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Comparison of parameters influencing the behavior of concentration of nitrates and phosphates during different extreme rainfall-runoff events in small watersheds

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Abstract

The behavior of solute concentrations during storm events is completely different from their behaviour under normal conditions, and very often results in hysteresis. This study aim is to explore the relationship between the biogeochemical and hydrological parameters describing natural conditions and the reciprocal interactions between changes in concentration of selected indicators of water quality in water and the discharge dynamics during different types of extreme rainfall-runoff events in the Jenínskỳ stream and the Kopaninskỳ stream catchment (Czech Republic). The relationship between concentrations and runoffs is explained by concentration-discharge hysteretic loops. As the statistical method used for cross analyzing the impact of the parameters there was chosen the RDA analysis. The relationships between the particular parameters were examined separately by conditions of spring snow melt and summer storm events. The results than confirmed the very strong relationship between parameters describing water quality and percentage of stable parts of the catchment and also of infiltration vulnerable sites.

1 Introduction

The quality of natural inland waters is related to geomorphology, climate and land-use in the catchment. The size and slope of the catchment, precipitation, wind, temperature, erosion, vegetation and soil structure – these all play a role in the catchment water quality (Schindler, 1997; Pačes, 1982; House and Warwick, 1998; Christopher et al., 2008). The quality of water that enters the aquatic system is also influenced by land management and use of the catchment for agriculture, forestry, horticulture, conservation, industry and urban areas (Johnes et al., 1996; Moss, 2009). As by normal runoff conditions the water quality is changing very slowly, by higher outflow it is changing very fast and markedly (Gergel and Bureš, 2004). An analysis of the storm events is the only possibility for understanding of all stream-catchment biogeochemical interactions

(Butturini et al., 2006). The analysis of particular element's hysteresis trajectories is one possibility of identifying the sources affecting water quality in a catchment (McDiffett et al., 1989). Meybeck et al. (1990) observed several types of concentrations behaviour during floods, which can last from a few hours to a few months, depending on the river size.

Variations in the concentration of substances in rivers during storm events often result in a hysteresis effect with different concentrations during the rising and falling limb of the hydrograph (Bowes et al., 2005; Toler, 1965). The shape and length of particular hydrograph limbs varies among the storm events and among the catchments (Bedient and Huber, 1988).

The form of the flood hydrograph depends on natural conditions and it is almost always multi-peaked (Reid et al., 1998). Such situation often results in non-unique concentration for a given value of stream discharge – called hysteresis (Rose, 2003). Hysteresis in the concentration–discharge relationship (c–q hysteresis) is often observed during storms, i.e. the concentration of a determinant, at a given discharge, is different on the rising and falling limb of a hydrograph (Hall, 1970). When plotted, such c–q relationships result in "loop trajectories" (Bowes et al., 2005; McDiffett et al., 1989; Bond, 1979; Hill, 1993). Evans and Davies (1998) proposed a classification of c–q hysteresis types according to their rotational pattern (clockwise – CLW/anticlockwise – ACLW), curvature (convex/concave) and trend (positive/negative/null).

Seeger et al. (2004) describes 3 basic possibilities of hysteretic loops: clockwise, anticlockwise and eight-shaped. The first two described types of hysteretic loops are the most common, in dependence with environmental conditions (Regüés et al., 2000). These two types Evans and Davies (1998) describe as C3 hysteresis for concave loops with clockwise rotation and A3 hysteresis for anticlockwise concave c–q loops. Clockwise hysteresis loop is produced when the concentration is highest on the rising limb and an anticlockwise loop when the concentration is higher on the falling limb (Bowes et al., 2005).

Also it was found out that a clockwise hysteresis occurs when sediment is derived from the bed and banks of the channel or areas adjacent to the channel, whereas an anti-clockwise hysteresis occurs when the sediment source area is in the upper part of the slopes (Klein, 1984). Some recent results show for some substances such as DOC opposite trend when anticlockwise hysteresis loop occur even if the source of the substance is directly in the riparian zone (Strohmeier et al., 2013). The third group of hysteresis, eight-shaped hysteresis, has only been described in a few publications e.g. Arnborg et al. (1967). Williams (1989) supplements the possible hysteresis development by c–q relationship with single valued relationship with constant concentrations.

According to House and Warwick (1998) the size and direction of hysteretic loops are described by the response factor and slope of the loop. These two factors were supplemented by Bowes et al. (2005) by the loop gradient constant. Despite its empirical nature, the constant may be related to real physical processes that occur during storm events. Hysteresis could be also controlled by catchment size, rainfall amount and soil moisture (Klein, 1984; de Boer and Campbell, 1989). One of the factors affecting the c–q hysteresis is also part of year and reason that caused the event. According to Alexandrov et al. (2007) the higher outflows resulting from convective storms predict the higher concentrations but correlation with water discharge is low, in contrast to frontal storm runoff causing lower concentration but the correlation with water discharge is better. Bowes et al. (2005) also expects the impact of antecedent conditions on hysteresis patterns to produce seasonal trends, with the largest clockwise loops following long dry periods. Butturini et al. (2006) estimated for each storm event three parameters describing the hydrological characteristics and also two descriptors of solute behavior.

Similar parameters were also chosen by Bertrand-Krajewski et al. (1998) for describing storm events. Evans and Davies (1998) have tested the hypothesis, that hysteresis is the result of pre-event and water mixing. But this type of evaluation sometimes may be doubtful according to some authors as claimed in Duffy and Cusumano (1998) or Joerin et al. (2002).

Abbaspour et al. (2007), Huber and Maidment (1992) or Prasuhn and Sieber (2005) found that during extreme events, surface runoff is particularly the important transport medium for the elements of the point sources, and in particular for nitrogen, phosphorus, sediments and pesticides from agricultural plots.

In contrast to these results Anderson et al. (1997) attribute the sudden changes in discharge rate and concentration of elements during rainfall-runoff events, especially to the influence of preferential flow in soil and rock environment. Montgomery and Dietrich (2002) and Vogel et al. (2010) reported as the main reason for the increased flow just preferential flow in macropores and other flow-through pathways. Kanwar and Bakhsh (2000) also believe that the sudden increase in flow after heavy rains and snow melting indicates the preferential flow of water into drainage systems or shallow groundwater. In contrast, Carpenter et al. (1998) these abrupt changes in discharge attributes to the rapid release of capillary water in the soil, and thus considered to be a major component of peak flow during rainfall-runoff events water from the events of the previous period.

In terms of nutrients loss Kanwar and Bakhsh (2000) see the evidence supporting the theory of preferential flow paths in soil and rocks, through which the nutrient poor rainwater rapidly penetrates into ground and surface water Wagner et al. (2008) in a sharp decrease in the concentrations of nitrate anions during rainfall-runoff events, especially in non arable locations. In contrast Vidon and Cuadra (2011) point to the significant rise of concentrations of total phosphorus and reactive phosphate during rainfall-runoff events recorded in the Midwest USA, due to washout of preferential flow paths in soils that are due to fertilizer use highly enriched by substances containing phosphorus. Gächter et al. (2004) found out the same conclusions by the monitoring of rainfall-runoff events in agricultural catchments in Switzerland.

The aim of this study is to evaluate the influence of land use and other factors that may affect the concentration changes of selected indicators of water quality during rainfall-runoff events. The study's aim is also testing the assumption that the

concentrations of chosen elements during rainfall – runoff events are affected by preferential flow.

2 Materials and methods

The experiments were carried out in two different localities, which are situated in upland parts of the Czech Republic (Fig. 1). First catchment – Kopaninskỳ stream – is located in Bohemian – Moravian highland near the town Pelhřimov in traditional agricultural area. The second catchment – Jenínskỳ stream – is situated close to the borders with Austria in the area which is used almost entirely as the intensive pasture.

2.1 Description of the catchments

2.1.1 Jenínský stream

Jenínskỳ stream catchment spreads out by the borders with Austria not far from Dolní Dvořiště (Fig. 1). It belongs to cadastral territories of Jenín and Horní Kaliště. The catchment area is 4683 km^2. The average altitude of the catchment is 753 m above sea level (a.s.l.). According to regional geomorphologic division of the Czech Republic the area is situated in the Šumavské podhůří unit. Jenínskỳ stream belongs to moderately warm climate region. The subsoil is formed by moldanubic pluton. The main rock types are the white mical biotitic gneiss and crystal diorite. From soils it prevails here dystric-cambisol, modal-cryptopodsol, modal-podsol, modal and fluvic-gleysol and gleyic-cambisol. Jenínskỳ stream is the right side affluent of Rybnickỳ stream. The spring of Jenínskỳ stream is located 3 kilometres from village Jenín by the peak Žibřidovskỳ vrch in the altitude 870 m a.s.l. Almost the whole catchment is artificially drained and it is used as the extensive pasture but only during summer period.

