Hydrol. Earth Syst. Sci. Discuss., 7, 2187–2220, 2010
www.hydrol-earth-syst-sci-discuss.net/7/2187/2010/

Hydrology and Earth System Sciences Discussions

This discussion paper is/has been under review for the journal Hydrology and Earth System Sciences (HESS). Please refer to the corresponding final paper in HESS if available.

Hydrochemical analysis of stream water in a tropical, mountainous headwater catchment in northern Thailand

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Received: 10 March 2010 – Accepted: 16 March 2010 – Published: 30 March 2010

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Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Land use in the vulnerable mountainous parts of the Mae Sa watershed, northern Thailand, has been changed from subsistence agriculture to market-driven production within the past decades. This change is reflected in an increased application of agrochemicals on agricultural areas to secure yields and control pests. Our study site is a steep and fast-responding headwater catchment (77 km^2), which transfers agrochemicals that might get lost from soils to waters quickly to the lowlands posing the risk of environmental contamination. This work describes the study, which has been carried out in a subcatchment (7 km^2) of the Mae Sa watershed to identify runoff generation processes and contributing flow paths to encircle potential flow paths of pesticides leaching from soil to surface water. We observed three events during the rainy seasons in 2007 and 2008, which were analysed on major ions and EC at high temporal resolution. Based on the samples a two-component hydrograph separation was carried out for three events. For two out of the three events a three-component hydrograph separation was performed to identify the contributions of baseflow, interflow and surface runoff. Baseflow remained the dominant flow fraction, but interflow outshined surface runoff in its amount. Interflow could be observed at the hillslope seeping from the soil in 2007, but not in 2008. We suggest, that interflow highly depends on a constant input of rainfall and requires a certain minimum amount of rainfall per season to be triggered and sustained. Former studies found that pesticides mainly get lost by interflow in this area. Hence, we can point out that pesticide leaching risk is particularly high after a certain amount of rainfall. Critical conditions are therefore mainly present, when the soil layers are close to saturation but not, when these layers are generated or degenerated.

1 Introduction

Land use in the vulnerable mountainous regions in northern Thailand has been intensified during the last decades due to increasing population pressure. Land use systems changed mainly from subsistence to market-oriented production. Fallow periods have been shortened or are completely omitted. Intensification is accompanied by an elevated amount of agrochemicals applied to increase and secure yields. This creates an increasing risk that agrochemicals appear in stream waters and leach to groundwater aquifers and contaminate the local environment. Recent studies in this area found pesticide residues in the breast milk of hilltribe women (Stuetz et al., 2000). Kruawal et al. (2004) point to water pollution as one of Thailand's most critical environmental issues.

Until now tropical regions are still among the most difficult and least understood in terms of their dominant hydrological processes (Montanari et al., 2008). Especially the summer-humid outer tropics (Weischet, 1991) – where our study site is located – suffer from lack of hydrological investigations. The bulk of runoff generation investigations has been carried out in humid temperate areas, with some surveys conducted under tropical conditions such as the Amazon basin (Elsenbeer, 2001) or the Malaysian archipelago (Negishi et al., 2007). The dominance of groundwater as main contributor to stormflows in temperate regions has been introduced by Sklash and Farvolden (1979) and has been consolidated by many other studies (e.g. Peters and Ratcliffe, 1998; Uhlenbrook and Hoeg, 2003). Some differences are expected when investigating runoff processes under tropical conditions (Bonell, 1993). Tropical areas often differ from temperate regions in soil physical properties (porosity, hydraulic conductivity), duration, amount and intensity of rainfall. The different weathering conditions of soils combined with a higher amount of rainfall and seasonal characteristics (drying and wetting of soils over the year) lead to other dominant runoff processes. Elsenbeer et al. (1995) confirmed the importance of overland flow under humid-tropical conditions in a small Amazonian watershed. The study found that overland flow occurs as return flow along hillslopes where soils are shallow. Subsequent investigations in the same region indicate that near-surface flow paths are important contributors to runoff generation but are difficult to separate into overland flow and pipeflow because they are coupled and overlap in response time (Elsenbeer and Vertessy, 2000). A review of Elsenbeer (2001) places more specific emphasis on near-surface and overland flow paths in Acrisol landscapes in tropical rain forests for runoff generation. However, the author recommended more field testing to strengthen this hypothesis. Dykes and Thornes (2000) state that overland flow is rare in undisturbed tropical forest (Borneo), but emphasize its occurrence likewise as return flow due to reduction of hydraulic conductivity with depth of soils on hillslopes. A more frequent and important occurrence of overland flow in our study region was shown by Ziegler et al. (2000) under disturbed conditions such as soil compaction along unpaved roads or foot paths versus agricultural areas. The authors observed Horton overland flow immediately after simulated rainfall on initially dry soils whereas agricultural areas required a high amount of rainfall to produce overland flow.

The importance of shallow groundwater and subsurface flow paths, such as preferential flow during stormflow, was shown by Negishi et al. (2007) in a study carried out in Peninsular Malaysia. Compared with the baseflow-dominant runoff generation of temperate areas Goller et al. (2005) found that two of three storm events in a tropical montane rain forest in Ecuador were dominated by event water. In addition, the temporal variability of stream flow generation over the seasons is more pronounced in tropical regions than in temperate areas. Chaves et al. (2008) identified different sources for overland flow in early and late wet season in their investigation area, the south-western Brazilian Amazon basin.

Numerous studies on losses of agrochemicals in temperate climates have been conducted (e.g. Müller et al., 2003; Freitas et al., 2008), but information of pesticide losses under tropical conditions is still lacking. The first study in northern Thailand (same research area as in this study) on losses of pesticides was carried out by Ciglasch et al. (2005). An important trigger for the present work was given by Kahl et al. (2007) and Kahl et al. (2008). The authors stated that the occurrence of preferential flow (interflow) is rather a function of rain amount and antecedent soil moisture than of rain intensity (Kahl et al., 2007). Furthermore the soil depth where interflow occurs changes in the course of the rainy season. Preferential interflow was found to be the main pathway for losses of pesticides to surface waters in the study area (Kahl et al., 2008). Pesticides applied on a hillslope were detected during periods of high rainfall mainly during the falling limb of the hydrograph or even shortly before peak flow. The authors interpreted this as a hint to a delayed runoff contributing process, which is the major flow path for pesticide losses to surface waters.

To extend their work to the regional scale and in order to better understand the transport and losses of agrochemicals to surface water and groundwater our work focuses on identifying and quantifying the dominant sources of runoff in a sub-watershed of the Mae Sa watershed. As investigations in such steep tropical terrains are rare (Dykes and Thornes, 2000), we want to contribute to a better understanding of these vulnerable areas. Activities in headwater catchments, especially in fast responding catchments, will have direct impacts on the lowlands. Revealing dominant flow paths and the transfer of solutes (i.e. pesticides) may help to improve the management of agrochemicals in the headwater areas and thereby reduce the risk of environmental contamination.

