during events; minimum, maximum and mean volume generated during events; and the mean Run-off Coefficient (RC) for water associated with run-off events.

	Number of monitored events	Yearly rainfall (mm)	Rainfall from March to October** (mm)	Rainfall of *m* monitored events** (mm)	Proportion of monitored rainfall/rainfall from March to October (%)	Discharge		Volume			RC* (%)
						Mean (l/s)	Max (l/s)	Min (m^3)	Max (m^3)	Mean (m^3)	
2003	12	359	265	101	38	4.8	127	1.2	198	62	1.6
2004	29	669	487	159	33	2.9	65	1	131	31	1.4
2005	8	470	407	105	26	3.6	19	6.7	117	64	1.1
2006	9	730	649	115	18	4.6	30	10.3	250	95	1.8
Mean		557	452	120	29	*4.0*	*60.3*	*4.8*	*174*	*63*	*1.475*
SD		172	160	27	8.9	*0.9*	*48.6*	*4.5*	*61.8*	*26.1*	*0.3*

*RC: Run-off coefficient.
**This period corresponds to the crop growing season.

management involving grass cover which was initially adopted for soil conservation and induces a decrease of surface run-off and (3) the fact that the effective area contributing to run-off is limited with respect to the total catchment area. Therefore, the mean volume generated during rainfall events is relatively low and ranged between 31 m^3 in 2004 and 95 m^3 in 2006 with a maximum value observed in 2006 (250 m^3) (Table 2). The infiltration process is predominant during the rainfall events. However, the pesticides in the surface water represent the main threat both for surface water and groundwater regionally. Indeed, the run-off produced from the vineyard catchment rapidly flows into downstream water bodies which are closely linked to the Rhenan aquifer.

3.2 *Pesticide inputs*

The survey response rates, expressed in proportion of the total vineyard catchment's area, are 75%, 83%, 57% and 61%, respectively, for 2003, 2004, 2005 and 2006. To take into account the missing information, a correcting ratio, i.e. ratio of investigated to total vineyard area, has been applied to estimate the total pesticide applied amount.

The difference of the total quantities of pesticides for 2003 and 2004 was low, i.e. 5% (Table 3) in spite of marked climatic variations (Table 2). This variation was higher for 2005 and 2006. For 2005, the total input decreased by 44% in comparison with the mean value calculated for 2003–2004. For 2006, we observed an increase of 66% compared to the mean values for the period 2003–2004, owing to the used of diuron and glyphosate by the Agricultural and Viticultural College of Rouffach (50% of the vineyard areas). Herbicides are the most used category of pesticides with 78% of the total amount applied (Table 3). Glyphosate was the most used herbicide and the yearly applied amount ranged from 18 to 61 kg. The highest input (61.4 kg for 2006) was associated with a very rainy year (730 mm, i.e. 22% more than the average inter-annual rainfall). In contrast, quantities of insecticides applied are marginal with nearly 1 kg annually. These quantities will continue to decrease due to the use of pheromones. Two hypotheses can be formulated to explain the frequency of determination of simazine banned since 2002: first, simazine was applied illegally on fields after 2002; secondly the fraction of simazine sorbed on field soil particles has progressively desorbed and transferred during run-off events. The survey results have confirmed the first hypothesis as simazine was been applied until 2004. However, in 2008 on the Hohrain catchment, simazine was systematically detected during the run-off events monitored (non published data). Consequently, the second hypothesis of desorption associated with low degradation kinetics in soil [37], cannot be excluded, in agreement with previous observations [11,29].

Figure 2 illustrates pesticide used in 2004. These results underline the diversity of compounds applied in 2004 (20 fungicides, 8 herbicides and 6 insecticides). However, three pesticides analysed between 2003 and 2006 were not applied in 2004 (Figure 2). Carbendazim and norflurazon were not applied during the studied period (2003–2006), according to the survey results, but analysed in 2003 and 2004. Indeed, these two pesticides belong to the priority list for groundwater survey and they had been applied in the past. The last year of their application was unknown.

