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A three-component hydrograph separation based on geochemical tracers in a tropical mountainous headwater catchment in northern Thailand

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Abstract. Land-use change in the mountainous parts of northern Thailand is reflected by an increased application of agrochemicals, which may be lost to surface and groundwater. The close relation between flow paths and contaminant transport within hydrological systems requires recognizing and understanding the dominant hydrological processes. To date, the vast majority of studies on runoff generation have been conducted in temperate regions. Tropical regions suffer from a general lack of data, and little is known about runoff generation processes. To fill this knowledge gap, a three-component hydrograph separation based on geochemical tracers was carried out in a steep, remote and monsoon-dominated study site (7 km^2) in northern Thailand. Silica and electrical conductivity (EC) were identified as useful tracers and were applied to calculate the fractions of groundwater (similar to pre-event water), shallow subsurface flow and surface runoff on stormflow. K^+ was a useful indicator for surface runoff dynamics, and Ca^{2+} provided insights into groundwater behaviour. Nevertheless, neither measure was applicable for the quantification of runoff components. Cl^- and further parameters (e.g. Na^+, K^+, and Mg^{2+}) were also not helpful for flow path identification, nor were their concentrations distinguishable among the components.

Groundwater contributed the largest fractions to stormflow (62–80 %) throughout all events, followed by shallow subsurface flow (17–36 %) and surface runoff (2–13 %). Our results provide important insights into the dynamics of the runoff processes in the study area and may be used to assess the transport pattern of contaminants (i.e. agrochemicals) here.

1 Introduction

Land use in the mountainous regions in northern Thailand has been intensifying over recent decades. Land-use systems have changed in many regions from subsistence- to market-oriented production. In the Mae Sa watershed, a study area close to Chiang Mai, Chiang Mai Province, remarkable changes have occurred. The proportion of annual cash crops increased from 8 to 39 % between 1974 and 2006, whereas rain-fed rice production declined from 21 to 0.5 % within the same time period (Schreinemachers and Sirijinda, 2008; Irwin, 1976). This intensification of cropping systems is accompanied by a higher input of agrochemicals to increase and secure yields. As a consequence, these agrochemicals may leach to groundwater aquifers and surface waters. Such water pollution has been postulated as one of Thailand's most critical environmental issues by Kruawal et al. (2004). Because the transport of agrochemicals within a hydrological system strongly depends on the dominant hydrological processes (i. e. Müller et al., 2006), it is important to understand the hydrology of the underlying system.

Runoff generation during stormflow events has been the subject of many research studies within the last decades. The dominance of groundwater as a main contributor to stormflow generation in a temperate study area was postulated, for example, by Sklash et al. (1976) and has been further consolidated by subsequent studies (e.g. Peters and Ratcliffe, 1998; Hoeg et al., 2000; Uhlenbrook and Hoeg, 2003).Whereas studies on runoff generation processes in temperate regions are plentiful, Giertz et al. (2006) stress a lack of studies

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within tropical regions. Chuan (2003) also notes a general lack of data on runoff generation processes in tropical regions, which applies especially for Southeast Asia. Examining these processes in the tropics is expected to yield different results based on characteristics of rainfall (Bonell, 1993): rainfall patterns here not only deviate from temperate ones, but there is also a strong variability. The amount of rainfall in the inner tropics can be twice as high as in the outer tropics (Table 1). Also, the seasonality of rainfall varies among the outer and inner tropics: the latter receive rainfall throughout the year; the former are characterized by a distinct wet and dry season. In addition to varying rainfall characteristics, the texture, mineralogy and structure of tropical and temperate soils may also promote different runoff generation, reflecting different soil hydraulic properties (Hodnett and Tomasella, 2002).

Although several studies have been conducted in tropics (i.e. Elsenbeer and Lack, 1996; Elsenbeer, 2001; Dykes and Thornes, 2000; Goller et al., 2005), comparisons are difficult because of the reported strong variations in the spatial and temporal distribution of rainfall. Such a comparison can be facilitated by listing them according to rainfall pattern (Table 1), which resembles a listing according to inner and outer tropical belt.

In contrast to the dominance of baseflow or pre-event water during stormflow generation in most temperate regions (i.e. Uhlenbrook and Hoeg, 2003), tropical studies agree on the importance of fast flow components (different terms, listed in Table 1). Despite this agreement, the dominant processes continue to be among the most difficult and least understood ones (Montanari et al., 2006).

Table 1 also shows the lack of attention to areas that receive < 2000 mm annual rainfall and are characterized by bimodal rainfall distribution with a distinct dry season (rainfall $\leq 20\,\mathrm{mm\,month^{-1}}$). Giertz and Diekkrüger (2003) and Liu et al. (2011) have helped close this gap. Ziegler et al. (2000) and Kahl et al. (2007) did not specifically investigate runoff generating processes, but delivered important hints for study sites in northern Thailand. During investigations on soil erosion, Ziegler et al. (2000) found that overland flow was very fast only on compacted soils, whereas less compacted areas required more rainfall to produce overland flow. Kahl et al. (2007, 2008) suggested the importance of interflow with regard to solute transport in a study area in northern Thailand. However, none of the runoff generation studies on catchments within the outer tropics have applied geochemical tracers to investigate runoff processes. This, and the persistent lack of runoff generation studies for steep catchments (i.e. Chappell, 2010) in the outer tropics, motivated the current investigation. We therefore investigated runoff generation in a steep catchment in northern Thailand using geochemical tracers. Prior to the runoff investigations, the geochemical tracers were tested with regard to their applicability in such an environment.

2 Materials and methods

2.1 Study area

The study area is a part of the Mae Sa watershed ($77\,\mathrm{km^2}$), which is located 35 km northwest of Chiang Mai in northern Thailand (Fig. 1). Measurements were conducted in the Mae Sa Noi subcatchment (18°54′ N, 98°54′ E; $7\,\mathrm{km^2}$) (Fig. 1), which is a very narrow and steep V-shaped (Fig. 1b) valley with an elevation ranging from 850 to 1560 m a.s.l. Soils are mainly Acrisols and Cambisols (Fig. 1b) on paragneiss and granite. Both soil types show a sharp decrease of hydraulic conductivity with increasing depth (Schuler, 2008). The bulk density of an Umbric Acrisol in the area ranged between 1.1 and $1.3\,\mathrm{g\,cm^{-3}}$ with increasing clay content within the first 100 cm (Spohrer et al., 2005). Hydraulic conductivity dropped from 1.04 to $0.54\,\mathrm{cm\,d^{-1}}$ within the first 20 cm. A slight increase to $0.7\,\mathrm{cm\,d^{-1}}$ at 40 cm was recorded, followed by a reduction to $0.2\,\mathrm{cm\,d^{-1}}$ in the layer below (70 cm) (Spohrer et al., 2005). Jantschke (2002) reported a soil water content ranging from 16 to 30 % by volume at 50 cm depths during irrigation experiments.

The vegetation is dominated by secondary forest and agricultural crops (Fig. 1a). The dry dipterocarp forest consists of a variety of evergreen and deciduous tree species. It also hosts scattered tree plantations including *Tectona grandis*, *Litchi chinensis*, and *Mangifera indica*. Around 30 % of the Mae Sa Noi area is covered by agricultural land, which can mainly be split into field crops (30 %) and litchi (50 %) (Schreinemachers and Sirijinda, 2008). Major field crops are cabbage and bell pepper, which are cultivated year round and irrigated if needed.

