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Article in *Agriculture Ecosystems & Environment* · January 2012

DOI: 10.1016/j.agee.2011.10.010

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Entry and toxicity of organic pesticides and copper in vineyard streams: Erosion rills jeopardise the efficiency of riparian buffer strips

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ARTICLE INFO

Article history:

Received 7 July 2011

Received in revised form 12 October 2011

Accepted 13 October 2011

Keywords:

Fungicide

Copper

Buffer strips

Surface water

Monitoring

Exposure

ABSTRACT

The present study was performed to characterise in-stream pesticide exposure within the Palatinate vineyard region in south-west Germany, evaluate the influence of buffer strip widths and identify mitigation measures for the relevant entry pathways. In-stream water and sediment samples that were taken at nine sampling sites of different buffer widths following intense rainfall, and edge-of-field runoff that were sampled in erosion rills were analysed regarding 28 active ingredients of pesticides including copper. In-stream samples contained a mix of 8 ± 4 pesticide compounds, resulting in total pesticide concentrations of $1.4\text{--}8.9 \mu\text{g l}^{-1}$ for water and $16\text{--}670 \mu\text{g kg}^{-1}$ dw for sediment. Following an exceptional rainfall event with a previous 34-day drought period, pesticide concentrations reached $7.0\text{--}83.4 \mu\text{g l}^{-1}$. Fungicides were the most important pesticides found and were significantly correlated with the pesticide application frequency and rate. The calculated toxicity values per sample (TU_{max}) indicated that both organic pesticides and copper concentrations likely cause ecotoxicological effects in the field. The buffer strip width was of little importance for pesticide in-stream concentrations because pesticide entry occurred mainly via the field path network and erosion rills. Pesticide in-stream concentrations were significantly and positively correlated with the concentrations detected in erosion rills ($R^2 = 0.56$). As possible risk mitigation measures, we suggest the implementation of grassed field paths and vegetated ditches or wetlands.

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1. Introduction

Risk mitigation measures are increasingly important, particularly because regulatory frameworks such as the European Water Framework Directive (2000/60/EC; European Commission, 2000), the framework of the European Union (EU) for the sustainable use of pesticides (2009/128/EC; European Commission, 2009a) and the placing of pesticides on the market (1107/2009; European Commission, 2009b) require higher standards. At present, in most EU member states, certain pesticide risk management measures (e.g., no-spray zones) have already been implemented in pesticide regulations (Van Vliet, 2001; DEFRA, 2002; Streloke et al., 2007). Nevertheless, there are numerous studies reporting pesticide residues in the aquatic environment, even at ecotoxicologically relevant concentrations (e.g., Schulz, 2004; Suess et al., 2006).

Current monitoring studies often focus on insecticide exposure, presumably due to their high acute toxicity to invertebrates. By

contrast, fungicide pollution, especially following pesticide application in vineyard areas, has rarely been addressed. This research area has gained importance in the last few years. Thus far, only four studies have dealt with the detection of fungicide residues in streams within vineyard catchments following runoff events (Bermudez-Couso et al., 2007; Hildebrandt et al., 2008; Gregoire et al., 2010; Rabiet et al., 2010). This small number of studies is particularly noticeable because fungicides are used intensively in vineyards and account for 96% of all pesticide applications (Rossberg, 2009).

Through diffuse entry pathways, applied pesticides may also reach non-target aquatic ecosystems, such as small streams draining the present study area (Palatinate vineyard region in south-west Germany). In this region, in addition to spray drift, which is of general importance for permanent crops (Ganzelmeier et al., 1995; Rautmann et al., 2001), runoff is regarded as a major contributor to pesticide entry in surface waters because slopes of more than 2% are common in the studied vineyard area (Ohliger and Schulz, 2010). Compared with runoff, management measures for reducing the risk from spray drift are much better developed (FOCUS, 2007). Therefore, the present investigation

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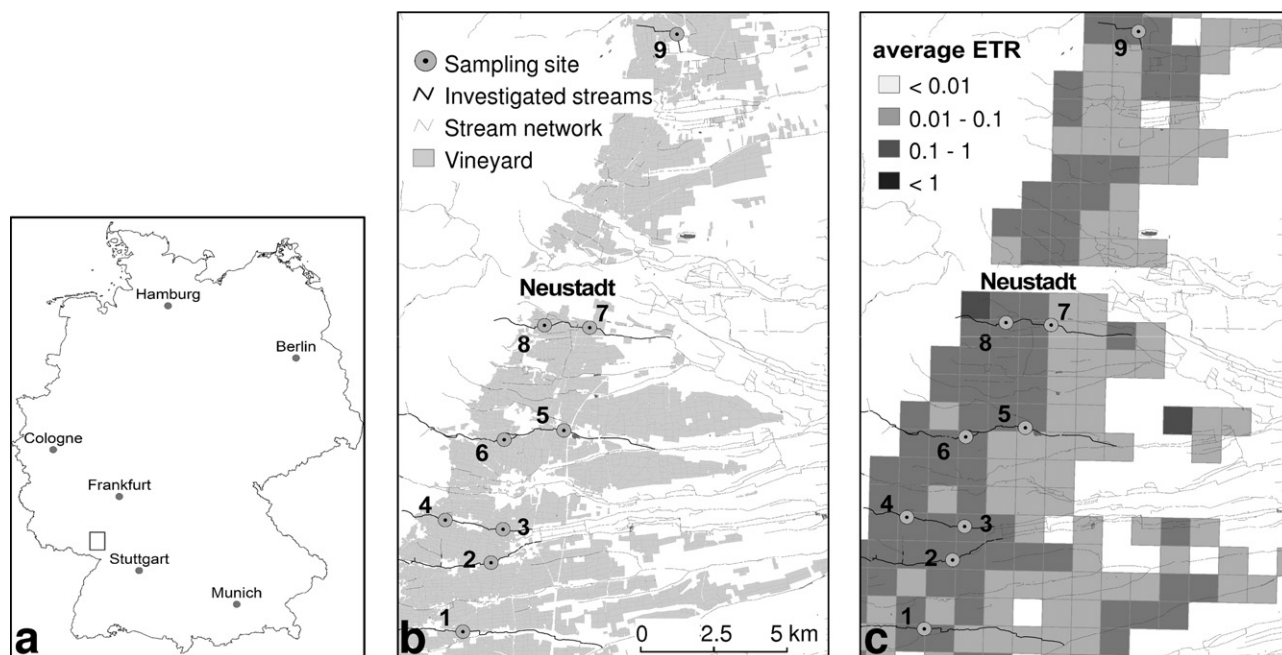


Fig. 1. Location of the study area, the Palatinate vineyard region in south-west Germany (a) and the sampling sites at the investigated streams (b). All sampling sites were located within 1 km grids with a high acute aquatic risk potential (average Exposure-Toxicity-Ratio (ETR) ≥ 0.1) modelled with SYNOPSIS-GIS (c).

focused on runoff. Runoff pesticide entries are determined by many influencing factors (e.g., soil moisture, rainfall amount and intensity, concentrated flow and properties of substances), which complicate the estimation of expected runoff entries (Schulz, 2001) and consequently the estimation of the reduction efficiency of risk management measures. Nevertheless, in some EU member states (Germany, France, Portugal), measures related to runoff, such as vegetated buffer strips, are also part of the regulatory framework (FOCUS, 2007). With more than 10 reviews available (e.g., Muscutt et al., 1993; Schulz, 2004; Lacas et al., 2005; Reichenberger et al., 2007; Zhang et al., 2010) and approximately 30 original research studies (e.g., Syversen and Bechmann, 2004; Vianello et al., 2005; Pätzold et al., 2007; Otto et al., 2008), vegetated buffer strips are one of the best studied management measures to reduce runoff pesticide entry. Nevertheless, reported reduction values are highly variable (0–100%), with most exceeding 60% (Reichenberger et al., 2007; Zhang et al., 2010). Although it is not the only factor, buffer strip width is often used to estimate respective reduction efficiency. For example, in Germany, densely vegetated buffers in widths of 5 m, 10 m and 20 m, pesticide reductions of 40%, 60% and 80%, respectively, for an even/uniform type of runoff are assumed for weakly absorbed pesticides while reductions of 40%, 85% and 95%, respectively, are assumed for moderately absorbed pesticides (Umweltbundesamt, 2011). Overall, current research in the field of pesticide reduction efficiency in vegetated buffer strips has concentrated mainly on herbicides (89% of studies), while only 32% and 11% of studies also focused on insecticides and fungicides, respectively. Moreover, experimental designs (experimental sites with simulated or natural rainfall) were used. An evaluation of the pesticide reduction efficiency of vegetated buffer strips in the field (which were not explicitly designed with the goal of pesticide mitigation) by a monitoring program has not been performed.

