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Spatial variability of herbicide mobilisation and transport at catchment scale: insights from a field experiment

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Abstract

During rain events, herbicides can be transported from their point of application to surface waters where they may harm aquatic organisms. Since the spatial pattern of mobilisation and transport is heterogeneous, the contributions of different fields to the herbicide load in the stream may differ considerably within one catchment. Therefore, the prediction of contributing areas could help to target mitigation measures efficiently to those locations where they reduce herbicide pollution the most.

Such spatial predictions require sufficient insight into the underlying transport processes. To improve the understanding of the process chain of herbicide mobilisation on the field and the subsequent transport through the catchment to the stream, we performed a controlled herbicide application on corn fields in a small agricultural catchment (ca. 1 km^2) with intensive crop production in the Swiss Plateau. For two months after application in 2009, water samples were taken at different locations in the catchment (overland flow, tile drains and open channel) with a high temporal resolution during rain events. We also analysed soil samples from the experimental fields and measured discharge, groundwater level, soil moisture and the occurrence of overland flow at several locations. Several rain events with varying intensities and magnitudes occurred during the study period. Overland flow and erosion were frequently observed in the entire catchment. Infiltration excess and saturation excess overland flow were both observed. However, the main herbicide loss event was dominated by infiltration excess. This is in contrast to earlier studies in the Swiss Plateau, demonstrating that saturation excess overland flow was the dominant process.

Despite the frequent and wide-spread occurrence of overland flow, most of this water did not directly reach the channel. It mostly got retained in small sinks in the catchment. From there, it reached the stream via macropores and tile drains. Manholes of the drainage system and catch basins for road and farmyard runoff acted as additional shortcuts to the stream.

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Although fast flow processes like overland and macropore flow reduce the influence of herbicide properties due to short travel times, sorption properties influenced the herbicide transfer from ponding overland flow to tile drains (macropore flow). However, no influence of sorption was observed during the mobilisation of the herbicides from soil to overland flow. These two observations on the role of herbicide properties contradict, to some degrees, previous findings. They demonstrate that valuable insight can be gained by spatially detailed observations along the flow paths.

1 Introduction

In modern agriculture, a wide variety of pesticides is used to increase crop productivity. Pesticides encompass a broad range of chemicals. They are used to control weeds, to fight plant diseases, insects, arachnids and other species. These substances can enter the water system where they can harm aquatic organisms even when present in low concentrations. Especially small streams in catchments with intensive crop production are at risk (Liess and Schulz, 1999); in these areas diffuse pollution from agricultural fields causes major inputs to the stream (Leu et al., 2010). Herbicides mainly enter surface waters during rain events when they are mobilised and transported with fast runoff (Thurman et al., 1991). Under Swiss conditions, the two most important input pathways in that context are overland flow and, when subsurface drains are present, preferential flow to the drainage system. Due to sorption and degradation, the pathway to groundwater and exfiltration into streams as baseflow is of little importance for most pesticides.

In several cases it has been shown that there are large differences of herbicide losses from different fields within a given catchment (Gomides Freitas et al., 2008; Leu et al., 2004b, 2005; Louchart et al., 2001). This implies that a relatively small proportion of a catchment causes the major part of surface water pollution with herbicides. The same has been observed for diffuse pollution of surface waters with phosphorus (Pionke et al., 1996, 2000). These observations did not come as surprises to hydrologists.

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Already in the 1960s and 1970s it was recognized that not all areas contribute to storm runoff (Betson, 1964; Dunne and Black, 1970) and that diffuse pollution should be expected from only a limited fraction of a catchment (Freeze, 1974). Such areas that contribute a large fraction of the pollution load are called critical source areas (CSAs) or contributing areas.

The insight that not all parts of a catchment have the same relevance for diffuse pollution offers efficient mitigation options because actions on a small proportion of the area can strongly reduce the substance input to the stream. The CSA concept can be expressed by three conditions that an area has to fulfil to become a critical source area: (1) the area needs to be a substance source. In the case of pesticides these are the areas where pesticides are applied. (2) The area has to be hydrologically active, meaning that the relevant mobilisation and transport processes are initiated on the area. For pesticides these are areas where overland flow and/or macropore flow occur. (3) The area has to be connected to the stream; for pesticides this implies that the overland flow or macropore flow with the mobilised pesticides has to reach the stream either directly or via the drainage system.

In the landscape, these three conditions can be represented by parts of the catchment, where the respective conditions are fulfilled. The spatial extent of the CSAs (A_{CSA}) can hence be interpreted as the spatial intersection of the spatial subsets:

$$A_{\mathrm{CSA}} = A_{\mathrm{source}} \cap A_{\mathrm{active}} \cap A_{\mathrm{connect}} \quad (1)$$

with A_{source} being the source area of a given compound, A_{active} being the hydrologically active area, and A_{connect} is that part of the catchment that is directly connected to the stream network. For pesticides, A_{source} depends on the pesticide applications and is not a property of the field per se. Every crop production field is a potential source area even though the pesticide applications change with crop rotation. However, the compound properties can modify A_{source} in space and time. Degradation and sorption both determine the amount of substance that is available for transport at the time of rainfall (Louchart et al., 2001). If there was substantial spatial variability in degradation rates and/or sorption of herbicides to soil, these properties may affect the spatial CSA

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distribution. Earlier studies in the Swiss Plateau (Leu et al., 2004b; Stamm et al., 2004) indicate, however, that degradation rates and sorption coefficients do not vary strongly between fields in a catchment and could not account for observed spatial differences in herbicide loss rates. Under these conditions, and under the assumption that the areas of pesticide applications are known, the CSA delineation reduces to a hydrological problem where A_{active} and A_{connect} have to be predicted.

For pesticide transport, the relevant flow components are fast flow like surface runoff and preferential flow to tile drains. Hence, A_{active} is determined by the spatial extent of areas where these processes are generated in relevant amounts. Two different processes can lead to overland flow. Horton (1933) described the occurrence of infiltration excess overland flow where rain intensity exceeds the infiltration capacity of the soil. On the other hand, saturation excess overland flow occurs when the soil gets saturated from below until the water table reaches the surface (Dunne and Black, 1970). It was recognized that saturation excess overland flow usually dominates in humid climate and in well vegetated catchments (Anderson and Burt, 1978; Dunne and Black, 1970; Moore et al., 1976). The dominance of saturation excess overland flow as transport process also seems to hold for phosphorus transport to surface waters in agricultural areas in humid climates (Easton et al., 2008; Lyon et al., 2006). Infiltration excess overland flow was found to be the dominant process in arid and semiarid climate (e.g., Goodrich et al., 1997). However, not all studies show a clear spatial separation of these two processes. Descroix et al. (2007) for example found that saturation excess overland flow can also be important in semiarid climate and infiltration excess overland flow does also occur in more humid climate. The simultaneous occurrence of infiltration excess and saturation excess overland flow was also observed in field experiments e.g. by Srinivasan et al. (2002). Preferential flow to tile drains is closely linked to the occurrence of surface runoff because preferential flow requires the lateral flow of water towards the preferential flow paths (Flühler et al., 1996; Weiler and Naef, 2003). Furthermore, preferential flow paths may intercept surface runoff and direct it towards tile drains (Stamm et al., 2002). Therefore, the two runoff-generating mechanisms

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(infiltration excess and saturation excess) are also relevant for the input of herbicides into surface waters via preferential flow to tile drains.

Regarding A_{connect}, the focus is on the connectivity of fast flow processes that are relevant for pesticide transport. In the analysis of overland flow connectivity, natural or anthropogenic depressions within a catchment are of major importance since they can retain large amounts of overland flow which then does not reach the stream (Barron et al., 2011; Frey et al., 2009; Kiesel et al., 2010). In addition to the depressions, man-made networks have a large influence on connectivity. Subsurface pipe networks (tile drains, road drainage etc.) can heavily increase connectivity. It can happen that areas outside the topographic catchment become contributing (Noll and Magee, 2009). Roads can act as barriers for overland flow or they can concentrate flow (Carluer and De Marsily, 2004; Payraudeau et al., 2009) and direct it to the stream via road drainage (e.g. Ledermann et al., 2010). Other small linear features like tramlines and field edges substantially influence flow directions and therefore also connectivity (e.g. Aurousseau et al., 2009; Heathwaite et al., 2005). Many of these spatial processes are subject to regional differences. They depend on climate and agricultural land management practices but also on general structural properties of agricultural catchments (field sizes, proportion of drained area, length and type of road network etc.).

A reliable spatial prediction of CSAs is necessary if site specific mitigation measures should be implemented in practice on CSAs. However, a sound prediction requires a detailed understanding of the governing processes and their interactions. The process understanding can be gained in field studies and field experiments at catchment scale where the processes and their interplay can be observed. For validating spatial predictions of herbicide losses within agricultural catchments, there are only few comprehensive field data sets available (Gomides Freitas et al., 2008; Leu et al., 2004a,b). In these studies, the herbicide input into the catchments and the output through the stream were controlled and monitored. This setup does not allow investigating the individual processes occurring along the transport pathway from the field to the stream. Furthermore, only limited data on the catchment hydrology were collected. These

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limitations were overcome in this study by taking samples along the whole transport pathway from field soil to overland flow and tile drains and finally to the open stream. In addition, we measured soil hydrologic fluxes and state variables at different sites across the study area (e.g. the spatial occurrence of overland flow). This procedure allowed us to link the hydrological processes with the observed herbicide concentration patterns and helped to improve the understanding of individual processes along the transport pathway.

Additionally, the earlier studies in Switzerland (Gomides Freitas et al., 2008; Leu et al., 2004a,b) have all been carried out in the same region southeast of Zürich (Greifensee) in a small number of test catchments. This raises the question how well these study sites represent conditions across the Swiss Plateau. To test the transferability of the process understanding gained in these studies, we performed our field experiment in another region of the Swiss Plateau with significantly drier climate (880 mm instead of 1200 mm mean annual precipitation), different topography and landform and more intensive crop production. Based on the knowledge from the studies mentioned above, we expected that saturation excess overland flow is the main transport process. Accordingly, soil hydrology and connectivity were expected to be the drivers for spatial differences. We therefore selected a catchment with soils differing in their soil water regimes.

