DYNAMICS OF STREAM WATER QUALITY DURING SNOWMELT AND FLASH FLOOD EVENTS IN A SMALL AGRICULTURAL CATCHMENT

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Introduction

Time behaviour of inorganic nitrogen and suspended solids concentrations in surface waters of small water courses is a very variable one in connection with the course of weather (season, precipitation intensity and space-time distribution, the length of the period without precipitation before effective rainfall, atmospheric deposition), soil and hydrogeological characteristics of the catchment, saturation of the soil profile (antecedent moisture / hydrological conditions in the catchment), time and intensity of fertiliser application, biochemical reactions in soil, land use and catchment morphology (Pačes, 1982; Webb and Walling, 1985; Burt *et al.*, 1993; House and Warwick, 1998; Čížek, 2002; Haygarth and Jarvis, 2002; Withers *et al.*, 2002; Doležal and Kvítek, 2004; Christopher *et al.*, 2008; Turgeon *et al.*, 2008). *C–q* hysteresis (loops) are observed in the case when a substance concentration is different for the same discharge on the rising and on the falling limb of a hydrograph. Meybeck, Chapman, Helmer (1990) describe some typical *c-q* relationships with the duration period from several hours to several days: (i) general concentration decrease with increasing discharge (dilution) – typical for main ions, more mineralised waters; (ii) confined increase connected to soil particles' washing out (organic solids, N forms) during runoff; (iii) concentration increase with increasing discharge, the concentrations' maximum follows their decrease caused by the dilution of matters' concentration in soil profile; (iv) exponential increase (suspended solids and connected components – metals, pesticides); (v) clockwise loop (suspended solids during floods), maximum concentration precluding maximum discharge; (vi) constant concentration caused by dominant portion of groundwater discharge (e. g. karst areas, water reservoir runoff). Bond (1979, cit. Butturini *et al.*, 2006) deliver the hypothesis, that hysteresis-course, -rotation and -extend are typical and periodical for each parameter and each catchment. Further explanation of the effect report House and Warwick (1998), Evans *et al.* (1999) and Rose (2003) when they describe the hysteresis as a result of two (pre-event and event water) or three (surface runoff, sub-surface-soil water, ground water) runoff components mixing; each component with different concentration prevailing in different parts of the event. Evans and Davies (1998, cit. Hornberger *et al.*, 2001; Rose, 2003; Butturini *et al.*, 2006) suggested *c-q* hysteresis classification on the basis of the hysteresis rotational pattern (clockwise, anticlockwise), curvature (convex, concave) and direction (positive, negative, null).

The aim of this study is to investigate, if and how it is possible to characterise and quantify relations among rainfall – runoff (R-R) events and related concentrations (NO_3^-, NH_4^+ and suspended solids) throughout different seasons of the year on the basis of detailed surface water sampling analysis and related discharges measurement, together with the evaluation of the antecedent hydrological (moisture) catchment's conditions.

Material and Methods

Site description

Observations were realized in the Kopaninský stream catchment located in the Bohemo-Moravian Highland, Pelhřimov district and lying within the drinking water reservoir basin Svihov (on the Zelivka river). The watershed is situated in the Czech crystalline complex. Major parent rock is paragneiss, other encountered ones are granite, orthogneiss and quartzite; sporadically sandy and loamy eluvium. There is characteristic shallow aquifer which is fixed to quaternary porous sediments or to weathering zones in the basement crystalline rocks or to zone of shallow disjunction of crevices. The dominant soil types are Cambisols and gleyic Stagnosols (Planosols). Catchment area to the outlet profile T7U is 7.1 km^2, altitude ranging between 478-620 m a.s.l. Main channel length is 4.2 km, average slope 2.6%. The Kopaninský stream represents a typical local small agricultural catchment (44.7% arable land, 36.7 forest, 13.1% meadows and pastures, 3.5 % other surfaces, 1 % gardens, 0.6% built up areas, 0.5% water ponds) with agricultural subsoil tile drainage systems (10% of the catchment area, 16% of the agricultural land).

Evaluated hydrological events and sampling strategy

For *c-q* analysis, 12 thoroughly examined R-R events occured in years 2005-2007 were selected; 9 events caused by rain (marked R), 3 events from snow thawing accompanied by some precipitation (symbol T). R-R event from march 2006 was composed of 6 shorter events (waves), which occured consequently and were analysed each in detail. Water sampling was realized in the closing profile of the catchment (T7U) in an intensive regime with every 0.5-4 hour extraction (till June 2006) or according the streamwater level dynamics (with approx. every 50 mm water level change; from July 2006). Authomatic sampler ISCO 6712 was used for water samples withdrawal. With every impulse of the sampler one water sample (of 1 liter volume) was taken all at once. Suction basket of the sampler was situated nearby the left brook bank, approx. 20 cm above the stream bottom and 0.5 m ahead of the weir crest. Water samples were analysed in the accredited laboratory of Research Institute for Soil and Water Conservation, Prague using standard methods. Stream water dynamics was measured continuously by an ultrasonic probe and recorded in a 10 minute step with a datalogger. Precipitation amounts were collected and registered in a 10 minute interval by an authomatic rain gauge (tipping bucket) with a datalogger, situated nearby the weir. In case of snow cover, the snow-water content was measured and added to the causal precipitation amount. In Figure 1 there is as an example one evaluated hydrological event displayed.

