

Article



# Drainage Runoff Separation of New and Old Water Based on Precipitation, Air, Water, and Soil Temperature Compared to Stable Isotopes <sup>18</sup>O and <sup>2</sup>H

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Abstract: In order to evaluate the proportion of old and new water in drainage runoff, we recorded air temperature, drainage discharge, drainage runoff temperature, soil temperature, precipitation totals, and temperature. The results of separation by temperature were compared with the results of chemical separation using the stable isotopes  $\delta^{18}$ O and  $\delta^{2}$ H measured in causal precipitation and monitored in drainage runoff. Separation was determined based on precipitation temperature in 18 rainfall–runoff events and on soil temperature in 20 rainfall–runoff events, with no significant difference between results of separation of drainage runoff based on temperature and that based on isotopes. Separation of runoff based on temperature is feasible only for simple isolated rainfall–runoff events as opposed to those involving multiple rainfalls. Time to peak discharge was identified as a viable factor to determine whether to employ separation based on soil temperature or on precipitation. The results suggest that, conditional on analysis of a larger dataset, isotope separation of drainage runoff and, possibly, runoff in watercourses may potentially be replaced with more economical and technically simple measurement of soil and precipitation/air temperature.

**Keywords:** tile drainage; rainfall–runoff event; runoff separation; stable isotope <sup>18</sup>O; stable isotope <sup>2</sup>H; temperature

# 1. Introduction

Runoff hydrograph separation based on natural tracer analysis [1] has been used in small catchments [2,3] since the mid-20th century. Analysis of natural stable isotopes in precipitation water, soil water, groundwater, and runoff has deepened our insight into the origins of runoff water and increased our knowledge of runoff generation processes on slopes [4]. Stable isotopes are frequently used for this purpose [5–7], Šanda et al. [8] reviewed their use for hydrograph separation. The advantage of using isotopes is their strictly conservative behavior passing through the environment [9,10]. Use of tracers is the most direct method of obtaining information on runoff paths and the duration of water residence in a catchment [11]. The most practical tracers are those that are least affected by their environment and that can be dissolved in or transported through water. The employment of the stable isotopes of oxygen ( $^{17}O$ ,  $^{18}O$ ) and hydrogen ( $^{2}H$ -deuterium) as natural components of water was suggested by Kendall and McDonnell [12]. Chemical tracers include silicon in the form of SiO<sub>2</sub> [13], potassium (K<sup>+</sup>) [14], calcium (Ca<sup>2+</sup>) [15], chlorine Cl<sup>-</sup> [16], and magnesium (Mg<sup>2+</sup>) [17]. The primary disadvantages of the use of



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). chemical tracers are the labor intensity and technical demands of frequent water sampling and the high costs of tracer concentration analysis of water samples.

Water temperature is a natural and non-conservative tracer originally considered only an important factor in biological and chemical processes of the aquatic environment. Since the 1970s, when the fundamentals of temperature as a groundwater tracer were published [18,19], it has been an important factor in catchment hydrology research. The advantages of using temperature as a tracer include its ready availability and simple, continuous, automatic measurability [20]. A disadvantage of using temperature in hydrology is its non-conservative trait, as its properties can change through contact with the environment through which it passes. This drawback is offset by economic and technical benefits [21]. Temperature tracing has been expanded to include a variety of hydrological and hydrogeological applications [22–25].

Water possesses higher heat capacity and its temperature changes slowly compared to the majority of natural materials [26], making its use as a tracer feasible, particularly to differentiate runoff components during rainfall-runoff events (RRE). Water temperature measurements were used to investigate runoff generation during storms in a forested catchment in the USA [27] and to distinguish inflow points of groundwater into the surface flow [28]. It was demonstrated that a sudden change in drainage runoff temperature indicates the contribution of a rainfall event [29]. Given that the groundwater temperature of deeper layers (at least 2 m below soil surface) remains nearly constant throughout the year, and the temperature of shallow subsurface water shows only seasonal oscillation, a sudden change of temperature of drainage runoff during a rainfall-runoff event is connected to the presence of water from the rainfall. When event water was detected in drainage runoff through separation based on  $\delta$  <sup>18</sup>O and  $\delta$  <sup>2</sup>H, a rapid change in water temperature was observed in the same dataset; therefore, rainfall temperature can be used as a proxy for air temperature [30]. In previous studies, only qualitative differentiation of the runoff components has been described [20,21,24,29,30]. The quantitative aspect of separation of drainage runoff based on water temperature remains a challenge.

In this work, we focus on rainfall-runoff processes in small agricultural catchments with conditions typical of central and eastern Europe. Nearly 30% of agricultural land in the Czech Republic has been tile-drained since 1950 [31]. Drainage system runoff represents a substantial portion of the total runoff from many such areas [32]. Despite benefits, such as increased crop production and transformation of surface runoff into shallow subsurface runoff [33], extensive artificial soil drainage has many disadvantages. It shortens water residence time in the drained area, reduces the groundwater table, and increases vulnerability to shallow subsurface water pollution, particularly by nutrients and pesticides [34]. Tile drainage systems in the foothills of the Bohemian-Moravian Highland and other similar areas of central Europe are typically located on slopes [35]. Drainage runoff from these widespread areas of Cambisol soils primarily consists of the following major components [30] differentiated according to typical residence time: (i) long-term, with residence time in the range of years to tens of years, which may be related to traditionally described base flow; (ii) medium-term, with residence time of weeks to months, which can be linked to hypodermic shallow subsurface flow; or (iii) immediate, with residence time of minutes to hours, corresponding to rapid runoff.