The sampling site itself was located along a hill slope in the lower catchment area (Fig. 1b), which is covered by an abandoned litchi orchard. This orchard was abandoned in 2006 and has not been agriculturally used since that time. This implies that no fertilizers had been applied several months before and during the sampling period. The climate in the area is controlled by the monsoon with distinct wet (May–October) and dry (November–April) seasons and a mean annual rainfall of 1200 mm. Based on a mean annual discharge of $623\,\mathrm{mm\,a^{-1}}$ (long-term runoff coefficient 0.52), evapotranspiration would be $577\,\mathrm{mm\,a^{-1}}$. The average annual air temperature is 21 °C, and relative humidity ranges between 40 and 100 %.

2.2 Measurements

Rainfall was monitored at four stations. Two of these were located within the Mae Sa Noi subcatchment (MSN and MSM, Fig. 1a), the other two (BMK and PNK, Fig. 1a) close-by. During events, the rainfall data were extracted from stations closest to the discharge flume (MSN and MSM, Fig. 1a). To ensure the data quality or to fill gaps, rainfall records were compared with the closest stations: BMK and PNK (Fig. 1a).

Table 1. Comparison of studies on runoff generation conducted in inner and outer tropical regions (information taken from literature).

Study	Location	Area size	Soils	Main vegetation	Annual rainfall (mm)	Dry season	Wet season	Dominant runoff processes/major runoff contributors	Separation/ identification of flow components
Dykes and Thornes (2000)	Northwest Borneo, Brunei	Kuala Belalong Field Studies Centre, hillslope study	orthic Acrisol	Mixed dipterocarp rainforest	4000–5000	All year rainfall, with highest rainfall from May to November		Subsurface stormflow/ return flow	Measurement of soil water by tensiometers
Elsenbeer and Lack (1996)	Western Amazonia	La Cuenca, 0.75 ha	Ultisols, Inceptisols	Rainforest	3300	All year rainfall, with totals below 100 mm month^{-1} from June to September and totals around 900 mm month^{-1}		Fast flow paths: overland flow, return flow	Molar ratio of potassium to silica
Elsenbeer and Vertessy (2000)	Western Amazonia	La Cuenca, 0.75 ha	Ultisols, Inceptisols	Rainforest	3300			Overland flow, near-surface flow	Measurement of soil hydraulic properties
Negishi et al. (2007)	Malaysia	Bukit Tarek Experimental Catchment, 0.328 km^2	Not specified	Rainforest	2800	All year rainfall, with peaks in May and November		Shallow groundwater and subsurface flow paths	Measurement of silica and electrical conductivity, overland flow detectors
Chaves et al. (2008)	Southwest Amazon Basin, Brazil	2 study sites at Rancho Grande, 1.37/0.73 ha	Ultisols, Oxisol, Inceptisols, Entisols	Forest, pasture	2330	All year rainfall, with totals <100 mm month^{-1} from June to August and higher values from September to May		Forest: throughfall, pasture: overland flow	Endmember mixing analysis, groundwater, soil water, throughfall or overland flow,respectively
Goller et al. (2005)	Ecuador	3 microcatchments, 0.08–0.13 km^2	Dystrudepts, Eutrudepts	Tropical rainforest	2182	All year rainfall, wettest month June (281 mm), driest month November (∼ 80 mm)		Vertical and lateral pathways, event water dominated stormflow generation	Measurement of ^{18}O
Muñoz-Villers and McDonnell (2012)	Central Veracruz, Mexico	Headwater montane cloud forest catchment, 24.6 ha	Umbric Andosols	Old-growth lower montane cloud forest	3200	November–April	May–October (80 % of annual rainfall)	Groundwater discharge from hillslope	Measurement of ^{2}H and ^{18}O
Godsey et al. (2004)	Central Panama	Lutz Creek, 9.37 ha; Conrad Trail Stream, 40.2 ha	Acrisol, Oxisols	Rainforest	2600	January–May	June–December	Strong overland flow influence for Lutz Creek, lower influence in Conrad Trail Stream	In situ measurement of soil saturated hydraulic conductivity, overland flow detectors
Wickel et al. (2008)	Eastern Amazonia, Brazil	2 subcatchments of Cumaro catchment, 0.1–0.34 km^2	Ultisols	Mix of agriculture and secondary forest	2500	Dry spell from October to December, rainfall ($\leq$ 50 mm day^{-1})	Frequent rainfall between January and September	Direct runoff from saturated source areas	Measurement of soil infiltrability, application of dye tracer
Liu et al. (2011)	Xishuangbanna, southwest China	Tropical rainforest catchment (TRFC), 51.1 ha; artificial rubber plantation catchment (ARPC), 19.3 ha	Lateritic soils	Tropical rainforest, rubber trees	1487	November–April	May–October	29–31 % event water fraction in TRFC; 62–69 % event water fraction in ARPC	Measurement of ^{18}O
Giertz and Diekkrüger (2003)	Central Benin, Aguima catchment	(1) Upper Niaou, 3.5 km^2 and (2) Upper Aguima, 3.2 km^2	Lixisols, Gleysols, Plinthisols	(1) Agricultural land, (2) Tree savannah, woodland	1100	May–October	November–April	Lateral subsurface flow	Estimation of saturated conductivity with TDR probes, hydraulic tensiometers and infiltration measurement

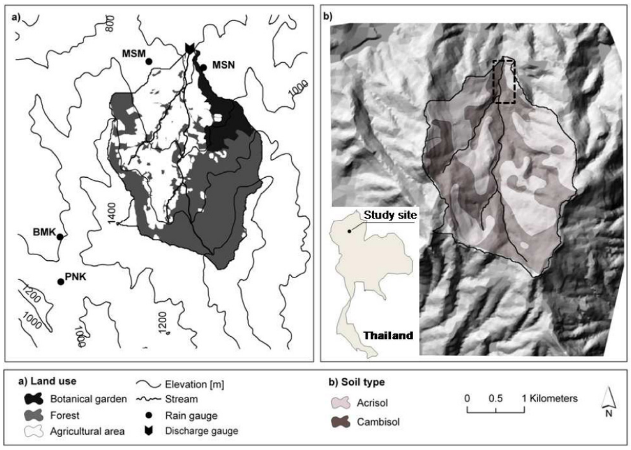

Fig. 1. Mae Sa Noi sub-catchment with **(a)** measurement devices (MSM, MSN, BMK, and PNK), land use in 2008 (modified after M. Lippe, SFB 564, Subproject C4.1) and **(b)** sampling area (black square), topography, and soil types (modified after Schuler et al., 2008).

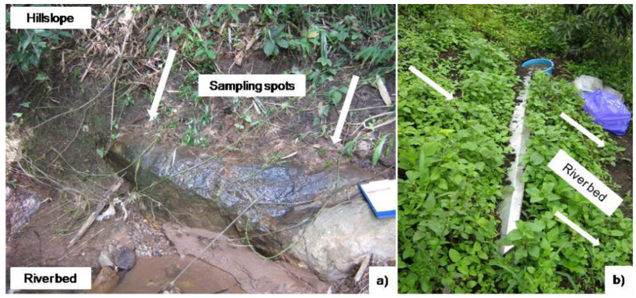

Fig. 2. Sampling of surface runoff (SUR) and (shallow) subsurface flow (SUB) at the study site (black square, Fig. 1b). **(a)** depicts the seep, which is defined as subsurface flow, **(b)** one of the steel gutters used to measure surface runoff along the hillslope.

