HYDROLOGICAL PROCESSES
Hydrol. Process. **20**, 2921–2934 (2006)
Published online 31 July 2006 in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/hyp.6169

On the relationship between hydrographs and chemographs

Andreas Kurtenbach,[1]* Steffen Möller,[2] Andreas Krein[1] and Wolfhard Symader[1]

[1] *Department of Hydrology, University of Trier, 54286 Trier, Germany*
[2] *Institute of Geographical Sciences, Physical Geography, Freie Universität Berlin, 12249 Berlin, Germany*

Abstract:

The spatial representativeness of gauging stations was investigated in two low-mountainous river basins near the city of Trier, southwest Germany. Longitudinal profiles during low and high flow conditions were sampled in order to identify sources of solutes and to characterize the alteration of flood wave properties during its travel downstream. Numerous hydrographs and chemographs of natural flood events were analysed in detail. Additionally, artificial flood events were investigated to study in-channel transport processes.

During dry weather conditions the gauging station was only representative for a short river segment upstream, owing to discharge and solute concentrations of sources contiguous to the measurement site. During artificial flood events the kinematic wave velocity was considerably faster than the movement of water body and solutes, refuting the idea of a simple mixing process of individual runoff components. Depending on hydrological boundary conditions, the wave at a specific gauge could be entirely composed of old in-channel water, which notably reduces the spatial representativeness of a sampling site. Natural flood events were characterized by a superimposition of local overland flow, riparian water and the kinematic wave process comprising the downstream conveyance of solutes. Summer floods in particular were marked by a chronological occurrence of distinct individual runoff components originating only from a few contributing areas adjacent to the stream and gauge. Thus, the representativeness of a gauge for processes in the whole basin depends on the distance of the nearest significant source to the station. The consequence of our study is that the assumptions of mixing models are not satisfied in river basins larger than 3 km^2. Copyright © 2006 John Wiley & Sons, Ltd.

KEY WORDS runoff generation; storm events; mixing models; kinematic waves; tracer; riparian water

INTRODUCTION

The analysis of flood wave hydrographs and chemographs is seen as a promising approach to understanding runoff-generation processes within a river basin. It is assumed that the output signal at a specific monitoring station can be attributed to a complex response of the upstream basin to an input signal. This concept has been applied to investigations of runoff generation and solute transport over a wide array of basin sizes (e.g. Kennedy *et al*., 1986; Buttle, 1994; Symader and Bierl, 1998; Krein and Bierl, 1999).

Differences between flood events and basin responses can be attributed to numerous controlling factors, such as spatial and temporal rainfall distribution and intensity, antecedent soil moisture, the number and magnitude of prior flood events, the morphology and size of the basin, the four-dimensional activation of sources, and anthropogenic influences (Pilgrim *et al*., 1982; Burt, 1989; Krein, 2000; Blake *et al*., 2003). Another substantial factor is the scale-dependent alteration of significant runoff processes. With increasing catchment size, the spatial distribution of rainfall and the superimposition of flood waves, as well as their

* Correspondence to: Andreas Kurtenbach, Department of Hydrology, University of Trier, 54286 Trier, Germany.
E-mail: hydrolog@uni-trier.de

Received 22 March 2004
Accepted 10 August 2005

movement within the river network, become more and more important (Walling and Webb, 1980; Burt, 1989; Blöschl and Sivapalan, 1995).

The investigation of runoff generation and solute transport at a monitoring station using mixing models is based on several assumptions that are rarely verified and inconstantly fulfilled under varying boundary conditions (Buttle, 1994; Bonell and Fritsch, 1997; Bonell 1998). The mixing model approach has mainly been used in small, homogeneous basins (e.g. Buttle, 1994), but has also been applied in mesoscale basins larger than 3 km^2 (e.g. Caissie *et al.*, 1996; Hoeg *et al.*, 2000; Soulsby *et al.*, 2003). However, the question of whether a flood wave is in fact composed of a mixture of individual runoff components remains unsolved. The 'end-member mixing analysis' (EMMA) concept established by Christophersen *et al.* (1990) and Hooper *et al.* (1990) postulates a mixing process of discrete, time-invariant runoff components. On the other hand, Anderson *et al.* (1997) deny the existence of stable end-members. It is indeed no surprise that mixing models show good results in small, homogeneous river catchments (Hooper *et al.*, 1990; Burns *et al.*, 2001). In contrast, Krein and DeSutter (2001) confirm the need to take account of both mixing and in-channel transport processes even in small basins, and Ball and Trudgill (1997) emphasize the limitations of solutes as EMMA tracers at very small scales due to lack of conservative and constant behaviour. Locating and characterizing the end-members and evaluating their relative contributions during single storm events leads to additional difficulties and large uncertainties (Hooper *et al.*, 1998; Uhlenbrook and Hoeg, 2003).

During natural floods, the chemical composition of the water body is influenced by transformation/degradation, adsorption/desorption, dissolution/precipitation and mixing processes on its way to the river network. In particular, flow pathways on and through near-stream soils may cause significant changes even over very short flow distances and during single storm events (Chapman *et al.*, 1993; Anderson *et al.*, 1997; Ball and Trudgill, 1997). Additionally, kinematic waves within the channel (describing the translation of flow with limited hydraulic dispersion or diffusion) induce time lags between discharge and chemical response (Glover and Johnson, 1974; Nolan and Hill, 1990; Jordan-Meille *et al.*, 1998), impeding the application of simple mixing models (Krein and DeSutter, 2001).

If a flood response at a gauging station is considered as an integrated output signal of the basin to a rainfall event, then two questions have to be answered. First, which parts of the basin contribute water and dissolved solids during an event? Second, can these parts be assumed to be invariant during an event? The variable source-area concept negates this assumption (Hewlett and Hibbert, 1967). Therefore, the factors controlling the temporal and spatial variability must be determined.

Against this background, there is still a need to establish for which part of a basin and at which stage of a flood a gauging station is representative. This will be crucial for all aspects dealing with river management strategies, monitoring programmes, land-use modifications and spatially distributed runoff models.

The objective of this paper, therefore, is to assess the spatial representativeness of a gauging station. Three strategies have been adopted:

1. longitudinal profiles of important ions and electrical conductivity have been analysed to characterize the spatial variability within the river basins;
2. artificial flood events were generated to investigate in-channel related processes;
3. natural flood events have been analysed at multiple locations to characterize the temporal dynamics of runoff generation and solute transport.

STUDY AREAS

The two mesoscale basins (Figure 1) under investigation are typical of the low mountain ranges around the city of Trier, southwest Germany. They show similar moderate climatic conditions, but differ in geology and topography and are characterized by heterogeneous land use and intense anthropogenic impacts (Table I).