Each runoff component exhibits characteristic chemical composition. The proportion of each runoff component usually varies according to aspects of the rainfall–runoff event, such as snowmelt, summer storms, and long periods of rain. Analysis of typical solute concentrations and their changes can be used to identify the prevailing component of each phase of the runoff process [30].

Studies of tile-drained agricultural micro-catchments found that nitrate–nitrogen, as well as pesticide metabolites, are closely connected with the medium-term runoff component that can be found in the subsurface layers prior to analyses of a rainfall event, whereas phosphorus and parental pesticide compounds are typical of the immediate component of runoff events [34,36].

Knowledge of the age of runoff and the runoff-forming pathways is crucial to understanding how a given substance or solution is transported from the surface to subsurface and further into water courses. Whereas mostly stable concentrations of pollutants were described in the long-term runoff component [37], medium-term and immediate runoff components play a major role in explaining solute concentration variations during periods of high runoff [34,36].

The aims of this research were (I) to compare separation of new and old water in total drainage runoff based on changes in stable isotope composition with that based on measurement of water, precipitation/air, and soil temperatures and (II) to identify a drainage runoff parameter suitable for deciding which temperature, air or soil, is optimal for characterization of individual rainfall–runoff events in small agricultural catchments influenced by tile drainage.

## 2. Materials and Methods

#### 2.1. Catchment Description and Data Collection

The research took place in three small agricultural catchments located in the Bohemian-Moravian Highlands, Czech Republic (Figure 1), with similar overall characteristics (Table 1) separated by approximately 3 km. Prevalent soil in the catchments is dystric Cambisol covering bedrock formed by paragneiss. Only shallow subsurface water movement was taken into consideration. Due to the low permeability of bedrock, deep groundwater interactions with the shallow water are negligible.



Figure 1. Map of study catchments.

	V	Watershed/Drainage Profile						
_	Kopaninský Stream (P6)	Dehtáře (KP)	Dehtáře (KL)					
Geographic coordinates	49°28′34″ N 15°18′32″ E	49°28′ N 15°12′ E	49°28′ N 15°12′ E					
Årea (ha)	15.73	28.30	29.60					
Altitude (m a.s.l.)	532-489	550-497	550-497					
Slope (%)	6.57	5.52	5.52					
Primary land use (ha)	Cultivated 15.08	Cultivated 24.20	Cultivated 20.20					
I filliary faile use (lia)	Grassland 0.38	Grassland 0.80	Grassland 9.00					
Tile-drained area (ha)	9.68	6.30	9.10					
Bedrock	Paragneiss	Paragneiss	Paragneiss					
	Haplic Cambisol	Haplic Cambisol	Haplic Cambisol					
Main soil types (WRB 2014)	Stagnic Cambisol	Stagnic Cambisol	Stagnic Cambisol					
	C C	Haplic Stagnosol	Haplic Stagnosol					
Mean annual precipitation (mm)	666	666	666					
Mean annual temperature (°C)	7.9	7.9	7.9					
Average discharge ( $l s^{-1}$ )	0.87	1.52	0.37					
Monitored period	2011–2012	2011-2014	2011-2014					

Table 1. Physical characteristics of the three small agricultural catchments studied.

A tile drainage system spaced at 13 m with a collecting drain depth of 1.0 m covers more than sixty percent of catchment P6. The systems in the Dehtáře catchment consist of collection drains spaced at 13 and 20 m and at 1.0 m depth; the depth of the conductive drains is 1.1 m. The intercepting drains for all sites are at a depth of 1.1–1.8 m and covered with gravel. Seasonal springs in the central areas of the slopes are intercepted by drainage [38].

Long-term continuous monitoring of precipitation; shallow groundwater level; drainage runoff; and the temperature of air, soil, and water was conducted. Water temperature was measured using a Pt100 temperature sensor (Fiedler-Mágr, Czech Republic) with a resolution of 0.001 °C and a measuring range of -50 °C to 80 °C. The precision of temperature measurements was 0.15 + 0.002\*t (°C). For the research catchments, the temperature range was set to 0–50 °C using software, with a resolution of 0.1 °C. Drainage discharge and water temperature were averaged at 10 min intervals based on continuous time series recorded by ultrasound water level sensors at the outlets of all drainage systems. Each outlet was equipped with an automatic sampler that collected samples of drainage water during the RREs at 20 min intervals. During base flow, samples were collected manually at the outlets fortnightly. Precipitation volume and intensity were measured using an automatic shuttle precipitation gauge located approximately in the center of the study location. Samples of rainfall water were collected using an automatic rainfall sampler located in the Kopaninský stream catchment.

For chemical separation, stable isotopes <sup>18</sup>O and <sup>2</sup>H were used. Analyses of the samples for stable isotope composition were performed at the Czech Technical University in Prague (Czech Republic) using a liquid water isotope analyzer (LGR Inc. Device). All <sup>18</sup>O values were expressed as  $\delta$  <sup>18</sup>O, and all <sup>2</sup>H values were expressed as  $\delta$  <sup>18</sup>H in ‰ of the Vienna Standard Mean Ocean Water (V-SMOW) [9,13]. The precision of  $\delta$  <sup>18</sup>O analysis was 0.15‰ V-SMOW and the precision of  $\delta$  <sup>2</sup>H analysis was 0.10‰ V-SMOW.