The variability among the stations was evaluated in terms of representativeness of each rainfall event during the field experiments by cross-correlation coefficients (CCRs). CCR was computed among the rain gauges and between each rain gauge and discharge measurement. The analysis was based on monthly data series with a resolution of 10 min, yielding CCR per month and station. If more details on CCR between stations were needed, a higher temporal resolution was applied (i.e. days or single events). The mean annual rainfall input for the Mae Sa Noi subcatchment was based on records of stations MSN and MSM.

Water level was measured at a fixed, rectangular cross section using an ISCO ultrasonic sensor at the discharge gauge. A stage–discharge rating curve was established by salt dilution measurements for different water levels in order to convert water level into discharge.

2.3 Sampling of the components

During September 2007 (E1) and October 2007 (E2), two event-based field campaigns were conducted to investigate runoff generation in the Mae Sa Noi subcatchment. In the frame of another sampling campaign in August 2009 (E4) and September 2009 (E5), two additional events were sampled (Duffner, 2010). Sampled components included rainfall, surface runoff, shallow subsurface flow, groundwater and stormflow. The terms component and endmember may be used interchangeably in the following text. Surface runoff (SUR) is defined as the component that flows above the soil surface during and/or shortly after events. Shallow subsurface flow (SUB) is water that seeps from the soil at the hill slope foot along the riverbed (Fig. 2b). Shallow subsurface flow is assumed to flow laterally along the hill slope between the bedrock and the soil cover, being forced to ex-filtrate at the end of the slope (Fig. 2b). Because of wet and dry seasons, the subsurface flow is temporal (episodic) and not active throughout the year. Once established, it takes place until rainfall events are intermittent and is understood to be mainly fed by macropore flow in the unsaturated zone along the hill slope. Discharge during the rainy season is believed to be sustained by a mixture of groundwater and contributions from saturated zones. This mixture is termed groundwater (GW) component within this study and is represented by the average stream flow concentration measured in between events. Note that a separation of both contributors is not possible and that the contributed proportions may vary in an unknown amount. Since the subcatchment is very steep and valley bottoms or riparian zones are rare, groundwater must originate from deeper soil layers and/or fissured and fractured rocks. The saturated zones may be distributed across the subcatchment and are most likely highly dynamic. All named components are thought to contribute to stormflow (SF) in varying magnitudes.

Rainfall samples were collected in a bulk collector and extracted immediately after or during a rainfall event. Surface runoff was collected along the hill slope close to the discharge gauge (Fig. 1a) by stainless steel gutters. The gutters were installed slope-parallel with a gentle inclination to route the water towards a bulk collector at the end of each gutter (Fig. 2a). The samples were extracted during or immediately after rainfall events. In 2009, two additional gutters at different positions extended the installation across the hill slope to cover the spatial variability of surface runoff. The distance between those gutters ranged between 50 and 100 m, covering a stretch of roughly 300 m along the slope (Fig. 1b). A mixture of surface runoff with return flow along the hill slope could not be excluded, although the samples were extracted directly during or after rainfall events. Shallow subsurface flow was sampled at three spots close to the discharge gauge (Fig. 1b) along the river banks (Fig. 2b). Samples were collected with a resolution of 15–20 min during events. Additional samples were taken before, after and randomly in between events. The hydrochemical signature of the groundwater endmember was obtained from samples collected during rainless periods and directly prior to stormflow. In order to apply a representative endmember signature, the average concentration of all samples related to an event was defined as the groundwater component. During the rainy season, sporadic groundwater samples were collected along the main reach. Stormflow samples were obtained every 5–10 min. A conductivity meter (WinLab Data Line, Windaus Labortechnik, Germany, measurement error: ±2 %) was used to measure electrical conductivity (EC) in situ. Major ions (Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Ca^{2+}, and Mg^{2+}) were analysed using ion chromatography (ion chromatograph, Metrohm). Silica samples were analysed by ICP-OES (inductively coupled plasma–optical emission spectrometry, Perkin Elmer). Detection limits for each ion and for silica are listed in Table 3. Analytical errors of silica concentration were specified as ±10 %, those of the major ions as ±7 % (Department of Chemistry, Chiang Mai University, personal communication, 2007).

To test the accuracy and consistency of the chemical analysis and the electrical conductivity measurements, the results were checked according to Appelo and Postma (2005). When checking the electrical balance, the sum of cations (μeqL^{-1}) and anions (μeqL^{-1}) should be similar. Measured EC was backed up by calculating the EC based on the molar conductivity of measured ion concentrations as shown by Appelo and Postma (2005).

2.4 Hydrograph separation

To divide the hydrograph into its flow components, a three-component hydrograph separation was performed. The chemically based hydrograph separation relies on the principle of mixing, where equations of continuity and mass balance govern the quantity of tracer flow.

The following equations define a three-component separation (modified after Ogunkoya and Jenkins, 1993):

$$Q_\mathrm{T} = Q_\mathrm{GW} + Q_\mathrm{SUB} + Q_\mathrm{SUR}, \quad (1)$$

$$Q_\mathrm{T} C_{i,\mathrm{T}} = Q_\mathrm{GW} C_{i,\mathrm{GW}} + Q_\mathrm{SUB} C_{i,\mathrm{SUB}} + Q_\mathrm{SUR} C_{i,\mathrm{SUR}}, \quad (2)$$

$$Q_\mathrm{T} C_{j,\mathrm{T}} = Q_\mathrm{GW} C_{j,\mathrm{GW}} + Q_\mathrm{SUB} C_{j,\mathrm{SUB}} + Q_\mathrm{SUR} C_{j,\mathrm{SUR}}, \quad (3)$$

where Q_T, Q_GW, Q_SUB, and Q_SUR (Q in $m^3 s^{-1}$) represent volumes of the measured discharge (Q_T), groundwater (GW), subsurface flow (SUB) and surface runoff (SUR) (see definition in Sect. 2.3), while C_T, C_GW, C_SUB, and C_SUR are the equivalent concentrations of two tracers i and j. The equations are solved for Q_GW, Q_SUB, and Q_SUR. The method is based on several assumptions, which are described in the literature (e.g. Ogunkoya and Jenkins, 1993). Note, however, that the method is only applicable if the components are chemically distinguishable and if tracers are conservative or their fluctuations measurable.

Uncertainty analysis for the three-component hydrograph separation included uncertainties of endmembers and laboratory analysis. The propagation of uncertainty was derived from equations presented by Genereux (1998).

Table 2. Annual rainfall and the number of rainy days recorded at four weather stations (for location of stations see Fig. 1).