2.1.2 Kopaninský stream

Kopaninskỳ stream catchment spreads out in Bohemian-Moravian highland not far from Pelhřimov (Fig. 1). It belongs to cadastral territories of Chvojnov, Kletečná u Humpolce, Onšovice u Dehtářů, Velkỳ Rybník u Humpolce and Žírov. The catchment area is 9178 km^2. The average altitude of the catchment is 545 m a.s.l. According to regional geomorphologic division of the Czech Republic the area is situated in the Křemešnická highland unit. The area of Kopaninskỳ stream belongs to moderately warm climate region. The subsoil is also formed by moldanubic pluton. The main rock types are the white mical biotitic gneiss and crystal diorite. From soils modal-cambisol, gleyic-cambisol and gleysol prevails here. Kopaninskỳ stream catchment is the left side affluent of Jankovskỳ stream. The spring of Kopaninskỳ stream is located in forest complex in the southernmost part of the catchment in the altitude 624 m a.s.l. This catchment is used for traditional intensive agriculture. Almost the whole locality is used as arable land.

2.2 Methods

2.2.1 Water quality monitoring

Discharge rates were measured on all selected profiles by ultrasonic water level sond (US1200), completed with recording units (M4016). Discharge rates and water levels are recorded in data loggers by normal runoff conditions in the ten-minute intervals and during extreme rainfall-runoff events in the one minute time step. During the whole year, on the particular profiles, discreet monitoring of water quality was carried out, in one month interval. These results are complemented by continuous monitoring of water quality during extreme rainfall-runoff events, when the sampling time step varies depending on the duration of the event within hours. Sampling is now on all the profiles provided by the continuous ISCO 6712 automatic sampler with sampling up to 24 water samples in a single program cycle. The study includes totally 26 episodes, of which

19 were from the catchment of Jenínskỳ stream and 7 of Kopaninskỳ stream catchment. For this study there were used only results from water quality analysis covering nitrate anions NO_3^- and phosphate anions PO_4^3. Analyses were carried out according to standard analytical methods in accredited laboratory.

2.2.2 Data analysis

Data about water quality and discharge rates obtained during the rainfall-runoff events were evaluated using the hysteresis loops described in the work Butturini et al. (2006). This method is based on the evaluation of the mutual relations of flow and concentration of selected substances in the rainfall-runoff episodes to capture the current timing of the event. Hysteresis loop can be described by a series of parameters that can be divided into biogeochemical and hydrological parameters as described in Butturini et al. (2008), Butturini et al. (2006) or Christopher et al. (2008). Biogeochemical parameters reflect the development of particular element concentrations in water during the monitored events, while hydrological parameters record the local environmental conditions, particularly the use of the area, moisture conditions and hydrographs of rainfall runoff events. These parameters are then statistically evaluated.

Among the biogeochemical parameters there are monitored only two characteristic values for each element describing the change of its concentration during the rainfall-runoff events.

→ dC [%] – parameter describing the relative change in concentrations during rainfall-runoff event. This parameter takes values in the range of −100 to +100, where negative values indicate a process of dilution and conversely positive values describe increased leaching of the substance

$$\mathrm{d}C = \frac{(C_\mathrm{s} - C_\mathrm{b})}{C_\mathrm{max}} \times 100, \tag{1}$$

where C_s is the concentration of the substance [mg L^{-1}] reached in the culminating moment of the flow, C_b is the concentration of the substance [mg L^{-1}] recorded by the base flow, C_{max} is the maximal recorded concentration of the substance [mg L^{-1}].

→ dR [%] 00 parameter which includes information describing the area and direction of hysteresis loop.

$$\mathrm{d}R = A_h \times R \times 100, \tag{2}$$

where A_h is the area of the hysteresis loop corresponding to the event, R is a parameter describing the direction of hysteresis loop. This parameter takes three possible values: +1 value that indicates rotation in a clockwise direction, 0 value that indicates the hysteresis loop with a vague rotation, or event, where it is not possible to indicate hysteresis, −1 value that indicates anticlockwise rotation.

Among the hydrological parameters nine values describing the environmental conditions were included. These include the following parameters:

→ dQ_t – parameter describing the amplitude of discharge between the value at the beginning of the rainfall-runoff event and peak discharge rate, relative to the value of the base discharge.

→ dQ_{t-1} – parameter describing the amplitude of discharge between the value at the beginning of the rainfall-runoff event and peak discharge rate, relative to the value of the base discharge of the previous rainfall-runoff event.

→ t [day] – parameter describing the time elapsed since the previous rainfall-runoff event.

→ precip [mm] – parameter describing the total amount of precipitation, which caused current rainfall-runoff event.

→ precip – 1 [mm] – parameter describing the total amount of precipitation that caused the previous rainfall-runoff event.

→ RIS : REC – parameter describing the ratio between the length of the ascending and descending branches of rainfall-runoff event hydrograph.

→ stable [%] – parameter describing the percentage of stable areas (grassland, forests, water areas) in the catchment area.

→ inf [%] – parameter describing the percentage of land classified in the I. and II. category of soil infiltration under appropriate methodology Janglová et al. (2003) in the catchment area.

→ slope [%] – a parameter describing the average slope of the catchment.

At first the c–q hysteretic loops were evaluated on the basis of their area and rotational pattern. According to Butturini et al. (2006) it is possible to sort these loops into four quadrants on the basis of different concentration and runoff changes during the particular rainfall-runoff events (dC, dR). In the quadrant A there are loops with CLW rotation and at the same time these loops have generally positive trend (d$C > 0$, d$R > 0$) – they explain the process of flushing. In the quadrant B there are the hysteretic loops also CLW but describing the process of dilution, so with the negative trend (d$C < 0$, d$R > 0$). In the quadrant C there we can find the loops which are ACLW and describing the negative trend (d$C < 0$, d$R < 0$) and those in quadrant D describe the positive trend and they are also ACLW (d$C > 0$, d$R < 0$).

2.2.3 Statistical evaluation

The statistical evaluation of the c–q hysteretic loops was processed in programs Microsoft Excel, Statistica and CANOCO 4 (Ter Braak and Šmilauer, 2002) with modules for data import WCanoImp, Canoco for Windows 4.5 for the analysis of data sets and CanoDraw for Windows 4.1 software for creating graphical output.

The relationships of concentrations, discharges and the parameters of the catchments were explored using the multivariate gradient redundancy analysis (RDA). RDA is the extension of linear multiple regression.

Distribution of the data inputs for the chosen multivariate statistical analysis results from the terminology of used software. Data is divided into the species data, environmental characteristics and covariates. Species data are the primary data characterizing the formation of links between discharge and concentration during rainfall-runoff events. This data enter into the analysis as the explained variables. Environmental characteristics include the parameters of relevant catchments, their formation and properties. These parameters are included in the analysis as the explaining variables. In the explanatory variables there are also included covariates. However, these are parameters that have known or at least expected influence on the explained variables.

All of the above biogeochemical parameters of rainfall-runoff events were selected as a species data for analysis and all selected hydrologic parameters described rainfall-runoff events were included as environmental characteristics. The parameters STABLE and INF were the only exception, when these were included in one analysis as covariates.

For this study, the significant hydrological parameters ($p < 0.05$) were selected after forward selection using a Monte Carlo permutation test.

The result of analysis is the ordination diagram where the species data are presented as arrows in the direction of the species abundances and environmental characteristics are shown as arrows in the direction of increasing value. Those vectors pointing in the same direction indicate a positive correlation, vectors crossing at right angles indicate a near zero correlation, and vectors pointing in opposite directions show a high negative correlation.

Rainfall-runoff events were first tested and evaluated together as a whole and then events resulting from short term or long term precipitation and events associated with the spring snow melt were evaluated separately.