2 Materials and methods

2.1 Study area

The study area is a sub-catchment of the Mae Sa watershed (77 km^2), which is located 35 km northwest of Chiang Mai in northern Thailand. The catchment includes two gauged sub-catchments, the headwater (28 km^2) and the Mae Sa Noi sub-catchment (7 km^2). The latter one was the area of investigation and can be found on the southern boundary of the catchment (Fig. 1). The sub-catchment is a very narrow and steep V-shaped valley and the elevation ranges from 850 to 1560 m a.s.l. The creek shows mountainous characteristics with a rocky streambed and an average bed slope of 11%

over a length of 2.6 km. The soils are mainly Acrisols and Cambisols. They have a highly developed macro pore network. The Acrisols in the area can reach a soil thickness of up to 5 m and are mainly located in the lower areas. The Cambisols are usually located in the higher parts and on steeper slopes and may have a thickness of over 3 m (Schuler, 2008). The parent material is mainly granite and paragneiss.

The main natural vegetation type in Mae Sa Noi is secondary forest and bamboo along the river sides., The main agricultural products are vegetables (e.g. bell pepper, salad, cabbage) and tree crops such as *Mangifera indica* or *Litchi sinensis*. Scattered tree plantations include *Tectona grandis and Pinus spp*. The climate in the area is controlled by the monsoons with distinct rainy (May to October) and dry (November to April) seasons. The average annual rainfall is 1200 mm. The average annual air temperature is 21 °C.

2.2 Measurements

The sub-catchment Mae Sa Noi is equipped with a weather station, a rain gauge and a discharge gauge. Discharge is measured at a fixed flume in the sub-catchment using an Ultra Sonic Sensor (ISCO Flow module 710, USA) equipped with an automatic sampler (ISCO 6712 portable sampler, USA) to collect pesticide samples in a continuous mode. The stage-discharge relationship was calibrated by salt-dilution at several water levels. In Fig. 1 the location of the devices can be seen, which also shows the additional equipment for the whole catchment installed in the beginning of 2007. This includes an additional weather station, 13 rain gauges and 2 more discharge gauges with automatic samplers.

During September and October in 2007 and October 2008 event-based field measuring campaigns were carried out to investigate the runoff generation and to gather information on the flow path distribution in the Mae Sa Noi sub-catchment. In total, three events were sampled, which are named in following E1 to E3.

Due to high spatial variability of rainfall, the rain gauges closest to the discharge gauge and sampling points (MSN and MSM; Fig. 1) were at times not representative to capture the spatial variability of rainfall during the observed events. Therefore, stations outside the watershed boundary were included in the study (PNK, BMK, Fig. 1).

2.3 Sampling of the components

During the measurement campaigns samples of baseflow (water in the stream during periods without rainfall), interflow (water seeping out at the foothill between parent material and soil cover), surface runoff and rainfall were collected and measured.

Rainfall was collected and measured in a bulk collector. Buckets were emptied after each rainfall event and samples extracted immediately after or during rainfall events (daily or more often). Surface runoff was sampled using a simple construction involving a slope-parallel trench and a bucket collector at the end, where the grab samples were taken. These samples were collected at least once during an event.

The interflow component was sampled and collected at the foothill, where water drained out between soil and parent material. These samples were taken in varying intervals (approx. 5–20 min) during events and non-event periods, as long as this component was activated.

The baseflow component was determined by sampling stream water prior to events and during non-event episodes. During events samples were taken from the stream and measured in 5-min intervals. The analysis of major ions (Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Ca^{2+}, and Mg^{2+}) was carried out in the laboratory using an ion chromatograph. Prior analysis, water samples were filtered through 0.45 µm cellulose acetate filter paper (Whatman Inc., USA). All filtered samples were stored at 4 °C before ion analysis.

2.4 End-member mixing diagrams

Hydrochemical mixing diagrams (Burns et al., 2000) were used to identify and select suitable tracers for separating the three components. The assumption of this method is that the stream water is a mixture of water from sources within the catchment and that the components are chemically distinguishable. In the case of a three-component mixing model, the stream water sample concentrations should be bound by a triangle, which is defined by the end-members of each particular event. If samples are not well bound, the components are either non-conservative and/or non-representative.

2.5 Hydrograph separation

To partition the hydrograph into its flow components a two- and a three-component hydrograph separation was performed. The chemically based hydrograph separation relies on the principle of mixing where the equations of continuity and mass balance govern the quantity of tracer flow (Ogunkoya and Jenkins, 1993) as an example for a three-component separation:

$$Q_T = Q_{BF} + Q_{SF} + Q_{IF}$$
$$Q_T C_T = Q_{BF} C_{BF} + Q_{SF} C_{SF} + Q_{IF} C_{IF}$$

where Q_T, Q_{BF} and Q_{SF} and Q_{IF} (Q in $m^3 s^{-1}$) represent volumes of current stream flow, baseflow, surface runoff and interflow, respectively, and C_T, C_{BF}, C_{SF} and C_{IF} (C in $mg\,l^{-1}$ or $\mu S\,cm^{-1}$) are the corresponding concentrations of solutes or electrical conductivity. To separate (n) components ($n-1$) tracers are needed. Of course, the method is only applicable if the components are chemically distinguishable. The assumptions underlying this method are widely discussed in the literature (e.g. Sklash and Farvolden, 1979).

3 Results

3.1 General hydrological conditions

The major peak of rainfall in 2007 in the investigation area (MSN and MSM) was recorded in May, whereas the major peak in 2008 occurred in September. The average annual rainfall measured at both stations was 1503 mm a^{-1} in 2007 and 1272 mm a^{-1} in 2008. The amount of rainy days in 2007 was 178 for MSM and 157 for MSN. In 2008 it was 161 for MSM and 152 for MSN. The maximum daily amount of rainfall in 2007 was recorded at MSM (60.4 mm day^{-1}, 15 September 2007; MSN: 59.2 mm day^{-1}, same day). In 2008, the daily maximum was recorded at MSN (46.7 mm day^{-1}, 3 May 2008; MSM: 44.9 mm day^{-1}, 9 June 2008). At the beginning of the event-based sampling in 2007 the total rainfall input was 1284 mm. At 9 October 2007 the measured rainfall was 1327 mm.

In the second year the rainfall input until 9 October was lower (1069 mm).

The annual discharge at Mae Sa Noi was thus higher in 2007 (720 mm a^{-1}) than in 2008 (490 mm a^{-1}). The runoff-rainfall ratio was 0.47 and 0.38 in 2007 and 2008, respectively. The monthly ratio was 0.3 (September 2007), 0.5 (October 2007) and 0.3 (October 2008). The daily average discharge in 2007 was 0.16 $m^3 s^{-1}$ and 0.1 $m^3 s^{-1}$ in 2008. Evapotranspiration is, based on a simple water balance approach, given with 783 mm a^{-1} for 2007 and with 782 mm a^{-1} almost the same amount for 2008.