Drainage discharge recorded incessantly (even during dry periods) at all measured sites confirms the presence of runoff components from long-term, medium-term, and immediate sources. The pathways to the flow gauge differed, resulting in variations in the runoff volume ratio over time.

The focus of this research was chiefly the immediate component of runoff, which causes a rapid increase in flow rate in the monitored RREs. Thermal and isotope separation were conducted to determine the proportion of new water from an RRE contained in the total runoff.

## 2.2. Analysis of Rainfall-Runoff Events

A set of 39 RREs was analyzed from the data recorded in subcatchments KP, KL (2011–2014), and P6 (2011–2012) during the growing season (Table 2). RREs with significant water temperature changes were selected for analysis. It is expected that new water contribution will elicit a detectable change in runoff water temperature [29].

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RRE ID	Precipitation Total Until Peak Discharge (mm)	Precipitation Duration (min)	Precipitation Intensity (mm/h)	Increase in Runoff [l/s] During RRE	Time to peak Discharge (min)	Increase in Drainage Runoff Temperature (°C) during RRE	Weighted Avg. of Causal Precipitation Temperature (°C)	Avg. Soil Temperature at 40–70 cm Depth before RRE (°C)
1-P6 8 June 2011	10.1	60	10.10	4.11	40	0.8	14.21	16.35
1-KL 8 June 2011	18.6	190	5.87	0.63	180	0.9	12.34	16.39
1-KP 8 June 2011	18.6	190	5.87	1.35	170	3.9	12.34	16.39
2-P6 22 June 2011	28.4	70	24.34	66.33	40	2.1	16.95	15.26
2-KL 22 June 2011	23.9	80	17.93	1.30	40	0.8	16.84	15.23
3-P6 13 July 2011	16	90	10.67	9.92	80	1.3	17.47	17.79
3-KL 13 July 2011	21.1	90	14.07	0.77	70	0.8	17.53	17.67
2-KP 13 July 2011	21.1	90	14.07	1.56	50	4.3	17.53	17.67
4-P6 20 July 2011	28.2	780	2.17	2.16	760	1.8	13.23	16.19
4-KL 20 July 2011	24.7	920	1.61	0.87	620	0.5	13.44	16.17
3-KP 20 July 2011	24.7	882	1.68	0.95	710	0.6	13.44	16.17
5-P6 30 July 2011	20.6	1545	0.80	2.09	870	1.3	12.29	15.03
6-P6 4 August 2011	26.7	110	14.56	244.08	100	2.2	16.30	16.83
7-P6 15 August 2011	14.3	380	2.26	0.89	370	0.7	15.44	20.47
5-KL 15 August 2011	14.4	270	3.20	0.88	200	0.5	15.39	15.79
4-KP 15 August 2011	14.4	250	3.46	2.14	220	2.5	15.39	15.79
8-P6 5 September 2011	34.3	360	5.72	2.40	340	1.6	16.05	16.72
6-KL 5 September 2011	19.5	170	6.88	0.36	140	0.3	16.02	16.91
5-KP 5 September 2011	19.5	170	6.88	2.18	270	2.5	16.02	16.91
9-P6 3 May 2012	70.2	80	52.65	71.76	80	3.4	0.75	8.86
7-KL 1 July 2012	21.4	50	25.68	1.99	40	1.1	18.04	17.67
8-KL 6 August 2012	7.5	30	15.00	1.73	40	0.6	16.38	17.69
6-KP 6 August 2012	17.6	60	17.60	1.86	60	3.7	16.38	17.69
10-KL 24 June 2013	56.6	1220	2.78	3.22	1610	1.7	10.59	16.58
8-KP 24 June 2013	56.6	1220	2.78	3.18	490	2.0	10.59	16.58
11-KL 29 July 2013	8.5	100	5.10	2.62	100	1.7	19.75	16.60
12-KL 18 May 2014	9.6	520	1.11	0.30	310	0.4	8.19	10.24
9-KP 18 May 2014	9.6	520	1.11	0.56	570	0.3	8.19	10.24
13-KL 23 May 2014	7.8	80	5.85	0.90	100	0.7	15.53	11.19
10-KP 23 May 2014	7.8	80	5.85	0.72	100	5.1	15.53	11.19
14-KL 29 May 2014	10.7	680	0.94	1.26	610	0.8	9.20	13.49
11-KP 29 May 2014	10.7	970	0.94	1.67	680	1.3	9.20	13.49
15-KL 27 July 2014	15.5	40	8.45	0.47	30	0.5	19.06	16.70
16-KL 31 July 2014	18.2	520	4.96	0.46	60	0.5	16.84	17.15
12-KP 27 August 2014	18.7	80	3.87	1.05	200	0.4	11.30	15.73
17-KL 12 September 2014	32.2	680	1.99	0.58	470	0.8	12.65	15.76
13-KP 12 September 2014	32.2	970	1.99	9.78	640	0.6	12.65	15.76
18-KL 15 September 2014	11.3	40	16.95	0.40	130	0.8	20.75	15.48
14-KP 15 September 2014	11.3	40	16.95	9.97	110	1.7	20.75	15.48