Station	2007		2009	
	[mm]	[days]	[mm]	[days]
PNK	1222	122	1123	105
BMK	1400	121	847	70
MSM	1228	118	785	98
MSN	1309	132	719	91
Average	1289	115	869	91
Standard deviation	83	6	178	15

2.5 Mixing plots

Mixing plots were used to explore the chemical composition of stormflow during an event (Christophersen et al., 1990). The basic assumption of mixing plots is that discharge during events is generated by different runoff components – each of which has its own chemical signature (fingerprint). The concentrations of the components serve as vertices of a triangle in which concentrations of stormflow samples should be bound in, if stormflow involves the selected runoff components. If the stormflow concentration is not framed by the concentration of the components, then the selected components are non-distinguishable or non-representative.

3 Results

3.1 Rainfall records

Annual rainfall and the amount of rainy days at the stations MSM, MSN, BMK, and PNK are given in Table 2. In E1, only very little rainfall was recorded at the lower stations (MSN and MSM, 0.7 mm). There, the transferability of rainfall data from the surrounding stations was tested by CCR. Single rainfall events between all four stations recorded two days prior and after E1 with a temporal resolution of 10 min were used as input data. For the single events within these 4 days, CCR ranged between 0.6 and 0.8. Hence, the transferability of rainfall data between the upper (BMK and PNK) and lower (MSM and MSN, Fig. 1) rain gauges was considered as representative and was applied for the evaluation of E1. Ultimately, the cross-correlation between the two lower rain gauges (MSM and MSN) and measured discharge yielded CCR = 0.6 with a lag time of 60 min between onset of rainfall and discharge peak in September and CCR = 0.7 in October. Discharge and rainfall from the upper two gauges (BMK and PNK) correlated well after a lag time of 80 min (CCR = 0.6).

Table 3. Electrical conductivity and ion concentrations in water samples of groundwater, shallow subsurface flow, surface runoff and rainfall taken during September–October 2007 and August–September 2009.

		DL**	Groundwater ($n = 20/15$)*	Shallow subsurface flow ($n = 20/10$)*	Surface runoff ($n = 7/7$)*	Rainfall ($n = 4/0$)*
			Mean ± standard deviation			
2007	EC [$\mu S\,cm^{-1}$]	–	135.86 ± 9.22	29.35 ± 1.04	37.95 ± 23.21	9.48 ± 5.88
	Silica [$mg\,L^{-1}$]	0.012	19.89 ± 1.10	14.64 ± 6.18	11.84 ± 0.88	n.a.
	Cl^- [$mg\,L^{-1}$]	0.011	1.31 ± 0.12	0.07 ± 0.03	0.97 ± 0.78	0.42 ± 0.47
	NO_3^- [$mg\,L^{-1}$]	0.009	2.45 ± 0.46	3.39 ± 0.94	5.29 ± 3.29	0.69 ± 0.37
	SO_4^{2-} [$mg\,L^{-1}$]	0.007	1.41 ± 0.18	0.13 ± 0.02	2.29 ± 1.54	0.83 ± 0.72
	Na^+ [$mg\,L^{-1}$]	0.008	4.90 ± 0.36	4.62 ± 0.79	0.27 ± 0.19	0.29 ± 0.34
	NH_4^+ [$mg\,L^{-1}$]	0.014	n.d.	n.d.	5.52 ± 3.17	0.72 ± 0.23
	K^+ [$mg\,L^{-1}$]	0.040	5.46 ± 0.85	1.72 ± 0.27	7.62 ± 3.47	0.39 ± 0.24
	Ca^{2+} [$mg\,L^{-1}$]	0.030	22.90 ± 5.63	1.20 ± 0.31	1.55 ± 0.8	0.52 ± 0.28
	Mg^{2+} [$mg\,L^{-1}$]	0.031	5.89 ± 0.95	0.16 ± 0.02	0.63 ± 0.37	0.12 ± 0.04
			($n = 24/24$)*	($n = 12/7$)*	($n = 6/6$)*	($n = 3/3$)*
2009	EC [$\mu S\,cm^{-1}$]	–	184.78 ± 14.09	35.17 ± 5.60	58.43 ± 12.41	5.35 ± 2.51
	Silica [$mg\,L^{-1}$]	0.012	14.7 ± 0.60	9.06 ± 1.71	1.32 ± 0.15	0.09 ± 0.01

(n.a.: not available; n.d.: not detected; * numbers of silica samples vary and are given on the second position; ** DL: detection limit.)

3.2 Event-based measurements

Rainfall during E1 had a low intensity, with a total amount of 6.9 mm in 50 min, and was recorded only at stations PNK and BMK (Fig. 3a). Discharge peaked at $0.42\,m^3\,s^{-1}$ ($60\,L\,s^{-1}\,km^{-2}$) within 20 min and caused a decline in EC by $36\,\mu S\,cm^{-1}$ within the same period (Fig. 3b). Major anions showed similar dynamics. The drop of silica (Fig. 3b) and the slight increase of Cl^- ($0.5\,mg\,L^{-1}$, Fig. 3c) prior to the event were probably induced by an earlier event (not shown in Fig. 3) on that day. A clear decrease in the concentration of silica coincided with the rise of the hydrograph. The Ca^{2+} concentration (Fig. 3c) was reduced by $10\,mg\,L^{-1}$ along the recession limb. Na^+, Mg^{2+}, and K^+ behaved similarly during the event (Fig. 3c).

Event E2 was monitored a few days later, on 9 October 2007. Total rainfall was 17.2 mm in 40 min and was recorded at all four stations. The discharge at E2 rose to $0.46\,m^3\,s^{-1}$ ($65.7\,L\,s^{-1}\,km^{-2}$) (Fig. 4a) after 60 min of rainfall. EC (Fig. 4b) rapidly sank by $53\,\mu S\,cm^{-1}$. Silica concentrations dropped by $4\,mg\,L^{-1}$ (Fig. 4b). The dynamics of the major cations is given in Fig. 4c. A decrease in concentration with the beginning of peak flow was observed for all measured ions. The sharpest drop was recorded for Ca^{2+}, ($15\,mg\,L^{-1}$), the lowest for Na^+. The most significant increase was observed for K^+ ($10\,mg\,L^{-1}$), which occurred parallel to the drop of EC and silica. Initial concentrations were reached by all major cations and Cl^-, but not by silica. At both events, Ca^{2+} had by far the highest concentrations amongst all ions and reacted similarly as silica concentrations (Figs. 3c, 4c)

Compared to surface runoff, major ion concentrations and EC values of shallow subsurface flow were stable during E1 and E2 (Table 3). Only silica concentrations varied considerably.

In fact, silica concentration of shallow subsurface flow showed high fluctuations between samples from rainy days ($7.5 \pm 1.1\,mg\,L^{-1}$) and dry days ($19.4 \pm 0.9\,mg\,L^{-1}$).

During the two events in 2009 (E4 and E5), only EC and silica concentration were measured. For both events, rainfall data from the closest stations (MSN and MSM) were available. E4 was initiated by 10.6 mm rainfall. Discharge slowly increased from 0.1 to $0.28\,m^3\,s^{-1}$ ($40.0\,L\,s^{-1}\,km^{-2}$) (Fig. 5a). Silica concentration declined by $2.5\,mg\,L^{-1}$ (Fig. 5b). EC values fell gradually (Fig. 5b) and reached $139\,\mu S\,cm^{-1}$ after 50 min.