3.2 Event-based measurements

The hydrological conditions of the stream and the average rainfall a few days prior, during and after the measured events are depicted in Fig. 2. The average rainfall recorded at the station MSN and MSM and at BKM and PNK, respectively, are plotted in Fig. 2 as well, to show the spatial variability. Event E1 (28 September 2007) had a minor peak in discharge before the measurements were started. E2 (9 October 2007) also shows a minor peak in advance, but which was much lower than the one of E1. E3 (9 October 2008) is an isolated peak and the only one recorded on that day.

During E1 rainfall was recorded at stations PNK and BMK but not at the stations MSN and MSM. Therefore, the rainfall data of PNK and BMK was used. The rainfall had a low measured intensity with a total amount of 6.9 mm in 50 min. Initial discharge for E1 was 0.2 $m^3 s^{-1}$. Discharge peaked to 0.4 $m^3 s^{-1}$ within 20 min. The response time to rainfall was 80 min and initial discharge was reached again after 350 min (Fig. 3). The maximum peak flow reached in September was 3.4 $m^3 s^{-1}$. Electrical conductivity decreased from 120 $\mu S cm^{-1}$ to 85 $\mu S cm^{-1}$ (Fig. 3a). The initial value was not reached again during the sampling period.

Major anions showed similar dynamics. The drop of silica and the peaks of NO_3^- and Cl^- prior the event were probably caused by an earlier event. A clear drop in the concentration of SO_4^{2-}, Cl^- and silica coincided with the rise of the hydrograph. The concentration of Cl^- dropped by 0.5 $mg l^{-1}$. Both concentrations fluctuated in a range of 1 $mg l^{-1}$. At the same time, silica concentration dropped from 19.5 $mg l^{-1}$ to 17 $mg l^{-1}$.

The concentration of Ca^{2+} is the highest one measured (22 $mg l^{-1}$) in the beginning of the event. It shows a clear drop in concentration (12 $mg l^{-1}$) when the hydrograph increased. The concentration slowly increased again with the falling limb. Where Na^+ almost does not react to flow dynamics. Mg^{2+} and K^+ show similar patterns. A rise in the beginning of the peakflow is followed by a quick drop by 4 $mg l^{-1}$. Pre-peakflow values were reached again after 20 min.

E2 was measured a few days later, on 9 October 2007. Total rainfall (Fig. 4a) was 17.2 mm in 40 min recorded at the stations BMK and PNK, with the major rainfall peak recorded at PNK.

The discharge of E2 peaked after 60 min of rainfall. Within 30 min it increased from a baseflow volume of 0.1 $m^3 s^{-1}$ to 0.4 $m^3 s^{-1}$. The first 50 min of the recession limb show a somewhat noisy behavior before the hydrograph passes over into a smoother outflow and reaches initial baseflow again after 270 min (Fig. 4c).

EC (Fig. 4a) dropped from 145 $\mu S cm^{-1}$ to 92 $\mu S cm^{-1}$ in 10 min, slowly rising again during the falling limb of the hydrograph. The concentration of the chloride and silica concentrations in the stream are shown in Fig. 4b. Chloride concentration increased from a stable pre-event concentration to 2.6 $mg l^{-1}$. Silica concentration reacted differently; it decreased from an initial concentration of 20 $mg l^{-1}$ to 16 $mg l^{-1}$.

The dynamics of the major cations are shown in Fig. 4c. The same pattern – a drop in concentration with the beginning of the peak flow – can be seen for all measured ions. The sharpest drop was recorded for Ca^{2+}, the lowest for Na^{+}. The decrease of the concentrations changes when a change in the behavior of the recession limb occured. For all ions concentrations increased again – most significantly for K^{+} (10 mg l^{-1}). The patterns of Cl^{-} and K^{+} are similar considering the time of peak concentration and duration. All major cations and Cl^{-} reach the initial concentration along the recession limb while silica does not.

During both events in 2007 interflow seeped out between soil cover and bedrock and could be sampled close to the river bank. In the third event in October 2008 this component was not activated and could therefore not be sampled directly.

Concentrations of the surface runoff water varied much more than those of interflow samples (Table 1). As surface runoff is directly influenced by rainfall its variability is dominated by the variability of rainfall concentrations. Interflow concentrations are buffered much more strongly. Silica concentrations in the interflow water showed a high variability between samples taken during rainy days (7.5±1.1 mg l^{-1}) and samples taken on non-rainy days (19.4±0.9 mg l^{-1}). The lower concentrations on rainy days may have occurred due to dilution by quickly infiltrating rainfall water.

The third event, E3, was sampled on 9 October 2008 (Fig. 5). In 2008, the second peak of the bimodal rainfall distribution (first peak in May) was shifted towards the end of October. Rainfall initiating E3 occurred close to the discharge gauge (stations MSM and MSN) with a total amount of 2.2 mm in 70 min. There was no rainfall recorded at the other stations (PNK and BMK) which points at the high variability and local occurrence of rainfall in that region. In fact, rainfall causing the peak must have been much higher than 2.2 mm in 70 min. The maximum peak flow appeared at the end of the month and reached 4 $m^{3} s^{-1}$. Seventy minutes after rainfall input discharge peaked beginning from a flow volume of 0.2 $m^{3} s^{-1}$ within 30 min to 0.8 $m^{3} s^{-1}$. The initial baseflow volume was reached again after 180 min. EC values dropped from 115 $\mu S cm^{-1}$ to 82 $\mu S cm^{-1}$ and increased quickly again after the discharge peak.

Compared with E1 and E2, the hydrograph of E3 shows a quicker throughflow and also a shorter falling limb, which suggests a higher influence of fast flow components such as surface runoff and shallow subsurface flow. The recession limb was also rather smooth compared to E1 and E2.

3.3 End-member mixing diagrams

The relation of discharge volume to silica concentration and EC values during the hydrograph is shown in Fig. 6. The circular behavior during the rising and falling limb is clearer for E1. However, initial values are reached again with similar discharge volumes. The mixing diagrams were generated for E1 and E2 based on EC and silica to check whether the components are chosen representatively and are applicable for a three-component hydrograph separation (Fig. 7).

The components are represented by interflow, which has been sampled on rainy days (IFR) and on non-rainy days (IFNR), as well as surface runoff (SF) and baseflow (BF). The triangles in each graph indicate the range given by the average concentration of the end members and represent the range within which the stream water concentration should be bound in. If the stream water concentration is bound well by the triangle, the components were chosen representatively. If not, the stream water is mixing with another component and the selected component is not representative.

The silica concentration in interflow differs between samples taken during rainfall days (IFR) and non-rainfall (IFNR) days. In Fig. 7 the different boundaries of the hydrochemical triangles are owed to variability of the interflow component and are indicated by triangles with solid lines (IFR) and dashed lines (IFNR). Based on the rainy-day interflow component the stream water concentrations for E2 (Fig. 7b) are bound better than based on the non-rainy interflow component. In Fig. 7a the stream water concentration is well bound in the triangle based on IFR component but not at all bound where based on the IFNR component. The different magnitudes of rainfall input (E2: 17.2 mm; E1: 6.9 mm) could explain this finding.