Separation of drainage runoff was calculated at 10 min intervals using mixed equations (Equations (1) and (2)) previously used in [30,39]. In the case of 20 min interval measurements, the input data were linearly interpolated to a 10 min interval.

$$Q_t = Q_0 + Q_n \tag{1}$$

$$Q_t \times C_t = Q_o \times C_o + Q_n \times C_n \tag{2}$$

where:

 $Q_t$  = total drainage discharge;

Q<sub>o</sub> = discharge of old water;

 $Q_n$  = discharge of new water;

 $C_t$  = concentration of the tracer ( $\delta^{18}$ O or  $\delta^{2}$ H value) in the total runoff;

 $C_0$  = concentration of the tracer ( $\delta$  <sup>18</sup>O or  $\delta$  <sup>2</sup>H value) in old water;

 $C_n$  = concentration of the tracer ( $\delta$  <sup>18</sup>O or  $\delta$  <sup>2</sup>H value) in new water.

## 2.3. Runoff Separation

As an initial step, isotopic separation of runoff for all RREs was carried out on event precipitation using Equation (3) with  $\delta^{18}$ O or  $\delta^{2}$ H values.

$$Q_{o} = Q_{t} \times (C_{t} - C_{n1}) / (C_{o} - C_{n1})$$
(3)

where  $C_{n1}$  = weighted mean of  $\delta$  <sup>18</sup>O or  $\delta$  <sup>2</sup>H values of causal precipitation (precipitation that caused an increase in the drainage flow) until the peak discharge.

Separation via stable isotopes was based on  $\delta$ <sup>18</sup>O and  $\delta$ <sup>2</sup>H values in the causal precipitation and in the monitored drainage runoff. The concentration of isotopes in the drainage water Co (before RRE) was determined from the most recent value (usually 1–7 days before the RRE) from a manually collected sample. The  $\delta$ <sup>18</sup>O and  $\delta$ <sup>2</sup>H values in the precipitation water were determined as the weighted mean of  $\delta$ <sup>18</sup>O and  $\delta$ <sup>2</sup>H values and precipitation.

In the initial step, an assumption was made that the mean error (ME<sub>1</sub>; Equation (4)) between the measured discharge (Q<sub>t</sub>) of the assessed RRE and the proportion of old water (Q<sub>o</sub>) calculated by isotope separation would be greater than 0. If this was not the case, it followed that, on average, for a given RRE, the quantity of old water in the total runoff was overestimated and new water underestimated and that the separation of event precipitation by isotopes did not reflect the real ratio of new-to-old water in the runoff.

$$ME_1 = \frac{\sum_{i=1}^{n} (Qt_i - Qo_i)}{n}$$
(4)

where:

 $Q_{ti}$  = total discharge;

 $Q_{oi}$  = old water according to the isotope separation of event precipitation;

n = number of observations.

In the second step, runoff was separated using water, air, and soil temperature according to Equations (5)–(7). The analysis stems from the assumption that based on changes in the temperature of the drainage water during the rising limb of the RRE, it is possible to distinguish the runoff components [40], and a change in temperature is an indicator of the presence of an immediate component in runoff [29].

$$Q_t \times T_t = Q_o \times T_o + Q_n \times T_n$$
(5)

$$Q_{o} = Q_{t} \times (T_{t} - T_{n1}) / (T_{o} - T_{n1})$$
(6)

$$Q_{o} = Q_{t} \times (T_{t} - T_{n2}) / (T_{o} - T_{n2})$$
(7)

where:

T<sub>t</sub> = drainage water temperature;

 $T_o$  = old water temperature immediately prior to an increase in discharge during the RRE;  $T_{n1}$  = precipitation temperature or air temperature (indicating new water);  $T_{n2}$  = soil temperature (indicating old water).

 $T_{\rm m2} = 500$  temperature (intercating of a water).

To determine the ratio of old-to-new water in the drainage runoff, the runoff temperature immediately prior to the increase in discharge during the RRE and the discrete value of the drainage water temperature during the RRE were compared. An additional factor in the calculation was precipitation temperature or soil temperature as a weighted mean of temperature of causal precipitation until peak discharge of the RRE.

The third step of the analysis was to categorize the 39 RREs according to the  $ME_1$  criterion (total runoff volume greater than the old water component) based on isotope analysis. Events not fulfilling the  $ME_1$  criterion were subjected to separate analysis.

The fourth step of the analysis focused on RREs that met the  $ME_1$  assumption. The results of runoff component analysis based on temperature and on isotope concentrations were compared.

The agreement of the isotope and temperature models was evaluated using the Nash–Sutcliffe model efficiency (NSE) coefficient (Equation (8)) [41].

$$NSE = 1 - \frac{\sum_{i=1}^{n} (Qiso_i - Qtemp_i)^2}{\sum_{i=1}^{n} (Qiso_i - Qisoavg)^2}$$
(8)

where:

 $Q_{isoI}$  = calculated value of discharge for time i by isotope separation;  $Q_{tempI}$  = calculated value of discharge for time i by temperature separation;  $Q_{isoavg.}$  = mean value of calculated discharge by isotopic separation. NSE is expressed as a value from  $-\infty$  to 1. NSE = 1(perfect match of the model and the measured data);

NSE = 0 (the efficiency of the model is the same as the mean of the measured data);

NSE < 0 (the mean of the measured values is a better predictor than the model itself).

The NSE coefficient values were separated into three ranges of model match (Table 3) [42].