3 Results and discussion

The identification of individual events in the intact long-term data series of discharge measured at the closure profiles of Jenínskỳ stream catchment (subcatchment J1 and J2) – Fig. 2, and Kopaninskỳ stream catchment (subcatchment P23) – Fig. 3, was the first step in the evaluation of rainfall-runoff events. In case of both subcatchments of Jenínskỳ stream catchment there was also made the identification of individual events in the long-term data series of periodically measured concentrations of nitrate and phosphate anions. In the case of profile P23 there could not be presented similar long-term data series due to the very low and often zero discharge values during the year. During the monitored years, the various periods of zero flow occurred repeatedly – most during late summer and autumn of 2008. Therefore the periodic monitoring of water quality was impossible. In contrast in subcatchments J1 and J2 in Jenínskỳ stream catchment zero discharge rates were not recorded at all, minimal discharge was still moving in the immediate vicinity of a zero limit (0.1–0.6 $\mathrm{L\,s^{-1}}$). In all of these above mentioned cases the comparison between the data series for years 2006–2010 will be presented. The basic characteristics of the discharge and nutrient concentrations long-term data series are in the Table 1.

High maximum discharge rates in relatively stabilized grassed Jenínskỳ stream catchment, which range from 311.9 to 575.8 $\mathrm{L\,s^{-1}}$, are unusual. The discharges are 1.6–3 times higher than the maximum values observed in arable and intensively cultivated subcatchment P23 in Kopaninskỳ stream catchment. These maximum values were achieved during the spring snow melt even the rainfall amount was almost zero.

This result is contrary to the results from the comparable drained intensively farmed catchment and catchment with permanent grassland or pastures that are involved into work of Siriwardena et al. (2006), which points to a lower flow rate in the grassy catchments in Queensland, up to 59 %.

The greater volatility of discharges on a grassy area, as evidenced by a coefficient of variation on the river J1 and J2, 3.91 or 3.92 respectively, compared to the value of the coefficient of variation 2.74 in P23 catchment, is also unusual. The probable causal of these high values of discharges is the higher average altitude of Jenínskỳ stream catchment which is also associated with higher snow cover in winter and therefore, higher peak discharge in the spring snow melt period. Due to terrain configuration there is also very frequent occurrence of rapid summer storm events during which very high rainfall volume is recorded in the Jenínskỳ stream catchment, and thus there are achieved high levels of discharges. Both situations contribute to the high volatility of discharges in an otherwise relatively small watercourse with low water level.

This fact is fully consistent with the results of Butturini et al. (2006) and Novotny (2003), who attribute the high variability of flows during the year also primarily to the impact of solid and liquid precipitation. In contrast Wegehenkel (2003) described the major contribution to balanced discharge throughout the year without any major fluctuations of land use change from arable land to a more stable type of land use in the case study from northeastern Germany. This fact also confirms Fohrer et al. (2005) on river Aar, where grassing also leads to a reduction of the maximum discharges and hence flood risk locations.

In the case of concentrations of individual ions only two subcatchments of Jenínskỳ stream catchment were compared with each other. In the Kopaninsky stream catchment profile P23 concentrations of ions cannot be measured periodically due to the very low to zero discharge during the year. The both compared areas have almost identical assessment and utilization, despite the results are slightly different. By the concentration of nitrate (NO_3^-) and phosphate (PO_4^{3-}) anions there were observed differences not only in absolute concentrations, but also in basic descriptive characteristics.

In the case of the two monitored ions always higher concentrations were detected in subcatchment J1, while this subcatchment exhibits in the case of phosphate anions greater variation in concentration values (coefficient of variation 0.863). These results are affected by the fact that the subcatchment J1 is contaminated by nutrients from adjacent agricultural building, which was used for cattle breeding.

This assumption is confirmed by researches of Moore et al. (1978) and Miner et al. (2000) from the vicinity of similar objects in the middle of the USA, who assign these objects to 30 % of the impact of the environment on the total annual loss of nutrients.

In contrast, greater variation in concentrations of phosphate anions in the subcatchment J2 is given by the localization of functional pastures sites (water source, feeding, and places for rest in shade) where the incidence of grazing cattle is irregular, and thus there is an irregular contribution of this source to the total concentration of phosphates in the closure profile. Localization of a weekend house without sewerage in subcatchment J2 also contributes to volatility of particular elements concentrations.

In the second step the rainfall-runoff events were divided into three groups according to the origin of the event and these groups were described by the basic characteristics that describe their run. These values are summarized in Table 2.

From totally evaluated 26 rainfall-runoff events, 6 events arose as a result of snow melt, 10 events occurred after a long lasting rain and causal of remaining 10 events was short heavy rain. In terms of volume of discharge change significant differences were between different types of events. Short rainfall caused more general increase in discharge during the rainfall-runoff events (mean change of discharge is 84.8 $L\,s^{-1}$), while the difference in discharge by events from long lasting rain is usually much lower (mean change of discharge is 47.78 $L\,s^{-1}$). High amplitude of discharge is also registered in the events associated with the snow melting in early spring. During these events there is the average change in discharge 85.2 $L\,s^{-1}$. The cause of these differences can be seen in comparing the duration of the rainfall-runoff events and the total sum and intensity of the causal precipitation. Overall, the rainfall-runoff events caused by short-term rainfall has shorter duration (average duration 8.1 h), but the intensity of rainfall is very high (average intensity 4.5 $mm\,h^{-1}$). In contrast, events due to a long sustained period of rain have an average duration 13.4 h, but are not exceptional events lasting more than 20 h. Precipitation that has caused these events, compared to the previous type of events, has significantly lower intensity (average intensity of 0.8 $mm\,h^{-1}$). These changes in the discharge associated with the origin of the rainfall-runoff events are confirmed by the results obtained in the Sharon and Kutiel (1986) for Negev (Israel) and also Butturini et al. (2006) for Fuirosos catchment in the north of Spain. Butturini et al. (2006) also describe a larger increase in the discharge during events associated with rainfall from summer thunderstorms mainly over the persistent rain.

Rainfall-runoff events resulting from snow melting have quite a unique position. As already stated, these events are characterized by high amplitude of the discharge. Recorded rainfall volume during the rainfall-runoff event is not usually their main cause. These rainfalls have mostly very low intensity (average intensity $0.2\,\mathrm{mm\,h^{-1}}$). The reason of these events is rather an increase in air temperature. Precipitations at these events are only a supporting factor that contributes to increased discharge.

3.1 Characteristic development of nitrate anions NO_3^- concentrations

In the case of nitrate anions the events with a negative rate of change of the concentration of the ion were recorded almost exclusively. The dilution of the nitrate ions concentration occurs during rainfall-runoff episodes ($\mathrm{d}C < 0$) in all three catchments. Only overall in five recorded rainfall-runoff events (19 %) the parameter describing the change in concentration during rainfall-runoff events ($\mathrm{d}C$) achieved positive values. At the same time most of the recorded hysteresis loops (61 %) describing nitrate anions have the negative value of the parameter $\mathrm{d}R$. These negative values indicate negative direction of rotation, i.e. the direction is anticlockwise.

Hysteresis loops describing the development of nitrate anions, as they were recorded during 26 rainfall-runoff events, are located exclusively in quadrants B and C (Fig. 4). These loops have differently large areas and are oriented from 58 % anticlockwise, from 27 % in a clockwise direction and the remaining 15 % of the loops have unclear course, i.e. the parameter R describing the rotation of the hysteresis loop has a zero value.

With the exception of three events in the Jenínskỳ stream catchment, however, all the hysteresis loops describe the process of dilution of nitrate anions during rainfall-runoff events. A typical example of concentration development, depending on the discharge during rainfall-runoff events is shown in the Fig. 5.

In the first phase of the rainfall-runoff event (rising limb of hydrograph) a sharp decline of nitrate concentrations occurs in Jenínskỳ and Kopaninskỳ stream catchment. The probable causal of this sudden decrease in the concentrations of nitrate anions is dilution by leaking of rainwater poor on nitrate anions. The maximum concentration of nitrate anions is mostly recorded at the beginning of the rainfall-runoff events. After reaching the peak discharge a slight increase in concentration of nitrate anions is observed again. The return to the original values before the rainfall-runoff event is very slow as shown in Fig. 5, which shows the typical hysteresis loop. The original value is mostly observed after the end of the event. For individual rainfall-runoff events all characteristics describing the hysteresis loops for nitrate anions are listed in Table 3.

This behaviour of nitrate ions is described also in the research of Toler (1965) for the Southwest Georgia (USA), Butturini et al. (2006) for northern Spain and Jordan and Smith (2005) for the agricultural region of Northern Ireland. Baresel and Destouni (2006) in a case study in southern Sweden in Norrström catchment note that other development of nitrate anions concentrations during rainfall-runoff events than their dilution was never recorded.