2 Materials and methods

2.1 Site description

The study catchment is located in the northeast of Switzerland (see Fig. 1). The catchment area is 1.2 km^2, topography is moderate with altitudes ranging from 423 to 477 m a.s.l. and an average slope of 4.3° (min = 0°, max = 42°, based on 2 × 2 m digital elevation model (DEM) swisstopo, 2003). The twenty year mean annual precipitation at the closest permanent measurement station (Schaffhausen, 11 km north from the

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catchment) is 883 mm (Meteoschweiz, 2009). The soils developed on moraine material with a thickness of around ten meters which is underlain with Süsswassermolasse (swisstopo, 2007). Soils in the centre of the catchment are poorly drained gleysoils. Well drained cambisols, and eroded regosols are located in the higher parts of the catchment (FAL, 1997, see Fig. 1). Soil thickness varies between 30 cm at the eroded locations and more than 2 m in the depressions and near the stream. The catchment is heavily modified by human activities; it encompasses a road network with a total length of 11.5 km. The dominant land use is crop production (75 % of the area) with the main crops being corn, sugar beet, winter wheat and rape seed. Around 13 % of the catchment are covered by forest, and a small settlement area is located in the southeast of the catchment. Three farms lie at least partly within the catchment (see Fig. 1). 47 % of the agricultural land is artificially drained by tile drains; the pipe network has a total length of more than 21 km (Gemeinde Ossingen, 1995, the open stream has a length of 550 m). The stream system consists of two branches, an open ditch that was partly built as recipient for the drainage water, and the main branch of the stream that is running in a culvert (see Fig. 1). The stream also receives the runoff from the two main roads and from two farm yards (Gemeinde Ossingen, 2008).

2.2 Hydrological measurements

In the period from summer 2008 to autumn 2009 several hydrological parameters were monitored in the catchment. Not all measurements cover the whole time period. However, during the experimental period from February 2009 to October 2009 all measurements as depicted in Fig. 1 were running.

2.2.1 Discharge and electrical conductivity of stream and drainage water

At five locations in the catchment, discharge was measured. At four sites (O_d, O_u, S_d, S_u, see Fig. 2), water level and flow velocity were measured using a Doppler probe and a pressure transducer (Isco 750 area velocity flow module, Teledyne Inc., Los

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Angeles). Discharge was calculated using the exact cross section of these sites. At the fifth site (O_m, Fig. 2), discharge was determined by measuring the water level at a V-weir with a pressure transducer (Keller PR-46X, KELLER AG für Druckmesstechnik, Winterthur CH) and using a rating curve of the form $Q = \alpha \times (h - \beta)^{\gamma}$, where h is the water level (Herschy, 1995). The curve was fitted to 15 data points obtained by dilution experiments with NaCl (6 data points, CS547 Conductivity and Temperature Probe, Campbell Scientific, Inc., Loughborough UK) and bucket measurements (9 data points). Discharge data from all stations were stored at five-minute intervals, either by the data logger of the sampler (ISCO 6700, ISCO 6712, Teledyne Inc., Los Angeles USA), or by an external data logger (CR10X; Campell Scientific Inc., Loughborough UK).

At four discharge measurement stations (O_d, O_m, O_u, S_d, Fig. 2), we also obtained electrical conductivity data in 5 min intervals (STS DL/N, STS Sensor Technik Sirnach AG, Sirnach CH and CS547 Conductivity and Temperature Probe, Campbell Scientific, Inc., Loughborough UK).

2.2.2 Weather stations

At weather station 1 (see Fig. 1) precipitation was measured at 15 min resolution with a tipping bucket rain gauge (R102, Campbell Scientific, Inc., Loughborough UK). This rain gauge was out of order for 22 days (4 June 2009–25 June 2009). During this time, rain data from weather station 2 (see Fig. 1) were used (a mobile HP 100 Station run by Agroscope ART with a tipping bucket rain gauge: HP 100, Lufft GmbH, Fellbach Germany). For two of the major rain events in the experimental period (Events E2 and E9 in Table 2) rain data from both rain gauges are available.

2.2.3 Piezometers

We installed 11 piezometers to monitor groundwater levels and groundwater temperature in 15 min intervals (STS DL/N, STS Sensor Technik Sirnach AG, Sirnach CH and

Keller DCX-22, KELLER AG für Druckmesstechnik, Winterthur CH). The installation depth varied between 1.5 and 2.7 m below the surface. In eight of the piezometers, we also obtained the electrical conductivity of the groundwater (STS DL/N, STS Sensor Technik Sirnach AG, Sirnach CH).

2.2.4 Soil moisture and temperature

We instrumented four soil profiles with TDR probes, tensiometers and temperature probes to measure soil water content, suction pressure and soil temperature in four different depths between 0.1 and 1.1 m below the surface. The exact depths at the different locations were selected according to the soil horizons. In each depth we installed two TDR probes (TDR100, Campell Scientific Inc., Loughborough UK and two rod probes), three tensiometers (Ceramic cubs: High Flow Porous Ceramic Cub 6531B1M3 1 bar, Soil Moisture Equipment, Goleta, CA; Pressure transducers: 26 PC-CFA3D, Honeywell, Minneapolis, MN) and one temperature probe (T108; Campell Scientific Inc., Loughborough UK). All soil profile data were stored at hourly intervals in a data logger (CR10X; Campell Scientific Inc., Loughborough UK).

2.2.5 Overland flow and erosion

Two different devices were used to detect overland flow:

1. The runoff sensor is an electronic device based on the idea by Srinivasan et al. (2000). It detects overland flow by electric contacts on a small v-notch weir and stores the data in a data logger. This system delivers time resolved occurrence of overland flow.

2. The overland flow detector is a simple collection bottle similar to the device described by Kirkby et al. (1976). The overland flow detectors have to be controlled and emptied after every rain event. They do not only provide a signal if there

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was overland flow at the location, but they additionally provide a sample of the overland flow.

A total of 16 overland flow detectors and eleven runoff sensors were installed at 23 locations (four locations were equipped with both instruments, see Fig. 1). Additionally grab samples of overland flow were taken at several locations during events E2 and E9 (see Table 2). During and after some of the events, signs of overland flow, ponding and erosion were mapped (see Fig. 4). Although the mapping was carried out on an ad-hoc basis by different people and without a systematic coverage of the entire catchment, it complements the information on the spatial extent of overland flow and erosion from the point measurements of the runoff sensors and overland flow detectors.

2.3 Herbicide application

On 19 May 2009, we performed a controlled herbicide application on corn fields in the catchment. The fields were divided into two groups. Six of the corn fields were selected as experimental fields (labelled 1 to 6 on Fig. 2) where we had full control over all the substances applied. They were all sprayed at the same day with the same spraying device. The rest of the corn fields in the catchment (called alternative fields) received a different herbicide mixture. Not all of the alternative fields could be sprayed at the same day with the same spraying device. On the six experimental fields we applied the herbicides atrazine (CAS Nr: 1912-24-9), S-metolachlor (87392-12-9), sulcotrione (99105-77-8) and simazine (122-34-9) (see Table 1) in two different mixtures. The experimental fields 1 to 4 received atrazine, S-metolachlor and sulcotrione (Mix A) while fields 5 and 6 were sprayed with simazine and Mix A (see Fig. 2). The alternative fields were sprayed with a mixture of terbuthylazine (5915-41-3) and mesotrione (104206-82-8) (Mix B in Fig. 2). None of these substances was used elsewhere in the catchment. Even though the application on the alternative fields was less controlled, we know the substance amounts and application dates of all corn fields.

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To ensure the correct dose and concentration in the spray solution, the experimental herbicides were weighted exactly before being mixed in the spraying tank. Tank solution samples from each tank filling were taken and analysed. The exact amount of spray solution applied on each field was determined by a flow meter mounted on the spraying equipment. As quality control for the applied volume per field a calibrated scale bar at the spraying tank was used in addition to the flow meter. The extent of the sprayed area was marked with wooden sticks; their exact location was determined by a differential GPS (Leica GPS1200, Leica Geosystems AG, Heerbrugg Switzerland). With these control measures the exact areas and applied rates are known for each field and each substance.

2.4 Water sampling

Water samples from stream and tile drains were taken at the five discharge measurement stations prior to the herbicide application and during two months after application. In the 13 rain events that occurred during the experimental period these five locations were sampled at high temporal resolution. The sampling strategy followed the strategy applied by Wittmer et al. (2010). Time-proportional samples were taken by automatic water samplers equipped with 24 PP bottles (ISCO 2900, 6700, 6712 Teledyne Inc., Los Angeles USA). The samplers were triggered when a predefined water level was exceeded. During the first six hours of an event, time-proportional 15-min composite samples (three aliquots every five minutes) were taken. Afterwards, the sampling frequency was reduced to one composite sample per hour (four aliquots every 15 min). This sampling strategy yielded enough samples for short events, and lasted long enough (max. 30 h) to restart the samplers during large events. Grab samples were taken during base flow periods.

To keep the number of samples in a feasible range for subsequent analyses in the lab, the samples were selected in a two-step procedure. First, they were pre-selected in the field to cover the entire hydrograph of the event. A total of 1500 samples was brought to the lab in 250 ml glass bottles and stored at 4 °C. Every second sample

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was additionally stored at −20 °C (150 ml in a 250 ml glass bottle). Out of the total of 1500 samples, six hundred were selected for analysis in a step-wise procedure. First, the seven events with the highest rain amounts were selected for analysis (events E1, E2, E3, E7, E9, E12, E13 in Table 2, see also Fig. 3) and a few samples per event were analysed (beginning, peak, recession). Finally, we selected further samples to adequately represent the dynamics of the chemograph.

2.5 Analytics water samples

Stability of the analytes was investigated over a period of four months at 4 °C. No degradation was observed for two months of storage. However, sulcotrione and mesotrione showed slight degradation after two months in unfiltered samples; therefore, data for these two analytes is only reported from samples stored at −20 °C after the elapsed time (two months).

Analysis of the herbicides was performed after the method described by Singer et al. (2010), which was also used by Wittmer et al. (2010). The samples were filtered through glass-fibre filters (GF/F, 0.7 µm, Whatman) and isotope-labelled internal standards of all compounds were spiked to 50 ml of filtered sample. The samples were analysed by online solid-phase extraction (SPE) coupled to liquid chromatography followed by a triple quadrupole mass spectrometer (LC-MS/MS). Sample enrichment was achieved on a Strata-X extraction cartridge (20 × 2.1 mm I.D. 33 µm particle size, Phenomenex, Brechbühler AG, Schlieren, Switzerland). LC separation was performed on a XBridge C18 column (50 mm × 2, Waters, Baden-Dättwil, Switzerland), and detection by a TSQ Quantum triple quadrupole MS (Thermo, San Jose, CA, USA). The limit of detection (LOD) was in the range of 2 to 10 ng l^{-1} for all compounds. Quality control consisted of aliquots of spiked and non-spiked environmental samples analysed with each analytical run. The resulting inter-day precision of the method was 5 to 12 % for the six compounds. The average accuracy for each analyte was between 101 and 105 %.

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2.6 Soil sampling and sample preparation

From each of the six experimental fields (see Fig. 2), seven soil samples were taken: a background concentration sample before herbicide application, a sample directly after application and samples on days 3, 7, 15, 30 and 60 after application. A stainless steel probe with 5.4 cm diameter was used for soil sampling. 20 sub-samples from 0 to 5 cm depth were taken randomly across each field and combined into a polypropylene box tightly sealed with a lid for storage.