3.4 Hydrograph separation

A two-component hydrograph separation was carried out for all three events. As described in the section above (Event-based measurements, Figs. 3 and 4) the characteristic ions were not significantly different, so they could not be used as end-member signature. However, for all three events a two-component hydrograph separation based on EC values was possible. An additional three-component hydrograph separation was calculated for E1 and E2 based on silica concentrations and EC values. To compare the results of E1 and E2 with E3, the two-component separations for E1 and E2 were calculated in different ways. Firstly, based on the interflow end-member and additionally based on surface the runoff end-member.

For each event baseflow was always used as end-member, but interflow and surface runoff are applied in a changing mode (Table 2). The end-members chosen for the two-component hydrograph separation for E1 are interflow (28.2 $\mu S\,cm^{-1}$) and baseflow (140.0 $\mu S\,cm^{-1}$) on the one hand. On the other hand a comparative separation was calculated based on the end-members of surface runoff (36.4 $\mu S\,cm^{-1}$) and baseflow (140.0 $\mu S\,cm^{-1}$) (Table 2). The end-members for E2 were slightly in concentrations, 29.9 $\mu S\,cm^{-1}$ for interflow and 41.7 $\mu S\,cm^{-1}$ for surface runoff. Baseflow as end-member remained the same (140.0 $\mu S\,cm^{-1}$) as in E1. The end-members for E3 were different because interflow was not activated, therefore the separation was calculated based on surface runoff (43.9 $\mu S\,cm^{-1}$) and baseflow (139 $\mu S\,cm^{-1}$) as end-members. The average EC of rainfall is given with 13 $\mu S\,cm^{-1}$ but was not considered a significant component. In 2007, both events calculated with EC were clearly dominated by the baseflow component (Table 2), no matter whether interflow or surface runoff was chosen as end-member. The same trend was found based on silica concentrations, but resulted in somewhat different fractions (Table 2). The event in September 2007 based on the calculations on interflow as end-member and EC shows a proportion of 62% of baseflow and 38% of event water. The event water for E1 and E2 was given by the interflow concentration but tests showed that applying surface runoff as end-member resulted also in a baseflow dominance (Table 2).

To see the difference in the fractions of flow components for E2 and E3 a comparative separation based on surface runoff as end-member was carried out. Interflow could not be applied as end-member for E3, because it was not activated and could not be sampled. The results are shown in Fig. 8 and listed in Table 2. The rainfall per event is given in Fig. 8a and d. EC values for each event are plotted in Fig. 8b and e. The results for E2, based on surface runoff, show a higher calculated fraction of baseflow compared to the separation based on interflow concentration.

The separation of E2 (77% baseflow and 23% surface runoff, Table 2) shows an immediate appearance of the event-triggered component with the rising peak and a fast reduction of this component. The fraction of baseflow appears in a double peak which can also be seen in the EC values (Fig. 8b) and in the hydrograph (Fig. 8c).

There is no unsteady behavior in the falling limb and also not in the fractions shown in Fig. 8f. The peaks of baseflow and surface runoff do nearly appear at the same time but are different in their dynamics. The EC values measured during the falling limb show a clear and undisturbed recession (Fig. 8b).

Based on the silica concentration and EC measurements collected during E1 and E2 a three-component hydrograph separation was carried out. As indicated by the hydrochemical mixing diagrams (Fig. 7) E1 is based on end-members BF, SF and IFNR. For E2 the same end-members, BF and SF were applied, but as suggested by the mixing diagram, IFR was chosen.

The results of the separation are displayed in Fig. 9. E1 (Fig. 9a) was mainly composed of baseflow (62%) and interflow (36%), while the fraction of surface runoff (2%) was minor. The baseflow peak appears with the peak of the hydrograph. Interflow peaked 100 min after the rainfall peak, when the recession limb of the hydrograph shows a small shoulder. Surface runoff shows a peak shortly after beginning of rainfall, the peak of interflow appears simultaneously.

Baseflow was also the dominating component of E2 (67%) (Fig. 9b). The peak is more expressed than it was during E1 and appears at the same time as the peak in the hydrograph. The pronounced shoulder of the recession limb represents baseflow and to a smaller part interflow and surface runoff.

Compared with the baseflow peak interflow (20%) is delayed and it occurs 90 min after the beginning of rainfall and drops back to almost zero, again with the falling limb. Surface runoff (13%) shows a peak 150 min after rainfall input and at the same time when the second minor peak (shoulder) in the hydrograph is recorded. During E1 the interflow exceeds the baseflow component shortly, but not during E2. Along the recession limb the surface runoff fraction is temporally higher than the interflow fraction, but none of the two components exceeds the baseflow volume.

4 Discussion

A significant difference in amount and temporal distribution of rainfall in the sub-catchment Mae Sa Noi for both years could be observed. The lower rainfall in October 2008 compared to October 2007 was obviously the cause for the fact that there was no interflow witnessed at the hillfoot of the research site. The fact that interflow was activated in 2007 suggests soil layers that are close to saturation and hence a highly connected network of soil pores and macropores (biogenic pores formed by detritivores, e.g. termites). Observations of a soil profile in the same sub-catchment by Kahl et al. (2007) showed, that macropores can be found down to a depth of 90 cm. The areal density of macropores is 30% in 15 to 30 cm depth and 5 to 10% in 60 to 90 cm depth.

The establishment and occurrence of interflow over the rainy season and its dependence on rainfall input has also been reported by Kahl et al. (2007). They state that the amount of rainfall and therefore antecedent soil moisture affects the amount of interflow. Furthermore, it controls the location of interflow, whether it takes place in the topsoil or subsoil. Similar results were found by Dykes and Thornes (2000) using tensiometer measurements on Acrisol hillslopes in a catchment in Brunei. They also state the strong seasonality of hillslope hydrological conditions (saturation of soils and therefore activation of interflow) and its effect on runoff generation. The threshold value of rainfall input, which is necessary to bring soils to a state close to saturation during the study period was about 1000 mm a^{-1}. If the rainfall amount was below that threshold, interflow could not be witnessed at the foot of the hillslope. The spatio-temporal distribution of rainfall over the hillslope and the catchment seems to be an important factor as well. The data recorded for E3 suggest, that the rainfall event was a very local downpour, because it was only recorded at the two closest stations (MSN and MSM, Fig. 1) and the amount of measured rainfall was very likely underestimated (2.2 mm). The abrupt peak of E3 and its rapid throughflow (180 min) compared to the slower E1 (270 min) and E2 (350 min) indicates a higher influence of fast flow components on runoff generation, as well as the fact, that baseflow after the peak almost drops to the same volume as before. This supports the assumption of lower ground water tables and therefore a lower buffering capacity of the system in terms of stream flow sustaining runoff sources. We found that E3 results in the highest amount of event-triggered runoff component (41% surface-runoff component) of all three events. An isotope-based two-component separation in a tropical montane forest in Ecuador by Goller et al. (2005) showed that event water fractions (rain water) on storm runoff can be higher than 44%. As the interflow drainage could not be observed in 2008, we conclude that the event-water runoff was most likely generated by Horton overland flow. In the same region, Ziegler et al. (2000) observed Horton overland flow on agricultural fields after rainfall simulations on initially dry soils. However, they state that it is a rare event on such surfaces and still has to be investigated in more detail.