On 15 September 2009, E5 received 17.6 mm rainfall within 70 min. Discharge peaked at $0.6\,m^3\,s^{-1}$ ($85.7\,L\,s^{-1}\,km^{-2}$) within 60 min (Fig. 6a). During the rise of the hydrograph, EC and the silica concentrations fell by $35\,\mu S\,cm^{-1}$ and $3\,mg\,L^{-1}$, respectively (Fig. 6b).

The ion balance showed gaps of up to $-30\,\%$, probably reflecting the missing HCO_3^- measurements. Calculated and measured electrical conductivity of all samples varied between 6 and 25 %. These deviations are also most likely explained by the missing HCO_3^- measurements in the samples.

For each component, mean and standard deviation of concentrations are listed in Table 3. EC values of stream flow were generally higher in 2009, and silica had lower concentrations in 2009. Table 3 reveals that EC values of shallow subsurface flow were lower than those of surface runoff, which was also the case for most major ions and silica.

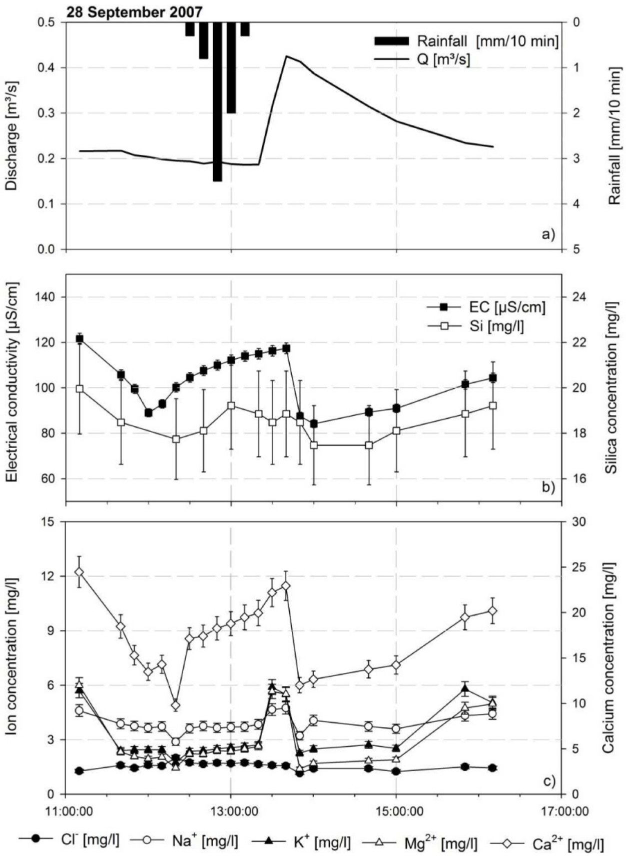

Fig. 3. Event E1 on 28 September 2007: **(a)** discharge and rainfall, **(b)** silica and Cl^- concentrations, and **(c)** concentrations of Na^+, Mg^{2+}, K^+, Ca^{2+}, and EC values. Error bars indicate measurement uncertainty of 7 % for ions and 10 % for silica.

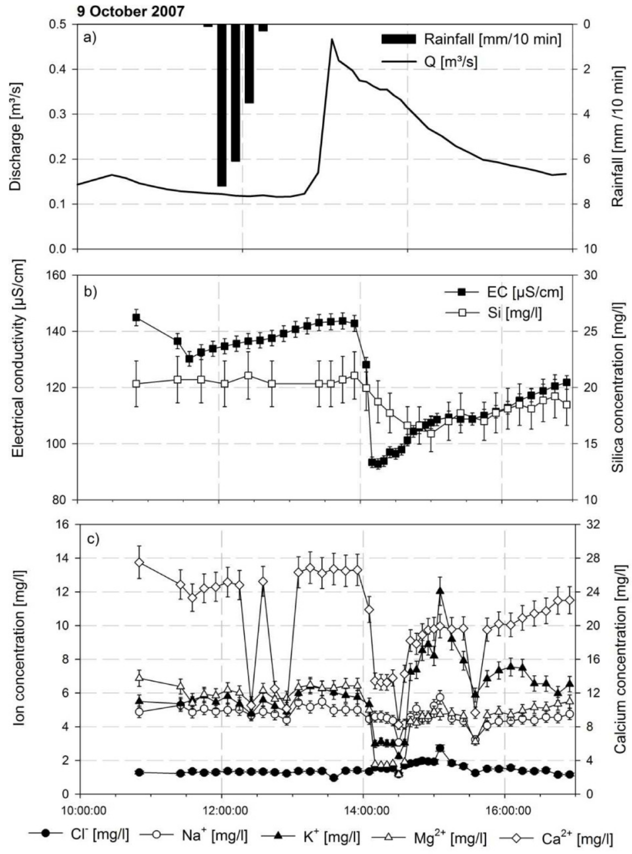

Fig. 4. Event E2 on 9 October 2007: **(a)** discharge and rainfall, **(b)** silica and Cl^- concentration, and **(c)** concentrations of Na^+, Mg^{2+},K^+, Ca^{2+}, and discharge. Error bars indicate measurement uncertainty of 7 % for ions and 10 % for silica.

Most major ions, which are commonly used for hydrograph separation (i.e. Cl^-), were hardly distinguishable between the components. Considerable differences were identified for K^+ and Ca^{2+}. The Ca^{2+} concentration in groundwater for E1 and E2 correlated well with EC ($0.8 \leq \text{CCR} \geq 0.86$) and silica ($0.8 \leq \text{CCR} \geq 0.82$).

3.3 Mixing plots

Mixing diagrams were plotted for E1, E2, E4, and E5 based on EC and silica concentrations (Fig. 7). The endmember concentrations are represented by surface runoff (SUR), shallow subsurface flow (SUB) and groundwater (GW).

Event E1 (Fig. 7a) was framed by SUR, SUB, and GW. Some stormflow concentrations during E1 and E2 were outside the GW endmember concentration. During E1 all but one concentration point were scattered within the range of the standard deviation (Fig. 7a). Most concentrations in E2 was clustered around the GW endmember concentration and were also covered by the standard deviation (Fig. 7b). We therefore assume that the GW endmember is representative. For the remaining events – E4 (Fig. 7c) and E5 (Fig. 7d) – most concentration points were located between GW and SUB. Those outside the boundaries are within the ranges of the standard deviations.

3.4 Hydrograph separation

A three-component hydrograph separation based on silica concentrations and EC values was performed for E1, E2, E4, and E5 (Fig. 8). Major ions were not applied for the three-component separation because the concentrations and/or the differences between the components were too low. Nevertheless, the results will be used for a qualitative assessment in the discussion.

During E1 (Fig. 8a), the discharge was mainly composed of groundwater (62 %) and shallow subsurface flow (36 %), whereas the fraction of surface runoff was very small (2 %). Groundwater was the first component which rose, followed by shallow subsurface flow. A first peak of surface runoff coincides with that of groundwater. E2 received 67 % of the groundwater (Fig. 8b). The pronounced shoulder of the recession limb was mainly constituted by groundwater and to a smaller extent by shallow subsurface flow and surface runoff.