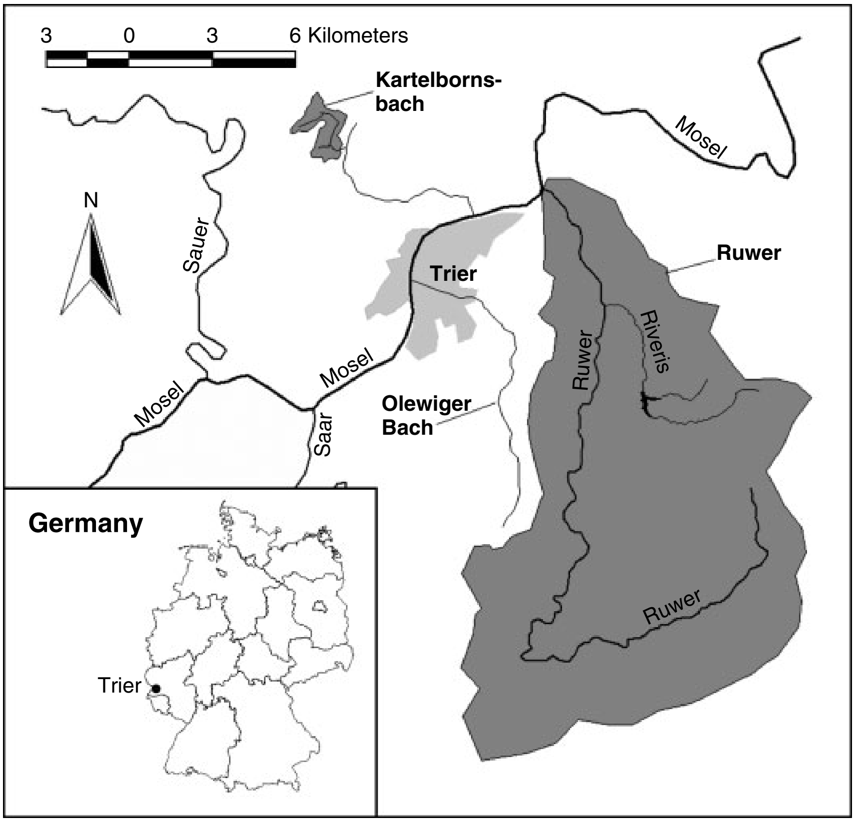

Figure 1. Map of the river basins investigated

The Kartelbornsbach catchment is situated 7 km northwest of Trier and covers an area of 3·2 km^2 (Figure 1). Triassic limestones, predominantly Upper and Middle limestone, dominate the underlying geology. Upper limestone consists mainly of calcium carbonate and Middle limestone is characterized by calcium sulphate. The catchment is covered by a mosaic of woodland, pasture and wasteland. A village with approximately 1000 inhabitants is located in the northern part of the catchment. Another small village is situated in the southern part of the catchment. The waste water of both villages has a considerable influence on the water quality of the Kartelbornsbach. Owing to the heterogeneity of the geology and land use, many sources for solutes can be found, such as diffuse and point sources of waste water, tile drains and variable inputs from groundwater and soil water.

The larger Ruwer basin, 238·5 km^2 in size, is located in the Hunsrück Mountains near the city of Trier (Figure 1). The bedrock predominantly consists of Devonian schist and quartzite. The land use is mainly arable on the broad ridges and pasture on the narrow valley bottoms. The steep, south-facing slopes in the lower reaches of the basin are planted with vineyards. North- and east-facing slopes are mainly forested. The water quality is influenced by waste-water treatment plants, several villages with minor industrial settlements, and some major streets.

MATERIAL AND METHODS

Water samples were collected midstream with 2 l polyethylene bottles. During the sampling procedure, temperature-compensated (at 25 °C) electrical conductivity and temperature were measured *in situ* using a

Table I. Characteristics of the basins investigated

	Kartelbornsbach[a]	Ruwer[b]
Catchment size (km^2)	3·2	238·5
Geology	Mainly Triassic bedrocks	Mainly quartzite and Devonian schist
Altitude (m)		
lowest	293·1	125·2
highest	392·6	707·3
Slope (°)		
mean	5·7	9·1
maximum	25·2	51·5
Mean annual temperature (°C)	8·6[c]	6 (higher ridges)[d]
	—	10 (lower valley)[d]
Mean annual precipitation (mm)	841[c]	700 (lower valley)[d]
	—	1100 (higher ridges)[d]
Land use[e] (%)		
crop land	41·8	15·8
green land	34·6	19·4
vineyards	—	1·6
forest	13·4	57·0
built-up area	10·2	3·8
water	—	0·2
deforested areas	—	2·2

[a] Selected data from Krein (2000).
[b] Selected data from Vohland *et al*. (2000).
[c] Time period 1961–1990 (Krein, 2000).
[d] Time period 1988–1993 (Vohland *et al*., 2000).
[e] Year of land-use classification: Kartelbornsbach, 2000; Ruwer, 1989.

mobile WTW conductivity meter. In the Ruwer basin, conductivity was additionally registered every 6 min by a data logger at the gauging station in Kasel. In the laboratory the water samples were filtered through Whatman GF/F glass-fibre filters, acidified with concentrated HNO_3 for metal analyses and stored prior to analysis at 4 °C. The dissolved anions (nitrate, sulphate, chloride) were analysed by ion chromatography (Metrohm 690 IC). Dissolved orthophosphate was determined with a photometer using the standardized molybdenum blue method recommended by the Deutsche Einheitsverfahren. The dissolved metals (calcium, magnesium, potassium, sodium, iron, manganese, zinc) were analysed by atomic absorption spectroscopy (AAS Varian-SpectrAA-640 GTA100; AAS Varian-SpectrAA-10). Reference materials were analysed and measurements were repeated to meet analytical quality assurance standards. Relative standard deviations of methods and determinations were lower than 7%. A number of metal analyses were additionally checked using an Agilent ICP-MS 7500i. Correlation coefficients between the atomic absorption spectroscopy and inductively coupled plasma mass spectrometry measurements of all elements were higher than 0·96. All statistical analyses were carried out with SPSS® for Windows.

Figure 2 shows the sampling locations during the artificial flood events in the Ruwer and Kartelbornsbach. In the Ruwer channel, the artificial flood events were generated by the release of water from a drinking-water reservoir in cooperation with the Trier municipal water works (Figure 2). In the Kartelbornsbach, the artificial flood wave was generated in cooperation with the ‘Technisches Hilfswerk’ by pumping low conductivity water out of a small reservoir into the river. Channels of both basins are predominantly rectangular shaped with medium channel slope. For instance, channel slope in the Ruwer reach between Waldrach and Kasel amounts to 0·75%.