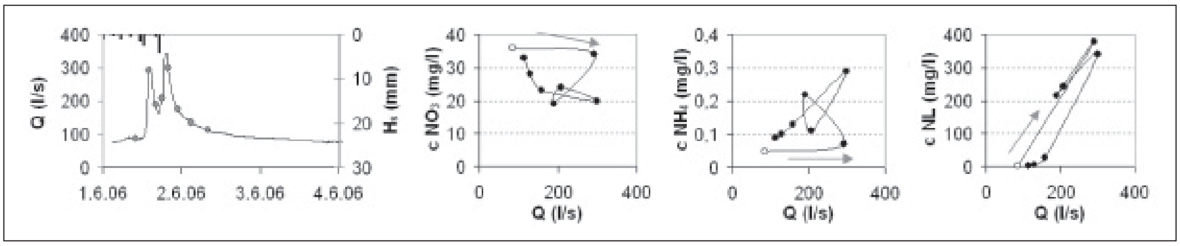

Figure 1. Example of a R-R event hydrogram (Q – discharge, H_s – 1hour total rainfall) with the sampling terms (points in the graph) and *c-q* hysteresis (Q – discharge, c – solute concentration; empty point describes the first sample of the episode, arrow indicates the *c-q* hysteresis rotation)

Compilation of parameters used and employed statistical methods

Hydrological characteristics of each R-R event represent parameters: Q_t (%) – the magnitude of the storm event, *k* (1/day) – the slope of the initial phase of the hydrograph recession limb, *SL* (SLOPE) – linear regression slope of the initial phase (2 hours) of the hydrograph recession limb, *RL* (%) – the relative length of the rising limb – in relation to the length of the entire hydrograph.

Each *c-q* loop was also characterised by solute behaviour descriptors δC and δR. Parameter δC (%) defines relative changes in solute concentrations and hysteresis trend, δR (%) integrates information about the area and rotational pattern of the hysteresis.

Furthermore, each R-R event was characterised by rainfall parameters (h_s – total precipitation height from the beginning till the end of the R-R event, h_{sQmax} – -"- till the runoff culmination, h_{iavg} – average rainfall intensity per 1 hour, h_{imax} – maximal rainfall intensity per 1 hour), runoff height h_o and runoff coeficient *f*, antecedent moisture conditions (*API* – 5 days precipitation sum prior to an event, h_{so} – number of days without rainfalls). Analogous selection and construction of parameters which describe each *c-q* hysteresis and moisture conditions in the catchment mention Butturini *et al.* (2006), Christopher *et al.* (2008) and Turgeon *et al.* (2008).

For the data evaluation, standard statistical methods were conducted; correlation, regression and multidimensional analysis (PCA – principal component analysis) with MsExcel and QcExpert 2.5 software. All testing and analysis were carried on the significance level under the null hypothesis $\alpha = 0.05$. Water quality and related discharges data sets were tested for distribution (normality and outliers occurrence) prior to analysis. Parameters described above entered the multidimensional (principal component) analysis, esults are depicted in Figure 2. Points represent each R-R events, lines (beams) represent parameters. Close row vectors (points) or column (lines) are cross correlated. Row vectors lying in the direction of some column vector have in this column higher or lower value.