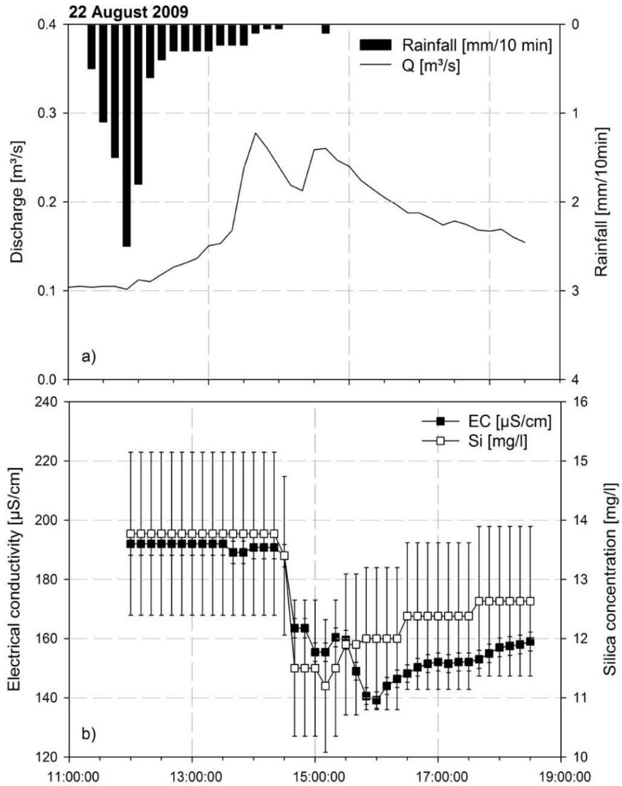

Fig. 5. Event on 22 August 2009 (E4) showing **(a)** rainfall and discharge and **(b)** EC values and silica. Error bars indicate measurement uncertainty of 2 % for EC and 10 % for silica.

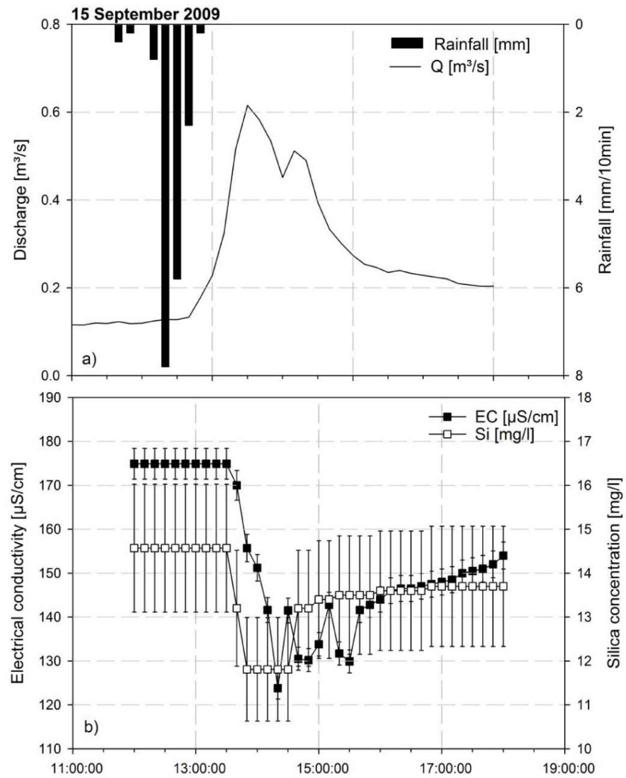

Fig. 6. Event on 15 September 2009 (E5) showing **(a)** rainfall and discharge and **(b)** EC values and silica. Error bars indicate measurement uncertainty of 2 % for EC and 10 % for silica.

Compared to the groundwater peak, shallow subsurface flow (20 %) was slightly delayed. Surface runoff (13 %) showed a peak during a gentle shoulder along the hydrograph.

In 2009, both runoff events were dominated by groundwater (E4: 80 %; E5: 76 %). While the role of surface runoff (2 %) was marginal (Fig. 8c), shallow subsurface flow contributed about 18 % to stormflow. Next to the groundwater component, the shallow subsurface flow constituted 17 %, surface runoff 7 % (Fig. 8d).

The computed uncertainties of each fraction are depicted in Fig. 8. Table 4 shows the mean uncertainties and standard deviations of each component during each event. The highest mean uncertainty occurred for the shallow subsurface flow component during E4, which is also visible in Fig. 8c. Overall uncertainties are within the expected range and do not weaken the order of contribution of the flow components. The errors of surface runoff are particularly high towards the end of E2. These errors and the uncertainties of shallow subsurface flow within E4 were the largest within the analysis.

4 Discussion

4.1 Hydrochemical analysis and applicability of tracers

As reported by other studies (i.e. Elsenbeer et al., 1994; Hoeg et al., 2000; Negishi et al., 2007; Mul et al., 2008), silica and EC proved to be appropriate tracers for the hydrograph separation in the Mae Sa Noi subcatchment. Despite the usefulness of EC, none of the analysed major ions were applicable at the study site because of generally low concentrations. As EC is a combined measure of dissolved ions within a sample, this may seem to be inconsistent at first glance. Comparisons between measured and calculated EC (differences from 6 to 25 %) and the check of the ion balance (up to −30 % for anions) suggest that the missing HCO_3^- analysis can explain the differences. Whereas EC is a variable correlated with the ion concentration of solutes, silica originates mainly from weathering processes. Therefore, water from deeper sources is considered to have higher silica concentrations (e.g. Scanlon et al., 2001) because of longer residence and contact times. This is well represented in the data: silica concentrations in groundwater were the highest among the components. This supports the assumption that groundwater is fed by deeper soil layers, from fissures and fractures in the rock and from saprolite zones in the catchment.