After sampling, all soil samples were stored at −20 °C. Prior to the analyses, all soil samples were crushed with a hammer mill in frozen state by the addition of dry ice. After milling, the soils were left outside for twelve hours with open lids to allow all the CO_2 added during milling to evaporate. Subsequently, the soil samples were again stored at −20 °C until further analysis.

2.7 Soil extraction and analytics

Herbicide concentrations were measured in all soil samples by two different extraction methods. For the total soil concentration we used pressurized liquid extraction (PLE), the pore water concentration was determined in a pore water sample obtained by centrifugation (see below). Pore water concentration was used as a proxy to determine the dissolved fraction in the soil samples.

2.7.1 Total soil concentration

The herbicides were extracted by PLE using an ASE 350 Accelerated Solvent Extractor (Dionex, Sunnyvale, CA). Extraction took place with a solvent mixture of acetone: 1 % phosphoric acid, 70:30 (volume ratio) at 100 °C. The PLE extract was stored at −20 °C. The clean-up of the PLE extract was done in four main steps after an internal standard solution was added. (1) The acetone was removed by rotary evaporation at 35 °C. (2) For the liquid-liquid extraction, HPLC grade water, 3.9 g of acetonitrile, 1.6 g

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of anhydrous magnesium sulfate and 0.3 g of ammonium chloride were added to the remaining extract. The tube was shaken for about 2 min and centrifuged for 4 min at 500 × g (Ultrafuge Filtron, Heraeus) to separate the acetonitrile phase. (3) The acetonitrile phase was blown down under a nitrogen stream to a volume of 500 µl, to which 500 µl of methanol were added. (4) The solution was filtered with a syringe through a 0.2 µm PTFE filter and stored at 4 °C until quantification.

2.7.2 Pore water

To obtain the pore water sample, a weighed amount of approximately 3 g of thawed soil sample was placed into a centrifuge filter tube with a 0.45 µm PTFE membrane (Ultrafree-CL, Millipore). For dry soil samples (<80 % of the water holding capacity (WHC)) the water content of the soil was adjusted to 80 % of the WHC by addition of water to the appropriate weight. The centrifuge tubes were then stored at 4 °C for roughly 24 h to obtain an apparent equilibrium between the pore water and the solid phase. After centrifugation, the internal standard mixture was added to the collected pore water, the solution was stored at 4 °C until quantification.

2.7.3 Quantification

Analysis of the extracts was done with liquid chromatography coupled to a triple quadrupole mass spectrometer (LC-MS/MS). Compounds were separated by reversed-phase LC using a Synergi C18, polar RP column (100 × 3 mm ID, 2.5 µm particle size, equipped with an inline-filter, Phenomenex, Torrance CA) and detected by a TSQ Quantum triple quadrupole MS (Thermo, San Jose, CA, USA).

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2.7.4 Distribution coefficients

In all of the soil samples the distribution of the herbicides between the dissolved and the sorbed phase was expressed by the apparent distribution coefficient K_d:

$$K_d = \frac{C_{\text{sorbed}}}{C_{\text{porewater}}} = \frac{C_{\text{PLE}} - C_{\text{PWfraction}}}{C_{\text{porewater}}} \quad (2)$$

C_{PLE} is the concentration obtained by PLE, expressed per mass of dry soil, $C_{\text{PWfraction}}$ is the pore water concentration expressed per mass of dry soil, and $C_{\text{porewater}}$ is the measured pore water concentration in the water phase. A more detailed description of soil extraction and analysis is given in Camenzuli (2010).

2.8 GIS analysis

The catchment boundary was calculated in ArcGIS (ESRI, ArcGIS Desktop, 9.3.1) based on the 2 × 2 m DEM (swisstopo, 2003) and manually adapted after field observations. The topographical catchment does not coincide with the subsurface catchment everywhere. In some areas that topographically belong to the catchment the tile drains divert the water outside of the catchment. These areas were excluded. On the other hand, the settlement area in the southeast was kept in the catchment, even though the water from sealed areas in the settlement leaves the catchment. The subcatchments of the discharge and sampling stations were delineated based on topography and the detailed tile drain map (swisstopo, 2003; Gemeinde Ossingen, 1995). Catchments calculated from surface topography were not always congruent with the tile drain catchments. Priority was given to the tile drain catchments. The drained area was calculated as a buffer of 15 m around the drainage pipes.

For the analysis of surface connectivity, the original 2 × 2 m DEM (swisstopo, 2003) was used. In a first step, very small or shallow depressions were removed; these can be artefacts in the DEM or they are too shallow to trap significant amounts of overland flow. Depressions consisting of one or two cells and those with a maximum depth of

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less than 5 cm were filled. In a second correction step, the cells in the open stream were incised to the depth of the average water level. Depression analysis and filling as well as stream incision were performed in TAS (TAS geographical information system version 2.0.9, John Lindsey 2005). Based on this corrected DEM, flow directions and flow accumulation were calculated in ArcGIS (ESRI, ArcGIS Desktop, 9.3.1). The lowest stream channel cell was used as pour point for the catchment calculation to determine the area connected directly to the stream on the surface. For the determination of areas connected to manholes of the drainage system or to catch basins for road and farmyard runoff, the locations of these features were used as pour points for the catchment calculation (Gemeinde Ossingen, 1995, 2008). Where it was appropriate, the feature locations were manually shifted to cells with higher flow accumulation.

3 Results

3.1 Rainfall and hydrological processes

The period before the herbicide application was very dry. There was hardly any rain for more than a month prior to application (Fig. 3). Afterwards, the weather conditions changed: from 19 May 2009 to 21 July 2009 thirteen rain events of more than five mm were recorded. Five of them had more than 20 mm of rain; a total of 333 mm rainfall was measured in this period (see Fig. 3 and Table 2). From the five largest events (E2, E3, E9, E12, E13), four were thunderstorms with rather high rain intensities and short duration; only event E13 was a longer lasting, low intensity rain event (see Fig. 3 and Table 2).

The human modification had a strong influence on the catchment hydrology. The largest part of the stream network is situated subsurface and tile drains provided most of the discharge. Even though the catchment has a large storage capacity due to the artificial drainage and therefore reacts slowly (low runoff ratios, see Table 2), the hydrograph at some of the measurement stations was very peaky because road and

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farm yard runoff is directly connected to the drainage system and the stream (see Figs. 10 and 11).

3.1.1 Overland flow and erosion

During the experimental period, we frequently observed overland flow and erosion on different fields distributed in the whole catchment (see Fig. 4 and Table 2). Overland flow was observed at least at one location in all of the rain events (Table 2). Based on the observed groundwater levels and the electrical conductivity of overland flow samples, we concluded that both, infiltration excess and saturation excess overland flow occurred during the study period. Piezometer data showed that the groundwater level was often low before and during rain events. During events E2, E3 and E9 it rose to a level of less than 30 cm from the surface in only two, one and three piezometers, respectively. Four piezometers reached this level during event E12. However, during event E13 groundwater level rose close to the surface in seven out of nine piezometers (Table 2). Within the four soil profiles we never observed hanging water tables. Rising groundwater levels were therefore always regional and not limited to locations with low conductivity layers in the soil profile.

Electrical conductivity as measured in the overland flow samples supports the interpretation of infiltration excess overland flow being the main process for most of the events. Since rain typically has a very low electrical conductivity (<50 $\mu S\,cm^{-1}$) we expected infiltration excess overland flow to also have low conductivities. On the other hand, areas that produce saturation excess overland flow often also produce return flow (exfiltrating groundwater) because the groundwater table is at the surface. We therefore expected that the overland flow on saturation excess areas consisted of a mixture of return flow, pre event pore water and rain. It was therefore expected to have higher electrical conductivities (electrical conductivity of baseflow in this catchment was around 800 $\mu S\,cm^{-1}$). Table 2 shows the mean electrical conductivities in the overland flow samples of eight events. Except for events E2 and E13, the values

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were low and therefore indicated infiltration excess overland flow as the main process. Event two was a special case because fertilizer was applied directly before the event. The high electrical conductivity in the overland flow was probably caused by dissolved fertilizer in this case. Therefore, we concluded that the herbicides were mainly mobilised by infiltration excess overland flow and only during event E13 saturation excess overland flow was the more important process (Hirzel, 2009).

Figure 4 gives a spatial overview of the field observations concerning overland flow and erosion. None of these processes was limited to locations with high groundwater levels. Both were distributed across the whole catchment area. However, erosion was only observed on corn fields during the study period, never on wheat fields with high soil coverage. In addition, the land management on the corn fields played an important role for the risk of infiltration excess overland flow. The type of ploughing and harrowing as well as the addition of organic material in the past years seemed to be important factors affecting the infiltration capacity of a field. This can be illustrated with fields (A) and (B) on Fig. 4. Both were corn fields with comparable soil coverage, furthermore soil texture and topography are very similar. Erosion and overland flow were frequently observed on field (A), but rarely so on field (B). The differences can be explained with the land management: field (A) was harrowed very finely, leading to very small and crushed soil aggregates at the surface, low surface roughness and small detention storage. On the other hand, field (B) was harrowed only roughly, leading to a more irregular soil surface with intact soil aggregates, a high surface roughness and larger detention storage. Additionally solid manure was applied on field (B) before ploughing.

3.1.2 Connectivity

Only 4.4 % of the catchment area are directly connected to the stream on the surface (see Fig. 2) because depressions within the catchment or topographic barriers (e.g. field roads) prevent the overland flow from directly flowing to the stream (see Fig. 4 showing that ponding was often observed beside roads). However, the extended

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pipe network in the underground (tile drains as well as road and farm yard drainage), which is directly connected to the stream, offered two additional fast transport pathways for herbicides in overland flow: (i) direct shortcuts via maintenance manholes of the drainage system, or catch basins for road and farm yard runoff and (ii) ponding of overland flow in depressions and macropore flow to the drainage system. Figure 5 shows examples of these two pathways observed during event E2. The connectivity analysis revealed that the area connected to shortcuts is much larger (23 % of the catchment area) than the area directly connected to the stream (Fig. 2). This connectivity analysis is based on the assumption that all the overland flow in the catchment of a shortcut also enters the shortcut, which is a worst-case assumption. Several reasons can prevent overland flow from entering shortcuts: (1) manholes with closed lids do not collect all the water that reaches them. (2) Small scale topography around the potential shortcut can divert overland flow in another direction. (3) The rim of manholes can be slightly higher than ground surface and prevent overland flow from entering. Furthermore, overland flow can re-infiltrate on its way to the shortcut. Despite these possible restrictions, several shortcuts were observed to be active during the experiment. Figure 4 shows all shortcuts that were observed to be active at least once, Fig. 5 shows an example of an active shortcut.