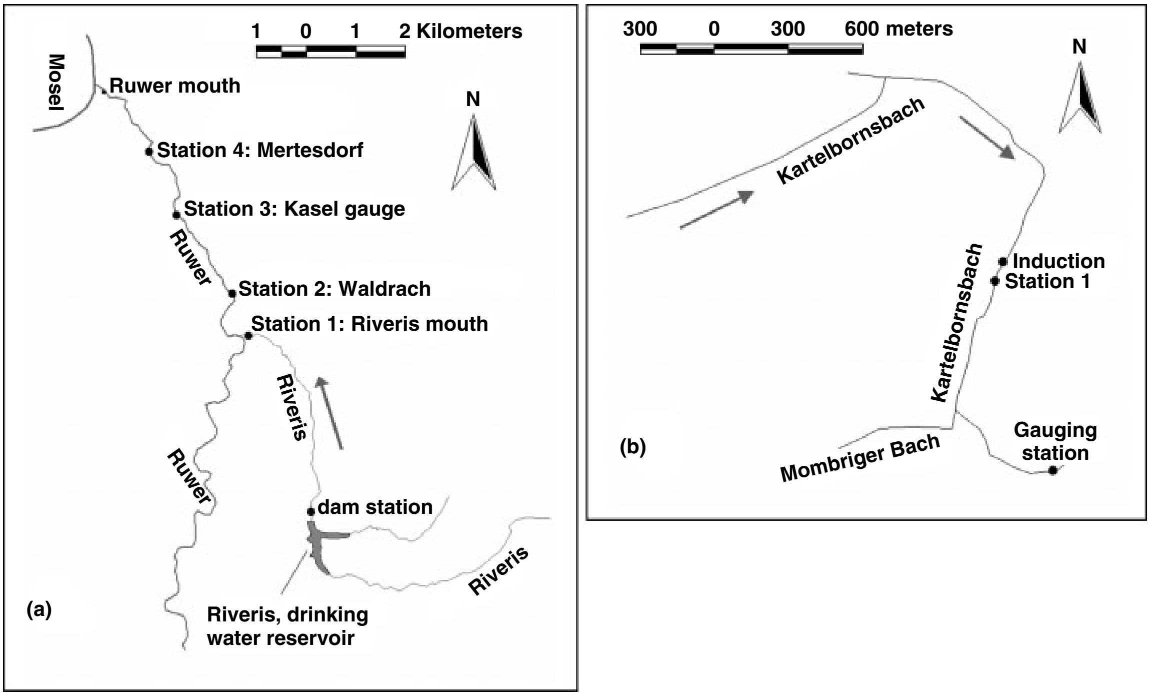

Figure 2. Sampling sites used during the artificial flood events on (a) the Ruwer and (b) the Kartelbornsbach

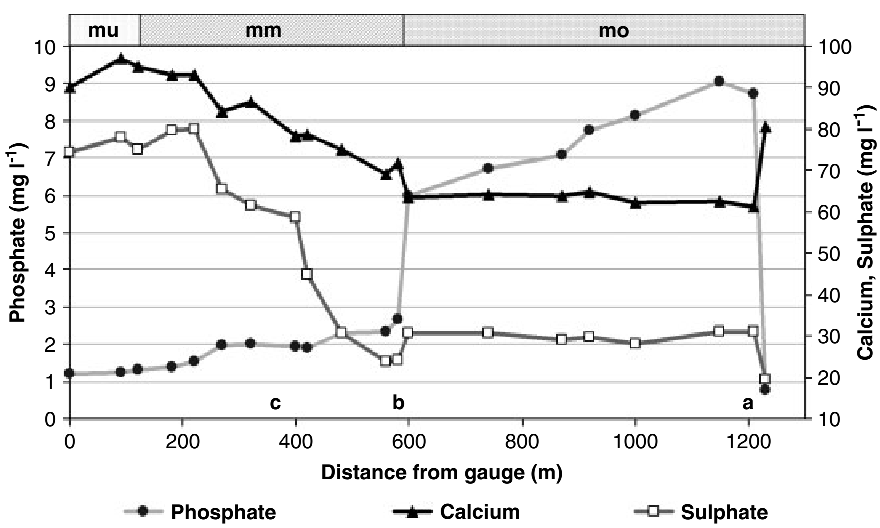

Figure 3. Longitudinal profiles of dissolved calcium, sulphate and phosphate along the Kartelbornsbach on 19 June 2000. The course of the Kartelbornsbach River flows through outcrops of Upper limestone (mo), Middle limestone (mm) and Lower limestone (mu)

RESULTS AND DISCUSSION

The spatial representativeness of a gauging station during dry weather conditions

The heterogeneity in geology and the various anthropogenic impacts within the Kartelbornsbach catchment result in a complex pattern of potential solute sources. Figure 3 depicts the variability of phosphate, calcium and sulphate along a typical dry-weather longitudinal profile on 19 June 2000. Three major sources are responsible for significant solute and conductivity changes along the river course. The first is the outflow of a sewage treatment plant (a). Its waste water is predominantly characterized by high phosphate and low calcium concentrations. During extreme summer conditions, the upper course of the Kartelbornsbach is dry and the outflow of the sewage treatment plant is the sole source of the river. The second major source is a spring, the Kartelborn (b), located on the boundary between the Upper and Middle limestone. This source delivers water with medium amounts of calcium, magnesium and hydrogen carbonate and low concentrations of sulphate. Because of relatively high discharge amounts even during dry summer periods, this spring has a considerable influence on the water quality and significantly dilutes the high phosphate concentrations released by the sewage treatment plant. The third source is a diffuse input of groundwater and soil water rich in calcium sulphate from the Middle limestone entering the river via various tile drains (c). Maximum sulphate concentrations up to 1040 mg l^{-1} have been measured at this source. Despite relatively low discharge amounts, these tile drains are responsible for marked longitudinal variability of electric conductivity, calcium and sulphate concentrations (Möller and Symader, 2001). Consequently, the lower course of the Kartelbornsbach is dominated by geological inputs, whereas the major part of the middle course is characterized by anthropogenic impacts.

In order to determine the sources that contribute significantly to dry-weather flow, a statistical analysis was carried out involving 25 longitudinal profiles of conductivity as a parameter reflecting the sum of the major ions in the Kartelbornsbach (Möller, 2002). Correlation coefficients between the conductivity at the gauging station and the conductivity at each single sampling site were calculated. The upper graph in Figure 4 depicts the results of this analysis. The correlation coefficient between the conductivity at the gauging station and a specific sampling site exceeds |0·7| only for the last 480 m of the river course. Thus, only for this river segment could more than 49% of the variance of the conductivity record at the gauging station be explained by the variation of conductivity at a single sampling site.