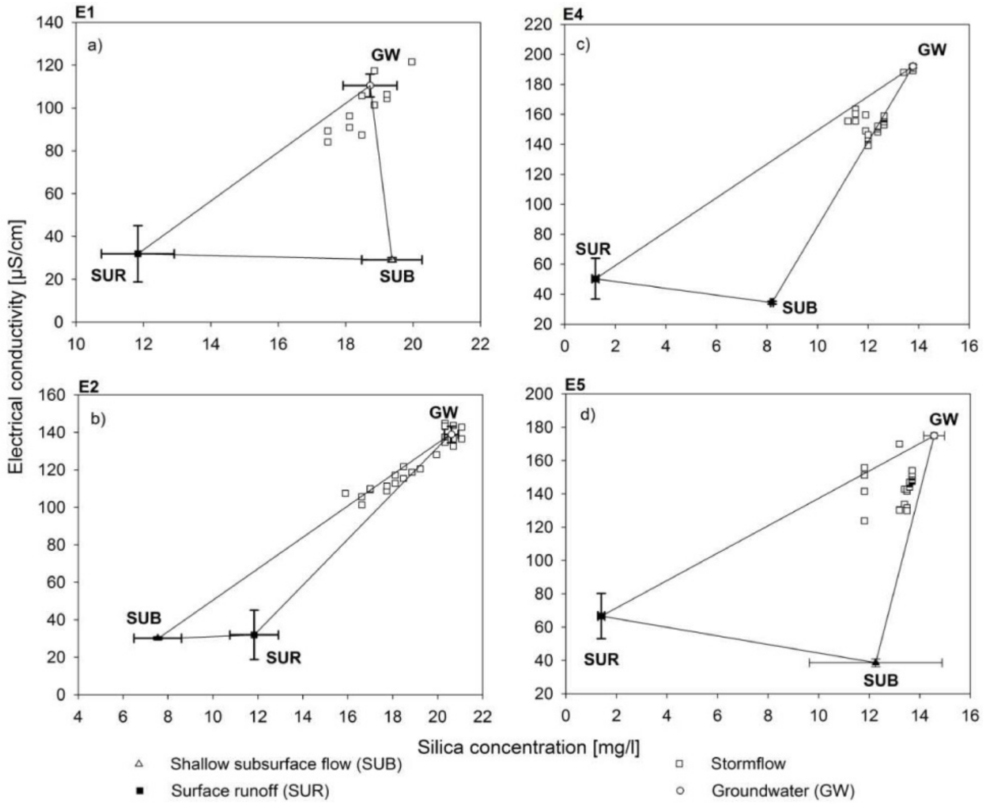

Fig. 7. Hydrochemical mixing diagrams for **(a)** 28 September 2007 (E1), **(b)** 9 October 2007 (E2), **(c)** 22 August 2009 (E4), and **(d)** 15 September 2009 (E5) based on endmembers of shallow subsurface flow (SUB), surface runoff (SUR) and groundwater (GW). Bars indicate standard deviations.

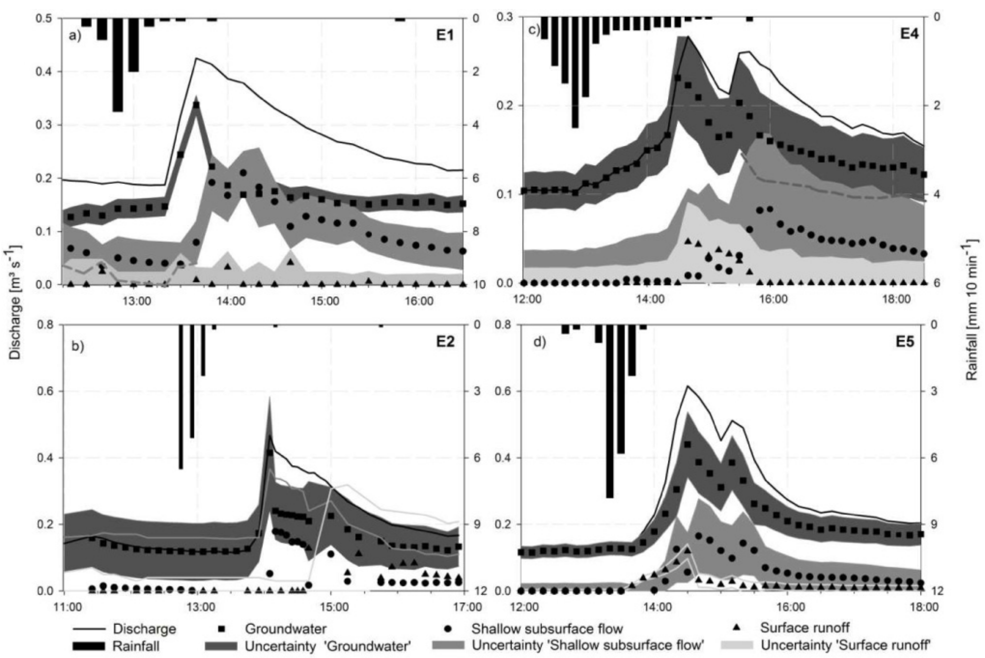

Fig. 8. Results of the three-component hydrograph separation and uncertainty bands for the monitored events: **(a)** E1 (28 September 2007), **(b)** E2 (9 October 2007), **(c)** E4 (22 August 2009), and **(d)** E5 (15 September 2009). Uncertainty is depicted with lines or areas, depending on overlay and intersections.

Table 4. Mean and standard deviation of the relative uncertainty of the separated components during E1, E2, E4, and E5.

Event	Groundwater		Shallow subsurface flow		Surface runoff	
	Mean (%)	Standard dev. (%)	Mean (%)	Standard dev. (%)	Mean (%)	Standard dev. (%)
E1	6.9	2.0	15.6	4.6	9.9	4.5
E2	26.5	10.9	18.0	16.4	11.9	6.7
E4	19.6	0.1	35.2	0.02	15.4	1.4
E5	16.0	0.04	10.2	8.7	3.6	0.03

The comparatively high Ca^{2+} concentrations in groundwater showed similar characteristics to silica. Christophersen et al. (1990) pointed at Ca^{2+} as an indicator for water from deeper soil layers at their temperate study site. Although we monitored a tropical site, this suggests a different, deeper source for this component than the one for shallow subsurface flow and surface runoff; this also strengthens the assumption of a groundwater source in a deeper soil layer. Besides EC and silica, K^+ has been described in the literature as a suitable tracer for hydrograph separation, particularly to divide overland flow and shallow subsurface flow from groundwater. Sharp rises of K^+ with the onset of fast-flow components were reported from tropical (e.g. Elsenbeer et al., 1995; Kinner and Stallard, 2004; Mul et al., 2008) and temperate study sites (Uhlenbrook et al., 2008). Within the present study, a similar pattern was monitored during E2. There, K^+ concentration increased shortly after peak flow. Additional indicators favour K^+ as a suitable tracer for surface runoff: throughout the monitored period, K^+ values in surface runoff were higher than concentrations in shallow subsurface flow. This finding matches well with measured data from Schuler (2008), who identified higher K^+ values in the topsoil (up to 20 cm) with decreasing concentration in the subsoil of a soil profile at the same study site. Since shallow subsurface flow samples were extracted from a soil depth of about 50 cm, the lower concentrations are congruent with Schuler (2008). However, the applicability of K^+ and Ca^{2+} as tracers for hydrograph separation in the Mae Sa Noi subcatchment needs more testing.

The single Cl^- peak during E2 is difficult to explain because none of the sampled components yielded concentrations with similar magnitudes. Although the samples were collected in non-agricultural areas, the single peak may originate from agricultural areas upstream, which were not covered by the sampling. The low Cl^- concentrations in all components (GW, SUB, SUR) and the presence of small agricultural patches within the catchment hamper the suitability of Cl^- as a tracer for this study site. Other ions were not applicable because of their low concentrations and similarity among the components. To bypass the limitations of non-distinguishable concentrations among the components, or their non-conservative behaviour, the application of isotopes (i.e. ^{18}O, ^{2}H) for hydrograph separation should be considered. Although present studies on isotope-based hydrograph separations are limited in tropical and subtropical areas (Klaus and McDonnell, 2013), a combination of stable isotopes and geochemical tracers could help to improve the understanding of runoff processes in the Mae Sa Noi subcatchment. Because chloride concentrations of the monitored components were low and non-distinguishable, silica should be favoured for a hydrograph separation based on isotopic and geochemical tracers. Combinations of O−18 and silica have been demonstrated by Uhlenbrook and Hoeg (2003) and Iwagami et al. (2010), for example.