Spatial sequences of different processes at different locations did also cause transport to the stream, even from fields that did not seem to be connected to the stream in any way. This was observed for experimental field 4, which is not directly connected to the stream and only small parts of the field are potentially connected to direct shortcuts (see Fig. 2). Furthermore, only one drainage tube crosses a corner of the field, which lies entirely on well drained soils and regosols (Fig. 1). Therefore, we did not expect any herbicides from field 4 to be found in the stream. However, we observed the experimental substances in sampling station S_u with field 4 being the only possible source area. Field observations during and after rain events revealed that overland flow and erosion occurred on field 4, the flow including the herbicides was routed off-field to a depression on the neighbouring field, where ponding was observed (see Fig. 4 for

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observed flowpaths and ponding and Fig. 9 for the catchment of the depression). The depression is drained and herbicides reached the stream via macropore flow to the drainage system (concentration data not shown).

3.2 Influence of compound properties

3.2.1 Herbicide dissipation and sorption

We calculated the herbicide's half-life in soil based on the total soil concentrations (corresponding to the concentration measured with PLE) with first-order kinetics. Dissipation of sulcotrione on all fields and of atrazine and S-metolachlor on some fields slowed down after day 30. For these cases only concentration data until day 30 were used for the calculation of the half-lives while for the other cases all data points (until day 60) were used. Average half-lives on the six experimental fields were 9.5, 13.8 and 5.5 days for atrazine, S-metolachlor and sulcotrione, respectively (Camenzuli, 2010). These values are well within the range reported in literature (see Table 1).

Sorption of the herbicides to soil was assessed by the distribution coefficient K_d between the sorbed and the dissolved fraction (Eq. 2). On all the experimental fields, sorption was strongest for S-metolachlor followed by atrazine and sulcotrione. At the application day, the K_d values on the experimental fields were in the range of 0.7 to 1.5 $\mathrm{l\,kg^{-1}}$, 1.4 to 2.6 $\mathrm{l\,kg^{-1}}$, and 0.1 to 0.2 $\mathrm{l\,kg^{-1}}$ for atrazine, S-metolachlor and sulcotrione, respectively. The distribution coefficient K_d of all substances increased with time. The magnitude of this aging effect was largest for sulcotrione (3.2 to 14 fold increase from day 0 to day 30) followed by atrazine (1.3 to 10 fold increase) and S-metolachlor (1.3 to 2.5 fold increase). As it can be seen from the large ranges of K_d increase, the variance between the different fields was large (Camenzuli, 2010). The magnitude of the aging effect and its variability are comparable to the observations reported by Gomides Freitas et al. (2008).

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3.2.2 Substance property dependence of mobilisation

Herbicide concentrations in the overland flow samples varied heavily in space and time. The concentrations at each overland flow sampling station decreased with time while the absolute magnitude of the concentrations at the stations mainly depended on the proportion of sample water that directly originated from a treated field. The concentrations in overland flow samples measured during event E2 differed by three orders of magnitude depending on the sampling location (atrazine: 0.58 to 426.3 $\mu g\,l^{-1}$, S-metolachlor: 0.42 to 466.8 $\mu g\,l^{-1}$, sulcotrione: <0.125 to 97.9 $\mu g\,l^{-1}$).

The mobilisation of the herbicides was expected to depend on the sorption behaviour of the substance. A mobilisation coefficient M was used to compare the mobilisation of different herbicides from soil to overland flow. The coefficient M is defined as the ratio of overland flow concentration to total soil concentration (PLE concentration). However, M could only be used to compare substances in the same sample, because the overland flow concentration was mainly determined by the mixing ratio of overland flow from different sources (dilution with uncontaminated water). Therefore, for investigating the influence of sorption on the mobilisation process, we used overland flow samples where the origin of the water could be attributed to one single experimental field. We calculated M ratios for all substance pairs and compared them with the respective ratios of K_d values. We used the distribution coefficients that had been determined in the last soil sample taken before the respective rain event. We expected that substances that show stronger sorption are less mobilised as compared to less sorbing substances. Hence, one can expect that the ratio of the M values of two compounds decreases as a function of the respective K_d-ratio. This expected behaviour is also implemented in simulation models like e.g. SWAT. This model describes the mobilisation of herbicides into mobile water as follows:

$$m_{rel} = \exp\left(\frac{-1}{\theta_{sat} + K_d \times \rho} \times \frac{q_{mobile}}{z}\right) \tag{3}$$

Where m_{rel} is the amount of mobilised pesticide relative to the initial amount, q_{mobile} is

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the flux of mobile water per time-step, θ_{sat} is the water content at saturation, K_d is the distribution coefficient, ρ is soil bulk density and z is the depth of the soil layer (Neitsch et al., 2005). In Fig. 6 we show two lines based on this equation with the following assumptions: $z = 50$ mm, $\theta_{sat} = 0.5$, $\rho = 1.2\,\mathrm{g\,cm^{-3}}$ and $q_{mobile} = 10$ mm (dashed line) and $q_{mobile} = 100$ mm (solid line).

Figure 6 also shows the field data from all experimental substances, all the events with overland flow samples and different experimental fields. In contrast to the expectation, no dependence could be detected between M ratios and K_d ratios. All M ratios scattered around one. Obviously, the different substances were mobilised into overland flow to a similar degree, independent of their distribution coefficients K_d. This implies that the influence of substance properties affected mobilisation in a different manner than expected and/or that other factors were more influential (e.g. size of soil aggregates).

3.2.3 Retardation during infiltration

While the field data do not show an influence of substance properties on the mobilisation process, the data suggest that the transport through macropores was affected by sorption. To describe the herbicide transport from ponding overland flow to tile drains we defined a retention coefficient R as the ratio of overland flow concentration on a given field to the concentration in the tile drain of that field at the corresponding time. For event E2, we calculated retention coefficients for all the experimental substances on experimental field 1. Two samples of the ponding overland flow were available, one at the beginning of the event and one at the end. These samples were used for calculating R together with the two samples from station O_u that were taken briefly after sampling the overland flow. The absolute value of R mainly depended on the dilution of the infiltrated overland flow with other drainage water (groundwater and infiltrate from other fields). However, we could compare retention coefficients of different substances (all applied together on field 1) within the same samples. Figure 7 shows the ratio of R of two substances plotted against the K_d ratio of the respective substances. The figure

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reveals that the retention coefficients were larger for substances with higher K_d values. This means that sorption played a role during the fast transport from ponding overland flow through macropores to tile drains. From the compounds dissolved in ponding water, a larger fraction of the stronger sorbing compounds was retained in the soil. This implies that the herbicide load was reduced during the soil passage, even though the flow was fast and the travel time short.

3.3 Concentration dynamics

During all of the sampled events (Table 2) we observed elevated concentrations of all the applied substances in the stream and in tile drains as compared to base flow. Additionally we observed that substances applied to the same fields, always showed the same dynamics. Atrazine, S-metolachlor and sulcotrione (the substances on the experimental fields) always peaked at the same time. The same holds for terbuthylazine and mesotrione, which were spayed on the alternative fields. However, the dynamics of these two mixtures differed during most events implying that the concentration dynamics was substantially influenced by the spatial origin of the compounds and the flow paths but not by substance properties.

Based on previous studies (Gomides Freitas et al., 2008; Leu et al., 2004a,b, 2005) we expected the concentrations to follow the hydrograph dynamics very closely. This pattern was indeed observed in event E13 for terbuthylazine (see Fig. 8). For atrazine and S-metolachlor the same holds for load as well (data not shown). The concentrations however, revealed a slight decrease during the discharge peak. Obviously, the proportion of water containing terbuthylazine increased more than the proportion of water containing atrazine and S-metolachlor during that part of the hydrograph. More drastic deviations from the expected pattern can be seen in Figs. 10 and 11. These data suggest a decoupling of discharge and concentration peaks for atrazine, S-metolachlor and sulcotrione in several events.

In order to understand these chemographs and the apparent contradiction to previous observations, one has to consider the relevant flow paths that have been observed

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in this catchment. Based on our results and field observations, we distinguish three major flow components:

1. Surface runoff that entered the system via shortcuts. This includes runoff from roads and farm yards but also overland flow from fields that entered one of the above mentioned shortcuts. This is the fastest flow component; it dominated discharge during times with high rain intensities and its proportion in discharge mainly followed the rain intensity pattern.

2. Macropore flow to tile drains. This water partly consisted of overland flow that ponded in small depressions that are drained; but it can contain water from other sources. This is also a fast flow component that was only active during rain events, but slower and longer lasting than component one.

3. Groundwater flow to tile drains. This is the slowest flow component that made up the base flow and increased with rising ground water tables during rain events. It was characterized by low herbicide concentrations.

The observed chemograph of a given compound was the result of the mixing of these three flow components and their respective herbicide concentrations. The connectivity analysis revealed that not all measuring sites were affected by the first two flow components to the same degree. Only small parts of the experimental fields – receiving atrazine, S-metolachlor and sulcotrione – in the catchment of S_d (fields 3 and 4) for example, were connected to a direct shortcut (see Fig. 2). The largest part of the fields drained into three important depressions (Fig. 9), from where overland flow reached the tile drains via macropore flow (flow component 2). Large areas of alternative corn fields – receiving terbuthylazine – were, however, connected to shortcuts (Fig. 2; flow component 1). This led to faster transport and therefore a sharper concentration peak (Fig. 10). Due to the different travel times along the two different fast flowpaths, the chemographs of the two herbicide mixtures differed.

This interpretation is supported by the electrical conductivity data. Measurements at S_d showed that the terbuthylazine peak occurred simultaneously with lowest electrical

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conductivity, indicating transport with water that did not experience a soil passage (Fig. 10). On the other hand, atrazine and sulcotrione had their peak concentration simultaneously with the time of higher electrical conductivity within the event. This was the time of less intensive rainfall; discharge was now dominated by the macropore flow from ponding overland flow to the tile drains. This flow component carried atrazine and sulcotrione and had a higher electrical conductivity because it experienced a soil passage.

A similar behaviour was observed at station O_u (Fig. 11), where the situation was even simpler with only one experimental (field 1) and two alternative corn fields in the catchment. Experimental field 1 was only connected to the stream via infiltration to the drainage system, direct shortcuts were not present (Fig. 2). Overland flow from the field was collected in a depression on field 1 from where it could infiltrate to the drainage system (see Fig. 9 for the catchment of the depression. Figure 5 shows a picture of this depression). Overland flow originating from the alternative fields in O_u's catchment (terbuthylazine) could take two flow paths. It either flowed to the depression on field one and infiltrated to the drainage system or it could enter the stream via catch basins for road runoff (Figs. 2 and 9). Figure 11 shows that concentration of the experimental substances (atrazine and sulcotrione) again correlated well with the electrical conductivity in the stream during the event. At this sampling station, discharge peaks were clearly dominated by road runoff, which led to strong dilution of herbicide concentration and to low electrical conductivities during times with intensive rainfall. Again, the concentration dynamics clearly supported the connectivity analysis; both indicated transport via infiltration to the drainage system. The terbuthylazine concentration dynamics reflected the two flow paths that the water from the fields could take: the very fast pathway via catch basins for road runoff and the pathway via infiltration to the drainage system. The resulting concentration dynamics of terbuthylazine was an overlay of the two processes. However, as soon as groundwater flow into the drains dominated discharge (at the end of the event and in base flow periods) concentrations were low and did not correlate anymore with electrical conductivity.