A dilution of Silica concentration in stream water as observed during E1 and E2 has been reported by other studies, in temperate regions (Hoeg et al., 2000) and particularly in the tropics (Elsenbeer et al., 1994). Silica concentration in rain water could not be measured, but was analyzed in a study in Malaysia by Negishi et al. (2007) and was below 1 mg l^{-1}. We assume that the value is similar at our study site.

The decrease of silica concentration in stream water of E2 during the event implies a dilution by a component with much lower silica concentration, such as rainfall and surface runoff. The rainfall recorded for E2 (17.2 mm 40 min^{-1}) was higher than for E1 (6.9 mm 50 min^{-1}), which explains the stronger dilution of stream flow concentration. The three-component hydrograph separation results in a 10 times higher amount of surface runoff during E2 (20%) as compared to E1 (2%). The increase of the K^+ concentration during E2 occurred with a change in the recession of the hydrograph. In general K^+ is considered an indicator of fast shallow subsurface flow components and overland flow in the tropics (Elsenbeer et al., 1994; Kinner and Stallard, 2004) and other areas.

The importance of temporal rainfall distribution mentioned earlier is confirmed by the differences in temporal rainfall patterns of E1 and E2 during the 10 days before events E1 and E2. Before E1, at 6 out of 10 days rainfall was observed. Before E2, 8 out of 10 days had rainfall, but no rainfall was recorded the day before E2. Rainfall was also not recorded in 2008 the day before E3 was measured. Based on the assumption that the unsteady refilling of soil pores (soil pipes and macropores) by infiltrating rainfall – and therefore their depletion – forces flow paths to switch to different, more shallow soil layers where soil water probably gets mixed with surface runoff and newly infiltrated rainwater. This could explain the lower Silica concentration of stream water. The importance of the saturated zone contribution to run-off generation and its dependence on a steady refill of the soils was also found by Wickel et al. (2008) in a study in Brazil. They conjecture a reduction of the influence of saturated zones while the soil is depleted and not refilled. Combining these findings with the results of the three-component separation the higher surface runoff in E2 is propably mainly due to higher rainfall input and the missing rainfall input during the day before. Soil pipes start to drain first, if not permanently refilled. Hence, their influence on runoff generation via interflow contribution is reduced first as well. A switch of interflow between different soil layers depending on rainfall input has also been reported by Kahl et al. (2007) at the same study site. The importance of soil pipes (biogenic soil pipes) and macropores for such fast flow components (shallow subsurface flow and overland flow) has been emphasized by Elsenbeer and Vertessy (2000). They suggest that it is not possible to differentiate between overland flow and subsurface stormflow and introduce the term of near-surface-flowpaths.

Even though surface runoff has been stated to be the most important pathway for pesticide losses (e.g. Schriever et al., 2007), we conclude that interflow plays a very important role as well – particularly at our study site. Pesticide leaching via matrix flow has been found not to be as important as the flow through macropores and soil pipes (Kahl et al., 2007). Pesticide peaks during discharge peaks in the stream in our study site observed by Kahl et al. (2008) were short (<6 h), which is congruent with the results from the hydrograph separation: interflow peaks appear delayed to the discharge peak. Surface runoff is most likely involved in pesticide transport as well, as it also appears delayed to discharge peak. The pesticide peaks which occur prior to the peak flow (Kahl et al., 2008) can not be explained well by our newly gained information, but it is most likely connected with a refill-release function of water in the soil pipes and macropores along the hillslope. On the other hand, the delayed pesticide peaks can be explained very well. Pesticide peaks measured along the recession limb can only be due to interflow dynamics revealed by the hydrograph separation. However, this will only be the case as long as soils are close to saturation. The fact that pesticides applied to the hillslope by Kahl et al. (2008) were recovered in the topsoil supports a transfer of pesticides to the stream by interflow as well.

Afore-mentioned facts lead to two different conceptual hillslope runoff models (Fig. 10). Figure 10a shows the hillslope model at times with low rainfall input (about 1000 mm a^{-1}) and therefore unsaturated conditions. Low rainfall input implies lower soil moisture and hence, a soil matrix in which pores are not well connected and flow rates through soil matrix are slow. Infiltrating water contributes to soil water and indirectly later on to runoff. Based on the observation that no interflow occurred at the hillfoot in the year 2008, we conclude that the observed overland flow during E3 is Horton overland flow rather then saturation excess overland flow or return flow. Figure 10b shows the system with a fully saturated zone during periods as in 2007. Evidence for the saturated zone is given by a constantly leaking interflow layer during the sampling period in 2007. A quick transfer of water by interflow is supported by very similar EC values measured for rainfall (13 µS cm^{-1} in average), surface runoff (45 µS cm^{-1} in average) and interflow (28 µS cm^{-1}). Surface runoff occurring in that state of the system is most likely a mixture of saturation excess overland flow, return flow and Horton overland flow. However, the dominance of baseflow in E1 and E2 under saturated conditions can be explained by the temporal storage of water along the hillslope combined with a stepwise release at the foothill. A similar finding by Kim et al. (2005) shows that the deeper the water percolates into the saturated zone – which is given for E1 and E2 – the more water is released at the foothill. Due to a high degree of saturation along the hillslope a functional and well-connected network of soil pores can be expected and facilitates a high percolation rate from the surface to deeper soil layers.

5 Conclusion

The application of the three-component hydrograph separation shows, that interflow plays a significant role in the runoff generation at the test site. It depends on a certain amount of rainfall (observed threshold about 1000 mm a^{-1}) and its continuity which allows the shallow saturated zone in the hillslope to be developed and trigger interflow in certain soil layers. Linking our results with the findings of Kahl et al. (2008), who are pointing at lateral preferential flow (interflow) as a major pathway for the observed loss of pesticides to the stream, we conclude that the risk of leaching is higher while the system is under high moisture or saturated conditions. As we could identify the different fractions of interflow during two events we expect the losses of pesticides during generation and degeneration of the saturated zone to be lower than in a mid-season period. The surface runoff components which are formed by return flow and saturation excess might have a similar potential for losses of pesticides as interflow. Horton overland flow in the beginning of the rainy season poses a higher risk of pesticide losses to stream (wash-off effect) than later in the rainy season, because on the one hand pesticides have decayed and, on the other hand, the pesticide residues are most likely already washed off the surfaces. We learned that the runoff generating components change in their priority and dominance in the course of the season and are highly dependent on the state of soil moisture and its prior-event conditions, such as prior rainfall events, amount of rainfall, offset between rainfall events etc. However, we suggest a more detailed investigation of how the saturated zone is established and the subsurface flow processes, especially in terms of threshold values of annual water balance and the spatial variability of rainfall. Observations of groundwater chemistry and groundwater tables during the course of the rainy season will yield more detailed information on the contribution and distribution of runoff components and thereby the potential sources of pesticides losses.