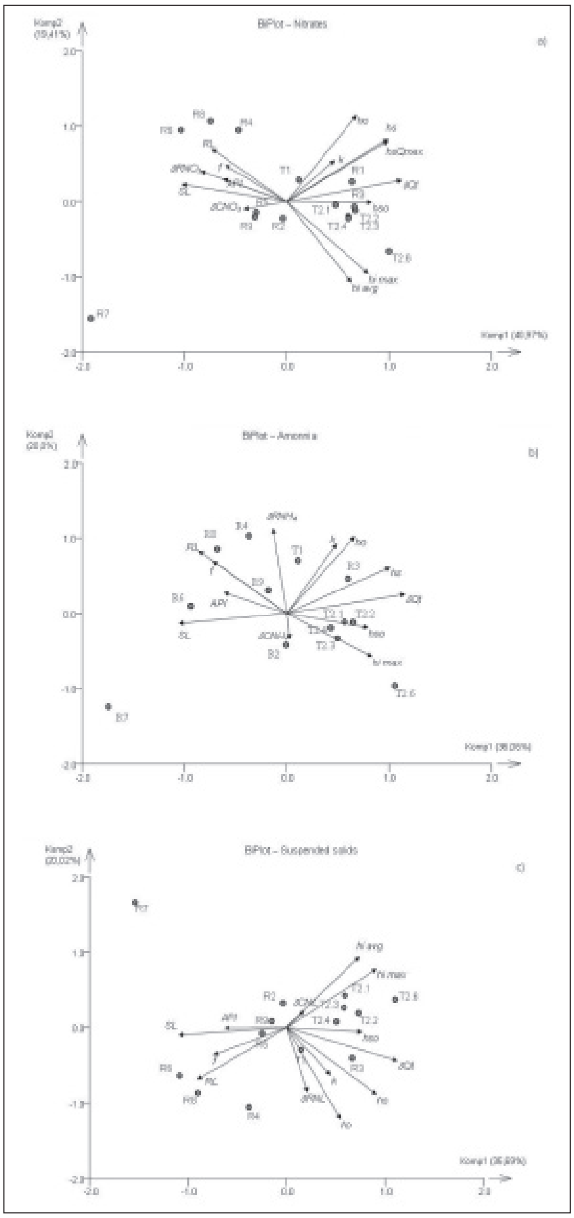

Figure 2. a, b, c. PCA BiPlots for NO_3^-, NH_4^+ and suspended solids

Results and discussion

From samples analysed within this study we noted two patterns of *c-q* hysteresis (clockwise and anticlokckwise) and their dual curvature (convex and concave).

For nitrates was found out:

1. anticlockwise movement direction of *c-q* hysteresis; togehter with rising of the discharge nitrate concentrations moderately increase (or are stable) up to discharge culmination, further, during the fall of discharge, the nitrate concentrations increase again along the concave shaped curve (events both from snowmelt as well as from the precipitation),
2. clockwise movement direction of *c-q* hysteresis; within the discharge increase the nitrate concentration are slightly decreasing, after the discharge peak the nitrates begin to rise, following either (more likely) the concave or less frequently the convex type of curve; both snowmelt and precipitation events take up these two curvature patterns.

Correlation analysis proved in the statistically significant cases predominantly negative linear relationships; with the rising discharge the nitrate concentrations were decreasing. Positive correlations were statistically insignificant, except the only one *c-q* hystersis from a snowmelt event during the spring 2006, when the correlation was positive. The PCA results showed, that the area and direction of a *c-q* hysteresis has the closest positive relations to the parameters *RL*, *SL*, further then to the *API* and *f* parameters. From the mutual positions of the factors δQt, δRNO_3 and δCNO_3 it can be assumed for a weak inverse relation among them, which has been confirmed by correlation and regression analysis. Accordingly, values of δCNO_3 parameters are for the majority of evaluated *c-q* hysteresis of a negative sign.

In the case of ammonia, *c-q* hysteresis patterns and curvatures were observed mostly with an opposite course than those for nitrates; with discharge growth the ammonia concentrations were usually rising. Statistically significant coefficients (positive) were revealed only in three cases and because of their high values they indicate for a close Q-C relation.

The course of suspended solids (SS) *c-q* hysteresis was unambiguous; in the prevailing cases there were discovered positive and quite close relationships between the actual discharge and suspended solids concentrations. In some cases those relations fit to the exponential shape of regression curves, which means a steep increase of suspended solids concentration with discharge growth. This principle is obvious and generally well known and documented.

Conclusion

The comprehensive statistical analysis were applied to characterise *c-q* hysteresis of selected substances in streamwater of a small agriculture catchment located in the Bohemo-Moravian Highland. From the results of surface water quality analysis (NO_3^-, NH_4^-, SS) and discharge dynamics both from snowmelt and precipitation events it was recognised, that except the suspended solids concentration there was no explicit pattern of behaviour of solutes and related discharges. Nitrate concentrations showed a dual course; during some events the concentrations slightly increased immediately with the beggining of a flood wave, when the concentration was usually similar to the value of a sample taken prior to event within the regular 14 day sampling (in accordance with a particular season). Further, with subsequent discharge ascent, a recession of nitrates happened due to dillution effect, untill or shortly after the moment of discharge peak. As the discharge declined, the concentrations rose up again. In other cases, a dillution effect appeared immediately with the discharge growth and the nitrate concentrations decreased. After discharge peak subsided, the concentrations returned to the similar rates, as prior to the event. It was found that variability of an area and rotation direction of NO_3^- *c-q* hysteresis is related mostly to the relative lenght of the hydrograph rising limb, slope of the initial phase of the hydrograph recession limb, 5 days precipitation sum prior to the event and to the runoff coefficient. Relative change of the nitrate concentrations during an event showed to be without a linkage to any of analysed factors. For ammonia, the concentration usually arose with discharge growth; the principal component analysis displayed no mutual relationships among investigated factors. Suspended solids concentration during all the events followed unambiguous relation to the discharge; it steeply rose with the discharge increase.

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