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4 Discussion

The rationale behind this study was to improve the understanding of the spatial occurrence of the hydrological processes controlling the transfer of herbicides from arable fields to small streams as a prerequisite to make spatial predictions on the extent of critical source areas (Eq. 1). In the following, we discuss and summarize what can be concluded from our results with respect to the CSA concept.

4.1 Transport processes and CSAs

While previous studies on herbicide transport (Leu et al., 2004a, 2010; Gomides Freitas et al., 2008) have indicated that saturation excess overland flow was a crucial process controlling diffuse herbicide pollution in the Swiss Plateau, this study clearly revealed that infiltration excess overland flow can be an important mobilisation process even in humid climate and on moderate topography.

These differences are most probably caused by very different rainfall characteristics of the events that led to the main herbicide losses. In the studies by Leu et al. (2004a) and Gomides Freitas (2005) the maximum rainfall intensity of the events that led to the main herbicide losses were 3.2 and 2.4 mm $(15\,\mathrm{min})^{-1}$, respectively. In contrast, the main loss event in this study had a maximum intensity of 12 mm $(15\,\mathrm{min})^{-1}$ (see Fig. 12 and Table 2). Figure 12 shows the histograms of rain intensities of the months Mai to July in these three field studies (Leu et al., 2004a; Gomides Freitas, 2005, and this study) together with the 30 yr average intensities during these months at Schaffhausen (closest permanent meteo-station from this study site, Meteoschweiz, 2012). The figure shows that the timing of the rain events was essential to determine the process that leads to the main herbicide losses. If the first event with a substantial hydrological response after the application was a high intensity event, infiltration excess overland flow was dominant, if it was a low intensity event saturation excess overland flow dominated the herbicide losses. The histograms also show that none of the field experiment years was an extreme year if compared to the 30 yr average. However, in the years 2003 and 2009 high intensities were much more common than in 2000.

Saturation excess and infiltration excess overland flow are influenced by different site characteristics. While the position in the relief and the subsoil properties play a major role in triggering saturation excess runoff, infiltration excess overland flow is strongly affected by topsoil properties. Accordingly, one may expect the two runoff processes to occur in different parts in the landscape. Equation (1) can be re-formulated to take this into consideration:

$$A_{\text{CSA}} = (A_{\text{source}} \cap A_{\text{inf\_ex}} \cap A_{\text{connect}}) \cup (A_{\text{source}} \cap A_{\text{sat\_ex}} \cap A_{\text{connect}}) \tag{4}$$

This equation states that the CSA extent is an overlay of CSAs with active areas for infiltration excess with those causing saturation excess runoff. As discussed above, the occurrence of the two processes may differ substantially in time depending on the meteorological conditions.

The distinction between the two processes has further implications for CSA management. The risk for pesticide transport by infiltration excess overland flow depends on the crop that is grown and on the stage of the crop at the time of pesticide application. Additionally land management practices play a role for soil surface properties. This makes $A_{\text{inf\_ex}}$ very variable in time and hardly predictable without very local information on the actual land management. Furthermore, the spatial pattern of infiltration excess overland flow can be dominated by the spatial variability of rain intensity. Especially during thunderstorms this variability can be large. The comparison of the rain data from the two weather stations for event E9 showed that variability. Maximum intensities were 9.4 and 7.2 mm $(15\,\text{min})^{-1}$ at the weather stations 1 and 2, respectively, the total rain depths of event E9 were 36.8 and 24 mm. These disadvantages for the prediction of infiltration excess runoff areas go together with the advantage that prevention of infiltration excess overland flow is much easier as compared to saturation excess overland flow. Because infiltration excess depends strongly on topsoil properties, it can be influenced by land management and cropping practices. This is much less of an option for saturation excess overland flow, which is strongly controlled by constant site characteristics like the position in the landscape.

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4.2 Connectivity

This study confirmed previous work (Frey et al., 2009; Kiesel et al., 2010; Barron et al., 2011) by demonstrating that only a very small part of the catchment has a direct surface connectivity to the open stream; the largest part of the catchment is connected to topographic depressions within the catchment. One main reason for the low surface connectivity is the moderate topography – which is typical for major crop production areas – in the catchments. In areas with more pronounced topography it can be expected that larger areas are directly connected to the stream. Additionally, field roads, which are common in crop production regions, often act as small topographic barriers for overland flow. Figure 4 shows that ponding was often mapped directly alongside field roads as shown earlier by Frey et al. (2009).

However, the road network can also have the opposite effect and can increase connectivity by offering new routes for fast transport (Payraudeau et al., 2009; Ledermann et al., 2010). This holds especially true for Switzerland, where a large percentage of roads have a drainage system conveying runoff water directly to the stream network. For natural catchments it may be sufficient to analyse the topography in order to assess the connectivity to the stream network. For agricultural areas like the Swiss Plateau such an analysis has to be complemented by information on all kind of human interventions affecting the routing of water through the catchment. Such interventions may be quite region-specific and difficult to generalize. The study also showed that the risk for herbicide transport can not be assessed by investigating single fields; fields always have to be seen in their context within the catchment. Fields that do not produce overland flow, can be affected by run-on from an upslope field (Ledermann et al., 2010). On the other hand, a field that is neither connected to the stream or a shortcut nor drained can still be a contributing area because overland flow from the field can pond in a drained depression on a neighbouring field from where it enters the drainage system via macropores as shown for experimental field 4.

Although most of the fields were not connected on the surface to the stream network, herbicides were lost from the fields to the stream network. Obviously, herbicides were transported to the stream even if they were accumulating first in depressions in the landscape. In this context it is relevant that areas connected to the stream via different pathways do not pose the same risk for losses to the stream. Areas connected via shortcuts are less risky than those directly connected to the stream because parts of the overland flow might miss the inlet to the shortcut. Furthermore, areas connected to drained depressions pose an even lower risk because of sorption during the transport to the drainage system (see Sect. 3.2.3). In addition to sorption it has to be considered that ponding of overland flow in depressions lowers peak concentrations also through retarding the contaminated water. This leads to elevated concentrations for a longer time but lower peak concentration (compare e.g. atrazine (ponding) and terbuthylazine (no ponding) in Fig. 10). It has already been shown that drainage water typically has lower concentrations than surface runoff (Brown and van Beinum, 2009). Our findings concerning connectivity suggest that the question weather an area is connected to the stream can not be answered with yes or no. The question should rather be how well an area is connected to the stream.

4.3 Substance properties and transport

Previous observations had shown that the loss rates of herbicides depended on the K_d values of the substances (lower loss rates for substances with higher K_d) and that the sorption strengths did not affect the timing of concentration peaks. Based on these observations it was concluded that the substance properties of the herbicides have an influence on how much of a compound is mobilised into fast flow, but that these properties do not affect the transport of the compound once it got into the fast flow component (Leu et al., 2004a; Gomides Freitas et al., 2008). Interestingly, the results observed in this study were the opposite of what we expected: sorption did not yield any measurable influence on the mobilisation of the compounds into surface runoff (Fig. 6) but it did so during the transport by preferential flow towards tile drains (Fig. 7).

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These (apparent) contradictions can probably be explained by the different level of detail of investigating transport along the flow paths. In previous work, the interpretation was based on the knowledge of input into and output from the catchments. In this study, we also obtained information along the flow path by sampling e.g. ponding water. This more detailed information indicates that sorption affected the transport through preferential flow paths to tile drains. However, the retardation was not visible in the timing of the peak concentrations; this can have two reasons. First, the water at sampling station O_u was a mixture of the three flow components described in Sect. 3.3 where the retardation only appeared in the macropore flow (flow component 2). The timing of the concentration peak of all substances, however, was determined by the mixing ratio of the three flow components; this can mask the retardation occurring in one flow component. Second, the travel times were so short that any retardation effects were too subtle to be detected with our temporal sampling scheme.

The lack of sorption effect with regard to the mobilisation of the compounds may be caused by the fact that the equilibrium concept behind the K_d values is not adequate to describe the mobilisation of the herbicides from soil to overland flow, which is a fast process. It is possible that differing sorption kinetics compensated for differing equilibrium concentrations. Villaverde et al. (2009) postulated that sorption and desorption kinetics in undisturbed soil aggregates are negatively correlated with sorption strength. They argue that stronger sorbing compounds sorb at the surface of the soil aggregates while compounds with weaker sorption can diffuse into the soil aggregates. If diffusion into or out of soil aggregates is the rate limiting step, stronger sorbing compounds have a faster desorption kinetics. This could explain our results. Furthermore, it is possible that our soil sampling depth of 5 cm is not representative for the thin layer at the surface where mobilisation takes place. Stronger sorbing compounds could be overrepresented in the top layer as compared to our sampling depth. In addition, it has to be concidered that our substance selection does not cover the full range of sorption strengths. Possibly, the sorption effects during mobilazation were masked by other factors for our substances, but they would become visible for substances that differ more

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in their sorption properies. However, our results indicate that equilibrium sorption is not the only relevant process during herbicide mobilisation.

5 Conclusions

This field experiment aimed at improving the process understanding of herbicide transport from the fields of application to streams. This was done by controlling the herbicide input in an experimental way and by simultaneously analysing samples along the entire pathway of herbicide transport from the field to the stream (soil samples, overland flow samples, samples from drainage tubes and the open stream) and by monitoring a variety of hydrological state variables. This combination of observations was indeed crucial for improving the process understanding. It clarified the role of different hydrological processes for the transfer of the herbicides and elucidated the role of compound properties for transport. Both of these aspects also have implications for mitigation measures against diffuse herbicide pollution.

One of these measures starts from the concept of contributing areas CSA and aims at targeting measures to those parts of a catchment that contribute the main part of the pollution. In practice, this concept relies on the temporal stability of the spatial extent of CSAs for pesticide transport. This stability can be reasonably assumed for saturation excess runoff because it strongly depends on site characteristics like the topographic position that do not change over time scales relevant for these management issues. This study has, however, shown that infiltration excess can be an important process for herbicide transport in humid climate. In contrast to saturation excess overland flow, the spatial occurrence of infiltration excess overland flow may vary substantially through time due to crop growth, land management etc. Although the CSA concept may still be a useful heuristic for analysing transport in such situations, it renders the concept much more difficult to apply in practice. However, this disadvantage goes with the possibility to affect the risk for infiltration excess runoff relatively easily by adapting land management or crop rotations.