Acknowledgements. We thank Ittipon Sodsaard and Mai Tanarumgruang for their indispensable help during the data collection in the field and for assisting in the lab. This research was funded by the Deutsche Forschungsgemeinschaft (German Research Foundation) and was a part of the Special Research Program (SFB) 564.

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Table 1. Mean concentration and standard deviation of water samples of interflow, surface runoff and rainfall taken during September and October 2007.

	Interflow	Surface runoff	Rainfall
	Mean±standard deviation		
EC [µS cm^{-1}]	29.35±1.04	37.95±23.21	9.48±5.88
Silica [mg l^{-1}]	14.64±6.18	11.84±0.88	n.a.
Cl^- [mg l^{-1}]	0.07±0.03	0.97±0.78	0.42±0.47
NO_3^- [mg l^{-1}]	3.39±0.94	5.29±3.29	0.69±0.37
SO_4^{2-} [mg l^{-1}]	0.13±0.02	2.29±1.54	0.83±0.72
Na^+ [mg l^{-1}]	4.62±0.79	0.27±0.19	0.29±0.34
NH_4^+ [mg l^{-1}]	n.d.	5.52±3.17	0.72±0.23
K^+ [mg l^{-1}]	1.72±0.27	7.62±3.47	0.39±0.24
Ca^{2+} [mg l^{-1}]	1.20±0.31	1.55±0.8	0.52±0.28
Mg^{2+} [mg l^{-1}]	0.16±0.02	0.63±0.37	0.12±0.04

n.a.: not available; n.d.: not detected

Table 2. Runoff components of events E1, E2 and E3, determined by a two-component analysis based on either silica concentration or electrical conductivity.

	Silica concentration		Electrical conductivity	
	Surface runoff (%)	Interflow (%)	Surface runoff (%)	Interflow (%)
E1	19	35	29	38
E2	20	33	23	24
E3	–	–	41	–

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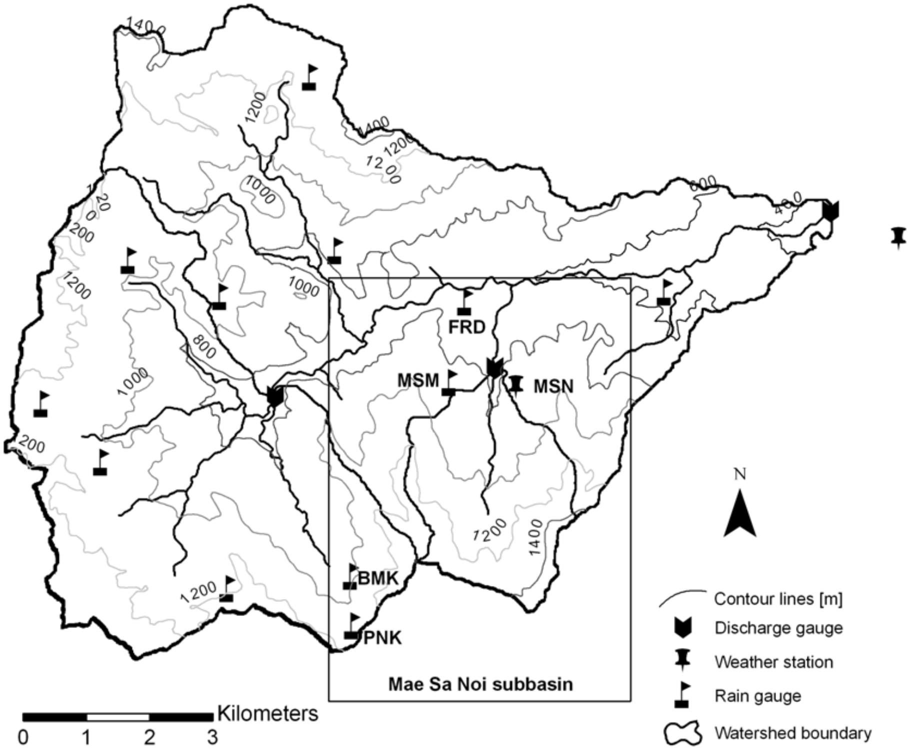

Fig. 1. Mae Sa watershed and Mae Sa Noi sub-catchment with measurement devices (FRD, MSM, MSN, BMK and PNK are representative rain gauges for the sub-catchment Mae Sa Noi).

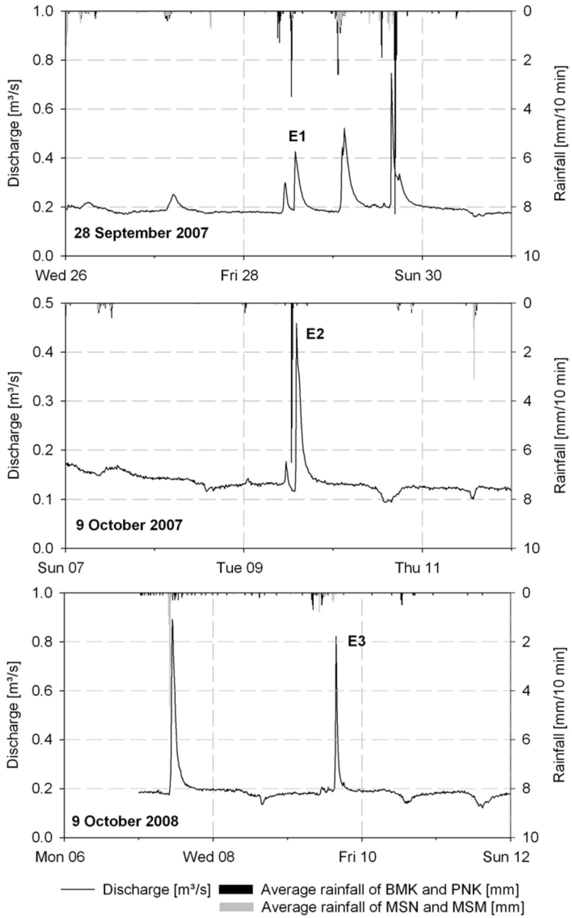

Fig. 2. Discharge and rainfall measured two days before, after and during the evaluated events (E1, E2 and E3). Rainfall is given as average of the closest stations (MSN, MSM, BMK or/and PNK).