Table 3. Evaluation of Nash–Sutcliffe efficiency (NSE) coefficient values.

NSE Coefficient	<b>Evaluation of Model Match</b>			
NSE > 0.75 NSE = 0.5=0.75	High Agreement (HA) Medium Agreement (MA)			
NSE < 0.5	Discrepancy (D)			

The results of separation based on precipitation temperature and that based on precipitation event isotopes were compared to identify those RREs in which runoff was significantly affected by causal rainwater seeping into the soil and entering the drainage runoff.

Rainfall–runoff events showing high and medium agreement (HA and MA) between separation based on precipitation temperature and those based on isotopes were excluded from further evaluation. It was demonstrated that runoff was affected by precipitation, and its components could be separated based on precipitation temperature with a high degree of validity.

As the fifth step of the analysis, RREs showing discrepancy were further processed with RREs in which  $ME_1$  was not reached. In RREs with NSE showing discrepancy, the origin of water measured in the drainage runoff was assumed to be from the soil and hypodermic runoff, i.e., old water. The water that infiltrated the soil in previous RREs and is at the soil temperature is expelled from the soil by precipitation and enters the runoff. Based on this assumption, the separation Equation (3) was modified to replace the concentration in causal precipitation with the concentration in the previous precipitation event (Equation (9)).

$$Q_{o} = Q_{t} \times (C_{t} - C_{n2}) / (C_{o} - C_{n2})$$
(9)

where  $C_{n2}$  = weighted mean of the  $\delta^{18}$ O and  $\delta^{2}$ H values of the total precipitation produced by the previous event.

By comparing and evaluating the NSE coefficient of RRE separation based on soil temperature with that using isotopes of previous precipitation, we determined whether a significant source of runoff was hypodermic runoff of previous precipitation.

Using the above-described method, the entire set of RREs was divided into two groups. The first included RREs that showed the presence of water from precipitation that caused an acute increase in discharge in a catchment (new water). The second group comprised RREs in which the increase in discharge was caused by soil water infiltrated into the soil during precipitation preceding the causal precipitation, or hypodermic/old water.

After statistical analysis (repeated measures ANOVA for dependent monitoring or general linear model) of the results of steps 1–5, a follow-up analysis was conducted with the aim of identifying a general parameter that could unambiguously define when the method of separation used can be based on soil temperature or precipitation/air temperature. Such

a factor would make it feasible to replace isotope separation with a more economical and user-friendly temperature-based method.

#### 3. Results

## 3.1. Analysis of Events

Of 39 monitored events, 28 met the criteria of  $ME_1$  (Table 4). Of the 11 RREs not meeting the criteria, one that failed to meet any set assumption (RRE ID 12 KP 27.8.2014, Table 4) was omitted from further analyses. The data measured in this event were consistent and probably without errors, and the data processing followed the procedures specified in the methodology. The runoff in that RRE was made up primarily of precipitation combined with water from a previous rainfall event, with temperature partly modified by soil. This illustrates that the methods under investigation may be most suitable for clearly separated isolated RREs.

**Table 4.** Comparison of separation based on precipitation temperature with that based on precipitation isotopes and comparison of separation based on soil temperature with separation based on isotopes in a previous precipitation event.