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In previous studies, where it was only possible to control herbicide input and measure the outflow (Leu et al., 2004a; Gomides Freitas et al., 2008), it was concluded that compound properties hardly had an effect on transport, once a compound had been mobilised into a fast flow component (being it surface runoff or preferential flow to tile drains). The detailed observations along the flow paths carried out in this study, however, suggest that the mobilisation process may be much less affected by sorption than expected. On the other hand, herbicides were partially retained even during the fast transport through preferential flowpaths underneath a depression with ponding water. This improved process understanding is not only of scientific interest; it also results in recommendations for practice in that hydraulic shortcuts should be avoided. A soil passage should be the goal even if preferential flow can convey herbicides quickly to tile drains.

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Table 1. The molecular structures of the applied substances with their sorption coefficient to organic carbon (K_{oc}) and their half life in field soil (DT_{50}). All data taken from PPDB (2010).

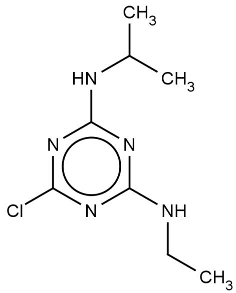
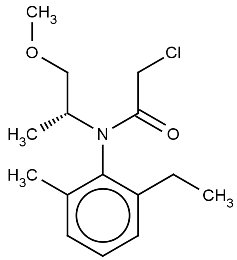
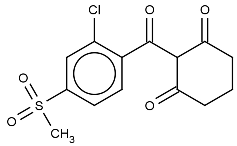
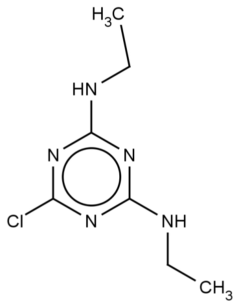
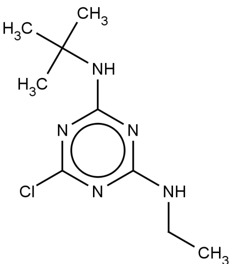
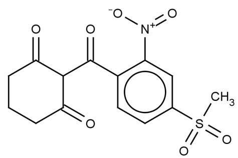
	Atrazine	S-Metolachlor	Sulcotrione
			
K_{oc} ($\mathrm{l\,kg^{-1}}$)	89 to 513	110 to 339	17 to 58
DT_{50} (d)	6 to 108	11 to 31	1 to 11
	Simazine	Terbuthylazine	Mesotrione
			
K_{oc} ($\mathrm{l\,kg^{-1}}$)	128 to 138	151 to 333	19 to 141
DT_{50} (d)	27 to 102	10 to 36	3 to 7

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Table 2. Characteristics of the 13 rain events with number of locations where overland flow (OF) was observed (results from runoff sensors and overland flow detectors), the number of overland flow samples, the average electrical conductivity (EC) in the overland flow samples and the number of piezometers that had maximum water levels (WL) less than 30 cm below the surface during the event.

Event	Rain depth mm	Max rain intensity mm 15 min^{-1}	Runoff ratio %	Locations with OF (out of 23)	Samples OF	Mean EC $\mu\text{S cm}^{-1}$	Piezometers with WL < 0.3 m
E1	9.8	4.2	6	1	0	–	0/10
E2	45.6	12.0	8	8	7	565*	2/10
E3	22.2	4.2	10	9	6	187	1/10
E4	7.8	1.3	13	1	0	–	0/10
E5	5.6	1.0	8	2	0	–	0/10
E6	9.6	0.8	9	4	0	–	0/10
E7	18.2	1.6	9	7	3	183	0/10
E8	14.6	1.4	12	7	4	206	0/10
E9	36.8	9.4	12	11	8	209	3/10
E10	6.4	0.6	4	5	0	–	0/9
E11	15.2	3.6	7	8	3	192	0/9
E12	51.6	8.8	12	15	12	167	4/9
E13	57	3.4	37	17	14	409	7/9

* Fertilizer applied at the day of the event.

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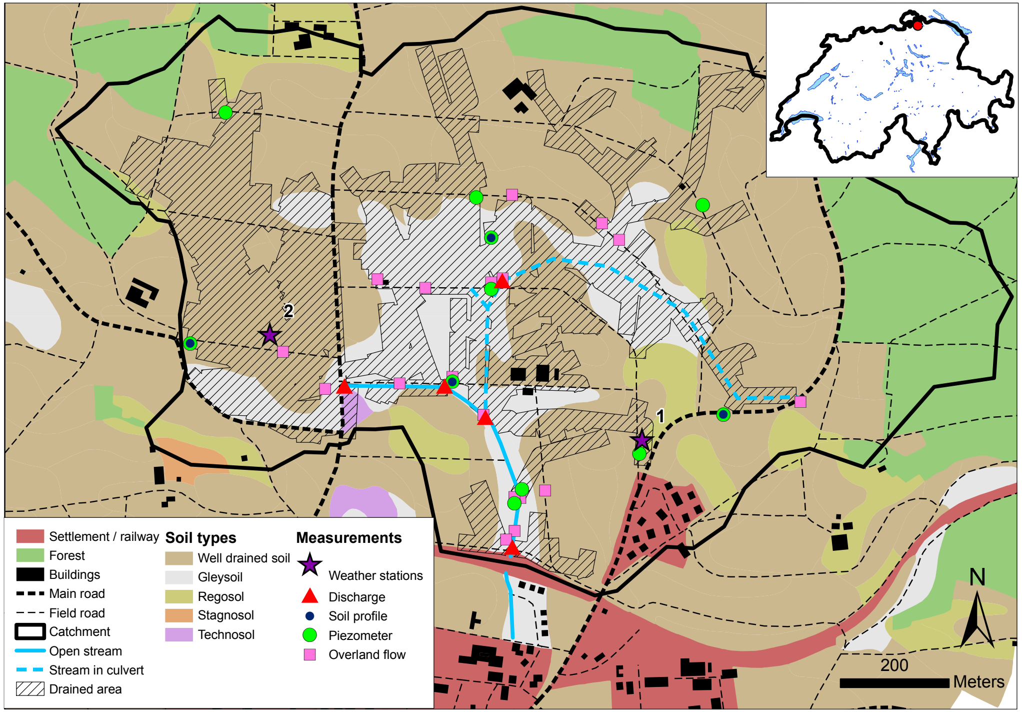

Fig. 1. The experimental catchment with soil types, land use and the hydrological measurement locations. The small map in the top right corner depicts the location of the study site within Switzerland. Sources: FAL (1997); swisstopo (2008); Gemeinde Ossingen (1995).

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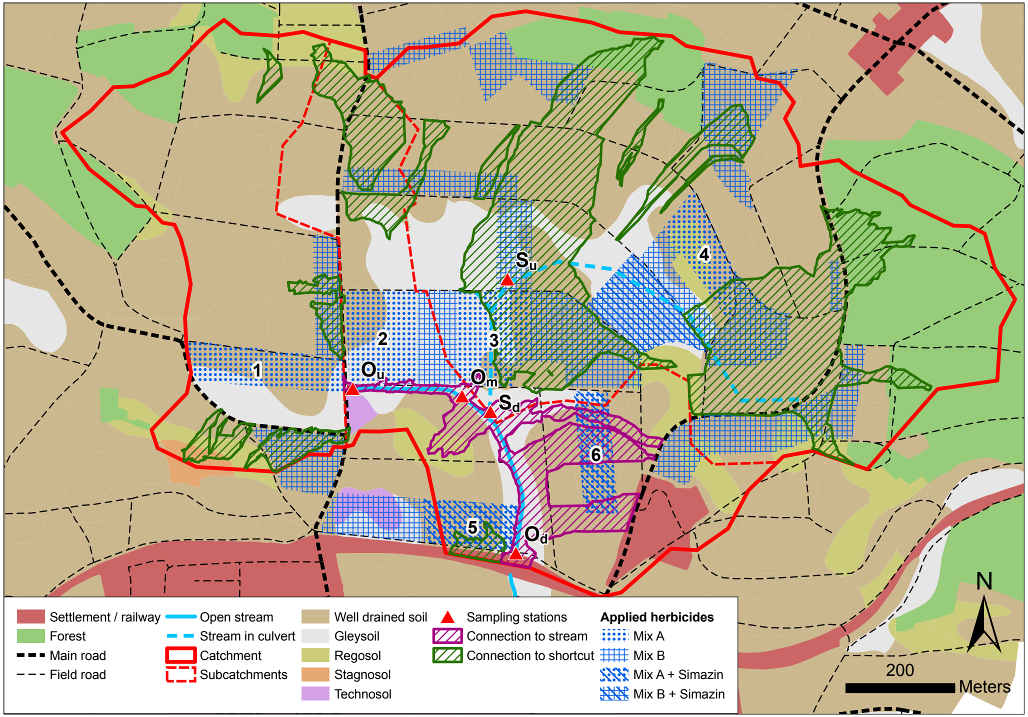

Fig. 2. Experimental setup with the six experimental fields (numbered 1 to 6, Mix A = atrazine, S-metolachlor and sulcotrione), the alternative fields (Mix B = terbuthylazine and mesotrione) and the five sampling locations: S_u and S_d (subsurface upstream and downstream) and O_u, O_m and O_d (open upstream, middle and downstream). The subcatchments of the sampling stations O_u and S_d are displayed. The area with a direct surface connection to the stream is shown together with the areas connected to manholes and catch basins (only connected areas $> 1000\,m^2$ are shown, see Sect. 3.1.2). Sources: swisstopo (2008); FAL (1997).

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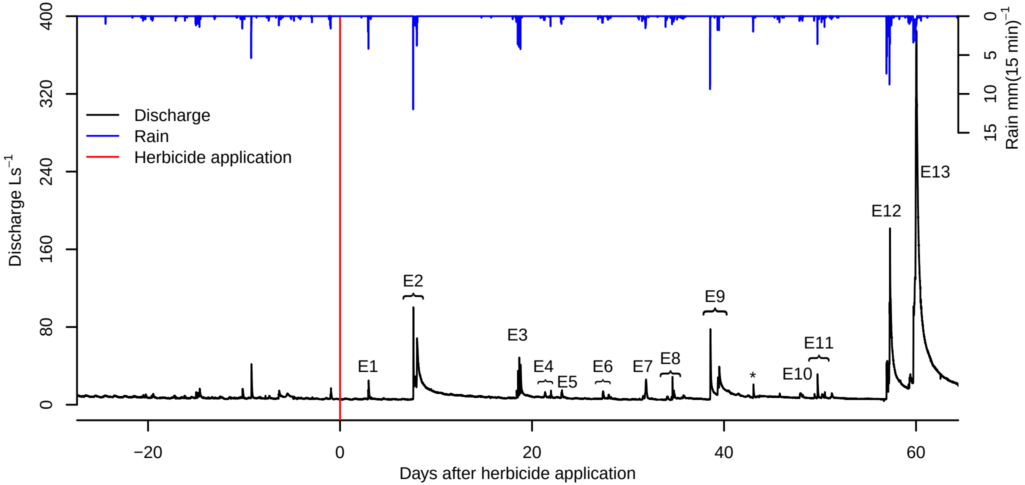

Fig. 3. Rainfall and discharge at the outlet of the catchment (station O_d) prior and after the controlled herbicide application. The numbers refer to the rain events described in Table 2. $\star$: event with <5 mm rain.