However, additional insight into runoff generation can be obtained by the ion concentrations and EC values of surface runoff and shallow subsurface flow. Most of the measured ion concentrations and EC values of surface runoff were larger than those of shallow subsurface water. Surface runoff is assumed to flow quickly at the soil surface. Hence, the contact time between water and soil is limited, and ion concentrations and EC values close to concentrations in rainfall are to be expected. During the investigated events, surface runoff showed an enrichment of ions compared to shallow subsurface flow. Except during event E2, silica concentrations were higher in shallow subsurface flow than in surface runoff. This exception may be explained by soil chemical investigations by Schuler (2008). Schuler (2008) reported maximum ion concentrations in the soil within the first 10 cm and a clear decrease below 20 cm. Hence, the hydrochemical composition of surface runoff indicates an infiltration of water into the topsoil at an uphill position. While laterally flowing downhill in the topsoil, the water may have been forced to ex-filtrate along the hill slope by the bedrock or topography. The observed surface runoff during the events may therefore actually be return flow. The difficulty in separating the two flow components in a tropical environment has already been stated by Elsenbeer et al. (1994) and is supported at the present study site. Similar characteristics of silica concentration, and EC values were reported by Negishi et al. (2007) from a Malaysian study site. They sampled bedrock seep and pipe flow. There, silica concentrations of bedrock seep were highest and EC values were the lowest among the observed components. In the Mae Sa Noi subcatchment, Schuler's (2008) data provide an explanation. He found highest clay contents at soil depths between 40 and 70 cm. In contrast, the measured ion concentrations within this 40–70 cm depth were lower than those in the first 20 cm.

Combining soil characteristics and our analysis, a possible pathway for silica-rich and low-ion concentration water may be a rapid bypass of the upper soil layer, which is enabled by vertical macropores (McDonnell, 1990). Kienzler and Naef (2008) also stated that vertical macropores and lateral preferential flow paths can transfer water quickly and directly into streams. Preferential interflow was identified at depths of 60–90 cm by Kahl et al. (2007) at the present site.

4.2 Hydrograph separation

Hydrograph separation based on silica and EC revealed that all stormflow events were dominated by groundwater. Although EC is considered to be a non-conservative tracer, the high temporal resolution of the monitoring allows the application within a hydrograph separation. The order of the components – GW >SUB >SUR – is congruent with most studies from temperate regions (Peters and Ratcliffe, 1998; Uhlenbrook and Hoeg, 2003), but deviates from findings in tropical areas (Table 1). Note, however, that most available studies were conducted in areas receiving much more rainfall than the Mae Sa Noi subcatchment (Table 1). Only reports from Giertz and Diekkrüger (2003) and Liu et al. (2011) are comparable regarding rainfall amounts, although rainfall had a unimodal distribution in the Beninese study area. Liu et al. (2011) delivered similar results to ours for runoff generation under a tropical rainforest (around 30 % event water contribution). Negishi et al. (2007) identified shallow groundwater as the main contributor to stormflow at a Malaysian study site, with a rainfall distribution equal to that reported here but with higher annual amounts. As groundwater within the present study was sampled only from the stream during the rainless periods, it may not have solely represented groundwater from deeper sources. A mixture of deep and shallow groundwater may also be possible, but could not be backed up with measurements.

In our study, the difficulty of separating shallow subsurface flow and groundwater is visible in the computed uncertainties. Compared with surface runoff, both components show relatively large uncertainties (Fig. 8, Table 4), particularly shallow subsurface flow during E4. This points to the necessity of more detailed measurements and, for example, sampling of deep groundwater to compare the geochemical pattern of the groundwater and the shallow subsurface flow components.

The low fractions of surface runoff identified in the current separation approach can be explained by the magnitude of the rainfall events and are congruent with the results of Ziegler et al. (2000). They stated that overland flow enhancement on undisturbed soils needs high amounts of rainfall. Other authors also stressed that overland flow in forested study catchments is rare, and subsurface flow components are more important (e.g. Wickel et al., 2008; Chaves et al., 2008; Negishi et al., 2007; Table 1). Other issues with regard to surface runoff include the higher silica concentrations of E2 in surface runoff compared to the concentrations in shallow subsurface flow. The increasing uncertainty of surface runoff towards the end of E2 (Fig. 8b) may reflect this problem. Therefore, the calculated fractions of surface runoff during E2 must be considered critically.

4.3 Representativeness of the study site

Although we monitored only four events with low rainfall intensity, the runoff patterns of all events were comparable with regard to dynamics, initial volumes and peak flow. Regarding the computed uncertainties, the separated fractions may deviate from the presented amounts, but the order of contributions of the components is maintained. During E2, the fraction of surface runoff seems to be underestimated, potentially due to the dimension of the rainfall event. Nevertheless, the dominance of groundwater during the event remains valid.

Some of the monitored silica concentrations and EC values during stormflow were not fully bound within the chemical triangles. This may reduce the reliability of the statements gained from the evaluated events. Nonetheless, most of the measured concentrations were within the triangles and within the ranges of the standard deviation of the endmembers, making the chosen endmembers defensible. The clustering of concentrations around the GW endmember during E1 and E2 may reflect a higher variability of the GW endmember in this study.

The spatial representativeness of surface runoff sampling was improved during the 2009 campaign. The extended collection did not reveal significant differences among the samples, but future studies should extend the sampling of both surface runoff and shallow subsurface flow across the whole catchment. Moreover, we did not monitor groundwater levels and soil moisture. This hampers the interpretation of the results and makes subsurface processes somewhat speculative.

Importantly, although the monitored years differed much in the amount and distribution of rainfall, the results are very much alike.

During the study period, most parts of the catchment area were secondary forests and managed tree plantations. Only smaller patches were used for cropping. The low concentrations of Cl^- and NO_3^- (Table 3) along with the minimal differences in soil cover (leaves, weeds, etc.) and soil properties among the land use types (Schuler, 2008) suggest that agricultural practices did not significantly influence the composition of water samples and that the selected site can be regarded as representative of the catchment.

Despite these limitations and uncertainties, the present study promotes our understanding of runoff generation in this particular tropical, mountainous catchment, for which no runoff investigations are available. Additionally, our results serve as a basis for further, more detailed studies and can be used to evaluate rainfall-runoff models or solute transport in the catchment.

5 Conclusions

The present study was conducted in a remote catchment in the outer tropics. For such catchments, only very few data on runoff generation are available. Suitable tracers were identified for hydrograph separation, and data of four monitored stormflow events were analysed. Silica and EC were found to be applicable at the study site. K^+ can serve as an indicator for surface runoff dynamics, Ca^{2+} as a groundwater marker. Both may deliver more information on runoff generation if continuously monitored. Other major ions were not found to be useful for geochemical separation: their concentrations were either too low or not distinguishable among the components. To bypass this limitation, isotope tracers could be considered as another tool to elucidate runoff generation processes in this catchment. The three-component hydrograph separation revealed groundwater as the major source of stormflow during all monitored events, followed by shallow subsurface flow and surface runoff. These results indicate that runoff generation during the monitored events in the Mae Sa Noi subcatchment is in good agreement with studies from the outer tropics but not with those from the inner tropics. The hydrochemical data indicate a complex system of flow paths within the study catchment; these should be investigated at a higher spatial–temporal resolution in the future. Especially the relation between rainfall and the occurrence of shallow subsurface flow during the rainy season needs more attention.

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