RRE ID	ME <sub>1</sub> <sup>2</sup> H	ME <sub>1</sub> <sup>18</sup> O	ME <sub>1</sub> Evaluation	NSE <sup>2</sup> H of CP vs. TP	NSE <sup>18</sup> O of CP vs. TP	NSE CP vs. TP Evaluation	NSE <sup>2</sup> H PP vs. TS	NSE <sup>18</sup> O PP vs. TS	NSE PP vs. TS Evaluation
1-P6 8 June 2011	0.0887	0.0993	Н	0.8933	0.9045	HA	NO	NO	NO
2-KL 22 June 2011	0.1044	0.1020	Н	0.5187	0.5334	MA	NO	NO	NO
2-P6 22 June 2011	0.9703	1.0998	Н	0.9482	0.8841	HA	NO	NO	NO
2-KP 13 July 2011	0.1810	0.1952	Н	0.7690	0.7281	MA	NO	NO	NO
3-KL 13 July 2011	0.0987	0.1072	Н	0.8443	0.7641	HA	NO	NO	NO
3-P6 13 July 2011	0.6227	0.6522	Н	0.9902	0.9856	HA	NO	NO	NO
4-P6 20 July 2011	0.8214	0.9553	Н	-428.2268	-931.5555	D	0.8425	0.8427	HA
3-KP 20 July 2011	0.2628	0.2595	Н	-371.1274	-449.9511	D	0.9619	0.9735	HA
4-KL 20 July 2011	0.2434	0.2096	Н	-45.1230	-22.7756	D	0.9376	0.9626	HA
5-P6 30 July 2011	0.4926	0.6105	Н	-1191.3665	-3594.7472	D	0.8826	0.6373	HA
6-P6 4 August 2011	5.2765	4.4635	Н	0.9801	0.9301	HA	NO	NO	NO
9-P6 3 May 2012	2.2548	2.5979	Н	0.9035	0.8457	HA	NO	NO	NO
7-KL 1 July 2012	0.1560	0.1662	Н	0.8666	0.6532	HA	NO	NO	NO
6-KP 6 August 2012	0.2020	0.2201	Η	0.8463	0.7779	HA	NO	NO	NO
8-KL 6 August 2012	0.1148	0.1180	Η	0.8441	0.8583	HA	NO	NO	NO
10-KL 24 June 2013	0.6418	0.6938	Н	-46.8710	-51.4948	D	0.8637	0.8464	HA
8-KP 24 June 2013	0.8087	1.0459	Η	-118.5586	-153.4816	D	0.6800	0.7401	MA
11-KL 29 July 2013	0.0734	0.0588	Н	0.9241	0.9154	HA	NO	NO	NO
12-KL 18 May 2014	0.0770	0.1467	Н	-3.7417	-44.6586	D	0.8491	0.9560	HA
9-KP 18 May 2014	0.1096	0.1620	Н	-9.1755	-20.7343	D	0.9567	0.9358	HA
10-KP 23 May 2014	0.0505	0.0462	Н	0.8231	0.8555	HA	NO	NO	NO
13-KL 23 May 2014	0.0615	0.0321	Н	0.9419	0.9747	HA	NO	NO	NO
11-KP 29 May 2014	0.0935	0.0822	Н	-1.2311	-1.2044	D	0.7817	0.7540	HA
14-KL 29 May 2014	0.1251	0.1273	Н	-2.3197	-2.3787	D	0.8210	0.7960	HA
15-KL 27 July 2014	0.0061	0.0075	Н	0.9843	0.9834	HA	NO	NO	NO
16-KL 31 July 2014	0.0407	0.0375	Н	0.8915	0.9525	HA	NO	NO	NO
14-KP 15 September 2014	0.7646	0.2242	Н	0.8715	0.9408	HA	NO	NO	NO
18-KL 15 September 2014	0.0348	0.0257	Н	0.9754	0.9643	HA	NO	NO	NO
1-KL 8 June 2011	-0.0383	-0.0481	D	NO	NO	NO	0.9595	0.9736	HA
1-KP 8 June 2011	-0.0632	-0.0744	D	NO	NO	NO	0.5234	0.5271	MA
7-P6 15 August 2011	-0.1186	-0.1424	D	NO	NO	NO	0.9492	0.9444	HA
5-KL 15 August 2011	-0.2375	-0.3432	D	NO	NO	NO	0.9331	0.9269	HA
4-KP 15 August 2011	-0.9948	-1.5619	D	NO	NO	NO	0.5542	0.5723	MA
8-P6 5 September 2011	-1.5087	-1.5030	D	NO	NO	NO	0.5839	0.7550	MA
6-KL 5 September 2011	-0.0551	-0.0424	D	NO	NO	NO	0.9574	0.9565	HA
5-KP 5 September 2011	-0.8332	-0.8302	D	NO	NO	NO	0.9301	0.9121	HA
12-KP 27 August 2014	-0.0748	-0.0970	D	0.1759	-0.0018	D	E	E	E
17-KL 12 September 2014	-0.1771	-0.1331	D	NO	NO	NO	0.6348	0.6518	MA
13-KP 12 September 2014	-0.8527	-0.6214	D	NO	NO	NO	0.9061	0.9034	HA

RRE ID = rainfall event identification;  $ME_1^{2}H$  = mean error between total discharge and old water discharge separated by <sup>2</sup>H;  $ME_1^{18}O$  = mean error between total discharge and old water discharge separated by <sup>18</sup>O; NSE <sup>2</sup>H of CP vs.TP = Nash–Sutcliffe coefficient of separation according to <sup>2</sup>H in casual precipitation (CP) and based on precipitation temperature (TP); NSE <sup>18</sup>O of CP vs.TP = Nash–Sutcliffe coefficient of separation according to <sup>18</sup>O in casual precipitation (CP) and based on precipitation temperature (TP); NSE <sup>18</sup>O of CP vs.TP = Nash–Sutcliffe coefficient of separation according to <sup>18</sup>O in casual precipitation (CP) and based on precipitation temperature (TP); NSE <sup>2</sup>H PP vs. TS = Nash–Sutcliffe coefficient of separation based on <sup>2</sup>H in preceding precipitation (PP) and on soil temperature (TS); NSE <sup>18</sup>O PP vs. TS = Nash–Sutcliffe coefficient of separation based on <sup>18</sup>O in preceding precipitation (PP) and on soil temperature (TS); NO = not evaluated, D = discrepancy, HA = high agreement, MA = medium agreement, E = error.

The efficiency of separation using temperature of causal precipitation was comparable to that based on stable isotopes of causal precipitation. Of the 28 RREs, 18 satisfied the

conditions of the NSE coefficient, with 16 obtaining high agreement (HA) and 2 registering medium agreement (MA). In these RREs, the increased discharge was due to the presence of event water, and separation based on precipitation temperature was successfully applied, as in, for example, RRE 1-P6 (Figure 2).



**Figure 2.** The course of runoff separation based on isotopes of causal precipitation and precipitation temperature in RRE 1-P6 (8 June 2011). Qt, total discharge; Qo d2H, discharge of the old water by separations using  $\delta$  <sup>2</sup>H values; Qo d18O, discharge of the old water by separations using  $\delta$  <sup>18</sup>O; Qo precipitation temperature, discharge of the old water by separations using precipitation temperature.