3.2 Characteristic development of phosphate anions PO_4^{3-} concentrations

By monitoring the trend of phosphate anions the concentrations has increased by leaching process of the substance in water during rainfall-runoff episodes in 71 % of cases, as indicated by positive values of $\mathrm{d}C$. At the same time the vast majority of rated events prevail with unclear or ambiguous direction of shaping of the hysteresis loop for this anion.

When evaluating the rainfall-runoff events in terms of phosphate anions the trend of hysteresis loops in terms of their size and direction is ambiguous and the location of events in each quadrant graph is completely random (Fig. 6). A large number of loops (42 %) have a relatively large area, and have a positive orientation – are oriented in a clockwise direction ($dR > 0$). Only 23 % of all recorded events has reversed rotation, that is anticlockwise ($dR < 0$). This phenomenon is generally very rare and is observed only in isolated cases. Typical hysteresis loops formation during rainfall-runoff events (34 %) remains the development with uncertain rotation ($dR = 0$). Such development of hysteresis loops was observed in the grassy area of the Jenínskỳ stream catchment in 45 % of all monitored rainfall-runoff events.

In contrast, the development of phosphate anion concentrations during the rainfall-runoff events is relatively clear. The 77 % of the events is describing a process of phosphate ions leaching, i.e. an increase of concentrations ($dC > 0$). A gradual escalation of phosphate anions concentrations usually occurs in the first phase of the rainfall-runoff event. This trend continues even after reaching the peak discharge (Fig. 7). The maximum concentration of phosphate anions is usually reached subsequently after a short time (approximately 1.3 h) from culmination of discharge. It is followed by a slow decline in concentrations until reaching baseline values before the rainfall-runoff events. The reason can be seen in the elution of phosphate ions from the rock and soil profile during leakage of rainwater in the initial phase of the rainfall-runoff events and also in higher concentrations of phosphate anions in rainwater. The inverse development of the phosphate anions concentrations is observed only in 23 % of the rainfall-runoff events. These are usually rainfall-runoff events with a shorter duration and low intensity of rainfall. The concentration changes reached in an average only 26.3 %. For individual rainfall-runoff events all characteristics describing the hysteresis loops for phosphate anions are listed in Table 3.

This result was observed also in other, agriculturally intensive but also extensively utilized catchments, such as the Eaton catchment in the Appalachians in the southeast USA (Carson et al., 1973) or agricultural catchment in Holbeck Yorkshire – United Kingdom (Klein, 1984). Randomness in direction and surface shaping of hysteresis loops is also confirmed by the results from other river basins in the United Kingdom

(Swale River Basin) described by Bowes et al. (2005) and the Colville River catchment in Alaska (USA) described by Arnborg et al. (1967).

Figure 8 demonstrates a comparison of the typical discharge rates and concentrations of nitrate and phosphate anions during rainfall-runoff events, as described in this section.

The graph clearly shows synchronous dilution of nitrate anions and increase in phosphate anions concentrations with increasing flow rate in the initial phase of the rainfall-runoff event (the rising limb of hydrograph). This is probably due to the above mentioned seepage of rain water through the soil profile, through preferential flow paths. In the case of nitrate anions the significant dilution of concentrations is caused by the rainwater poor on nitrate anions, similar to the events in the western USA described by Wagner et al. (2008). Unlike nitrate anions, the concentration of phosphate anions is during rainfall-runoff events increased by leaching of phosphate ions from the soil, through seepage of rainwater through runoff preferential flow paths as it was described during the rainfall-runoff events by Zajíček et al. (2011). The significant contribution of water percolating through preferential flow paths was shown also in research of (Cerro et al., 2013) in Alegria catchment in the north of Spain. This research confirmed that substances such as phosphorus are washed out mainly by increasing surface runoff and leaching directly to the stream channel, while the concentration of substances such as nitrates are reduced mainly by contributions of groundwater.

3.3 Evaluation of statistical RDA analysis

Ordination diagrams which are presented here are the result of statistical analysis between discharge rate and concentration of elements in rainfall-runoff events by using RDA analysis. The minimal, maximal and average values of individual environmental characteristics for each subcatchment are listed in Table 4.

All three monitored subcatchments of Jenínskỳ stream (J1, J2) and Kopaninskỳ stream (P23) catchments, according to the recorded values of parameters describing the rainfall-runoff events are comparable. The biggest difference can be seen in the measured amplitude of discharges, both directly during current rainfall-runoff event ($\mathrm{d}Q_t$), and also in the case of discharges by previous rainfall-runoff event ($\mathrm{d}Q_{t-1}$).

First, the data from all recorded events were included in the RDA analysis, entering all biogeochemical parameters as dependent variables and all hydrological parameters described in the methodology as explanatory variables without using covariates.

Based on Monte Carlo permutation test as statistically significant parameters INF, STABLE, $\mathrm{d}Q_t$ and precip – 1 were identified. Collectively, these four parameters explain 83 % of the variation, with the first two mentioned parameters, together explaining 47 % of the total variation.

By the analysis (Fig. 9) a positive correlation was mainly found between the parameter STABLE describing representation of stable parts of landscape in the catchment and the parameters that describe the change in concentration of nitrate ($\mathrm{NO_3}$–dC) and phosphate ($\mathrm{PO_4}$–dC) anions in the watercourse. The absence of stable part of the landscape (forests, grasslands and wetlands) has the greatest impact on increasing changes in the concentrations of both of monitored ions as it was expected. It can be said that the higher abundance of stable landscape structures in the catchment is significantly reducing changes in concentrations of phosphate but also of nitrate anions during rainfall-runoff events.

This result illustrates the reduction in the concentration of nitrate and phosphate anions in wooded and grassy catchments compared to arable land and it is comparable with results of Siwek et al. (2011) for catchments in similar geographical conditions as in the Czech Republic (the slopes of the Carpathians, Poland).

Parameter STABLE also has a significant influence on the formation of hysteresis loops of phosphate and nitrate anions in terms of their area and the direction of rotation. With decreasing proportion of stable parts of the landscape in the catchment the area of hysteresis loops is reducing and often falls in dR deeper below zero.

INF parameter describing the proportion of soils vulnerable to infiltration in the catchment also has a significant impact on the changes in the concentration of nitrate and phosphate anions during rainfall-runoff events. From the ordination diagram it can be

concluded that in catchments with a higher proportion of infiltration vulnerable soils leads to significant variation in concentrations of phosphate and nitrate anions during rainfall-runoff events.

INF parameter has irreplaceable importance also for the direction and size of the hysteresis loops of the two monitored ions. It has been shown that a higher proportion of infiltration vulnerable soils in the catchment will decrease the value of parameters describing the direction and magnitude of hysteresis loops during rainfall-runoff events, thus there is a reduction in the area of hysteresis loops and rotation of loops is anticlockwise.

The influence of the two described parameters (STABLE and INF), or their combination, on the formation of concentrations of nutrients during extreme rainfall-runoff events, as well as on the discharge, is also described by many authors such as Butturini et al. (2006), Worrall and Burt (1999), Stutter et al. (2008) or Poor and McDonnell (2007). In the Czech Republic, the impact of individual forms of land use and infiltration vulnerable soils, as described above by the two parameters (STABLE and INF), was studied primarily in the crystalline area. Crucially influence of these two parameters on the formation of surface, but also the drainage water in the catchment of water reservoir Švihov, was described in work Fučík et al. (2010) and Lexa et al. (2006).

Given that this analysis confirmed in advance expected significance of these two parameters. Because of that both variables were afterwards included in the RDA analysis as covariates, as described in Methods. The resulting ordination diagram of the subsequent analysis is shown in Fig. 10.

After using parameters STABIL and INF as covariates only two parameters reached statistically significant level, namely a parameter $\mathrm{d}Q_t$ and precip – 1 that collectively explain 36 % of the total variability of the data file. The binding of statistically conclusive parameter $\mathrm{d}Q_t$ to the parameters describing the changes in the concentration of nitrate and phosphate anions is very important. Generally, the higher increase in discharge during rainfall-runoff events usually causes a lower value of the dC–$\mathrm{NO_3}$, which describes the change in concentration of nitrate anions, while the value of the dC–PO_4, which describes the changes in concentrations of phosphate anions, is higher.