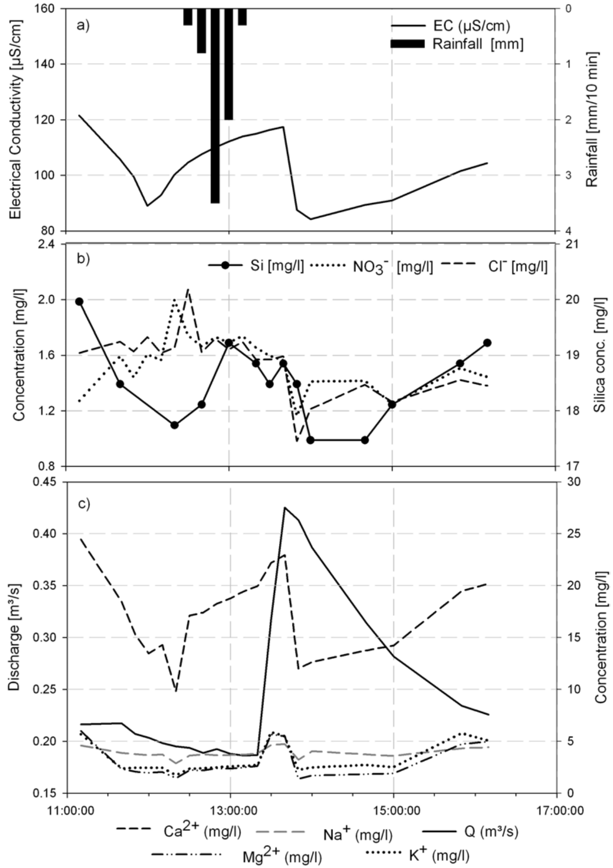

Fig. 3. Event on 28 September 2007 (E1) showing EC values, silica and ion concentrations, discharge and rainfall.

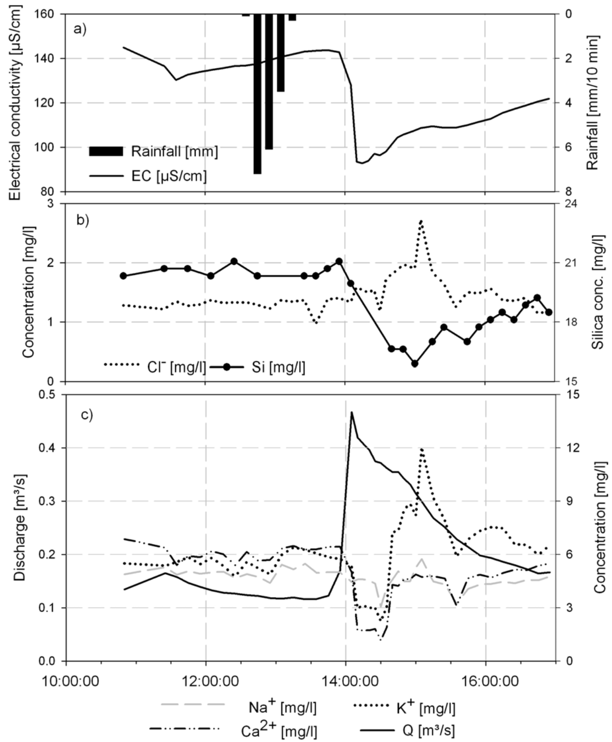

Fig. 4. Event on 9 October 2007 (E2) showing EC values, silica and ion concentrations, discharge and rainfall.

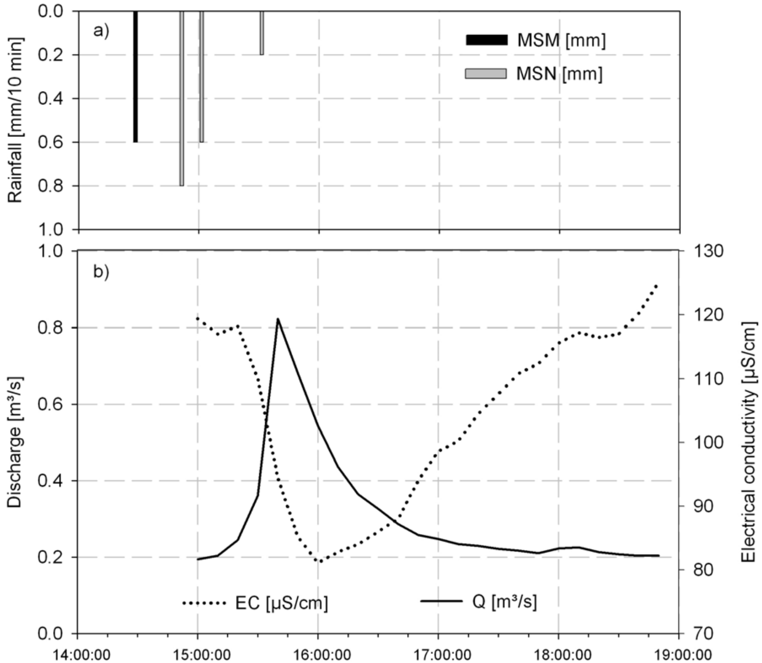

Fig. 5. Event on 9 October 2008 (E3) showing EC values, discharge and rainfall. Rainfall was recorded at Mae Sa Mai (MSM) and Mae Sa Noi (MSN), respectively.

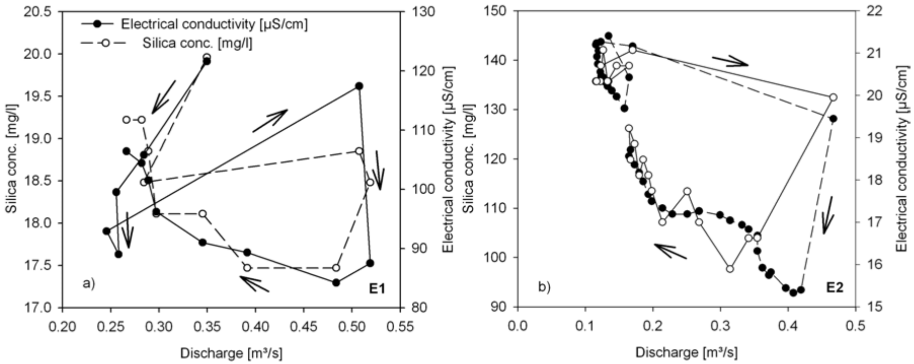

Fig. 6. Silica concentration and electrical conductivity during **(a)** 28 September 2007 (E1) and **(b)** 9 October 2007 (E2). Arrows indicate the course of time.