Ten RREs identified as showing "discrepancy" did not meet the criteria of the NSE coefficient for HA or MA. These events were further evaluated, along with the 10 events that did not meet the ME<sub>1</sub> criteria. In these 20 RREs, isotopic separation was conducted based on previous precipitation and on soil temperature. HA of the old water parameter was found in 15 RREs, and MA was achieved in 5 RREs (Table 4). These 20 separations by soil temperature were further distinguished into separations that did not meet the conditions of the NSE coefficient for HA or for MA (soil separation by temperature (SST-NSE)) and separations for which the ME<sub>1</sub> was not met (SST-ME<sub>1</sub>). Figure 3 depicts the course of drainage runoff in SST-NSE events based on the temperature of the previous precipitation versus soil temperature, with HA shown in RRE 10-KL. An example of separation by soil temperature in SST-ME<sub>1</sub> with HA in RRE 1-KL is shown in Figure 4.

The statistical hypothesis that the new water volumes as calculated by  $\delta$  <sup>18</sup>O and  $\delta$  <sup>2</sup>H and temperature did not differ from one another was tested by repeated measures analysis of variance (ANOVA for dependent monitoring). We did not find significant differences among results of these separation techniques (*p* = 0.18) (Figure 5).

Separation based on precipitation and soil temperatures provided results similar to those based on stable isotopes. Therefore, the dataset was divided into events separated by precipitation temperature and those separated by soil temperature. Subsequently, a double test was performed to determine whether the volumes of new water obtained by the separation based on  $\delta$  <sup>18</sup>O and  $\delta$  <sup>2</sup>H values and temperature differed. In both cases, a general linear model was used with the main effects separation method and block identity. The results showed no significant influence of separation method on the estimated volume of new water; *p*-value = 0.57 for precipitation temperature vs. isotopes and *p*-value = 0.25 for soil temperature vs.



**Figure 3.** The course of runoff separation in SST-NSE based on isotopes of previous precipitation and soil temperature in RRE 10-KL (24 June 2013). Qt, total discharge; Qo d2H, discharge of the old water by separations using  $\delta^{2}$ H values of previous precipitation; Qo d18O, discharge of the old water by separations using  $\delta^{18}$ O values of previous precipitation; Qo soil temperature, discharge of the old water by separations using previous precipitation temperature and soil temperature.



**Figure 4.** The course of runoff separation in SST-ME<sub>1</sub> based on isotopes of previous precipitation and soil temperature in RRE 1-KL (8 June 2011). Qt, total discharge; Qo d2H PP, discharge of the old water by separations using  $\delta$  <sup>2</sup>H values of previous precipitation; Qo d18O, discharge of the old water by separations using  $\delta$  <sup>18</sup>O of previous precipitation; Qo soil temperature, discharge of the old water by separations using soil temperature.



**Figure 5.** Evaluation of separation based on three tracers according to ANOVA with means and confidence intervals (mean  $\pm$  0.95 confidence interval).

Further comparison of methods for separation of runoff components was based on the volume of total runoff and that of new water in individual events (Figure 6). The small differences found between values are in agreement with the testing of the used methods of runoff separations by ANOVA and the general linear model.



**Figure 6.** Proportion of new water in total runoff volume according to separation based on <sup>2</sup>H and <sup>18</sup>O isotopes and on temperature in 38 events in three subcatchments.

## 3.2. Drainage Runoff Parameter to Determine Suitable Separation

Time to peak discharge (Tables 2 and 5) was examined in the 38 analyzed RREs as a potential common parameter to determine whether air temperature or soil temperature is the most suitable measure for separation of drainage runoff.

Separation Method/Origin of Water		Precipitatior Causal Pr	n Temperature/ recipitation	Soil Temperature/ Pre-Precipitation Water		
Parameter		Time to peak discharge (min)	Number of events	Time to peak discharge (min)	Number of events	
	KL	30-130	9	140-1610	8	
Drainage profile	KP	50-110	4	170-710	8	
	P6	40-100	5	340-870	4	

**Table 5.** Time to peak discharge (min) and number of events according to used separation method and origin of water.

Pre-precipitation water-water presented in the catchment before casual precipitation.

A comparison of separation methods based on temperature and time of runoff increase yielded the following results: in time to peak discharge from 0–130 min, new water was the main source of increase in flow rate, whereas rising flow beyond this time displayed an increase in discharge of old water (Table 5). This division was valid, regardless of the year of monitoring, rainfall intensity, or total precipitation volume. For drainage system P6, the cut-off time was 100 min; for KP, it was 110 min, and for KL, 130 min. The number of events evaluated was 17 in the KL subcatchment, 12 in KP, and 9 in P6. To specify the cut-off time of time to peak discharge more precisely, it would be necessary to evaluate more RREs in multiple drainage systems. Time to peak discharge can vary according to catchment area size, climate conditions, type and variety of soil, and soil parameters related to cultivated crops.

For all RREs, the time of rising discharge was strongly negatively correlated with rainfall intensity ( $y = 1009.9 * x^{-0.955}$ ,  $R^2 = 0.7507$ ) (Figure 7).



**Figure 7.** Relationship between the mean intensity of precipitation and the time to peak discharge of individual RREs.

Rainfall runoff events were grouped into three categories based on time to peak discharge (Table 6) with the appropriate separation method identified. For the 18 RREs characterized by the shortest discharge rise time (<130 min), separation by precipitation temperature (SPT) was used successfully. For the 10 RREs with time to peak discharge of 140–640 min (SST-ME<sub>1</sub>), as well for the 10 with the longest discharge rise time (SST-NSE), separation by soil temperature was optimal. Generally, characteristics of the time to peak discharge parameter decreased with increased precipitation intensity. The more new water

in the runoff, as indicated by precipitation temperature, the shorter the discharge increase in the hydrograph.