3.3 *Frequency of determination*

Table 4 synthesises the results of pesticide fate metrics, i.e. the frequency of determination (FOD) and the maximum C_{max} and mean C_{mean} concentrations calculated for the 58

Table 3. Use and fate pesticide metrics with input data from farmer surveys; output flux for 17 pesticides and 3 compounds of degradation (AMPA: amino-methyl phosphonic acid; DCPMU: 3,4-Dichlorophenyl-N-methyl urea and DCPU: 3,4-Dichlorophenyl urea) and the export coefficient (Ec) ("/"pesticide was not analysed; "n.a." the pesticide was not applied; and "n.c." the export coefficient could not be calculated.

Pesticides	Total applied amount (g)				Pesticide outputs (g)				Export coefficient (Ec) (%)			
	2003	2004	2005	2006	2003	2004	2005	2006	2003	2004	2005	2006
Fungicides applied												
Azoxystrobin	671	n.a.	n.a.	n.a.	0.11	0.04	/	/	0.016	n.c.	n.c.	n.c.
Cymoxanil	5846	5187	763	3364	0.02	0.03	/	/	0.0003	0.001	n.c.	n.c.
Dimetomorph	767	257	1003	190	0.51	0.26	/	0.11	0.066	0.099	n.c.	0.059
Kresoxim methyl	6039	3129	2608	1995	0.04	0.11	/	0.04	0.001	0.003	n.c.	0.0015
Penconazole	58	n.a.	33	33	0.02	/	0.01	/	0.033	n.c.	0.043	n.c.
Pyrimethanil	3185	2808	1246	n.a.	0.48	0.16	0.16	0.06	0.015	0.006	0.013	n.c.
Tetraconazole	54	68	n.a.	295	0.03	/	0.01	/	0.048	n.c.	n.c.	n.c.
Herbicides applied												
Diuron	289	1499	195	5199	0.31	0.55	0.68	2.71	0.106	0.037	0.035	0.052
Glufosinate	384	496	n.a.	n.a.	/	0.08	/	/	n.c.	0.017	n.c.	n.c.
Glyphosate	22816	28101	18459	61411	6.60	9.40	4.71	5.77	0.029	0.033	0.026	0.009
Isoxaben	42	n.a.	n.a.	n.a.	0.04	/	0.04	0.02	0.09	n.c.	n.c.	n.c.
Oryzalin	1663	2990	311	947	0.04	0.15	/	/	0.002	0.005	n.c.	n.c.
Terbuthylazine	n.a.	386	n.a.	n.a.	0.11	0.05	0.04	0.03	n.c.	0.013	n.c.	n.c.
Simazine	81	168	n.a.	n.a.	0.06	0.50	0.01	0.02	0.077	0.298	n.c.	n.c.
Insecticides applied												
Thiodicarb	1171	42	n.a.	n.a.	/	0.13	/	/	n.c.	0.317	n.c.	n.c.
Pesticides non applied												
Carbendazim (Fungicide)	n.a.	n.a.	n.a.	n.a.	0.02	0.03	/	/	n.c.	n.c.	n.c.	n.c.
Norflurazon (Herbicide)	n.a.	n.a.	n.a.	n.a.	0.08	0.11	/	/	n.c.	n.c.	n.c.	n.c.
Degradation products												
AMPA (from Glyphosate)	n.a.	n.a.	n.a.	n.a.	2.50	2.77	1.06	1.22	n.c.	n.c.	n.c.	n.c.
DCPMU (from Diuron)	n.a.	n.a.	n.a.	n.a.	/	/	/	0.027	n.c.	n.c.	n.c.	n.c.
DCPU (from Diuron)	n.a.	n.a.	n.a.	n.a.	/	/	/	/	n.c.	n.c.	n.c.	n.c.