The present monitoring field study was carried out at six streams in a vineyard area in southwest Germany during the pesticide application periods of 2009 and 2010 with the following main objectives:

- (1) Determination of pesticide exposure (with an emphasis on fungicide exposure) following runoff events in receiving

streams draining a vineyard area and identification of the main entry pathway.

- (2) In-field evaluation of buffer strip effectiveness to reduce pesticide runoff entries and to establish a relationship between the in-stream pesticide pollution level and the buffer strip width in the catchment area.
- (3) Derivation of appropriate mitigation measures based on the results.

2. Materials and methods

2.1. Study area and sampling sites

The present field study was carried out in the Palatinate wine-growing area (Fig. 1a and b), which is the second largest viticulture district of Germany, with more than 23,000 ha of vineyards (Statistisches Landesamt RLP, 2011). The sampling site selection was supported with the risk indicator model SYNOPSIS-GIS (model for the synoptic assessment of pesticide risk potential coupled with geo-information systems) (Gutsche and Strassmeyer, 2007; Strassmeyer and Gutsche, 2010). The model was used to identify 1-km² grid cells in the Palatinate region with relatively high aquatic risk potentials of vineyards due to the pesticide exposure pathways of spray drift, runoff and drainage. SYNOPSIS-GIS is a spatially explicit version of the SYNOPSIS model (Gutsche and Rossberg, 1997) that implements spatial databases on land use, elevation, soil conditions and climate data as well as data sets of regionalised surveys of pesticide application.

The results of the regional risk analysis for acute aquatic risk are illustrated in Fig. 1c. For this analysis, the environmental input parameters of more than 9000 vineyards were available, and 19 catchments with relevant wine growing activity were involved. The parameters were merged with a set of 38 application calendars (Rossberg, 2004). The field-based acute aquatic risk potentials calculated with SYNOPSIS-GIS were aggregated in space by calculating the average Exposure-Toxicity Ratio (ETR) of vineyards in 1-km² grids (Fig. 1c). The low risk potential level, defined as ETR = 0.1, is 1/10 of the lowest lethal concentration LC₅₀ from a set of aquatic

Table 1

Characteristics of the sampling sites regarding riparian buffer strips and hydrology and the respective catchment area.

Sampling site	Characteristics of the sampling site				Characteristics of the catchment area		
	Average riparian buffer strip width ¹ (m)	Surface water width ^{a,c} (m)	Water depth ^{a,c} (m)	Flow velocity ^a (m s ⁻¹)	Catchment area ^b (km ²)	Field path density ^b (km km ⁻² vineyard area in the catchment)	Erosion rills leading into the water body ^a (number km ⁻¹ flow length)
1	10.8	1.4	0.11	0.14	7.9	9	4.2
2	10.1	2.4	0.13	0.07	18.1	5	3.9
3	4.1	1.1	0.04	0.06	3.5	5	1.0
4	5.5	0.4	0.03	0.02	1.7	14	1.8
5	8.8	1.3	0.13	0.05	10.2	4	0.3
6	18.9	1.0	0.12	0.06	8.5	4	0.8
7	12.6	0.3	0.04	0.07	7.2	4	3.3
8	20.5	1.1	0.12	0.01	1.4	15	5.0
9	5.1	0.4	0.04	0.08	3.1	5	5.0

^a Determined by field survey.^b Determined on the basis of geo-data.^c Determined at normal water level.

reference organisms (Gutsche and Strassemeyer, 2007). All sampling sites were located in the grids with an acute aquatic risk potential above the defined level of low risk potential.

A total of six streams were investigated using nine sampling sites (Fig. 1b) during the application season from June to August 2009 to determine the levels of pesticide residues in the water and sediment phases following heavy rainfall events. The sampling sites differed regarding riparian buffer width and were specifically selected to represent a broad spectrum of width, varying from 4.0 to 20.5 m (Table 1). All the sampling sites had relatively small catchment areas of less than 18 km², which were characterised by the high numbers of field paths (4–14 km km⁻² vineyard area) and erosion rills (0.3–5 per km flow length), which are typical for this vineyard area (Ohliger and Schulz, 2010). At a normal water level, the average surface water width and depth ranged from 0.3 m to 2.4 m and from 0.03 m to 0.13 m, respectively. Nevertheless, following heavy rainfall events, the water level rose substantially, by a factor of up to seven, indicating that runoff is very important in this area.

A second monitoring period was performed between June and August 2010 and focused exclusively on the determination of pesticide exposure in the water phase at four streams using five sampling sites (1, 2, 3, 4 and 9). These were investigated in detail by also taking water samples upstream of the original sampling sites. Each sampling site was marked by a letter following the sampling site number (e.g., 1 is the original sampling site, 1a is upstream of sampling site 1, and 1b is upstream of site 1a). Additionally, the edge-of-field runoff samples taken from erosion rills, which led concentrated runoff from fields into the water bodies, were analysed in 2010 for pesticide residues.

2.2. Pesticide application

Fungicides are the most important pesticides for grapes, accounting for 96% of all applications, while herbicides (1.5%) and insecticides/acaricides (2.5%) are of minor importance (Rossberg, 2009). According to application recommendations in the study area released by the official extension service (DLR Rheinlandpfalz), the most important pesticide active ingredients (in the present study only described by the term “pesticides”) were identified and selected for the monitoring program (23 fungicides, 1 herbicide, 3 insecticides; Table 2). The main pests in vines are *Peronospora* sp., *Botrytis* sp. and *Oidium* sp., which are controlled by fungicides that are applied every 10–14 days during the application period. This application period lasted approximately from the end of April until the middle of August. Table 2 shows that a large number of different fungicides are available for application, which is very important regarding

fungicide anti-resistance management. The application of fungicides with a specific mode of action must be altered during the application period. However, there are a few fungicides with a non-specific mode of action (e.g., folpet and copper), which may be applied more often.

Because we could not observe the pesticide application process in the present study, we generally assumed that the farmers worked according to principles of good agricultural practice and followed pesticide specific requirements (e.g., drift-reducing techniques and non-spray zones).

2.3. Pesticide monitoring

2.3.1. Sampling methods

Water and suspended particles for pesticide analysis were collected following heavy rainfall events using event-triggered passive sampling systems according to Schulz et al. (2001) and Liess et al. (1996). For water sampling, two 1-litre brown glass bottles were fixed to a metal stake at the sampling sites with the bottle openings approximately 10 and 30 cm above the normal water level. Specially prepared bottle lids prevented precipitation from entering the jar, while a free inflow of stream water was provided. When the water level rose, bottles filled passively with water and the highest filled bottle was taken for pesticide analysis, assuming that the peak concentration of pesticides coincided with the increasing water level (Rabiet et al., 2010). Conductivity was determined (using a WTW handheld meter, Multi 340i, and WTW conductivity cell, Tetra Con[®] 325) in the water samples. Lower values than those detected during a normal water level situation in the stream gave evidence that the sample contained edge-of-field runoff water (Schulz and Liess, 1999).

Suspended particles were collected with samplers (modified according to Liess et al., 1996) consisting of a 750-ml plastic jar lined with aluminium foil that was placed with two metal stakes at the bottom of the stream. Through a hole in the lid of the jar (diameter of 2 cm) suspended particles transported through the water column entered and settled within the jar. The samplers were emptied weekly and stored at –18 °C until pesticide extraction.

Edge-of-field runoff water that was sampled directly in erosion rills was collected with a system developed by Schulz et al. (1998). One-litre brown glass bottles were either buried in the ground of the embankment or installed with metal stakes in the erosion rills, if the ground was paved. Additionally, roofs consisting of metal or plastic were installed to prevent rainfall from entering the bottles. Furthermore, edge-of-field runoff samples were taken by hand during rainfall events.

Table 2
Application information (corresponding to the official extension service, DLR Rheinpfalz) and properties (PPDB, 2009) of the 27 pesticide active ingredients included in the residue analysis.