Table 6. Time to peak discharge and precipitation intensity relative to the separation method.

Parameters of RREs								
Separation Method	No. of Events	Time to	Peak Dischar	ge (min)	Precipitation Intensity (mm/hour)			
		Min	Max	Median	Min	Max	Median	
SST-NSE	10	310	1610	650	0.8	2.8	1.4	
SST-ME1	10	140	640	245	2.0	6.9	4.6	
SPT	18	30	130	65	5.0	52.7	14.3	

SST-NSE = separation by soil temperature (discrepancy NSE); SST-ME<sub>1</sub> = separation by soil temperature (failed criterion ME<sub>1</sub>); SPT = separation by precipitation temperature.

Table 6 shows that the time to peak discharge is inversely related to rainfall intensity and that both time to peak discharge and rainfall intensity are relevant to the separation methods used.

# 4. Discussion

The structure of drainage runoff from rainfall in sloping crystalline conditions can take different forms depending on rainfall intensity (Table 6).

Intense rainfalls are accompanied by a sharp increase in flow rate, both in springs and in drainage systems that are associated with a rapid change in water temperature (events described as SPT in Table 6). There are several water drainage system pathways under sloping crystalline conditions [35]. The first of the possible rainfall–runoff pathways is through springs that were identified and retained by drainage systems during construction. The springs drain groundwater through fissures in shallow layers under the soil flowing at the interfaces of rock and soil and forming diffuse spring areas. The fissures have a porosity of secondary origin that is the result of tectonic exposure of the rocks [43] and are probably replenished with water during heavy rainfalls through intergranular porosity, which is characteristic of unconsolidated and poorly consolidated sediments typical of hilltops. These are usually shallow, stony soil types. The fissures can be replenished by preferential pathways of light Cambisols formed on weathered crystalline formations that exhibit a wide range of grain sizes [44].

Runoff patterns can also consist of preferential pathways located directly over the drains. It is currently not possible to distinguish water from these pathways from water flowing through fissures.

Short and heavy rainfall in a small forest brook in the Sumava basin resulted in a sudden flow wave characterized by a drop in conductivity [45]. It can therefore be assumed that rainwater, which has low ionic conductivity, participated in the runoff, changing the soil water/rainwater proportions of flowing water. The proportion of rainwater in brooks increases with increasing flow rate. As stated by Vondrka [45], decreased flow rates result in a lower proportion of rainwater in the outflow from the basin. This corresponds to our results. Therefore, this is probably also an event identified as feasible for separation by precipitation temperature (SPT).

A major volume of previously infiltrated water may also be released suddenly after a relatively light or low-intensity rainfall [46–49]. These are events described as SST-NSE in Table 6. In this case, water from the current rainfall event flows through the soil layers and expels water from previous rainfalls from the pore space. Its temperature should differ from that of the rainfall water, as it was retained in the soil for a longer period of time (this does not apply if the rainfall temperature is the same as the soil water temperature when the rainfall occurs at air temperatures similar to the soil temperature). Preferential pathways should also be taken into consideration. Water flows in the soil through a complex system of pores of various sizes [50] via a small number of waterlogged pathways [51]. Šír and Tesař [52] suggest the source of preferential flow to be a dynamic imbalance caused by

insufficient time for the preferentially flowing water to reach a balance with the more slowly flowing water contained in the pores of the soil matrix. Generally, there is a dynamic imbalance resulting from the significant difference in flow velocity in the pores of the matrix

Mixing of old and new water occurs in all rainfall events. According to Císlerová [44] and Šír and Tesař [53], preferential flow occurs first when, at the beginning of the spill phase, the newly infiltrated rainwater displaces the predominant old water from the soil, and rainwater with reduced ionic conductivity flows from the soil, combining water from the flow in the soil matrix with water that passed through preferential pathways. The mechanism of gravitationally destabilized flow occurs during the periods of higher values of soil moisture. Originally air-filled pores become conductively connected in the form of a larger water body than can be carried by the capillary forces. Such a water body therefore descends through the porous bed. As it contacts pores filled with old water, the old water is pushed into the highly permeable subsoil [45,54].

and in the pores forming the preferential paths [50].

### 5. Conclusions

The novel temperature-based drainage separation procedure described herein provides results similar to those obtained by isotope-based separation. The use of temperature-based drainage runoff separation for water, air, precipitation, and soil is limited to simple, discrete storm runoff events. However, this is also true for isotope-based runoff separation. The method has, so far, been successfully tested during the growing season with a range of measured air temperatures and weighted average precipitation temperatures from 0.7 °C to 20.8 °C and a range of average soil temperatures at a depth of 0.4–0.6 m from 8.8 °C to 20.5 °C.

Further research should focus on testing the findings and extending them to other geographical conditions. Identifying the threshold time to peak discharge under different conditions is key, as this is the cutoff for the use of runoff separation based on soil temperature or precipitation temperature.

A larger dataset may reveal the possibility of replacing isotope separation of drainage runoff or separation of runoff in watercourses by more economical and technically simpler measurements of soil temperature or precipitation/air temperature.

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