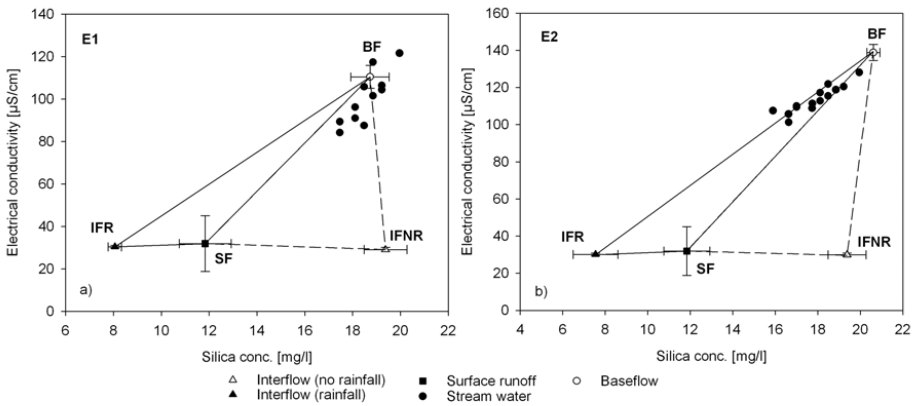

Fig. 7. Hydrochemical mixing diagrams for **(a)** 28 September 2007 (E1) and **(b)** 9 October 2007 (E2) based on end-members of interflow (IFR, IFNR), baseflow (BF), surface runoff (SF). The concentration of silica in the interflow components varies between rainy (IFR) and non-rainy sampling days (IFNR). Bars indicate standard deviation.

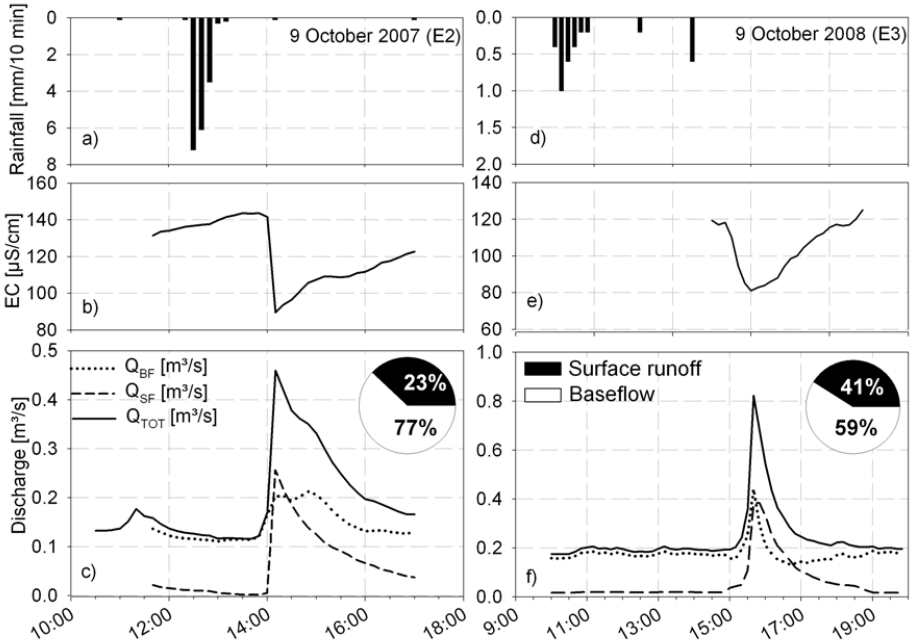

Fig. 8. Results of the two-component hydrograph separation for 9 October 2007 (E2) and 9 October 2008 (E3) based on surface runoff measurements. (Q_{TOT}: total discharge; Q_{SF}: surface runoff component, Q_{BF}: baseflow component).

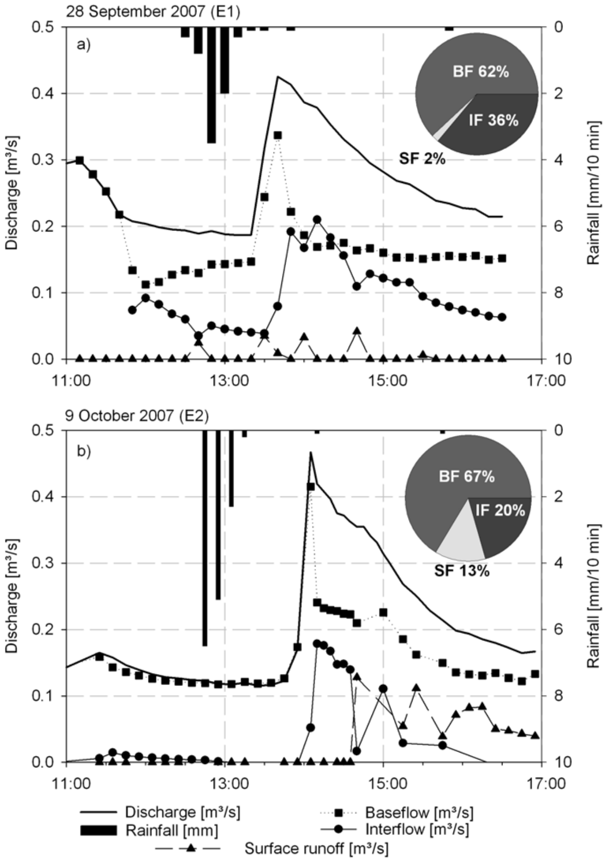

Fig. 9. Three component hydrograph separation for E1 (September 2007) and E2 (October 2007) showing fractions of baseflow (BF), interflow (IF) and surface runoff (SF) based on silica concentration and EC measurement.

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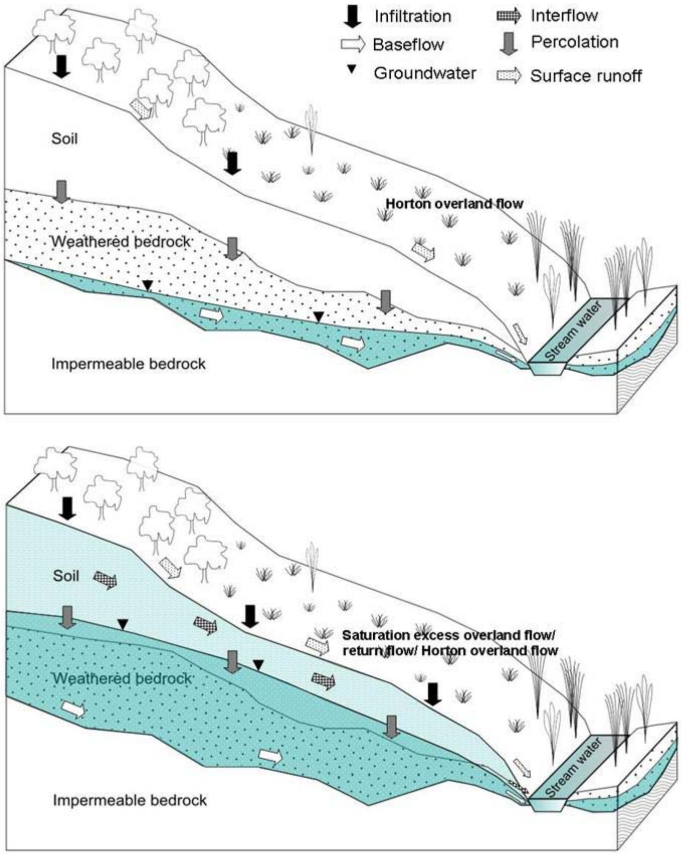

Fig. 10. Conceptual model of runoff generation at Mae Sa Noi hillslope during saturated and unsaturated conditions.