Active ingredient	Pest	Recommended application rate (kg a.i. ha ⁻¹) ^a	K _{OC}	EC ₅₀ /LC ₅₀ (most sensitive organism) (µg l ⁻¹)	NOEC <i>Chironomus riparius</i> (µg kg ⁻¹)
Fungicides					
Azoxystrobin ^b	O, P	0.22	423	230 (D)	
Boscalid ^b	B	0.60	809	2700 (F)	
Dimethomorph ^b	P	0.22	348	3400 (F)	
Cyazofamid ^b	P	0.08	1780	190 (D)	
Cyprodinil ^b	B	0.27	1706	33 (D)	
Famoxadone ^b	P	0.16	3740	11 (F)	
Fenarimol ^{b,c}	O	0.61	734	4100 (F)	
Fenhexamid ^b	B	0.18	475	1340 (F)	
Fludioxonil ^b	B	1.20	75,000	230 (F)	40,000
Folpet ^c	B, P	0.16	304	233 (F)	
Iprovalicarb ^b	B, P	0.09	106	19,800 (D)	
Kresoxim-methyl ^b	O	0.09	308	150 (F)	
Metalaxyl-M ^b	P	0.12	660	100,000 (D)	
Metrafenone ^b	O	0.05	3105	820 (F)	
Myclobutanil ^b	O	0.02	517	2000 (F)	
Penconazole ^b	O	0.61	2205	1130 (F)	25,200
Pyraclostrobin ^b	O, P	0.12	11,000	6 (F)	
Pyrimethanil ^b	B	0.60	301	2900 (D)	
Quinoxifen ^b	O	0.05	22,929	80 (D)	543
Spiroxamine ^b	O	0.30	2415	3 (A)	
Tebuconazole ^{b,e}	B, O, P	n.r.	769	2790 (D)	
Triadimenol ^{b,d}	O	n.r.	273	21,300 (F)	667
Trifloxystrobin ^b	O	0.09	2377	11 (D)	
Herbicides					
Carfentrazone-ethyl	S	0.6	866	12 (A)	
Insecticides					
Indoxacarb	G	0.05	6450	600 (D)	
Spirodiclofen	SM	0.50	31,037	35 (F)	
Tebuconazole ^b	SM	0.07	4204	23 (F)	640

O = *Oidium* sp.; P = *Peronospora* sp.; B = *Botrytis* sp.; S = stem shoots; G = grape leaf hoppers; SM = spider mites; n.r. = not recommended; D = *Daphnia*; F = fish; A = algae.
^a Application rate for the grapevine development stage BBCH 71, usually reached by the end of June/beginning of July. In cases where more than one commercial pesticide product was available for the active ingredient, the maximum application rate is shown.
^b Fungicide with specific mode of action.
^c Fungicide with unspecific mode of action.
^d Only registered for use until the end of 2009.
^e Only registered for use until the end of 2008.

2.3.2. Sample treatment

Stream water and edge-of field runoff samples were solid-phase extracted within 12 h after sampling. Prior to solid phase extraction (SPE), water samples were acidified with 2 M HCl to pH 2 and centrifuged for 15 min at 3000 rpm (Heraeus Multifuge 4KR, Thermo) to remove large particles. The SPE cartridges (C18, Chromabond, 0.45 µm filter) were conditioned with 12 ml methanol and 12 ml ultra pure water, as described by Schulz (2001), and 700–800 ml of each water sample was extracted. Finally, the cartridges were air dried for 10 min and stored at –18 °C.

Pesticide extraction of suspended particles was performed according to a slightly modified method of Schulz et al. (2001) using methanol as an organic solvent. Defrosted suspended particle samples were transferred to 1-l polypropylene bottles and, centrifuged (15 min, 3000 rpm, 19 °C), and the supernatant water was discarded. A total of 50 ml of methanol was added, mixed well with the suspended particles and then placed for 30 min in an ultrasonic bath (Sonorex digitec, Bandelin). After centrifugation, the supernatant methanol was poured into 500-ml glass beakers. The individual steps of the procedure were repeated resulting in 100 ml methanol containing the extracted pesticides that were diluted with ultra pure water to a volume of 500 ml. This solution was solid-phase extracted according to the method described above for the water samples and stored at –18 °C. Subsequently, the suspended particles were dried at 105 °C, and the dry weight was determined (all pesticide concentrations in the sediment are given in µg kg⁻¹ dry weight(dw)).

After drying the thawed C18 cartridges for 30 min in a stream of nitrogen, pesticides were eluted with 2 ml methanol and 3 ml of an acetone–toluene–dichloromethane (1:1:1) solvent mixture (Altmayer and Twertek, 2005). The resulting eluates were dried in a stream of nitrogen followed by a clean-up step to reduce coextractive matter that could interfere with quantification. According to a method by Altmayer and Twertek (2005), which was developed for vineyard pesticides, a column chromatography (3 ml) with 0.5 g silica gel (0.025–0.04 mm) and 5 ml of a solvent mixture of hexane–acetone (1:1) was performed. The eluate was dried in a stream of nitrogen and the residues were taken up in acetone. The recovery efficiencies for the elution and clean-up methods ranged from 84% to 98% (Altmayer and Twertek, 2005).

2.3.3. Trace analysis

Pesticide analysis was performed in the phytomedical laboratory of the DLR Rheinpfalz (Neustadt a.d. Weinstraße) for the chemicals listed in Table 2. Acetone dissolved extracts were analysed using a gas chromatograph (Trace, Thermo Quest) fitted with a nitrogen–phosphorus and electron-capture-detector (GC/NPD/ECD). Nitrogen–phosphorus detection (injector temperature 225 °C, make up gas nitrogen) was performed with an installed capillary column ZB-50 (30 m length, 0.25 mm i.d., 0.5 µm film thickness; Phenomenex) in 2009 and ZB-XLB (30 m length, 0.25 mm i.d., 0.5 µm film thickness; Phenomenex) in 2010. A volume of 2 µl was injected splitless with helium as the carrier gas (2.2 ml min⁻¹) and the following temperature programme was used: 50 °C (2.0 min, 20 °C min⁻¹), 180 °C (4.0 min, 20 °C min⁻¹),

200 °C (9.5 min, 20 °C min⁻¹), 220 °C (8.0 min, 20 °C min⁻¹), 240 °C (10.0 min, 30 °C min⁻¹), 300 °C (18 min). Electron-capture detection (injector temperature 200 °C in 2009 and 225 °C in 2010, make up gas nitrogen) was performed with an installed capillary column ZB-35 (30 m length, 0.25 mm i.d., 0.5 µm film thickness; Phenomenex). A volume of 2 µl was injected with a split factor of 20 using helium as the carrier gas (2.2 ml min⁻¹).

Pesticides were identified by retention times on two stationary phases (NPD, ECD). Unclear measures (substances that only show a signal on one detector) were confirmed by gas chromatography–mass spectrometry (GC/MS) (Finnigan 9001, Axel Semrau) in 2009. In 2010 confirmation was performed by a further measurement using GC/NPD/ECD (GC Trace Nr. 2, Thermo Fisher) in combination with a capillary column Thermo 5 (30 m length, 0.25 mm i.d., 0.25 µm film thickness, Thermo Fisher) for NPD and a capillary column ZB-1 (30 m length, 0.25 mm i.d., 0.5 µm film thickness) for ECD. Phosphorus–nitrogen detection was characterised using an injector temperature of 225 °C, make up gas nitrogen, injector volume of 2 µl splitless, carrier gas helium 2.2 ml min⁻¹, and the following temperature programme: 50 °C (2.0 min, 15 °C min⁻¹), 170 °C (10.0 min, 20 °C min⁻¹), 190 °C (7.5 min, 20 °C min⁻¹), 220 °C (7.5 min, 25 °C min⁻¹), 250 °C (6.3 min, 30 °C min⁻¹), 300 °C (13.3 min). Electron-capture detection was performed using an injector temperature of 225 °C and nitrogen as the carrier gas. In total, 2 µl was injected with a split factor of 20 using helium as the carrier gas.

Detection limits were in the range of 0.01–0.07 µg l⁻¹ and 0.2–5.0 µg kg⁻¹ dw for the water and sediment phase samples. However, the pesticides famoxadone, pyraclostrobin and folpet had higher detection limits in 2009 (0.2–0.6 µg l⁻¹; 0.4–50 µg kg⁻¹ dw), whereas folpet, dimethomorph, fenhexamid and indoxacarb had higher detection limits in 2010 (0.1–0.3 µg l⁻¹). Because of matrix loadings, pyraclostrobin, fludioxonil and cyazofamid could not be included in the trace analysis in 2010.