Sampling strategies at a gauging station often take the discharge variation into account. However, not much thought has been given to the question of over what upstream distance and for which upstream basin area the relationship between discharge and water quality and the conclusions drawn from this can be assumed to be representative. The lower graph shows the correlation between the discharge at the gauge and the conductivity

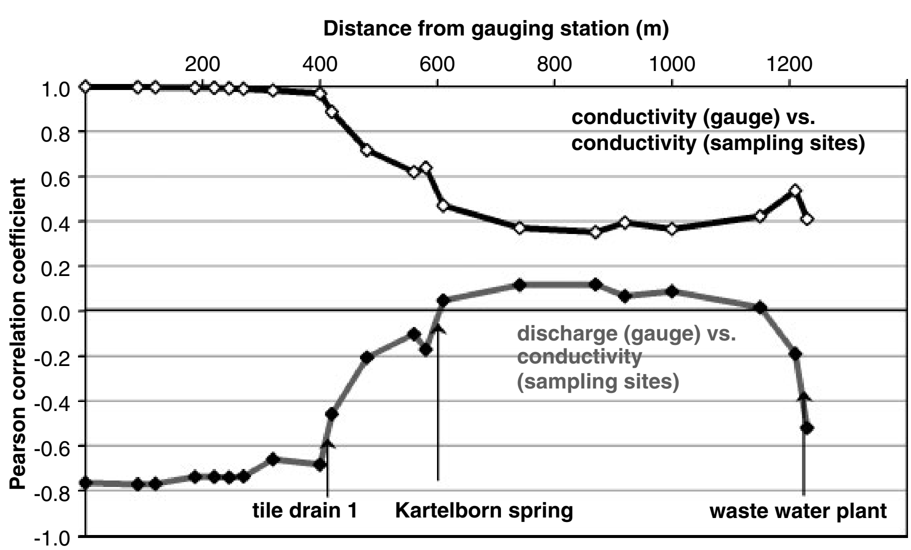

Figure 4. Correlation coefficients between electrical conductivity and discharge at the gauge and conductivity at the sampling sites along the Kartelbornsbach

at the sampling sites. Here, the situation is even worse than for the specific conductance values described above. Only for an upstream segment of 270 m does the relationship exceed |0·7|.

Although it is well known that the spatial distribution of solute sources is a controlling factor for the chemographs measured at a gauging station (e.g. Walling and Webb, 1980), the significance of a single source mostly remains unknown. Our results show that the representativeness of a gauge for processes in the upstream basin depends on the distance of the nearest significant source to the station. Consequently, analysis of the spatial and temporal behaviour of the sources is a prerequisite for establishing representative monitoring stations. Additionally, tracing the sources and upstream governing processes from a single gauging station, for instance by using mixing models, needs the consideration of the spatial significance of near-gauge sources.

The spatial representativeness of a gauging station during artificial flood waves

Artificial flood events provide a powerful tool for elucidating the impact of in-channel processes on the spatial representativeness of gauging stations. During these field experiments, hydrographs and chemographs at a specific sampling site can be attributed to the preceding dry-weather flow, certain autochthonous sources and the amount and composition of the water introduced.

Figure 5 depicts the change of discharge and solute transport during the downstream travel of an artificial flood event in the Ruwer basin on 12 July 2001. The locations of the sampling stations are illustrated in Figure 2. The discharge released (1000 l s^{-1} for 1 h) from the drinking water reservoir was five times higher than the long-term mean discharge of the Riveris tributary and approximately three times higher than the long-term lower discharge of the Ruwer. The water input from the drinking-water reservoir started at 09 : 35. The water introduced had a conductivity of 75 µS cm^{-1}, which is less than that of the receiving river.

At Station 1, representing the reaction of the Riveris tributary, the conductivity decreases nearly simultaneously with water rise due to the rapid arrival of the introduced water. The velocity of the wave to this station was approximately 0·87 m s^{-1}. At Stations 2 and 3, characterizing the transport patterns in the Ruwer, a distinct decoupling of the water rise and the arrival of the induced water was observed. The wave velocity up to Station 2 was 0·99 m s^{-1}. In contrast, the new water is transported at only 0·38 m s^{-1}. The wave velocity was calculated by dividing the distance between Stations 1 and 2 by the time difference between the first rise in water level at both stations, and the water velocity was calculated by dividing the distance by the time difference between the first change in conductivity at both stations. At Station 2, the time lag between the rising limb of the flood wave and the first recognizable change of conductivity was 36 min. At Station 3, this time lag between wave and water arrival increases to 110 min. Consequently, almost the entire flood wave was composed of old water. The wave velocity up to Station 3 was approximately 0·64 m s^{-1}. In contrast, the new introduced water is transported at only 0·27 m s^{-1}. The ratio of the wave speed to the water speed amounts to approximately 2·59 between Stations 1 and 2 and 2·33 between Stations 2 and 3. At both stations the water level regains its preceding value considerably faster than the conductivity. The short-term increase in conductivity evident at both stations (Figure 5a) was attributed to an increasing input of ion-rich Riveris water to the Ruwer at the beginning of the event at Station 1.

A similar decoupling of the wave and the water body was found in the smaller Kartelbornsbach after a travel distance of only 80 m (Figure 6). The artificial flood wave was generated on 8 August 2001 by introducing 1000 l of low-conductivity water into the river within 30 s. The conductivity remains constant during the steeply rising limb of the wave between 10 : 26 and 10 : 28. Again, the water level returns to its preceding value considerably faster than the conductivity.

The time lag demonstrated in both basins can be explained by kinematic wave theory (Singh, 1996; Krein and DeSutter, 2001; Wong, 2002). The discharge response develops like a kinematic wave (describing the translation of flow with limited hydraulic dispersion or diffusion), in contrast to the slower physical mass transport of the water body and the associated dissolved material. The disconnection between discharge response and solute transport is related to the flow distance (Figure 5), the antecedent dry-weather flow, the characteristics and size of the river network, the properties of the main and tributary channels (e.g. geometry