This assumption was confirmed in all three subcatchments both of Jenínskỳ stream (J1 and J2) and Kopaninsky stream (P23). There were during the rainfall-runoff events with lower amplitude of discharge recorded higher values and more often also positive values of NO_3–dC. These rainfall-runoff events can also demonstrate the influence of parameter dQ_t on the rotation and size of the hysteresis loops for nitrate anions described by parameters dR–NO_3. Even for this parameter it is true that by the rainfall-runoff events with minor changes of discharge positive values dR–NO_3 are recorded. This creates a hysteresis loop oriented clockwise with relatively large loop area. The same result was observed for the parameter dR–PO_4. Also for phosphate anions it was proved that the rainfall-runoff events with lower discharge changes produce hysteresis loops oriented either clockwise, or more often with vague rotation (dR = 0), and these loops have a larger area.

The significant influence of the discharge changes volume to changes in the concentration of nitrate and phosphate anions was presented in work on arable land catchments also by Butturini et al. (2006) in the catchments localized in northeast Spain and Jarvie et al. (2008) for the catchment in Wales (UK).

Parameter precip – 1 (describe precipitation volume during the previous rainfall-runoff event) has a strong positive effect on the changes of the concentration of nitrate anions. The stronger and more intensive is precipitation in the previous rainfall-runoff event, the higher is the value of the parameter dC–NO_3 and also the greater the loss of nitrate ions from the catchment. On the contrary, previous heavy rainfall adversely affects the changes in the levels of phosphate anions, which are due to the rainfall-runoff event washed out to a much lesser extent.

These results are entirely consistent with the research of Ramos and Martínez-Casasnovas (2009) in the vineyard region of northeastern Spain, where the same trend in changes of the nitrate anions levels was shown during rainfall-runoff events.

From the viewpoint of formation of hysteresis loops from ordination diagram it can be inferred the unambiguous relationship between the magnitude and direction of hysteresis loops of nitrate (NO_3–dR) and phosphate (PO_4–dR) anions with volume of previous precipitation volume (precip – 1). It can be said that the greater the previous precipitation volume, the more likely the formation of the hysteresis loops for nitrate anions with a relatively large area and clockwise rotations. For phosphate anions the dependent is totally opposite. With higher precipitations volume in the previous rainfall-runoff events the recorded hysteresis loops are with large loop area as ambiguous and less often with anticlockwise rotation.

Also Klein (1984) describes in his work this phenomenon for summer convective storms with high intensity rainfall.

Next analysis (Fig. 11) covered only episodes that were caused by long-term or short-term rainfall between 1 April and 31 October. It is therefore deliberately omitted 6 rainfall-runoff events caused by snow melting in the spring. Compared with the previous analysis, there were no parameters included as covariates.

Three parameters reached statistically significant level when testing the Monte Carlo permutation test, namely parameter STABLE, RIS : REC and precip. In total, these three factors explain 79 % of the total variability. The impact of STABLE (representation of stable parts of the landscape structure) on changes of the monitored substances concentrations is the same as when it was tested in all 26 rainfall-runoff events, including those caused by the spring snow melting.

Also during the growing period there was observed the dependence of changes in the levels of nitrate and phosphate anions on the arrangement of landscape structure and its stable components, or land use, confirmed by a number of authors. This dependence is described in the Švihov reservoir catchment in the publication Kvítek (1999) for concentrations of nitrate anions, in the southeast of Ireland in the publication Neill (1989) for nitrate and phosphate anions or Correll and Dixon (1980) in the Rhode River in Maryland (USA), where this variable (percentage of stable landscape parts) explained up to 89 % of the variability in concentrations of nitrates.

The remaining two parameters that were identified as statistically significant, i.e. the parameters RIS : REC (describing the ratio between the length of the ascending and descending branches of hydrograph) and precip (describing precipitation volume during rainfall-runoff events) play a significant role in shaping of the changes in concentrations of phosphate anions during rainfall-runoff events. Unlike phosphate, changes in the concentration of nitrate anions react to values of two described parameters very little. The same argument can be applied to the shaping of the direction and size of hysteresis loops for monitored anions. Generally in accordance with the results it can be stated that transport of phosphate anions from the catchment increased during substantial rainfall-runoff events with a faster onset. Changes in the concentration of nitrate anions during rainfall-runoff events are also affected by the two parameters and the main factor influencing their behavior during monitored events remain, as described above, land use, or the proportion of stable representation of landscape.

Influencing of changes in concentrations of phosphate and nitrate anions during rainfall-runoff events is also generally described within research of Bertrand-Krajewski et al. (1998), who for the 12 selected catchments in Germany also described the influence of precipitation and the speed of the flood event. Also Fučík et al. (2012) confirmed that strong relationship between nitrate anion concentration and shape of the hydrograph occurred during rainfall-runoff events. This confirmation and similar results are very valuable for this study, because the study Fučík et al. (2012) was carried out in the same conditions of Kopaninskỳ stream catchment.

The last analysis (Fig. 12) included only rainfall-runoff events that have arisen as a result of snowmelt in the spring.

Level of statistical significance was reached only by parameters dQ_t and RIS : REC. These rainfall-runoff events tend to have, unlike typical summer events, very specific course, usually with long deceleration time and thus with very low values of the parameter RIS : REC. For these events it can also be observed that the faster events with a greater increase in discharge is caused by melting due to rising air temperature and supported by rainfall, cause significant increase in concentration of phosphate anions

in water. In this type of rainfall-runoff events, on the other hand there is very little difference in the concentrations of nitrate anions. These are usually to a greater extent washed up in the period immediately following snowmelt.

The very strong link between the formation of hysteresis loops of nitrate ions and two hydrological parameters that were confirmed by RDA analysis as statistically significant (RIS : REC and dQ_t) was observed during these rainfall-runoff events caused by snow melting. During typical events of snow melting, as described above, i.e. with a longer running time and thus with low values of the parameter RIS : REC, hysteresis loops for nitrate anions with larger areas occur more frequently, but often with negative or ambiguous direction of rotation. Similar hysteresis loop, but with a smaller area, have been identified for the phosphate anions.

Bärlund et al. (2009) stated similar conclusions in his work from the catchment Mustajoki-Pääjärvi in Finland, also in the rainfall-runoff events associated with snowmelt. He described only small changes in the concentrations of nitrate anions and also drew attention to the subsequent increase in leaching of nitrate anion in deceleration of the flood wave, as well as confirmed by Petrone et al. (2007) for Kryklan catchment off the coast of the Baltic Sea.

4 Conclusions

Dilution of nitrate anions concentrations and increasing of phosphate anions concentrations with increasing discharge rate at the initial phase of the rainfall-runoff events (the ascending branch of hydrograph) is synchronous. The probable causal of sudden decrease in the concentrations of nitrate anions is dilution by leaking of the rainwater poor on nitrate anions through preferential flow pathways. The concentration of phosphate anions is during rainfall-runoff events increased by phosphate ions leaching from the soil, through seepage of rainwater also through these preferential flow pathways. The formation of hysteresis loops and changes in the concentration of nitrate and phosphate ions are during rainfall-runoff events mainly influenced by the representation permanent landscape cover – forest and grassland (STABLE), infiltration vulnerable zones (INF), but also by the amplitude of the flow (dQ_t) and total volume of precipitation, which caused previous rainfall-runoff event (precip – 1). By summer rainfall-runoff episodes the impact of parameters STABLE and INF on the formation of hysteresis loops and development of concentrations of ions is suppressed by the parameter describing the ratio of length of the rising and recession branches of hydrograph (RIS : REC). By rainfall-runoff events caused by snow melting snow the crucial factor in the formation of hysteresis loops and changes of concentrations of both ions is the parameter describing the amplitude of the flow (dQ_t) and the parameter describing the rate of onset of the flood wave (RIS : REC).

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Table 1. Basic characteristic of long time series of measured discharges [$\mathrm{L\,s^{-1}}$] and concentrations [$\mathrm{mg\,L^{-1}}$] of nitrate (NO_3^-) and phosphate anions (PO_4^{3-}) in Jenínskỳ stream catchment (subcatchment J1 and J2) and Kopaninskỳ stream catchment (subcatchment P23) during years 2006–2010.