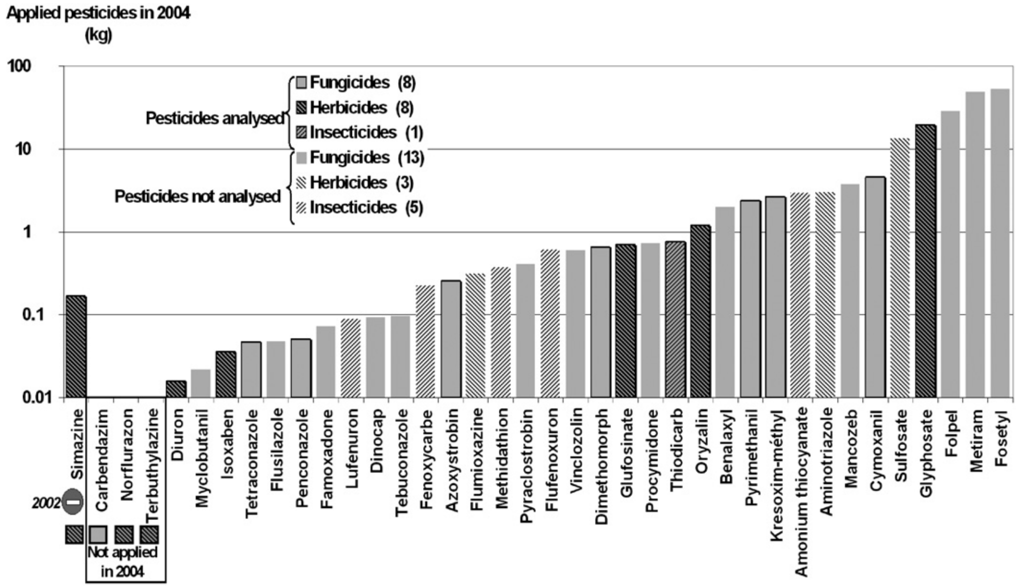

Figure 2. Total of pesticide amounts applied in 2004 (per kg) by distinguishing the pesticides (fungicides, herbicides and insecticides) analysed (black asterisk) or not during run-off events.

events between 2003 and 2006. The number of samples analysed is not the same for the different molecules in a same year. Indeed, owing to different technical constraints and timing of application, the numbers of sample for each pesticide can vary from one year to another.

The frequency of determination (FOD) (Equation (2)) was higher for herbicides (62%) than fungicides (30%). The rate is very low for the sole insecticide monitored (2%). The highest FOD have been observed for dimethomorph (74% on average for 2003–2006), pyrimethanil (67%), terbuthylazine (97.5%), diuron (98.5%) and glyphosate (99.75%) (Table 4). AMPA and DCPMU, degradation products of glyphosate and diuron, respectively, were always detected (100%) (Table 4). DCPU produced by the degradation of DCPMU [38] could not be detected during the events of 2006.

The pesticides studied involved a diverse group of chemical substances. Some older types in use, such as simazine, banned in France in 2002, persisted, with FODs of 100, 79, 24 and 42%, respectively, over the four years.

These frequencies of determination are relatively high with respect to the low run-off coefficient calculated. This could be explained by the hydrological connection of some areas within the catchment. Some vineyard fields located near the outlet may be directly connected to the impervious road network. Consequently, for all the run-off events, they would always contribute to both the discharge and to the pesticide loads.

The mean frequency of determination value for fungicide was about 50% lower than the herbicides with 28.4% (standard deviation: 32.3%) and 61.8% (standard deviation: 43.9%), respectively. These values were in agreement with the *a priori* higher availability of herbicides applied directly on soil compared to fungicides directly sprayed on the leaves. With only one export coefficient value (Table 3), it was not possible to compare the behaviour of insecticide with the one of herbicides and fungicides.

Table 4. Pesticide fate metrics for 17 pesticides and 3 degradation products (AMPA: amino-methyl phosphonic acid; DCPMU: 3,4-Dichlorophenyl-N-methyl urea and DCPU: 3,4-Dichlorophenyl urea) for 58 run-off events between 2003 and 2006: limit of quantification (LOQ); number of samples analysed by year; the annual frequency of determination (FOD); maximum concentrations C_{max} and mean concentrations C_{mean}; ("/" the pesticide was not analysed).