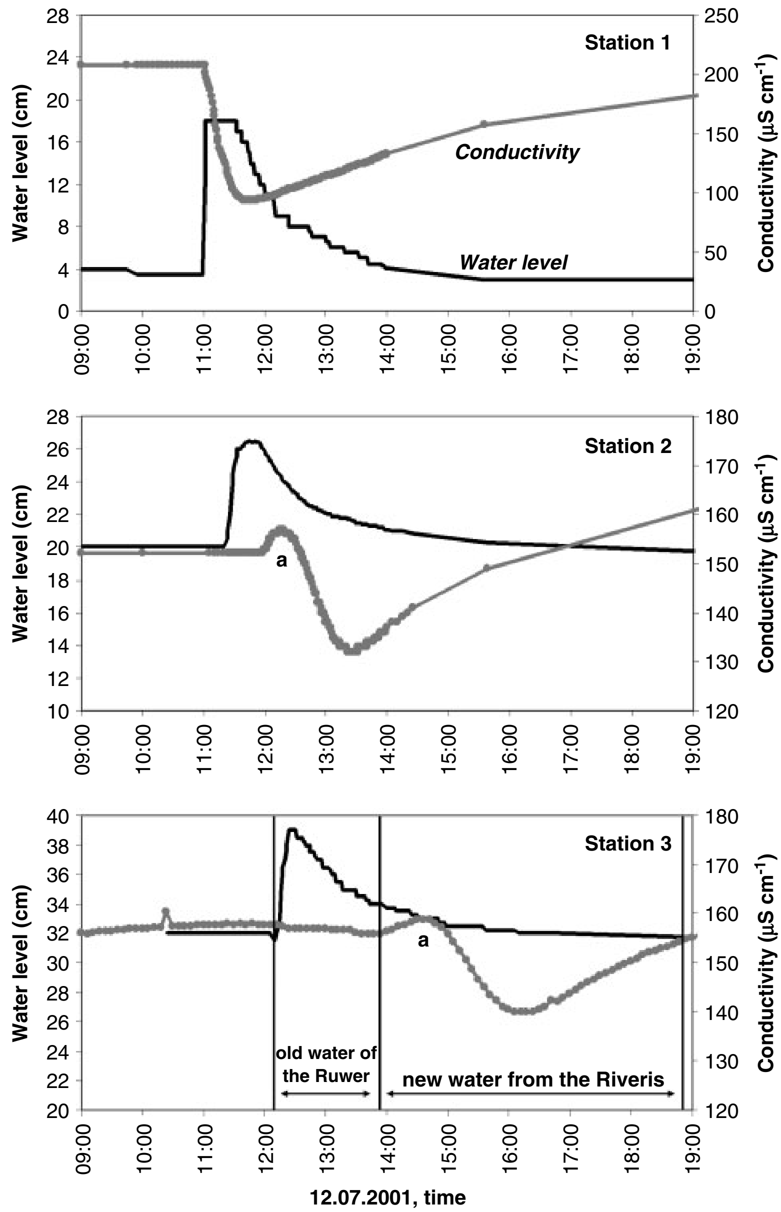

Figure 5. Runoff and conductivity dynamics during an artificial flood event in the Ruwer basin on 12 July 2001 (for sampling stations, see Figure 2a)

and slope), and the magnitude of the artificial discharge introduced. Table II depicts the influence of the introduced discharge and the antecedent hydrological conditions on the time lag between wave and water arrival in the Ruwer channel. The largest time lag at Waldrach and Kasel station gauges was found during an artificial wave with the lowest introduced discharge. Additionally, during the waves with 1500 l s^{-1} introduced discharge, the time lag increases with decreasing antecedent dry-weather flow. The latter could also be shown in the neighbouring, smaller basin of the Olewiger Bach (see Figure 1; Krein and DeSutter, 2001). The increasing time lag during low-flow conditions could be attributed to stronger friction losses on the water

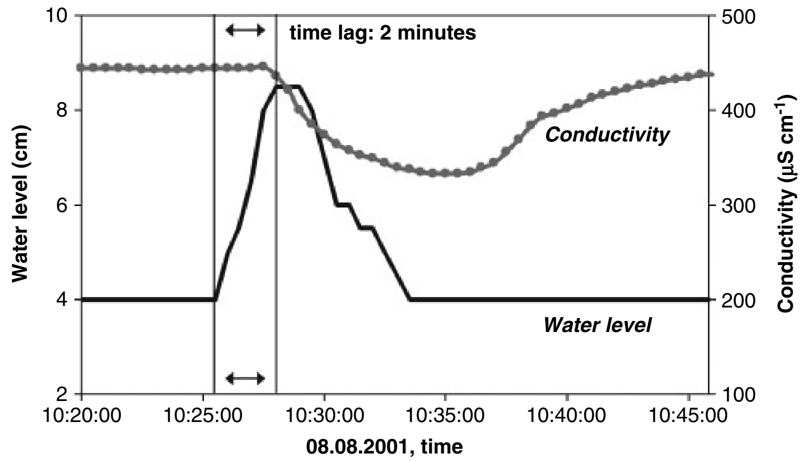

Figure 6. Runoff and conductivity dynamics during an artificial flood event in the Kartelbornsbach basin on 8 August 2001 at Station 1, 80 m below the introduction point (see Figure 2b)

Table II. Impacts of the introduced discharge and antecedent hydrological conditions on the time lag between wave and water arrival at two stations in the Ruwer channel

Date of artificial flood (2001)	12 July	30 July	6 August	16 July	28 May
Discharge released from water reservoir for 1 h (l s^{-1})	1000	1500	1500	1500	2000
Pre-event hydrological conditions					
Initial water level at Station Kasel gauge (cm)	32	30	35	40	42
Antecedent precipitation amount (mm)					
1 day[a]	0·2	0·0	4·5	0·0	0·0
7 days[a]	21·6	24·8	15·9	47·5	0·0
Time lag (min)					
Station 2 Waldrach	36	27	23	19	—
Station 3 Kasel gauge	110	76	71	63	40

[a] Rainfall station Avelsbach, Trier.

body and an increasing influence of morphological riffle–pool sequences, where the pools hold back the water body more strongly than the wave itself.

The greater velocity of the wave in comparison with the dissolved material was calculated for regular channels by Wong (2002). The kinematic wave process has been mainly described for large natural river channels (Glover and Johnson, 1974), but it could also be identified in very short channel sections and small basins (Nolan and Hill, 1990; Jordan-Meille *et al.*, 1998). Kinematic waves have also been utilized to describe pressure transmission processes in soils to provide a possible explanation for rapid pre-event water transport to the channel (Beven, 1989, 2001).

The different wave and water-body velocities refute the idea of a simple mixing process of individual runoff components. Additionally, if temporal variations in water quality are observed during the main part of the wave, then it can be concluded that their sources must be located contiguous to the measuring point. The flood wave from the Ruwer at Station 3 (Figure 5) consists totally of old water, which can only come from the 3·3 km Ruwer segment upstream (see Figure 2).

Kinematic wave theory provides a good framework for explaining the occurrence of natural flood waves consisting mainly of old water. Even in very small basins, the old water can come from the channel and from soil water, where similar pressure waves can be assumed (Bonell, 1998; Beven, 2001). Nolan and Hill (1990) note that the volume of dry-weather flow prior to the event is a limiting factor for in-channel kinematic waves. Nevertheless, our results reveal that considerable time lags and impacts of the old channel water could be identified at times of low antecedent dry-weather flow and even over very short travel distances.

The hydrograph and chemograph differ not only in travel time, but also in shape. In contrast to the kinematic wave, the temporal variation of solute concentration can vary considerably. Conservative tracers are influenced by longitudinal dispersion (e.g. Rutherford, 1994). Non-conservative tracers additionally change because of transformation/degradation, adsorption/desorption and precipitation processes (e.g. Jordan-Meille *et al.*, 1998). Figure 7 shows the impact of longitudinal dispersion during an artificial event in the Ruwer channel on 30 July 2001. The conductivity range at Station 4 is reduced to about 40% compared with Station 2 in a channel segment of only 3·7 km (of a total 46 km). This underlines the difficulty of inferring the contribution of a particular source at the measuring site in relation to a source in the upper basin by analysing hydrographs and chemographs at a single station.

The spatial representativeness of a gauging station during natural flood waves

Natural flood events are controlled by both in-channel and catchment processes. The results of the artificial wave experiments lead to the conclusion that all solute sources causing significant changes in water quality during an event are located near the station.