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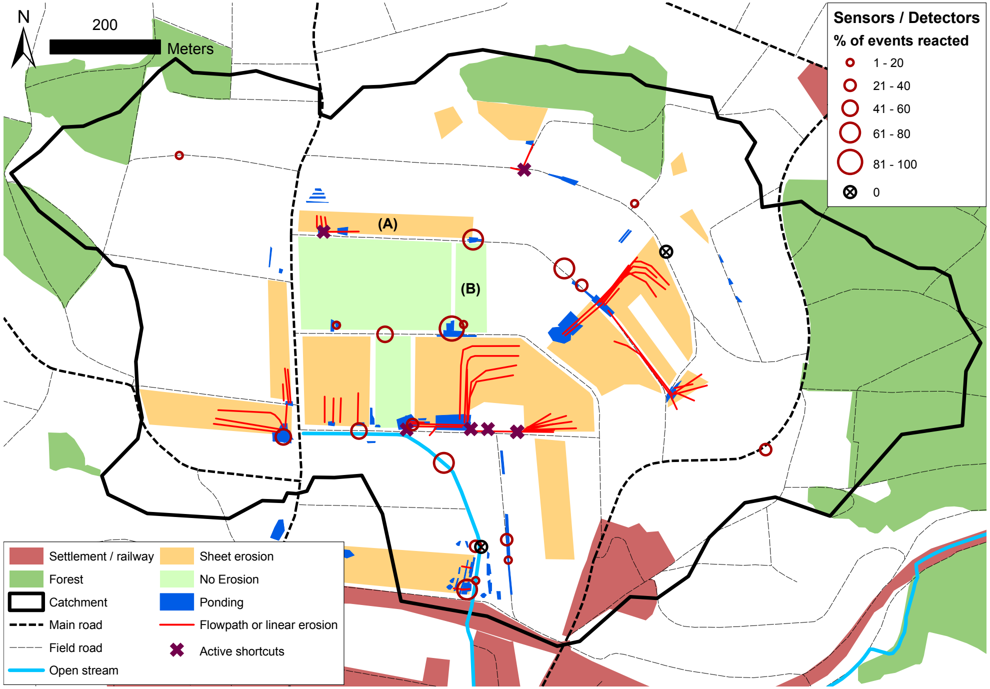

Fig. 4. Erosion mapping (sheet and linear erosion) from four events (E2, E9, E12, E13), direct observation of overland flowpaths (E2, E9, E13) and ponding (E2, E9, E12, E13) and results from runoff sensors and overland flow detectors showing the percentage of events in which overland flow occurred. (A) and (B) are two corn fields discussed in Sect. 3.1.1. White areas can be either unobserved areas or no erosion and overland flow was observed (see text). Fields labelled "No Erosion" were surveyed but did not show signs of erosion. Source: swisstopo (2008).

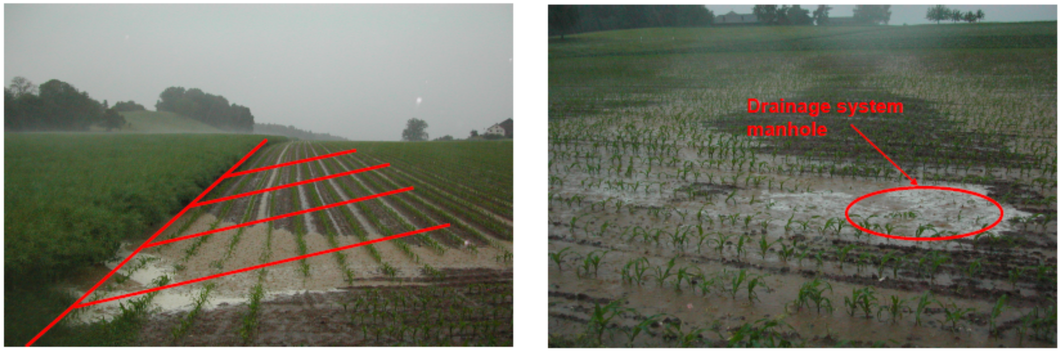

Fig. 5. Example pictures from event E2. Ponding overland flow in a drained depression on experimental field 1 (left) and overland flow entering a shortcut (right).

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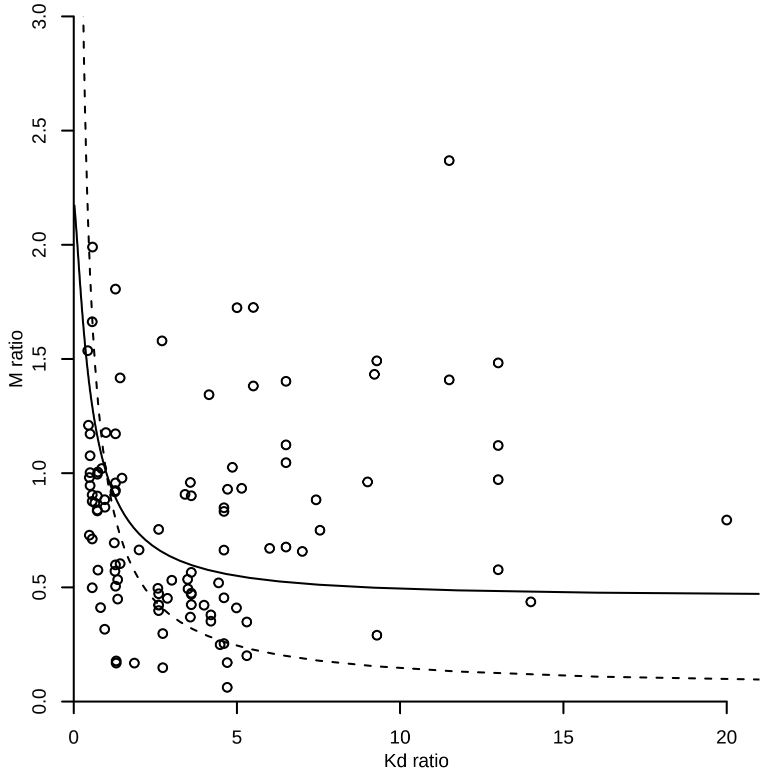

Fig. 6. The ratio of the mobilisation coefficients M of two substances in the same sample, plotted against the respective ratio of distribution coefficients K_d from the corresponding field. Dashed line: SWAT prediction with a flux of 10 mm of mobile water (see text), solid line: SWAT prediction with a flux of 100 mm of mobile water.

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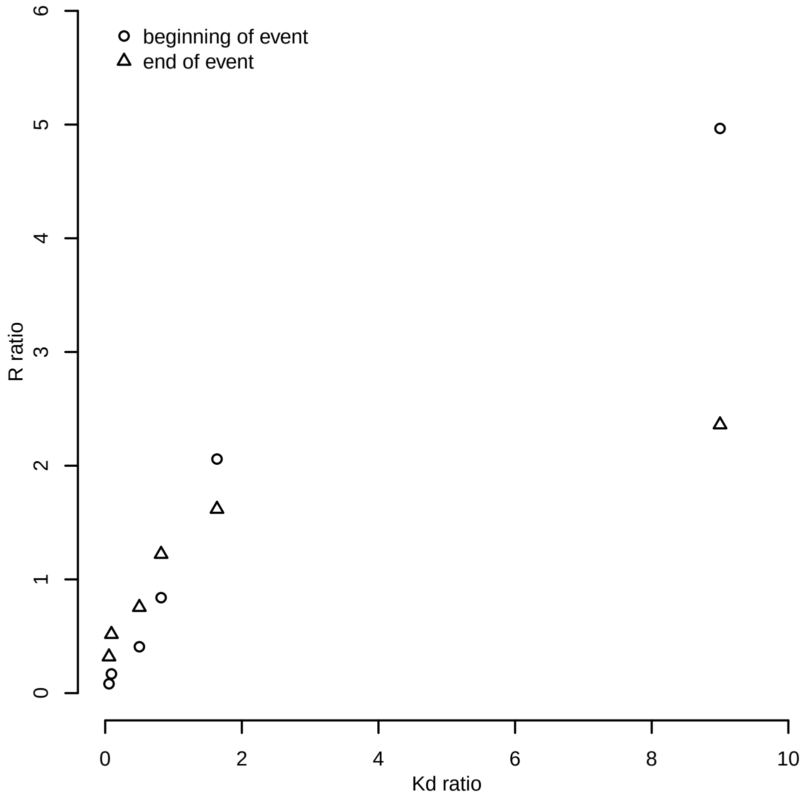

Fig. 7. Ratio of retention coefficients R of two substances plotted against the respective K_d ratio.

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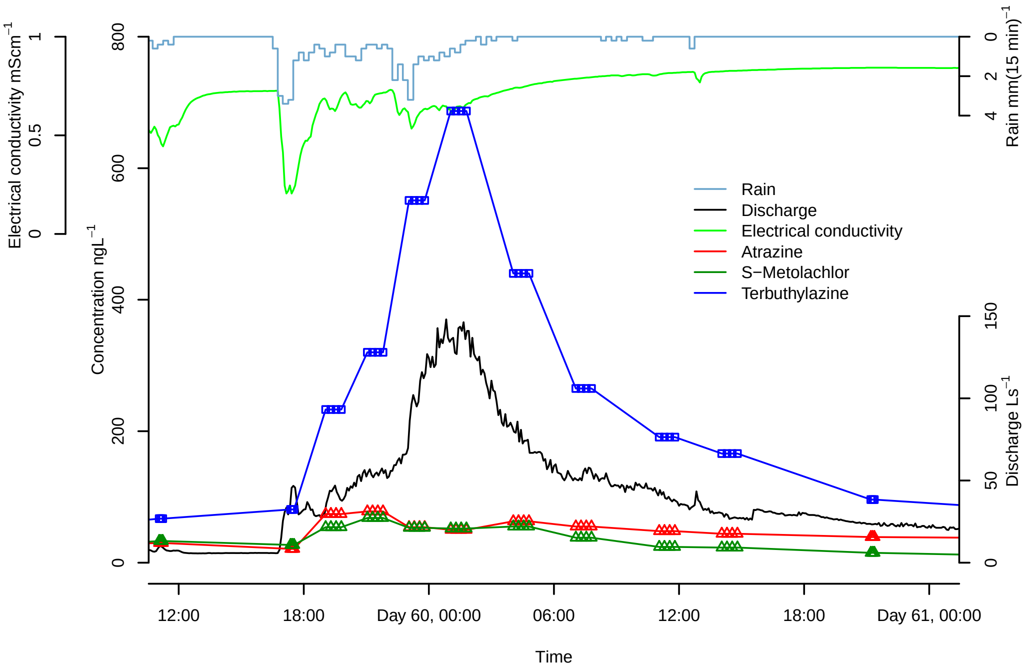

Fig. 8. Concentration dynamics of three substances at station S_d together with rain intensity, discharge, and electrical conductivity in the stream during event E13 (18 July 2009, 60 days after application). The symbols represent the sampling time of the individual sample aliquots (see Sect. 2.4).