2.4. Copper monitoring

As copper-based fungicides are frequently used in viticulture, total copper was monitored in the sediment and water samples (in-stream and edge-of-field runoff). The sediment phase was sampled during the application periods of 2009 and 2010 and outside the application season in March 2010 using passive samplers (described in Section 2.3.1 but without aluminium foil) that were placed at the bottom of the stream for two weeks. The samples were freeze-dried and treated as described by Duester et al. (2007). The copper concentration in the water was determined following the two latter rainfall events in 2010 (07/29/10 and 08/10/10). The water samples were filtered (0.45 µm filters) and acidified with ultrapure HNO₃ (65%). Measurements of water and sediment samples were performed with inductively coupled plasma mass spectrometry (ICP/MS) (XSeriesII, Thermo Fisher) according to Duester et al. (2011). The quantification limits were 0.18 µg l⁻¹ and 0.42 mg kg⁻¹ dw. Using this analytical approach, a distinction between the presence of different copper species was not possible.

2.5. Data analysis

To evaluate the toxicity of the detected pesticide exposure, the toxic unit (TU) concept was used. The maximum toxic units per sample were calculated as described by Schäfer et al. (2007):

$$TU_{\max} = \max_{i=1}^n \log \left(\frac{C_i}{Tox_i} \right) \quad (1)$$

where TU_{\max} is the maximum toxic unit of the n pesticide in the sample, C_i is the concentration of the pesticide i , and Tox_i is the toxicity value of the pesticide i for the respective test species. For the

Table 3
Characteristics of rainfall events.

Date	Amount of rainfall (mm event ⁻¹)	Maximum intensity (mm h ⁻¹)	Number of days without rainfall before ^a
<i>Monitoring period I</i>			
06/27/09	14–28 ^b	11–27	10
07/14/09	26–34	8–13	7
07/23/09	5–6	3–5	6
<i>Monitoring period II</i>			
07/14/10	8–9 ^b	8–9	34
07/29/10	6–11	4–11	6
08/12/10	6–11	3–5	6

Rainfall data were provided by meteorological weather stations of the DLR Rheinpfalz in the study area.

^a “Without rainfall” was defined as less than 4 mm rainfall per day.

^b No rainfall at sampling site 9.

water phase, the toxicity value for the most sensitive test species (daphnia, fish or algae) towards the respective pesticide i was used for the calculation (Table 2). However, all TU_{\max} per water phase sample given in the present study refer to daphnia or fish data because the only pesticides (carfentrazone-ethyl and spiroxamine) with the highest toxicity towards algae were rarely found. The calculation of TU_{\max} for measured pesticide residues in sediments is more difficult because the corresponding toxicity values for sediment dwelling organisms are often not available. The toxicity values in µg kg⁻¹ (NOEC for *Chironomus riparius*) existed for only five of the pesticides investigated in the present study (Table 2). Based on these values, TU_{\max} was calculated for the sediment samples.

We calculated TU_{\max} per sample instead of the mixture toxicity (TU_{SUM}), because the latter would require the assumption of a similar mode of action. Moreover, TU_{\max} has been shown to be a suitable measure for toxicity of in-field samples, which showed an even better relationship to biotic endpoints than TU_{SUM} (Liess and von der Ohe, 2005; Schäfer et al., 2011).

The statistical analysis was performed using the software programmes SPSS version 17.0.0 and R version 2.12.1. The data that were used for correlations were tested with the Spearman correlation analysis, because the variables were not normally distributed. Normal distribution was tested performing the Kolmogoroff–Smirnov test. To test the relationship between the pesticide pollution level and the buffer strip width we used linear and exponential curve fit models. To identify a relationship between pesticide pollution and application data, a multiple linear regression was applied followed by hierarchical partitioning, according to Chevan and Sutherland (1991). The level of significance α was ≤ 0.05 in all tests.

3. Results and discussion

3.1. Rainfall events

In general, rainfall events with precipitations amounts of approximately 10 mm day⁻¹ and above are assumed to cause pesticide runoff (Liess et al., 1999). In the present study, rainfall events meeting that definition occurred three times in both monitoring periods (Table 3). In 2009, there were two heavy rainfall events with precipitation amounts of more than 20 mm and high rainfall intensities of 8–27 mm h⁻¹. Furthermore, at the end of June, an event with a lower intensity occurred. In 2010, there were three rainfall events that were similar in precipitation amount and intensity. However, the first event was the only one that was characterised by a previous drought lasting for nearly five weeks (Table 3).

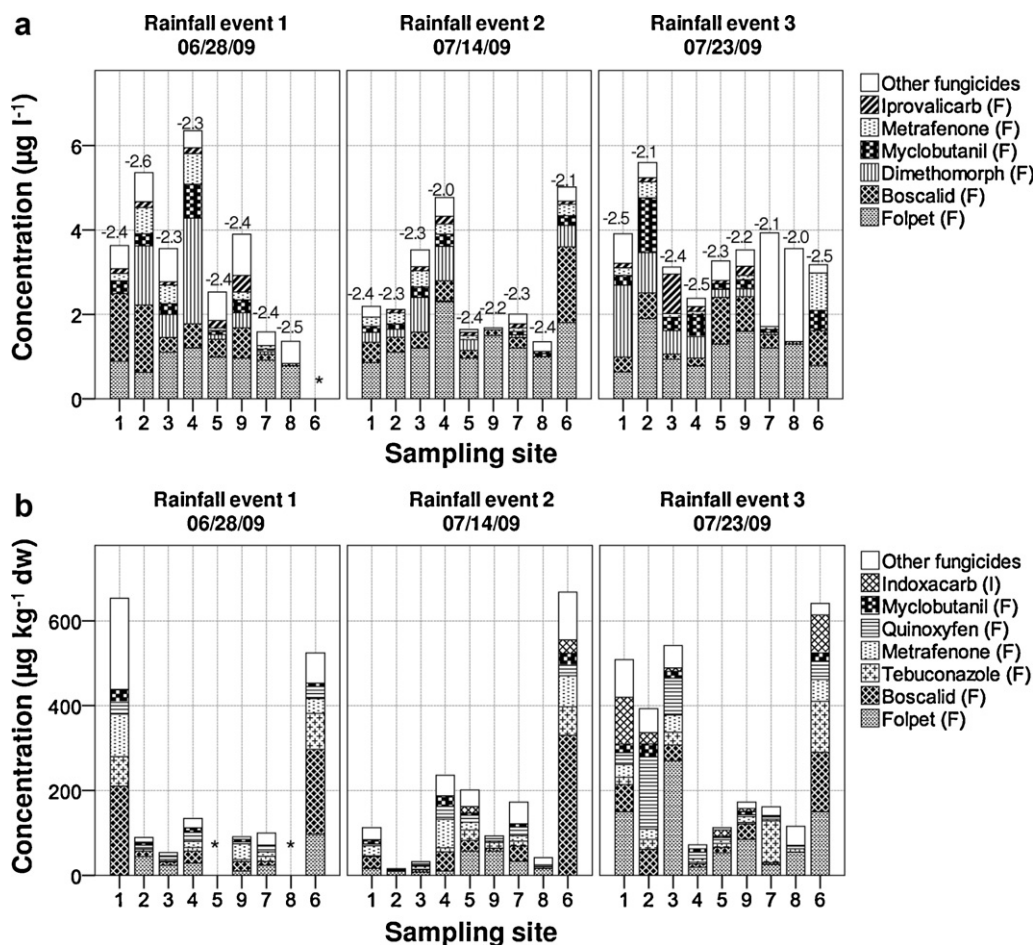


Fig. 2. Pesticide concentrations in the water phase (a) and sediment phase (b) at the sampling sites following three heavy rainfall events in 2009. Only the most frequently detected pesticides in the water phase (a) and sediment phase (b) are shown in detail. The values given above the bars indicate maximum toxic units (TU_{max}) per water samples (*: no data available; F: fungicide; I: insecticide).