Figure 8 illustrates a typical natural flood in the Kartelbornsbach basin following a short convective precipitation event on 23 July 1989 (modified according to Strunk (1992)). The wave starts with a small Hortonian preflush coming from impervious areas contiguous to the gauge and an additional input out of the sewer system. Subsequently, a distinct succession of three peaks of dissolved calcium, manganese and iron was found. The activated source area was riparian water released from different soil depths. Near-stream upper soil horizons release water rich in calcium. The increase in manganese is linked to an input from intermediate soil horizons. The delayed response of suspended iron indicates the influence of deeper soil water or groundwater. The successive release of manganese and iron is linked to a gradient of the redox potential. The chronology of the release of calcium, manganese and iron from different soil depths in the riparian zone was verified by sprinkling experiments in the Kartelbornsbach basin (Krein, 2000). The time lag

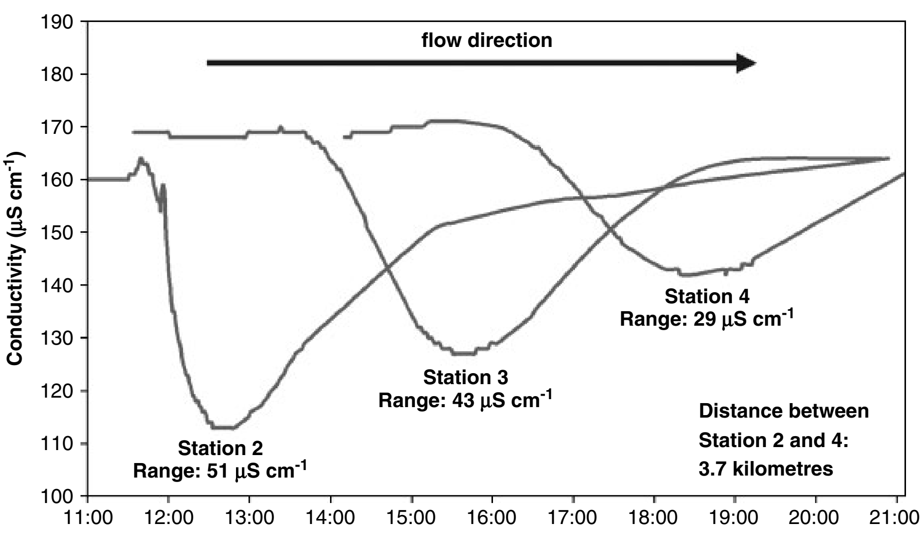

Figure 7. Longitudinal dispersion of conductivity during an artificial flood in the Ruwer basin on 30 July 2001 (for sampling stations, see Figure 2a)

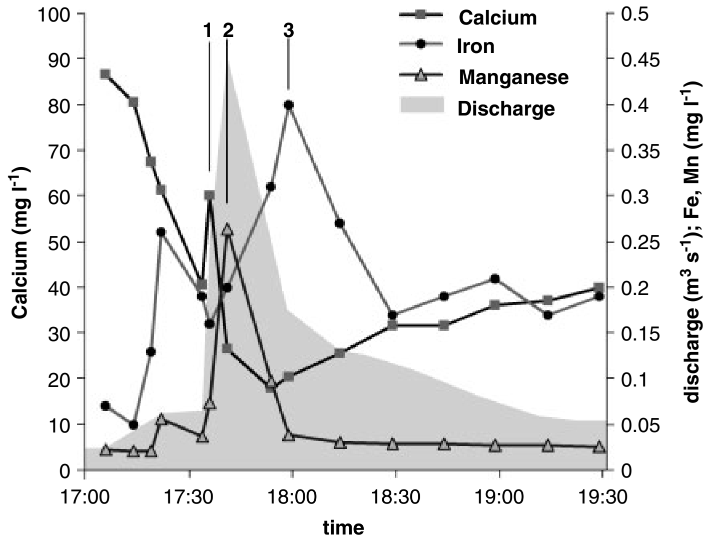

Figure 8. Temporal variation of calcium, manganese and iron concentrations during a single peaked flood wave on the Kartelbornsbach

between the peaks is mainly controlled by the water content of soils in the valley bottom. The development of the complete pattern requires a certain amount of rain. With decreasing precipitation amounts, first the peak in iron and then the peak in manganese fail to appear, whereas calcium, an indicator for contributions from the upper soil horizons, is mobilized even by small rain amounts.

Although the significant controlling processes change with increasing catchment size (Pilgrim *et al.* 1982; Blöschl and Sivapalan, 1995), the Hortonian flush and the delayed iron response in particular were also found in the larger Ruwer basin (Figure 9; Kurtenbach *et al.* (2002)). However, in this basin, the influence of these local inputs coming from the vicinity of the sampling site are superimposed on the influence of conveyance processes in the channel, as shown by a double-peaked natural flood at two stations in the Ruwer basin (Figure 9). The flood response was generated by a basin-wide precipitation event with its maximum around 23 : 30 on 6 July 2001. The first discharge peak is caused by contributing areas near the station (Figure 9a) and the second discharge peak shows the effect of the upper part of the basin (Figure 9b). Therefore, it can

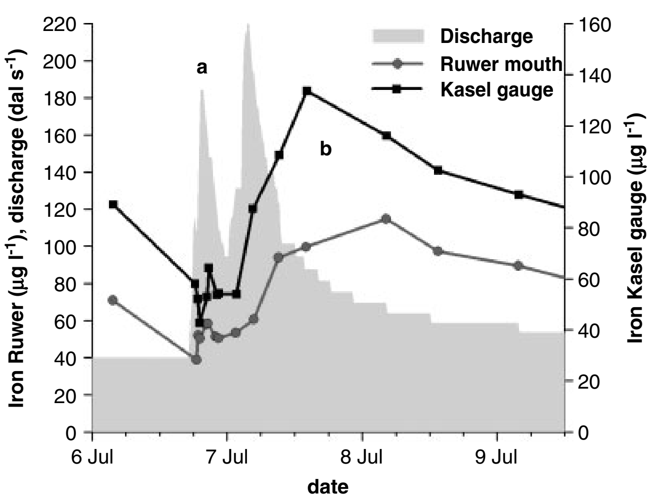

Figure 9. Iron dynamics during a natural flood event in the Ruwer basin on 7 July 2001; distance between the sampling sites 3·4 km

be concluded that the first variations in iron are caused by the contribution of sources in the vicinity of the sampling stations (Figure 9a).

However, by analysing hydrographs and chemographs only at the basin outlet, neither the exact location of the sources nor the possible participation of kinematic waves is assessable. Two explanations are always possible for the deferred rise in iron shown in Figures 8 and 9. The first is a delayed input of riparian water in the vicinity of the gauge. The second is a kinematic wave generated in the upper basin, which could produce the same hydrograph and delayed iron peak at the gauge. This ambiguity reinforces the problem described by Hooper *et al*. (1998), that the important influence of riparian zones on stream water chemistry complicates the inference of hydrological flow paths from stream water chemistry dynamics. This problem will still have to be overcome in future research projects.