		N	MIN	MAX	AVG	MED	SD	PERC C90	VAR
J1	Q	1826	0.100	575 800	9400	2500	33 950	7600	3910
	NO_3^-	56	4520	35 000	19 300	19 100	7540	30 000	0.390
	PO_4^{3-}	32	0.037	0.543	0.114	0.086	0.098	0.171	0.863
J2	Q	1826	0.600	311 900	6290	2200	24 640	6600	3920
	NO_3^-	56	1490	23 000	10 980	11 350	4460	16 530	0.410
	PO_4^{3-}	32	0.061	0.267	0.122	0.103	0.050	0.177	0.413
P23	Q	1826	0	189 960	10 800	0.400	29 600	30 300	2740

Table 2. Basic characteristics of discharges and precipitations during monitored rainfall-runoff events. (TYPE – origin of the rainfall-runoff event, SM – snow melting, STP – short time precipitation, LTP – long time precipitation; TIME - time length of the rainfall-runoff event [h]; MINQ – minimal recorded discharge during the rainfall-runoff event [$\mathrm{L\,s^{-1}}$]; MAXQ – maximal recorded discharge during the rainfall-runoff event [$\mathrm{L\,s^{-1}}$]; ΔQ – change of discharge during the rainfall-runoff event [$\mathrm{L\,s^{-1}}$] a [%]; $\sum$ PREC – total volume of precipitation during the rainfall-runoff event [mm].)

DATE		SITE	TYPE	TIME	MINQ	MAXQ	ΔQ	$\sum$ PREC
1.	27–31 Mar 2006	J1	SM	76.8	29.9	175.1	145.2	26.8
2.	27–31 Mar 2006	J2	SM	90.0	27.4	186.2	158.8	32.0
3.	7 Aug 2006	P23	LTP	3.0	29.0	165.8	136.8	11.8
4.	9 Aug 2006	P23	LTP	0.3	0.9	129.2	128.3	6.4
5.	9 Aug 2006	P23	LTP	0.5	3.4	72.3	68.9	7.9
6.	6 Jun 2007	P23	STP	1.5	0.6	95.2	94.6	7.4
7.	21 Jun 2007	P23	STP	1.1	0.6	100.9	100.3	8.1
8.	4 Jul 2007	P23	STP	2.8	0.1	28.3	28.2	14.6
9.	19 Jul 2007	P23	STP	2.2	5.6	156.7	151.1	11.9
10.	27 Sep 2007	J1	LTP	6.8	2.3	3	0.7	5.3
11.	27 Sep 2007	J2	LTP	5.5	2.3	3.1	0.8	6.2
12.	3 Jul 2008	J1	STP	3.3	30.9	224.2	193.3	28.6
13.	3 Jul 2008	J2	STP	3.3	19.0	62.5	43.5	27.9
14.	5–7 Mar 2009	J1	SM	55.5	6.5	133.2	126.7	14.5
15.	23–24 Jun 2009	J2	LTP	23.8	8.5	32.5	24.0	43.9
16.	24–25 Jun 2009	J2	LTP	13.0	10.5	40.4	29.9	7.1
17.	7–8 Jul 2009	J2	LTP	11.0	8.0	24.8	16.8	6.4
18.	18 Jul 2009	J2	STP	5.0	4.1	19.9	15.8	12.3
19.	23–24 Jul 2009	J2	STP	11.1	2.1	86.1	84	14.6
20.	27 Feb–1 Mar 2010	J2	SM	37.0	6.3	15.3	9.0	2.6
21.	1–4 Mar 2010	J2	SM	84.0	7.4	31.3	23.9	2.7
22.	18–24 Mar 2010	J2	SM	100.0	6.4	54.4	48.0	1.7
23.	13–15 May 2010	J2	LTP	46.0	8.2	65.6	58.4	11.8
24.	2–3 Jun 2010	J2	STP	7.0	13.8	137.5	123.7	19.8
25.	18 Jul 2010	J2	STP	6.0	4.7	18.6	13.9	8.5
26.	23–24 Jul 2010	J2	LTP	24.0	5.1	18.3	13.2	23.8

Table 3. Basic characteristics of hysteresis loops formation for nitrate anions NO_3^- and phosphate anions PO_4^{3-} concentration during monitored rainfall-runoff events. (dR [%] – parameter which includes information describing the area and direction of hysteresis loop; dC [%] – parameter describing the relative change in concentrations during rainfall-runoff event.)

			NO_3^-		PO_4^{3-}	
DATE		SITE	dR [%]	dC [%]	dR [%]	dC [%]
1.	27–31 Mar 2006	J1	−25.50	−72.10	43.75	53.23
2.	27–31 Mar 2006	J2	−40.30	8.40	30.30	66.96
3.	7 Aug 2006	P23	11.20	−70.00	−26.40	−66.67
4.	9 Aug 2006	P23	−13.47	−51.52	−20.90	39.71
5.	9 Aug 2006	P23	−20.56	−29.41	−19.87	45.67
6.	6 Jun 2007	P23	−33.62	−36.36	0	50.00
7.	21 Jun 2007	P23	0	−44.12	−20.66	−16.91
8.	4 Jul 2007	P23	−27.14	−23.53	32.70	−27.69
9.	19 Jul 2007	P23	0	−83.78	0	86.19
10.	27 Sep 2007	J1	13.95	−64.15	18.45	−51.69
11.	27 Sep 2007	J2	−32.50	20.00	13.97	−1.11
12.	3 Jul 2008	J1	−14.87	−61.13	−32.15	50.62
13.	3 Jul 2008	J2	−37.50	−29.95	24.23	52.28
14.	5–7 Mar 2009	J1	−5.37	−84.41	19.23	76.18
15.	23–24 Jun 2009	J2	0	−28.61	0	41.06
16.	24–25 Jun 2009	J2	4.36	−57.14	0	45.73
17.	7–8 Jul 2009	J2	−83.09	3.19	0	3.41
18.	18 Jul 2009	J2	−55.66	0	16.34	18.96
19.	23–24 Jul 2009	J2	−70.48	−164.00	12.43	35.75
20.	27 Feb–1 Mar 2010	J2	−68.39	−13.93	56.23	38.31
21.	1–4 Mar 2010	J2	−37.50	−29.65	0	38.49
22.	18–24 Mar 2010	J2	0	−47.25	0	58.32
23.	13–15 May 2010	J2	0	−41.89	0	−4.32
24.	2–3 Jun 2010	J2	38.73	14.46	−19.39	−15.89
25.	18 Jul 2010	J2	−32.44	−47.76	20.34	43.89
26.	23–24 Jul 2010	J2	40.94	1.49	0	22.49

Table 4. Parameters describing rainfall-runoff events in Jenínskỳ stream catchment (subcatchment J1 and J2) and Kopaninskỳ stream catchment (subcatchment P23) – average, minimal and maximal value of the parameters. (*N* – number of rainfall-runoff events; dQ_t – parameter describing the amplitude of flow between the value at the beginning of the rainfall-runoff event and peak flow rate, relative to the value of the base flow; dQ_{t-1} – parameter describing the amplitude of flow between the value at the beginning of the rainfall-runoff event and peak flow rate, relative to the value of the base flow of the previous rainfall-runoff event; *t* [day] – parameter describing the time elapsed since the previous rainfall-runoff event; precip [mm] – parameter describing the total amount of precipitation, which caused evaluated rainfall-runoff event; precip – 1 [mm] – parameter describing the total rainfall that caused the previous rainfall-runoff event; RIS : REC – parameter describing the ratio between the length of the ascending and descending branches of rainfall-runoff event hydrograph; stable [%] – parameter describing the percentage of stable sites (grassland, forests, water areas) on the catchment area; inf [%] – parameter describing the percentage of land classified in the I. and II. category of soil infiltration under appropriate methodology Janglová et al. (2003) on the catchment area; slope [%] – a parameter describing the average slope of the catchment.)

SITE		J1			J2			P23	
N		4			15			7	
	AVG	MIN	MAX	AVG	MIN	MAX	AVG	MIN	MAX
dQ_t	7.72	0.30	19.49	6.25	0.31	40.00	96.65	4.72	282.00
dQ_{t-1}	4.31	2.50	6.20	7.51	1.18	40.00	110.01	4.72	246.23
t	52.75	0.30	150.00	32.67	0.30	187.00	23.29	2.00	94.00
precip	15.33	0.40	27.90	14.10	0.40	27.90	12.81	10.50	16.30
precip – 1	13.63	0.40	31.40	15.90	0.40	31.40	13.44	10.50	16.30
RIS : REC	0.43	0.19	0.82	0.75	0.02	3.63	0.74	0.09	1.46
STABLE		0.98			0.98			0.24	
INF		73.23			65.44			57.74	
SLOPE	9.26	8.38	11.9	11.6	7.45	11.9	7.58	7.45	8.38

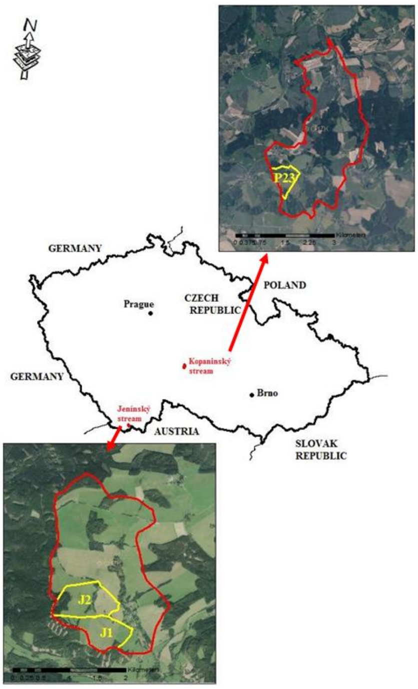

Fig. 1. Localization of Jenínskỳ and Kopaninskỳ stream catchments.