3.2. Pesticide exposure following runoff events

3.2.1. Pesticide residues in streams

The total pesticide concentrations detected were in the range of 1.4–8.9 $\mu\text{g l}^{-1}$ (mean concentration (C_{mean}) = $4.0 \pm 1.9 \mu\text{g l}^{-1}$) in the water phase samples and in the range of 16–670 $\mu\text{g kg}^{-1} \text{ dw}$ (C_{mean} = $284 \pm 234 \mu\text{g kg}^{-1} \text{ dw}$) in the sediment phase (Figs. 2 and 3). However, the first rainfall event in 2010 led with a range of 7.0–83.4 $\mu\text{g l}^{-1}$ (C_{mean} = $27.1 \pm 22.2 \mu\text{g l}^{-1}$) to concentrations that were an average of 6.8 times higher than the other events in 2009 and 2010. The rainfall characteristics did not differ in amount or intensity. This finding supports the results of Rabiet et al. (2010), who found that the maximum pesticide concentrations are not simply a function of water flow. Instead, the high in-stream pesticide concentrations found in 2010 appears to be attributed to the previous 34-day period without rainfall (Table 3). Considering that fungicides are applied continually every 10–14 days, pesticides could have been applied 3–4 times to each vineyard field during this period. Consequently, pesticide residues accumulated and were finally washed off by the rainfall event and transported to the receiving streams, causing considerably higher pesticide exposure. This result suggests that a long period between pesticide application and a rainfall event is not necessarily positive; it is negative under the present conditions of frequent applications of relatively persistent fungicides.

Fungicides contributed the main portion of total pesticide residues per sample ($98.8 \pm 3.5\%$), with insecticides/acaricides and

herbicides contributing only $1.2 \pm 3.5\%$ and $0.0 \pm 0.4\%$, respectively. The relatively low contribution of insecticides was expected because the main insect pest organism, the vine moth, is exclusively controlled with pheromones in most of the study area. As a consequence, insecticides are rarely used (Rossberg, 2009). By contrast, the importance of herbicide exposure may be higher than that indicated by our results, as the most important herbicide used in the study area, glyphosate, could not be included in the pesticide analysis for methodological reasons.

Figs. 2 and 3 show the in-stream pesticide concentrations for the respective rainfall events. On average, the samples contained a mixture of 8 ± 4 different pesticides, with a maximum of 15. In 2009, the most frequently detected pesticides were folpet (100% of samples with C_{mean} = $1.1 \mu\text{g l}^{-1}$), boscalid (96%; C_{mean} = $0.56 \mu\text{g l}^{-1}$), myclobutanil (85%; C_{mean} = $0.30 \mu\text{g l}^{-1}$), metrafenone (81%; C_{mean} = $0.27 \mu\text{g l}^{-1}$), dimethomorph (77%; C_{mean} = $0.60 \mu\text{g l}^{-1}$) and iprovalicarb (73%; C_{mean} = $0.17 \mu\text{g l}^{-1}$) in the water phase as well as quinoxifen (100%; C_{mean} = $23 \mu\text{g kg}^{-1} \text{ dw}$), tebuconazole (100%; C_{mean} = $26 \mu\text{g kg}^{-1} \text{ dw}$), metrafenone (96%; C_{mean} = $25 \mu\text{g kg}^{-1} \text{ dw}$), folpet (88%; C_{mean} = $57 \mu\text{g kg}^{-1} \text{ dw}$), boscalid (92%; μ = $58 \mu\text{g kg}^{-1} \text{ dw}$) and myclobutanil (88%; μ = $11 \mu\text{g kg}^{-1} \text{ dw}$) in the sediment phase. Moreover, the insecticide indoxacarb was detected in 13 (52%; C_{mean} = $24 \mu\text{g kg}^{-1} \text{ dw}$) sediment samples. Trifloxystrobin, famoxadone, pyraclostrobin and spiroadiclofen were not detected in the water or sediment phases in 2009.

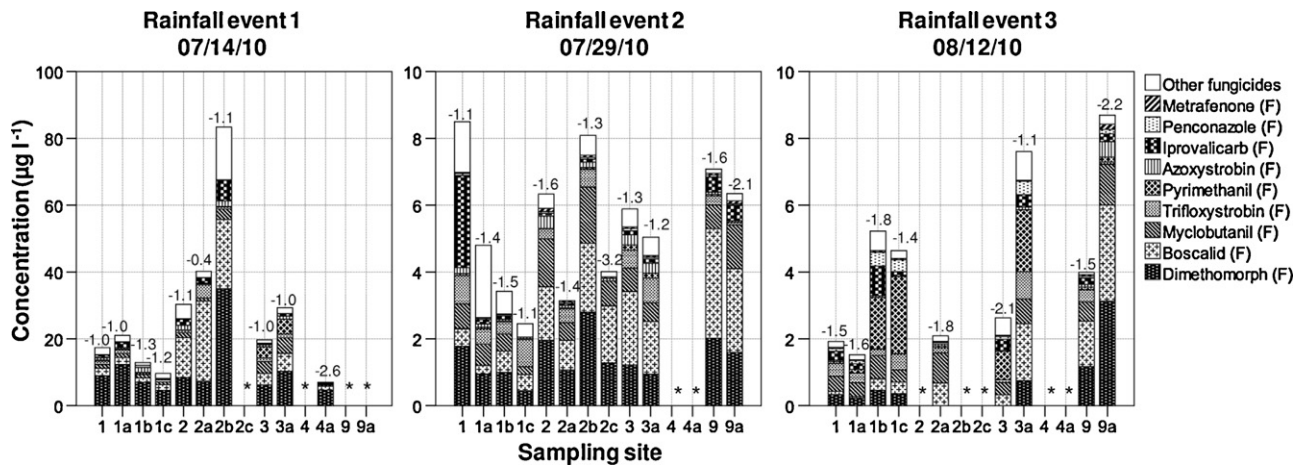


Fig. 3. Pesticide concentrations in the water phase ($\mu\text{g l}^{-1}$) at the sampling sites following three heavy rainfall events in 2010. Only the most frequently detected pesticides are shown in detail. The values given above the bars indicate maximum toxic units (TU_{max}) per sample (*: no data available; F: fungicide; I: insecticide).

The spectrum of pesticides that was found in the sediment phase was similar to residues found in the water phase in 2009 (Fig. 2). In the sediment, however, we also detected tebuconazole, quinoxifen and the insecticide indoxacarb, which were hardly found in the water phase. In the case of tebuconazole, this difference can be attributed to the fact that this substance was only allowed to be applied until the end of 2008. The residues detected in stream sediment samples might result from past applications that were still present in the sediment due to a high DT_{50} in soil in the field of 92 days (BVL, 2009). Degradation could even be slower in the sediment (BVL, 2009). In addition, quinoxifen and indoxacarb are expected to occur mainly in the sediment phase because of their very high K_{OC} values of, approximately 23,000 and 6450, respectively (Table 2). The frequent observation of quinoxifen is also in accordance with numerous findings concerning myclobutanil because quinoxifen is exclusively applied in a pesticide formulation containing both substances. Moreover, indoxacarb was identified by Rossberg (2009) as the most frequently applied insecticide in vineyard regions in Germany, accounting for more than 50% of all insecticide applications.

In 2010, the fungicides myclobutanil (100% of samples), boscalid (100%), pyrimethanil (97%), metrafenone (97%), trifloxystrobin (97%), dimethomorph (94%), iprovalicarb (87%), azoxystrobin (87%) and penconazole (84%) were most frequently detected in the water phase. The mean concentrations in these samples were higher in 2010 than in 2009, although rainfall events 2 and 3 were comparable to 2009 data: $C_{\text{mean}}(\text{myclobutanil}) = 0.74 \mu\text{g l}^{-1}$, $C_{\text{mean}}(\text{boscalid}) = 1.2 \mu\text{g l}^{-1}$, $C_{\text{mean}}(\text{pyrimethanil}) = 0.38 \mu\text{g l}^{-1}$, $C_{\text{mean}}(\text{metrafenone}) = 0.050 \mu\text{g l}^{-1}$, $C_{\text{mean}}(\text{trifloxystrobin}) = 0.41 \mu\text{g l}^{-1}$, $C_{\text{mean}}(\text{dimethomorph}) = 1.2 \mu\text{g l}^{-1}$, $C_{\text{mean}}(\text{iprovalicarb}) = 0.25 \mu\text{g l}^{-1}$, $C_{\text{mean}}(\text{azoxystrobin}) = 0.15 \mu\text{g l}^{-1}$ and $C_{\text{mean}}(\text{penconazole}) = 0.12 \mu\text{g l}^{-1}$. In addition, the spectrum of detected pesticides changed in 2010: folpet, which was the most frequently detected substance in 2009, was only found in 65% of the water samples, with a mean concentration of $0.16 \mu\text{g l}^{-1}$ (during rainfall events 2 and 3). The contributions of fungicides such as dimethomorph and boscalid in relation to the total pesticide concentration increased in 2010, and fungicides such as trifloxystrobin or penconazole, which were only rarely detected in 2009, became more common (Fig. 3). These differences are assumed to be related to a change in the pesticide spectrum used by farmers in 2010. In general, the applied pesticide formulation strongly depends on the respective disease pressure, which is influenced by specific climatic conditions or previous infections.