		Number of samples analysed				Frequency of determination (FOD) (%)				C_{max} ($\mu g\,L^{-1}$)				C_{mean} ($\mu g\,L^{-1}$)			
Pesticides	LOQ ($\mu g\,L^{-1}$)	2003	2004	2005	2006	2003	2004	2005	2006	2003	2004	2005	2006	2003	2004	2005	2006
Fungicides applied																	
Azoxystrobin	0.05	82	98	0	0	30	41	/	/	3.4	0.36	/	/	0.28	0.06	/	/
Cymoxanil	0.05	82	98	0	58	12	21	/	0	0.3	0.34	/	/	0.08	0.05	/	/
Dimetomorph	0.05	82	98	0	86	98	66	/	57	4.4	5.7	/	0.66	0.68	0.3	/	0.16
Kresoxim methyl	0.1	82	98	0	86	12	12	/	1	0.17	2.2	/	0.07	0.04	0.09	/	0.004
Penconazole	0.05	82	98	37	58	1	0	5	0	0.22	/	0.16	/	0.01	/	0.02	/
Pyrimethanil	0.1	82	98	37	86	48	80	100	39	5.8	1.5	1.8	0.39	0.45	0.2	0.23	0.1
Tetraconazole	0.05	82	98	37	58	21	0	9	0	0.14	/	0.09	/	0.05	/	0.01	/
Herbicides applied																	
Diuron	0.02	82	98	37	86	100	97	100	97	11	14	8.8	32	0.84	0.54	1.2	3.7
Glufosinate	0.1	82	98	0	0	0	16	/	/	/	1.3	/	/	/	0.26	/	/
Glyphosate	0.1	82	98	37	86	100	100	100	99	86	70	63	40	6.76	10.4	7.4	5.6
Isoxaben	0.1	82	98	37	86	4	0	8	2	0.28	/	1.9	0.07	0.04	/	0.15	0.001
Oryzalin	0.1	82	98	0	0	11	14	/	/	2.6	4.4	/	/	0.3	0.17	/	/
Terbuthylazine	0.025	82	98	37	86	100	99	100	91	5.6	0.27	0.22	0.12	0.44	0.05	0.07	0.04
Simazine	0.02	82	98	37	86	100	79	24	42	2.7	10.2	0.05	0.09	0.2	0.22	0.006	0.02
Insecticides applied																	
Thiodicarb	0.05	82	98	0	0	0	4	/	/	/	60	/	/	/	15	/	/
Pesticides not applied																	
Carbendazim (Fungicide)	0.05	82	98	0	0	10	19	/	/	0.19	0.18	/	/	0.03	0.03	/	/
Norflurazon (Herbicide)	0.1	82	98	0	0	24	49	/	/	1.6	4	/	/	0.32	0.2	/	/
Degradation products																	
AMPA (from Glyphosate)	0.1	82	98	37	86	100	100	100	100	23	44	8,5	5.5	2.76	2.9	1.9	1.4
DCPMU (from Diuron)	0.05	0	0	0	28	/	/	/	100	/	/	/	0.31	/	/	/	0.13
DCPU (from Diuron)	0.05	0	0	0	28	/	/	/	0	/	/	/	/	/	/	/	/

3.4 *Pesticide concentration*

Mean concentration values of herbicides was generally larger (1.7 $\mu g\,L^{-1}$ on average for the 2003–2006 period) than fungicides concentrations (0.15 $\mu g\,L^{-1}$). The largest concentrations were obtained for the herbicide glyphosate (7.5 $\mu g\,L^{-1}$ mean and 86 $\mu g\,L^{-1}$ max), the insecticide thiodicarb (15 $\mu g\,L^{-1}$ mean and 60 $\mu g\,L^{-1}$ max) and the glyphosate degradation product AMPA (2.9 $\mu g\,L^{-1}$ mean and 44 $\mu g\,L^{-1}$ max).

Concentrations detected in filtrated surface waters were one to three orders of magnitude larger than the drinking water limit (0.1 $\mu g\,L^{-1}$) (Table 4). Although water from the Hohrain catchment is not used directly for drinking water supply, such high pesticide concentrations could cause problems downstream.