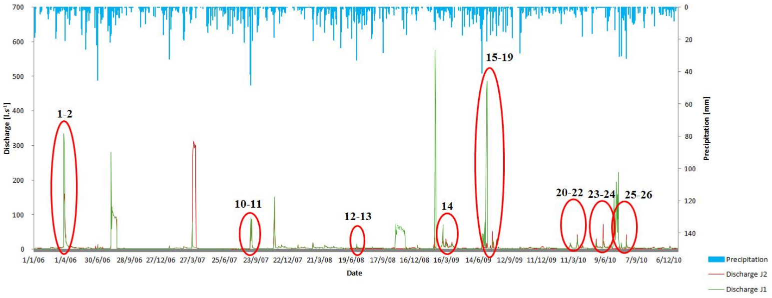

Fig. 2. Identification of rainfall-runoff events in the discharge time series from Jenínskỳ stream catchment – profile J1 and J2 – numbers of particular rainfall-runoff events according Table 2.

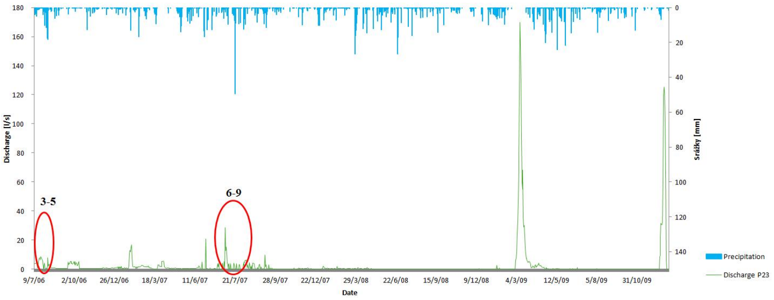

Fig. 3. Identification of rainfall-runoff events in the discharge time series from Kopaninskỳ stream catchment – profile P23 – numbers of particular rainfall-runoff events according Table 2.

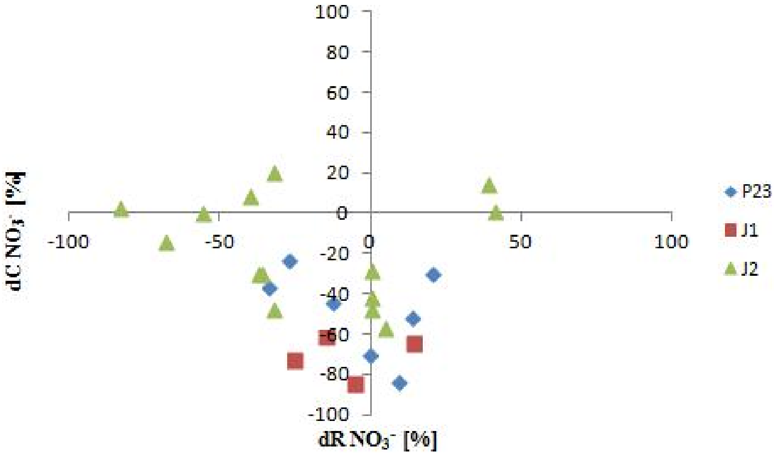

Fig. 4. Localization of rainfall-runoff events for nitrate anions NO_3^- by descriptive parameters d*C* (parameter describing the relative change in concentrations during rainfall-runoff event in %) and d*R* (parameter which includes information describing the area and direction of hysteresis loop in %) at three monitored subcatchment of Jenínskỳ and Kopaninskỳ stream (J1, J2 and P23).

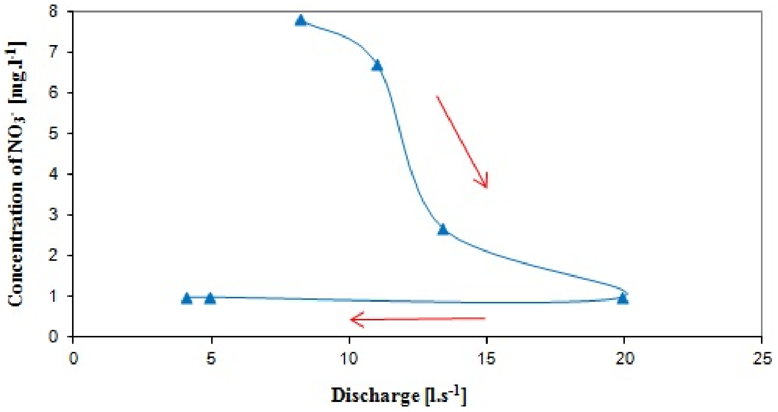

Fig. 5. Preview of hysteresis loop formation for nitrate anions NO_3^- for rainfall-runoff event recorded on the 24–25 June 2009 in the subcatchment J2 in Jenínskỳ stream catchment; arrows indicate the time course of the event.

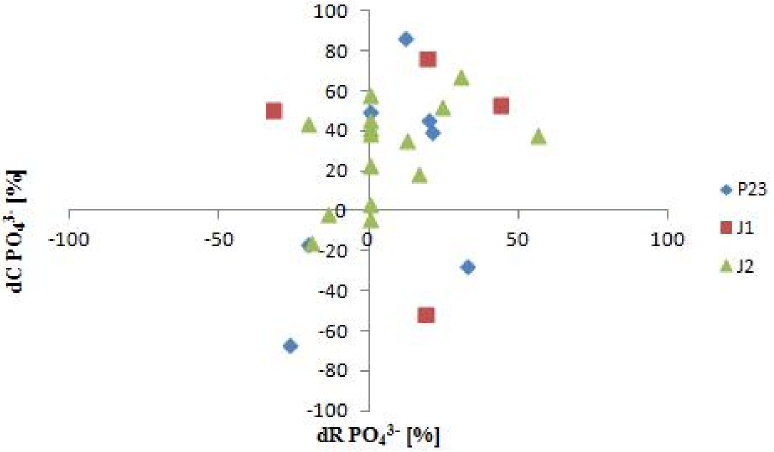

Fig. 6. Localization of rainfall-runoff events for phosphate anions PO_4^{3-} by descriptive parameters d*C* (parameter describing the relative change in concentrations during rainfall-runoff event in %) and d*R* (parameter which includes information describing the area and direction of hysteresis loop in %) at three monitored subcatchment of Jenínskỳ and Kopaninskỳ stream (J1, J2 and P23).

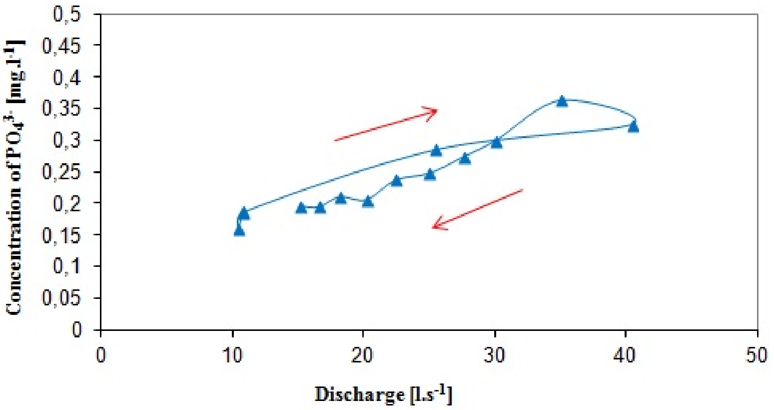

Fig. 7. Preview of hysteresis loop formation for phosphate anions PO_4^{3-} for rainfall-runoff event recorded on the 24–25 June 2009 in the subcatchment J2 in Jenínskỳ stream catchment; arrows indicate the time course of the event.