Further information concerning all pesticides listed in Table 2 can be found in the supplementary data. Apart from the first event in 2010, the concentrations found in the present study are comparable to findings from other studies of vineyard regions (Gregoire et al., 2010; Rabiet et al., 2010).

3.2.2. The relationship between fungicide detection and application data

Since 1999/2000, data on the actual use of pesticides in German agriculture have been collected for different crops by interviewing farmers within the NEPTUN-Project (Rossberg, 2007). The latest investigation from vineyard areas, which dates from the year 2009, gives the application frequency for single fungicide substances as percentages of all fungicide applications. In general, the amount of pesticides found in environmental samples should be influenced by their application frequency and their common application rates. This hypothesis was tested for the concentrations found in the water phase using a multiple regression, which showed that the total concentration ($\mu\text{g l}^{-1}$) for each of the single fungicides was well explained by the variables of application frequency (according to Rossberg, 2007) and recommended application rates (Table 2) in the study area ($R^2 = 0.78$, $p < 0.01$, $n = 19$). Hierarchical partitioning showed that application frequency was slightly more important, explaining the 59% of variance, compared with the application rate (41%).

3.3. Toxicity of pesticide residues to in-stream biota

The calculated TU_{max} for the water phase samples in 2009 are shown in Fig. 2 above the respective bars. All values ranged between -2.6 and -2.0 ($\mu = -2.3$). Considering a safety factor of 100 (which is common for acute risk assessment in the EU; Brock et al., 2009), effects should not occur at values greater than -2.0 . Nevertheless, several studies (Liess and von der Ohe, 2005; Schäfer et al., 2007) found significant reductions in sensitive species at risk for slightly polluted streams (TU of -3.5 to -2) compared to unpolluted sites (TU less than -3.5).

Fig. 3 shows the calculated TU_{max} per sample in 2010. For rainfall events 2 and 3 (most comparable to the rainfall events in 2009 regarding total pesticide entries), TU_{max} were equal or above the threshold value of -2.0 (used in acute risk assessment) in 86% of samples. Hence, the calculated toxicity was six times higher than in 2009, with a mean of -1.5 . This difference might be due to a switch in the pesticides used to substances with higher acute toxicities towards aquatic invertebrates or fish. These were, in most cases,

trifloxystrobin, but they also included cyprodinil, kresoxim-methyl and azoxystrobin. During the first rainfall event in 2010, the toxicity was even higher: 90% of the water samples exceeded the threshold value of -2.0 , and 50% were equal to or above the threshold value when assuming a safety factor of only 10 (Fig. 3). Thus, these pesticide concentrations might acutely affect the aquatic communities in the field.

Berenzen et al. (2005) showed a community shift towards less sensitive species for small pesticide-polluted streams (TU_{SUM} between -1.7 and -0.7) in central Germany. Sensitive groups such as Plecoptera, Ephemeroptera and Trichoptera were reduced in abundance. This finding was supported by Liess and von der Ohe (2005), who found a 60% reduction in sensitive species in highly polluted streams ($TU > -2$) from April to May. Therefore, the concentrations found in the present study likely affect the aquatic communities in the field.

Interestingly, all of the investigated fungicides (except spiroxamine) were most toxic towards fish species or daphnia (Table 2). Regarding algae, TU_{max} values (not shown in Figs. 2 and 3) were in 85% of cases below the threshold value of -1.0 (which is commonly used in chronic risk assessment; Brock et al., 2009), when not considering the exceptional rainfall event in 2010 (07/14/10). However, 15% of the concentrations may affect the algae community in the streams. Particularly the pesticide concentrations in the range of $20\text{--}80\text{ }\mu\text{g l}^{-1}$ that occurred following the first rainfall event in 2010, could lead to a reduction of fungal biomass as has been shown by Zubrod et al. (2011) for tebuconazole ($65\text{ }\mu\text{g l}^{-1}$). These fungal organisms play, however, an important role for stream ecosystem functions, such as leaf decomposition processes (Maltby et al., 2009).

For the sediment phase, the calculated TU_{max} values were based on the five pesticides for which NOEC values were available (see also Section 2.4) and are therefore not shown in Fig. 2. The values ranged between -2.8 to -0.5 with an average of -1.6 . Assuming a safety factor of 10 (common for chronic toxicity values; Brock et al., 2009), effects would be expected above a threshold value of -1.0 . According to this rather simplified procedure, the majority of samples are not expected to cause effects in the field. However, pesticide concentrations of two samples exceeded this threshold value, which was attributed to the high concentration of quinoxifen ($87\text{ }\mu\text{g kg}^{-1}\text{ dw}$ and $170\text{ }\mu\text{g kg}^{-1}\text{ dw}$). The results suggest that monitoring pesticide concentrations in sediments might be important, particularly when considering that the investigated samples contained pesticide residues in addition to the five pesticides that were considered in the calculation.

3.4. Copper exposure and toxicity to in-stream biota

The in-stream water sampled following heavy rainfall events contained $0\text{--}67.6\text{ }\mu\text{g l}^{-1}$ total dissolved copper, with a median value of $5.4\text{ }\mu\text{g l}^{-1}$ (Fig. 4). However, the availability of free copper ions, not the measured total copper concentration, is important for assessing the toxic effects on aquatic organisms (Kramer et al., 2004). This availability of free copper ions is mainly determined by the content of dissolved organic carbon (DOC) and the pH (De Schamphelaere and Janssen, 2004). As the analytical method did not allow a distinction between different copper species and the presence of free ions, the toxicity of total dissolved copper concentrations towards *Daphnia magna* was predicted according to De Schamphelaere and Janssen (2004). Accordingly, for the streams in the study area ($\text{DOC} = 3\text{--}24\text{ mg l}^{-1}$; $\text{pH} = 7.7\text{--}8.2$), the 21-day NOEC for *D. magna* was estimated as between 60 and $224\text{ }\mu\text{g l}^{-1}$ total copper. Considering a safety factor of 10, effects on sensitive aquatic organisms are expected as a result of the measured copper concentrations in the water phase of the studied streams.

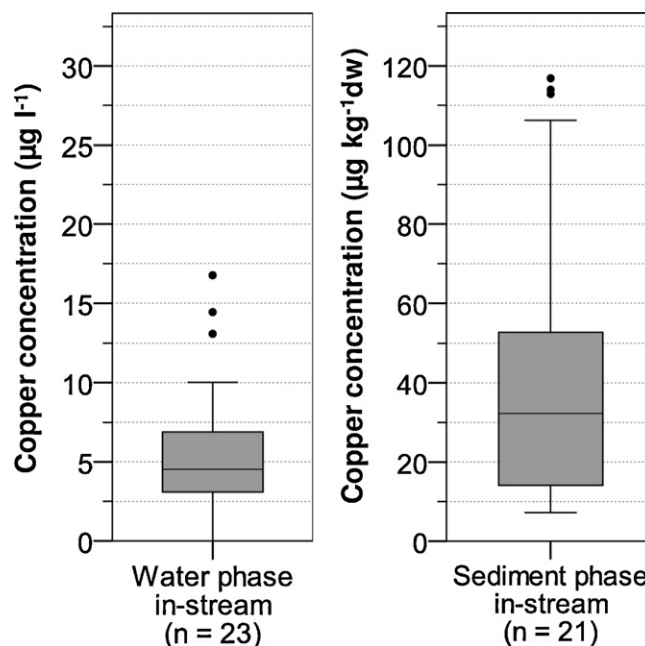


Fig. 4. Copper (Cu) concentration determined in the water and sediment phases following the rainfall events in 2009 and 2010. The black horizontal line marks the median, the box represents the 25th to 75th percentiles, the bars mark the range without outliers and the outliers are marked by black points.