Preliminary insight can be gained by tracing natural events downstream. In the Kartelbornsbach, five longitudinal profiles of electrical conductivity were measured during a natural flood event on 7 March 2001 (Möller, 2002). The five longitudinal profiles demonstrate the movement of the flood wave along the river course (Figure 10). During the first profile, at 08 : 30, the absolute minimum conductivity is located around 1200 m upstream of the gauging station (1). After 1 h, the minimum was located between 800 and 900 m (2). Between these two stations, no sources of surface runoff with low solute content could be found. The downstream movement of the conductivity minimum is, therefore, mainly caused by the travelling flood wave from the upper reaches.

In the third profile, at 10 : 25, the minimum conductivity was located around 245 m upstream of the gauging station (3). Simultaneously, a local conductivity minimum and the discharge maximum occur at the gauging station. This local minimum cannot be linked to the water from the upper basin. Activation of overland flow sources and an input of water of low solute content derived from impervious areas around the gauging station are primarily responsible for this conductivity minimum. The minimum from the upper basin appears at the gauging station in the fourth profile (4) at 11 : 15, whereas the chemograph of conductivity at this station shows a renewed rise. Hence, the conductivity minimum at the gauging station only reflects contributing areas located 245 m upstream of the gauging station. The conductivity minimum from the upper basin has only a minor influence in the recession limb of the wave. A sample taken during the discharge maximum is, therefore, only representative for 245 m upstream and mainly influenced by new water of low conductivity originating from impervious areas in the vicinity of the gauge.

These results show that the water from the upper basin reaches the gauge considerably later than the discharge maximum and is of minor importance due to longitudinal dispersion. The more important controlling factor for the local conductivity minimum is the contribution of sources near the gauge, resulting in the local minimum prior to the arrival of the conductivity minimum from the upper course. Therefore, the sources near

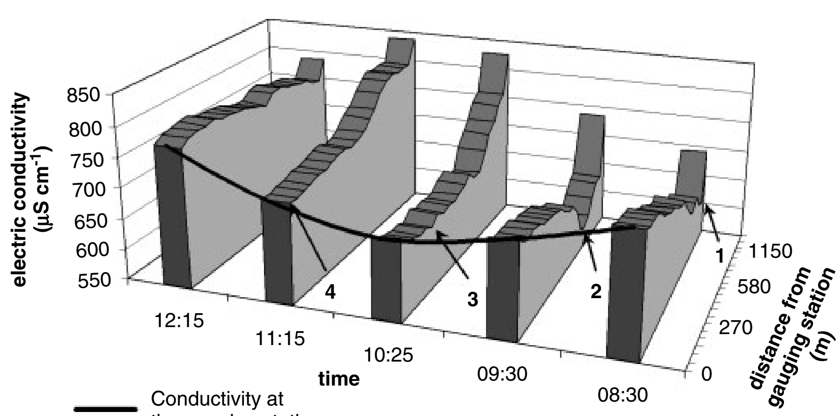

Figure 10. Longitudinal profiles of electrical conductivity during a natural flood event in the Kartelbornsbach basin on 7 March 2001. The numbers 1–4 mark the movement of the conductivity minimum

the gauge are important for understanding the hydrograph and chemograph variability during the main part of a flood wave, whereas the water from the upstream basin affects the recession limb.

CONCLUSIONS

The results presented demonstrate that near-gauge sources, in-stream processes and the spatial and temporal activation of contributing source areas have a considerable influence on the runoff response and solute transport in low-mountainous river basins. The following conclusions can be drawn:

1. During dry weather conditions, the spatial representativeness of a gauge is strongly controlled by the distribution, temporal behaviour and discharge of sources contiguous to the station. In the Kartelbornsbach catchment (3·2 km^2, 3 km river length) a sample collected from the gauging station is only representative for a river segment 400 to 500 m upstream.
2. Kinematic waves are not restricted to large basins. The kinematic wave process precludes a simple correlation of hydrograph and chemograph. The artificial wave in the Ruwer basin (238·5 km^2) was composed entirely of old water after travelling only 3 km. In the smaller Kartelbornsbach catchment, a disconnection between discharge response and solute transport was already evident after 80 m. This decoupling between water input and wave arrival results in a crucial reduction in the spatial representativeness of a gauge.
3. As a consequence of conclusion (2), the large amount of old water observed during the first stages of natural flood events is probably preceding dry-weather flow incorporated into the flood hydrograph by the kinematic wave process.
4. During natural summer floods, the spatial representativeness of a gauge is determined solely by a few hydrologically connected areas adjacent to the stream. During a natural flood in the Kartelbornsbach, chemographs and hydrographs for the rising limb and maximum were controlled by contributing areas located only 245 m upstream of the gauge. Longitudinal dispersion and the kinematic wave process are responsible for the limited relevance and delayed arrival of water parcels from the upper basin. The contribution of the sources depends on their spatial distribution and the flow pathways of the event water.
5. Use of mixing models to quantify the variability of the chemical composition of river water should be limited to very small basins and short river lengths.

ACKNOWLEDGEMENTS

This research project was supported financially by the German Research Foundation. We would like to thank the Trier municipal water works for generating the artificial floods in the Ruwer basin. Grateful thanks are also extended to the numerous field assistants and employees in the laboratory of the Department of Hydrology. The anonymous reviewers are acknowledged. We thank the "Landesamt für Wasserwirtschaft Rheinland-Pfalz", the "Struktur- und Genehmigungsdirektion Nord, Trier" and the "Dienstleistungszentren Ländlicher Raum Rheinland-Pfalz" for supplying discharge and precipitation data sets for the Ruwer basin.

REFERENCES

Anderson SP, Dietrich WE, Torres R, Montgomery DR, Louage K. 1997. Concentration–discharge relationships in runoff from a steep, unchanneled catchment. *Water Resources Research* **33**(1): 211–225.

Ball J, Trudgill S. 1997. Potentials and limitations in using geochemical tracers. In *Hydrochemistry*, Peters NE, Coudrain-Ribstein A (eds). IAHS Publication No. 244. IAHS Press: Wallingford; 165–185.

Beven KJ. 1989. Interflow. In *Unsaturated Flow in Hydrologic Modeling: Theory and Practice*, Morel-Seytoux HJ (ed.). Kluwer: Dordrecht; 191–219.

Beven KJ. 2001. *Rainfall-Runoff Modelling: The Primer*. Wiley: Chichester.

Blake WH, Walsh RPD, Barnsley MJ, Palmer G, Dyrynda P, James JG. 2003. Heavy metal concentrations during storm events in a rehabilitated industrialized catchment. *Hydrological Processes* **17**: 1923–1939.

Blöschl G, Sivapalan M. 1995. Scale issues in hydrological modelling: a review. *Hydrological Processes* **9**: 251–290.

Bonell M. 1998. Selected challenges in runoff generation research in forests from the hillslope to headwater drainage basins scale. *Journal of the American Water Resources Association* **34**(4): 765–785.