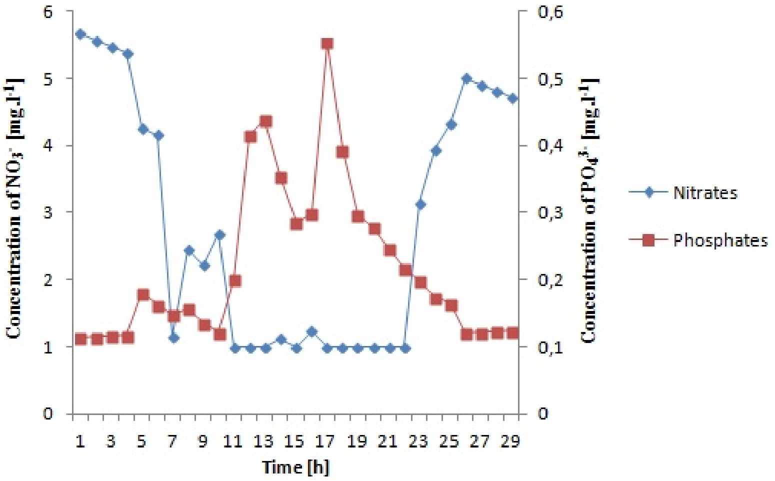

Fig. 8. Development of nitrate and phosphate anions concentration during rainfall-runoff events in the Jenínského stream catchment (J2) from 13–15 May 2010.

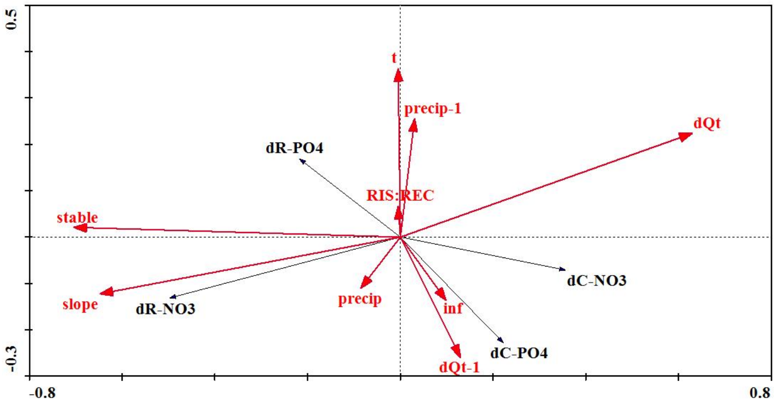

Fig. 9. RDA analysis ordination diagram – the impact of hydrological parameters on concentration values and formation of hysteresis loops. (dC [%] – relative change in concentrations during an event; dR [%] – the area and direction of hysteresis loop; dQ_t – amplitude of flow; dQ_{t-1} – amplitude of flow of the previous rainfall-runoff event; t [day] – time elapsed since the previous rainfall-runoff event; precip [mm] – total amount of precipitation, which caused evaluated event; precip – 1 [mm] – total rainfall that caused the previous rainfall-runoff event; RIS : REC – ratio between the length of the ascending and descending branches of hydrograph; stable [%] – percentage of stable sites on the catchment area; inf [%] – percentage of land classified in the I. and II. category of soil infiltration on the catchment area; slope [%] – the average slope of the catchment)

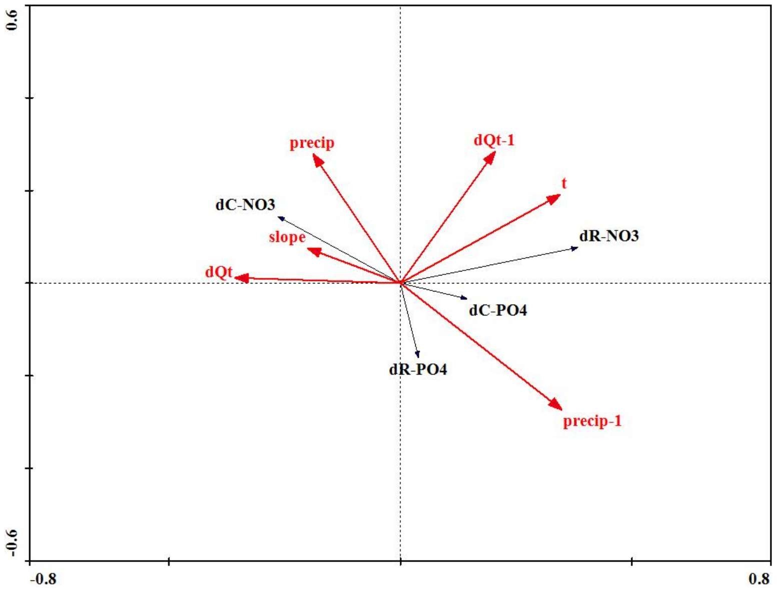

Fig. 10. RDA analysis ordination diagram – the impact of hydrological parameters on concentration values and formation of hysteresis loops by using the parameters STABLE and INF as covariates (used labels is same as in Fig. 9)

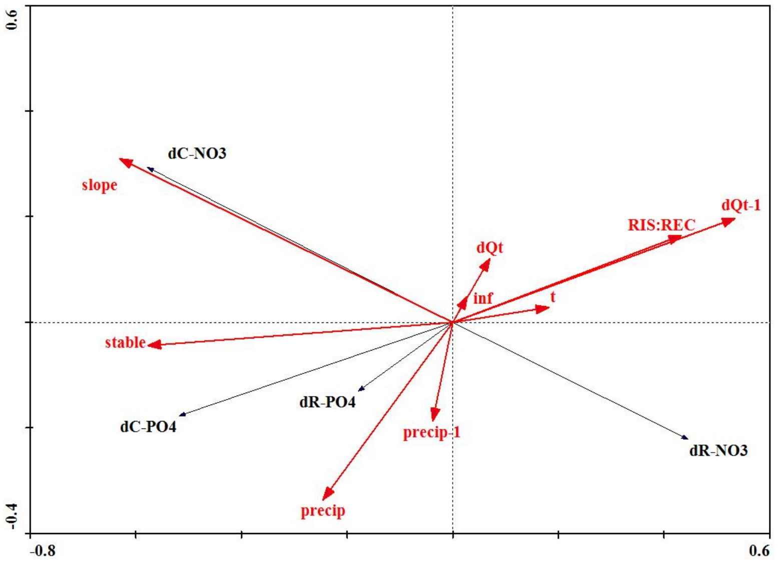

Fig. 11. RDA analysis ordination diagram – the impact of hydrological parameters on concentration values and formation of hysteresis loops during summer rainfall-runoff events (1 April–31 October) (used labels is same as in Fig. 9).

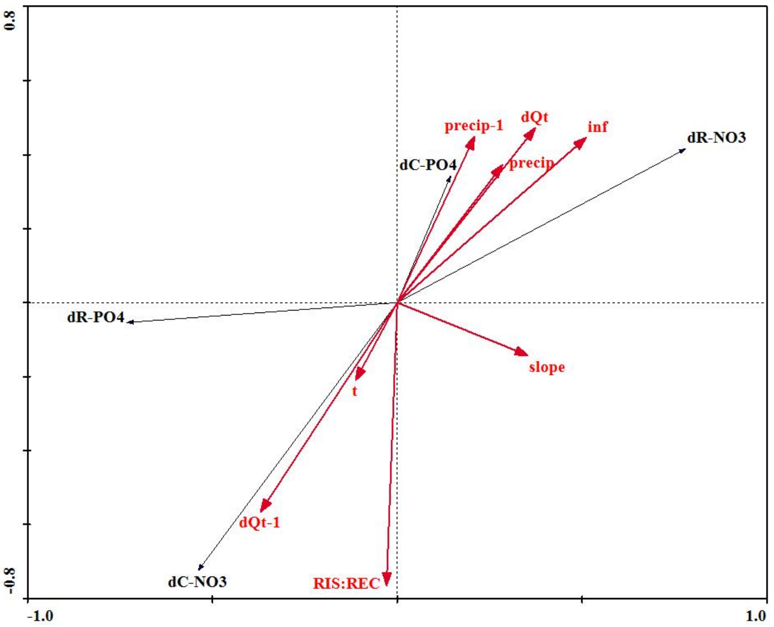

Fig. 12. RDA analysis ordination diagram – the impact of hydrological parameters on concentration values and formation of hysteresis loops during events caused by snow melting (used labels is same as in Fig. 9).