Regarding the copper concentrations in the sediment phase, there was no significant difference between samples taken during and outside the application period. Therefore, all data were pooled (Fig. 4). The concentration ranged between 7.3 and $116.9\text{ mg kg}^{-1}\text{ dw}$ and was an average of 10 times higher than the geological background concentration of $1.6\text{--}6.7\text{ mg kg}^{-1}\text{ dw}$ that has been determined for forested upstream regions. Fifty-seven percent of the samples were critically or highly polluted according to Wachs (1998). The effects on organism emergence and reproduction were shown in laboratory experiments at copper concentrations of $59\text{--}105\text{ mg kg}^{-1}\text{ dw}$ (Roman et al., 2007), highlighting the ecotoxicological relevance of the copper concentrations detected in the sediment phase. Interestingly, the measured copper level in the surface water sediments were in the same range as those actually measured in cultivated vineyard soils in the Palatinate wine-growing region (approximately $68\text{ mg kg}^{-1}\text{ soil dw}$; 95% CI: $48\text{--}88\text{ mg kg}^{-1}\text{ soil dw}$; background level: about $35\text{ mg kg}^{-1}\text{ soil dw}$) during a recent study (Strumpf et al., 2011). This finding illustrates the great extent to which copper is transported from vineyards into adjacent surface waters.

3.5. Influence of riparian buffer strip width on pesticide runoff entries

To determine the influence of riparian buffer strip width on in-stream pesticide concentrations, we used the results for 2009, because we possessed a complete dataset for all sampling sites (Table 1) as well as water and sediment phases data for this year. A clear negative relationship between the measured pesticide concentration and the average riparian buffer strip width was not observed in the water phase (linear curve fit: $R^2 = 0.14$, $p = 0.06$, $n = 26$; exponential curve fit: $R^2 = 0.17$, $p = 0.03$, $n = 26$; Fig. 5a) or sediment phase (linear curve fit: $R^2 = 0.13$, $p = 0.07$, $n = 25$; exponential curve fit: $R^2 = 0.07$, $p = 0.22$, $n = 25$; Fig. 5b). There was a tendency towards lower contamination with increasing buffer strip width. However, in absolute numbers, the average concentrations decreased only from 4.0 to $2.6\text{ }\mu\text{g l}^{-1}$ in the water phase and from

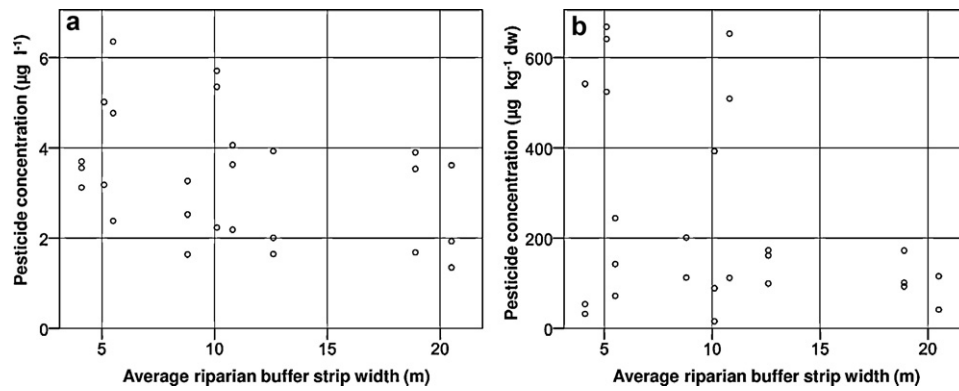


Fig. 5. Total pesticide concentration in the water ($\mu\text{g l}^{-1}$) and the sediment ($\mu\text{g kg}^{-1} \text{ dw}$) phases detected at the sampling sites as a function of the average riparian buffer strip width. Linear (a: $R^2 = 0.14$, $p = 0.06$, $n = 26$; b: $R^2 = 0.13$, $p = 0.08$, $n = 25$) and exponential curve fit models (a: $R^2 = 0.17$, $p = 0.03$, $n = 26$; $R^2 = 0.07$, $p = 0.22$, $n = 25$) showed no clear negative relationship.

345 to $103 \mu\text{g kg}^{-1} \text{ dw}$ in the sediment phase when the buffer strips increased from width below 5.5 m to widths of 19–20 m. This finding indicates that for the sites in the present study, contrary to the current assumptions used in regulatory exposure assessment for even/constant runoff, the presence of wider buffer strips neighbouring streams provides no substantial protection against dissolved runoff-related pesticide entries. The effectiveness of these strips seem to be only slightly higher for pesticides transported as bound on particles.

To explain these results, a closer look at the landscape characteristics of the sampling sites and their catchment areas was required (Table 1). All investigated catchments were characterised by a high number of field paths (density: $4\text{--}14 \text{ km km}^{-2}$ vineyard area), which are often paved or at least consist of heavily compacted bare soil. Runoff is assumed to be concentrated by these paths and reaches the streams via erosion rills that are present at the investigated streams, with a frequency of $0.3\text{--}5.0$ erosion rills per km flow length (Table 1). Field paths were also pointed out by Altmayer (2002) as one of the most important pathways for pesticide loss in the study area. Consequently, wide vegetated buffers cannot fulfil the function of filtering pesticide entries because drainage occurs via the field path network, and laminar sheet flow in the vegetated buffer strips, as required for effective pesticide reduction (Dosskey, 2001; Blanco-Canqui et al., 2006), is not possible. Whether buffer strips are more effective under other conditions allowing laminar sheet flow remains to be proven.

3.6. Pesticide residues in runoff samples and relationship to in-stream exposure

In addition to stream water samples, edge-of-field runoff water that was directly sampled in erosion rills was analysed in 2010. The total pesticide exposure and concentrations of the four most important pesticides detected in these samples are compared in Fig. 6 to the in-stream concentrations at the corresponding downstream sampling sites for the same event. The stream water samples showed the same pesticide residues as the edge-of-field runoff samples but at generally lower concentrations (see supplementary data). Only at sampling site 2b was the in-stream pesticide concentration higher than in the investigated erosion rills upstream following rainfall event 1. This finding might be attributed to further erosion rills that were not sampled within the monitoring program.

Fig. 7 confirms that the concentrations of pesticides in-stream are significantly positively correlated with the concentrations detected in edge-of-field runoff of erosion rills (Spearman $R^2 = 0.56$, $p < 0.01$, $n = 13$ sample pairs $\times 24$ analysed pesticides + 2 sample

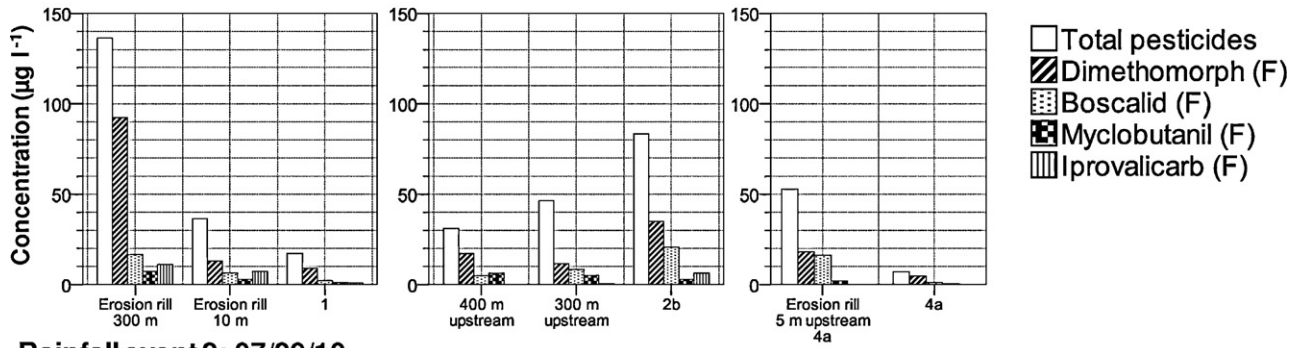
pairs analysed with respect to copper = 314). The ratios of the two variables varied greatly due to many other influencing factors that occurred during field studies, including differences in discharge and dilution, differences in the sampling method, unmonitored erosion rills and other entry pathways. These factors also contributed to the finding that in some cases, pesticide substances were found in the stream even though they were not detected in the respective upstream erosion rill (Fig. 7). However, a pesticide substance that was detected in-stream was also found in the respective erosion rill in 85% of cases, at a concentration that was higher by a median factor of 2.1 (25th to 75th percentile = $1.1\text{--}6.7$). Similar findings were made by Schulz and Liess (1999) in an agriculturally intensive field crop area in northern Germany. In 6 out of 8 cases (75%), insecticides that were found in a small headwater stream were also observed in the erosion rill at a concentration that was a median of 2.8 times higher. The generally lower in-stream concentrations might be attributed to dilution processes that occur as a result of direct rainfall or runoff water coming from uncontaminated sites (e.g., upstream wooded areas).