Bonell M, Fritsch JM. 1997. Combining hydrometric-hydrochemistry methods: a challenge for advancing runoff generation process research. In *Hydrochemistry*, Peters NE, Coudrain-Ribstein A (eds). IAHS Publication No. 244. IAHS Press: Wallingford; 165–184.

Burns DA, McDonnell JJ, Hooper RP, Peters NE, Freer JE, Kendall C, Beven K. 2001. Quantifying contributions to storm runoff through end-member mixing analysis and hydrologic measurements at the Panola Mountain Research Watershed (Georgia, USA). *Hydrological Processes* **15**: 1903–1924.

Burt TP. 1989. Storm runoff generation in small catchments in relation to the flood response of large catchments. In *Floods—Hydrological, Sedimentological and Geomorphological Implications*, Beven K, Carling P (eds). Wiley: Chichester; 11–35.

Buttle JM. 1994. Isotope hydrograph separations and rapid delivery of pre-event water from drainage catchments. *Progress in Physical Geography* **18**(1): 16–41.

Caissie D, Pollock TL, Cunjak RA. 1996. Variation in stream water chemistry and hydrograph separation in a small drainage basin. *Journal of Hydrology* **178**: 137–157.

Chapman PJ, Wheater HS, Reynolds B. 1993. The effect of geochemical reactions along flowpaths on storm water chemistry in headwater catchments. In *Tracers in Hydrology*, Peters NE, Hoehn E, Leibundgut Ch, Tase N, Walling DE (eds). IAHS Publication No. 215. IAHS Press: Wallingford; 23–30.

Christophersen N, Neal C, Hooper RP, Vogt RD, Andersen S. 1990. Modelling stream water chemistry as a mixture of soil water endmembers—a step towards second generation acidification models. *Journal of Hydrology* **116**: 307–320.

Glover BJ, Johnson P. 1974. Variations in the natural chemical concentration of river water during flood flows, and the lag effect. *Journal of Hydrology* **22**: 303–316.

Hewlett JD, Hibbert AR. 1967. Factors affecting the response of small watersheds to precipitation in humid areas. In *Forest Hydrology*, Sopper WE, Lull HW (eds). Pergamon: Oxford; 275–290.

Hoeg S, Uhlenbrook S, Leibundgut C. 2000. Hydrograph separation in a mountainous catchment—combining hydrochemical and isotopic tracers. *Hydrological Processes* **14**: 1199–1216.

Hooper RP, Christophersen N, Peters NE. 1990. Modelling stream water chemistry as a mixture of soil endmembers—an application to the Panola Mountain catchment, Georgia. *Journal of Hydrology* **116**: 321–343.

Hooper RP, Aulenbach BT, Burns DA, McDonnell JJ, Freer J, Kendall C, Beven K. 1998. Riparian control of stream water chemistry: implications for hydrochemical models. In *Hydrology, Water Resources and Ecology in Headwaters*, Kovar K, Tappeiner U, Peters NE, Craig RG (eds). IAHS Publication No. 248. IAHS Press: Wallingford; 451–458.

Jordan-Meille L, Dorioz JM, Mathieu N. 1998. Approche expérimentale par crue artificielle de la participation du réseau hydrographique a l'exportation de phosphore par un petit bassin versant rural. *Water Research* **32**(6): 1801–1810.

Kennedy VC, Kendall C, Zellweger GW, Wyerman TA, Avanzino RJ. 1986. Determination of the components of stormflow using water chemistry and environmental isotopes, Mattole river basin, California. *Journal of Hydrology* **84**: 107–140.

Krein A. 2000. Influences of the soil on the shape of the hydrograph and solute transport during floods in small catchments. *Hydrologie und Wasserbewirtschaftung* **44**(1): 19–27 (in German).

Krein A, Bierl R. 1999. Identifying major sources of organic micropollutants and heavy metals during flood events in a partly urbanized headwater catchment. In *Impacts of Urban Growth on Surface water and Groundwater Quality*, Ellis JB (ed.). IAHS Publication No. 259. IAHS Press: Wallingford; 263–268.

Krein A, DeSutter R. 2001. Use of artificial flood events to demonstrate the invalidity of simple mixing models. *Hydrological Sciences Journal* **46**(4): 611–622.

Kurtenbach A, Krein A, Symader W. 2002. The dynamics of contaminant transport at different scales during natural and artificial flood events. In *International Conference on Flood Estimation*, Berne, Switzerland, Spreafico M, Weingartner R (eds). CHR/KHR report no. II-17, International Commission for the Hydrology of the Rhine Basin; 165–174.

Möller S. 2002. *Räumliche und zeitliche Analyse von Stoffquellen und Abflussprozessen im Einzugsgebiet des Kartelbornsbaches*. PhD thesis, University of Trier, dissertation.de Verlag im Internet GmbH: Berlin.

Möller S, Symader W. 2001. Spatial distribution and temporal behaviour of dry weather flow components in a small drainage catchment. In *Runoff Generation and Implications for River Basin Modelling*, Leibundgut Ch, Uhlenbrook S, McDonnell J (eds). Freiburger Schriften zur Hydrologie, Band 13. Institute of Hydrology, University of Freiburg: Freiburg; 54–59.

Nolan KM, Hill BR. 1990. Storm-runoff generation in the Permanente Creek drainage catchment, west central California—an example of flood-wave effects on runoff composition. *Journal of Hydrology* **113**: 343–367.

Pilgrim DH, Cordery I, Baron BC. 1982. Effects of catchment size on runoff relationships. *Journal of Hydrology* **58**: 205–221.

Rutherford JC. 1994. *River Mixing*. Wiley: Chichester.

Singh VP. 1996. *Kinematic Wave Modelling in Water Resources: Surface Water Hydrology*. Wiley: New York.

Soulsby C, Rodgers P, Smart R, Dawson J, Dunn S. 2003. A tracer-based assessment of hydrological pathways at different spatial scales in a mesoscale Scottish catchment. *Hydrological Processes* **17**: 759–777.

Strunk N. 1992. Case studies of variations in suspended matter transport in small catchments. *Hydrobiologia* **235–236**: 247–255.

Symader W, Bierl R. 1998. The heterogeneity of runoff and its significance for water quality problems. *Hydrological Sciences Journal* **43**(1): 103–113.

Uhlenbrook S, Hoeg S. 2003. Quantifying uncertainties in tracer-based hydrograph separations: a case study for two-, three- and five-component hydrograph separations in a mountainous catchment. *Hydrological Processes* **17**: 431–453.

Vohland M, Treis A, Krein A, Udelhoven T, Hill J. 2000. Land use related modelling of flood relevant flow components in the Ruwer basin. (in German) *Hydrologie und Wasserbewirtschaftung* **44**(4): 190–200.

Walling DE, Webb BW. 1980. The spatial dimension in the interpretation of stream solute behaviour. *Journal of Hydrology* **47**: 129–149.

Wong TSW. 2002. Discussion of: Use of artificial flood events to demonstrate the invalidity of simple mixing models. *Hydrological Sciences Journal* **47**(5): 833–837.