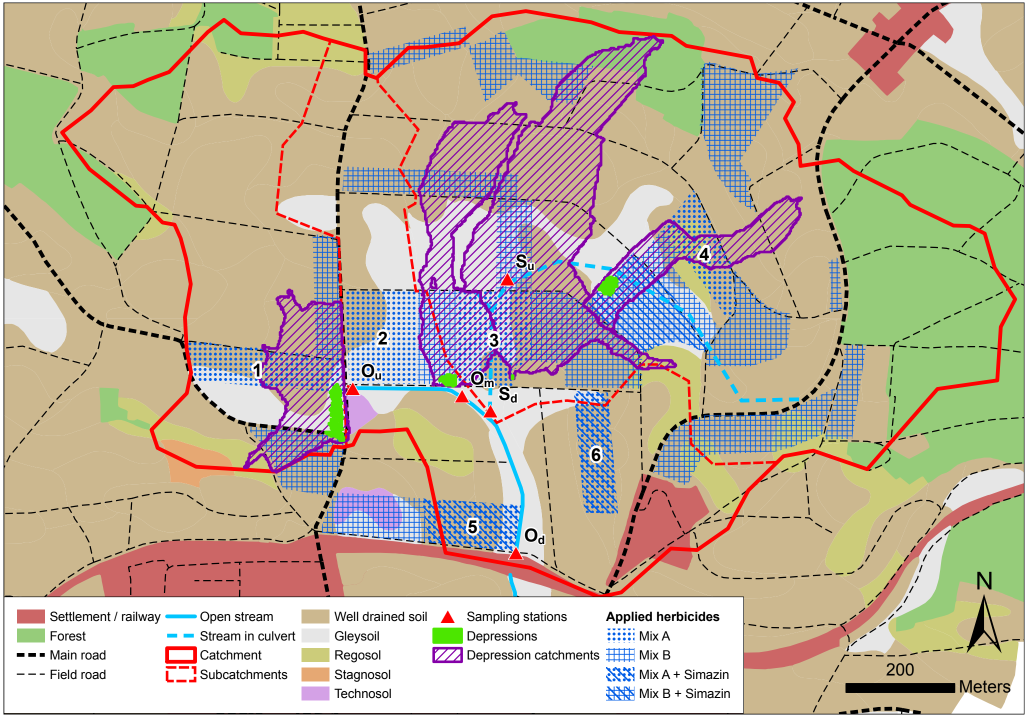

Fig. 9. Map of four major depressions and their corresponding topographic catchments together with the subcatchments of the sampling stations O_u and S_d. Sources: swisstopo (2008); FAL (1997).

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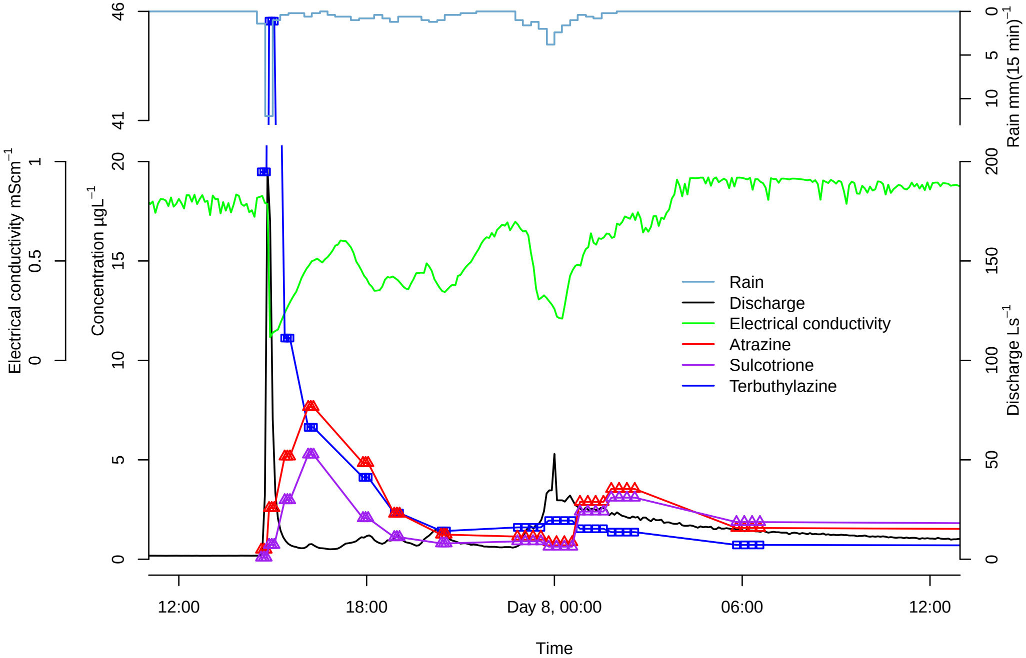

Fig. 10. Concentration dynamics of three substances at station S_d together with rain intensity, discharge, and electrical conductivity in the stream during event E2 (26 June 2009, seven days after application). The symbols represent the sampling time of the individual sample aliquots (see Sect. 2.4).

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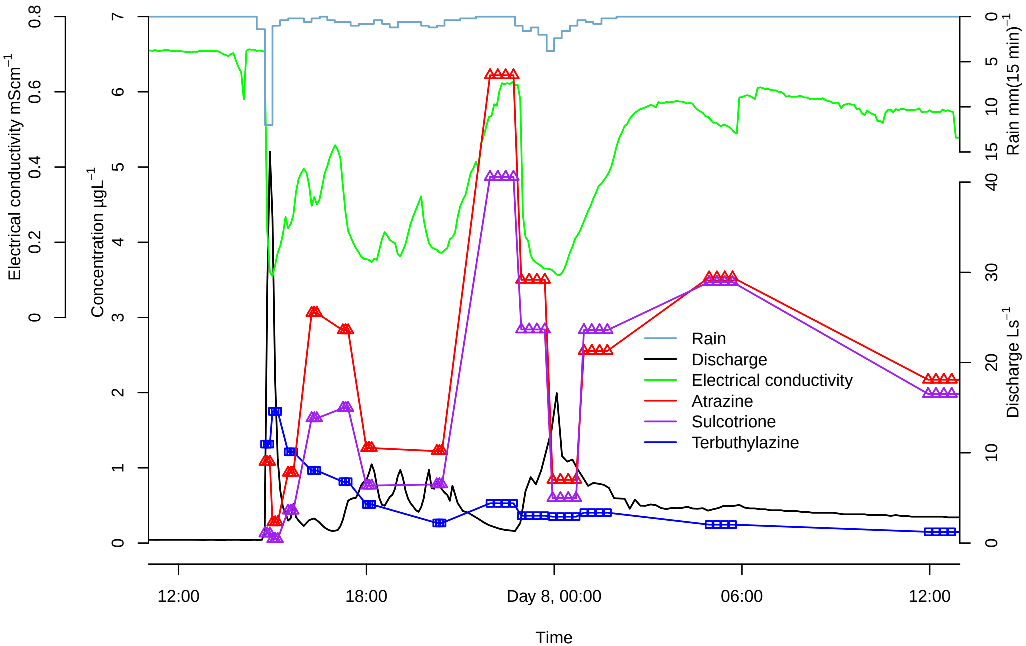

Fig. 11. Concentration dynamics of three substances at station O_u together with rain intensity, discharge, and electrical conductivity in the stream during event E2 (26 June 2009, seven days after application). The symbols represent the sampling time of the individual sample aliquots (see Sect. 2.4).

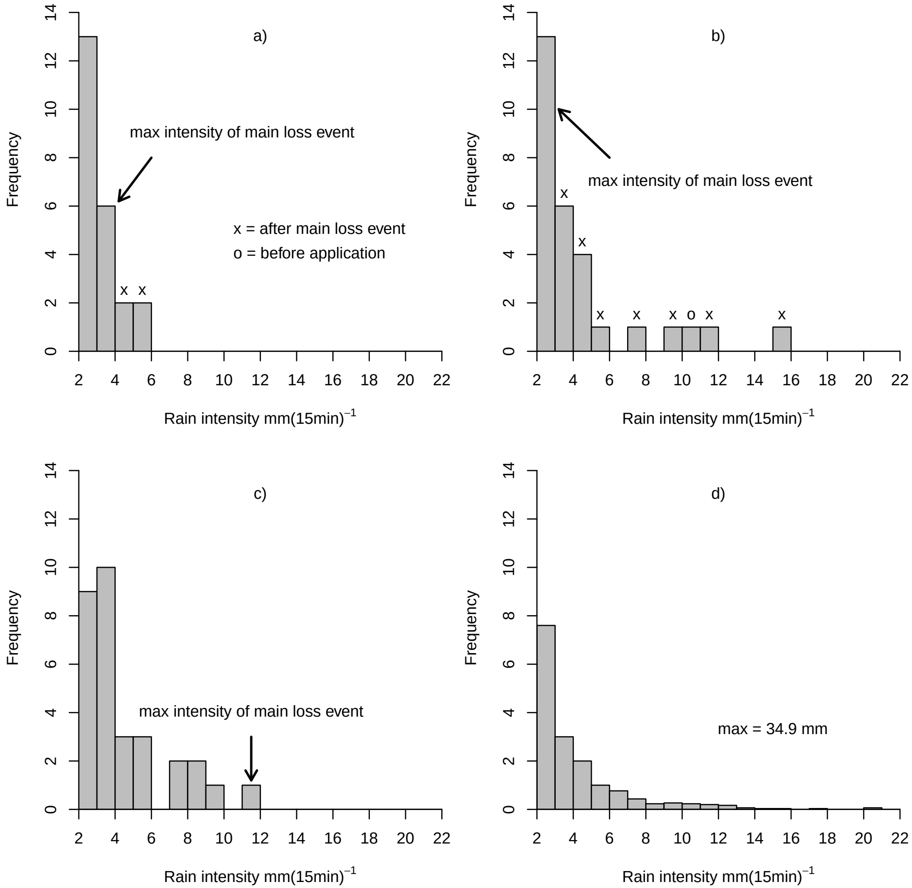

Fig. 12. Comparison of frequencies of rain intensities $> 2\,\text{mm}\,(15\,\text{min})^{-1}$ for the period May to July from **(a)** the field experiment in 2000 (Leu et al., 2004a), **(b)** the field experiment in 2003 (Gomides Freitas et al., 2008), **(c)** this field experiment and **(d)** the 30 yr average at the permanent meteo-station in Schaffhausen (Meteoschweiz, 2012).

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