3.7. Risk mitigation measures

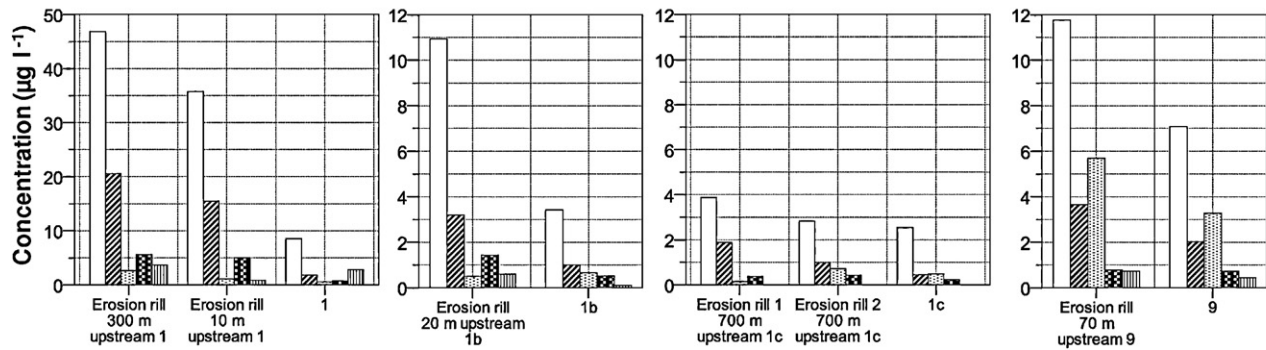
The results clearly show the important role of pesticide edge-of-field runoff transported via a field path network and erosion rills as a route of entry in the studied area and its strong contribution to pesticide exposure in streams. The results provide evidence that although wide vegetated buffers are present in parts of the study area, their contribution to the protection of pesticide runoff entry is very low. Once the runoff reaches the field path, it is transported rapidly to the stream with no noticeable reduction in pesticide concentration. This phenomenon was also shown for diuron by Louchart et al. (2001) in a Mediterranean vineyard area: at the outlet of a drainage ditch system, the diuron concentration was even slightly higher than the concentration measured at the edge of the field, indicating that a reduction in the pesticide concentration did not occur. The situation in the present study is further complicated by the fact that pesticides are also directly deposited onto field paths during the pesticide application stage through overspraying when machines turn around or via spray drift. These deposited pesticides are remobilised following rainfall events, as pointed out by Altmayer et al. (2003). To provide effective risk management, measures must address the identified and most important input pathway (concentrated runoff via erosion rills) and must be designed correspondingly.

A possible appropriate measure would be to establish grassed field paths instead of concrete paths, which could function in the manner described for grassed waterways (USDA, 2000; Lovell and

Rainfall event 1: 07/14/10



Rainfall event 2: 07/29/10



Rainfall event 3: 08/12/10

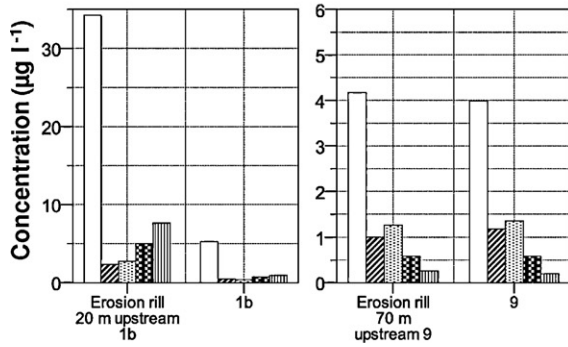


Fig. 6. Detected pesticide concentrations in edge-of-field runoff sampled in erosion rills and associated pesticide in-stream concentrations following three heavy rainfall events in 2010. The detected spectrum of pesticides in-stream corresponds to the spectrum detected in erosion rills, but in-stream concentrations are generally lower (only the four most important pesticides found in edge-of-field runoff are shown in detail; F= fungicide).

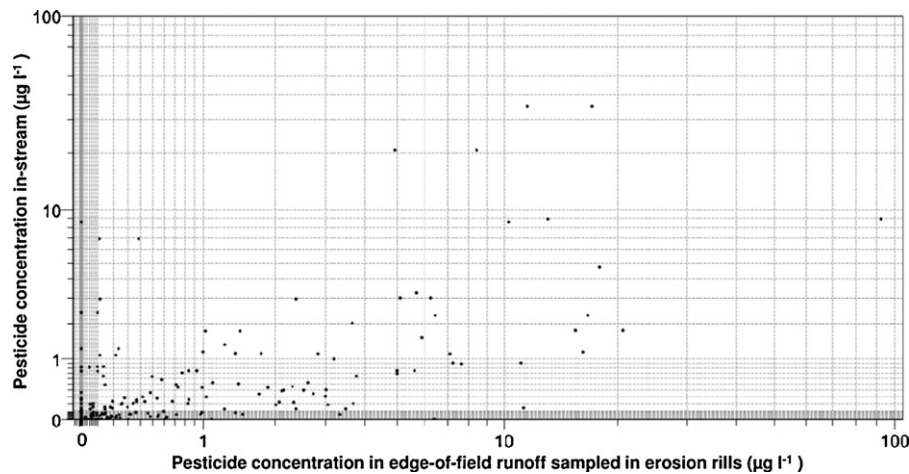


Fig. 7. Correlation between pesticide concentrations found in runoff as sampled in erosion rills and detected in streams. The individual substances measured in runoff water were plotted against the values measured in the associated in-stream samples (Spearman's $R^2 = 0.56$, $p < 0.01$, $n = 314$).

Sullivan, 2006). An infiltration of runoff water associated with a reduction in pesticide load is then provided. Reduction efficiencies of 70–96% were reported for a 24.4-m grassed waterway (Asmussen et al., 1977; Rohde et al., 1980). Paved field paths are often favoured in the study area because a rapid transport of runoff water from the fields is desired. Grassed field pathways should at least be designed parallel to and adjacent to streams to provide a laminar sheet flow of runoff water in the vegetated buffer strips, which were often present. Another measure with a similar effect would be grassed machine tracks between vine rows, which are recommended from a soil and environmental conservation point of view by the official extension service in the study area.

In addition, previous filtration in vegetated wetlands or ditches before the edge-of-field runoff enters the stream is assumed to be a suitable measure. By reducing the flow velocity and increasing the sedimentation and adsorption to aquatic macrophytes, such systems can efficiently reduce pesticide entries (Stehle et al., 2011). For example, for vegetated wetlands, pesticide reduction efficiencies of 60–99% have been reported (Schulz, 2004), and effective pesticide mitigation of vegetated ditches has been shown by numerous authors (Bennett et al., 2005). The effectiveness of this type of risk mitigation measure in the study area will be investigated in the final part of this research project.

4. Conclusions

The results of the present study show that the identification of effective risk management measures (in the context of (EC) 1107/2009, WFD) requires a previous detailed analysis of the pesticide pollution pattern and the main entry pathways in the catchment. The effective management of the identified main pesticide entry pathways (e.g., field paths and erosion rills in this study area) might be relevant if “hot spot” management became a goal in the national action plans for the sustainable use of pesticides that are developed by the EU member states according to 2009/128/EC (European Commission, 2009a). Moreover, our results might be particularly supportive of the identification of appropriate risk mitigation measures during the pesticide regulation process, because further measures (as proposed in this study for the vineyard region) could potentially be implemented in the regulation process.

Acknowledgements

This study is part of the research project “Risikominderungsmaßnahmen für Pflanzenschutzmitteleinträge in Gewässer”, which is funded by the Federal Office of Consumer Protection and Food Safety (BVL), and additionally financially supported by the Federal Ministry of Environment, Forestry and Consumer Protection Rheinland-Pfalz (MUFV-RLP). We would like to thank Bernd Altmayer and Michael Twertek for their support in pesticide analysis and their helpful advice on the pesticide application data. We would also like to thank Claudia Janoske and Kathrin Maaßen for their help with field and laboratory work, Ralf B. Schäfer for statistical support and the members of the project advisory committee. Furthermore we thank the two anonymous reviewers for the helpful comments on earlier drafts of the manuscript.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.agee.2011.10.010.

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