Schulz [34] reported a negative correlation (with a significance of $p = 0.0025$) between the log-transformed maximum insecticide concentration and the catchment size. The high pesticide concentration values obtained in the Hohrain catchment, 42 ha, are in agreement with this correlation. The Koc values of the monitored pesticides range from 44 L Kg-1 (cymoxanil, fungicide) to 21 699 L Kg-1 (glyphosate, herbicide). It may be noted that this range is similar to those mentioned by Schulz [34], suggesting similar fate processes. These results are of particular importance with regard to the European Water Framework Directive [3], which currently only covers catchment areas over 10 km^2. As discussed by Schulz [34], this directive thus excludes aquatic habitats that are potentially at the highest risk of being negatively affected by high pesticide concentrations.

3.5 *Export coefficient*

Knowledge of both pesticide input and output is used to calculate an export coefficient Ec (Equation (4)). The export coefficients calculated at the catchment scale were always less than 1% and often less than 0.1% (Table 4). The pesticides with higher export coefficients were thiodicarb and simazine (0.31%). The lower ratio is observed for fungicides such as cymoxanil (0.0003%). Despite these low export coefficients, all water samples were above the drinking water limit (0.1 $\mu g\,L^{-1}$). A comparison between the 4 years shows a relative constant export coefficient. No significant relationship can be determined between the export coefficient and (1) the characteristics of rainfall calculated yearly, or (2) the physico-chemical properties of each pesticide.

The export coefficients calculated for the Hohrain catchment were lower than the values obtained in similar studies, e.g. between 0.09% and 0.87% for Poissan *et al.* [11]; between 0.2% and 17.5% for Blanchoud *et al.* [29] and between 0.26% and 0.57% for Baran *et al.* [25].

Considering mean and standard deviation values of export coefficient, no difference of availability can be determined at the catchment scale between fungicides (mean: 0.027%; standard deviation: 0.03%) and herbicides (mean: 0.055%; standard deviation: 0.074%).

As discussed in the hydrology results Section 3.1, the main run-off events, i.e. with more than 8 m^3, represented each year only 29% of the total rainfall amount between March and October (Table 2) and so the export coefficient values likely underestimate the total annual pesticide loads.

4. Conclusions

More than 80 kg of pesticides can be applied annually to the Hohrain vineyard catchment during a growing season. Pesticides studied were a diverse group of chemical substances.

Some compounds were frequently detected at the outlet of the catchment for the 2003–2006 period (dimethomorph: 74%, pyrimethanil: 67%, diuron: 98.5% and glyphosate: 99%). AMPA and DCPMU, degradation products of glyphosate and diuron, respectively, were detected in every sample.

Glyphosate and diuron are the most extensively used pesticides on the Hohrain catchment. Overall, pesticides losses from Hohrain catchment were systematically less than 0.1%. Surprisingly, considering the high variability of applied amounts and weather conditions, this value (0.1%) seems to be stable over the study period.

Pesticides and their degradation products were present in the Hohrain catchment with maximum concentrations of $86\,\mu g\,L^{-1}$ for the herbicide glyphosate and $44\,\mu g\,L^{-1}$ for its degradation product AMPA.

The results from this 4 year study underscore that pesticide behaviour at the catchment scale varies both over time and according to the type of pesticide considered. Assessing the fate of pesticide in agro-ecosystems based on land use patterns is not a straightforward exercise. Indeed, the quantification of the export coefficient, expressing a mass balance requires also significant investment both to collect information on pesticides application amount and timing as well as to calculate the pesticides loads at the catchment scale.

Because a broad spectrum of pesticides has been detected in natural water, the effect of mixtures should also be taken into account; because the overall toxicity could be higher than the sum of toxicities caused by the concentrations of the individual pesticides.

The database corresponding to the 58 events characteristics will be used to develop fate indicators, fate models and to evaluate bio-remediation strategies for pesticide mitigation, such as artificial wetland located at the downstream of the catchment [39].

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