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Linking soils and streams during events: response of stream water K^+ concentration to soil exchangeable K^+ concentration in small catchments with fragipan soils (Carpathian Foothills, Poland)

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Abstract: The study aimed to determine the linkage between soil exchangeable potassium (K^+) concentration and stream water K^+ concentration during rainfall and snowmelt events in small catchments with different land use (Carpathian Foothills, Poland). The complementary geochemical and hydrochemical approach used in the study produced new information on the role of particular soil horizons and contributing areas such as hillslope or riparian areas in K^+ delivery to stream channels during events. Horizons lying above the nearly impermeable fragipan (Btx) play the most important role in the process of K^+ influx to streams during most event types except snowmelts with frozen soils, in all the studied catchments. In the woodland catchment, rapid flushing of K^+ from the topsoil Ah horizon with higher hydraulic conductivity (K_{sat}) and higher exchangeable K^+ concentrations than in the lying lower E horizon resulted in a clockwise hysteresis of K^+ in stream water during most events. In agricultural catchments, changes in stream water K^+ concentration during events were determined by distinct differences between soil exchangeable K^+ concentrations on hillslopes and in riparian areas.

Keywords: Hystereses of K^+; Rainfall and snowmelt events; Soil exchangeable K^+ concentration; Fragipan; Agricultural and woodland catchments; Carpathian Foothills.

INTRODUCTION

Potassium (K) – along with nitrogen (N) and phosphorus (P) – are three of the most important biogenic elements in the natural environment (Anderson et al., 1997; Barré et al., 2007; Dobermann et al., 1996; Hem, 1985; Likens et al., 1994; Tripler et al., 2006). The amount of data on the effects of environmental factors impacting the circulation of potassium in soil and water is markedly smaller than that for nitrogen and phosphorus (Alfaro et al., 2004a, b; Kayser and Isselstein, 2005; Simonsson et al., 2007; Tripler et al., 2006).

One critical store of catchment potassium is the soil, where the K^+ concentration varies due to a number of factors including natural variation of the K^+ concentration in soil parent material (Irmak and Sürücü, 1999), different clay mineral content (Barré et al., 2007, 2008; Kayser and Isselstein, 2005), as well as different hydrologic properties of soils that determine the onset of so-called macropore (preferential) flow rich in K^+ (Alfaro et al., 2004a). One major source of potassium in surface soil horizons is decaying organic matter (McDowell and Liptzin, 2014; Stottlemyer, 2001). The acquisition of potassium from the soil by plants leads to the enrichment of the upper soil horizons with potassium thanks to the process of potassium uptake (Jobbágy and Jackson, 2004; Ulery et al., 1995). In woodland catchments, soils may become enriched in K^+ ions via throughfall (Evans and Davis, 1998; Likens, 2013; Likens et al., 1994; Małek and Astel, 2008; Rothe et al., 2002; Stachurski and Zimka, 2002). In the case of agricultural catchments, soils are strongly enriched with potassium via the use of mineral and organic fertilizers (Alfaro et al., 2004 a, b).

As in the case of other solutes, the quantity of K^+ flushed out of the soil determines its concentration in stream water (Christophersen et al., 1990; Mulder et al., 1991, 1995). The significance of the soil in the K^+ concentration in stream water is demonstrated by the close relationship between K^+ in streams and soil moisture conditions in catchments (Foster, 1978). Griffioen (2001) and Williams et al. (2001) note that cation-exchange processes usually drive the downward transport of K^+, which is easily adsorbed by clay minerals and organic matter (Barré et al., 2007, 2008; Likens et al., 1994). The quantity of potassium released from the soil is determined by soil texture and the application of fertilizer (Alfaro et al., 2004b; Simonsson et al., 2007).

The largest amounts of K^+ are flushed out of the soil during rainfall and snowmelt events. The flushing of K^+ from the soil is controlled not only by the pool of available potassium in soils but also by the hydrologic properties of soils (Alfaro et al., 2004b). One interesting example is the fragipan, which exhibits higher bulk density and lower porosity than overlying soil horizons, and therefore, restricts the infiltration of water (Lindbo et al., 1994; Szymański et al., 2011, 2012; Witty and Knox, 1989). The fragipan is characterized by very low hydraulic conductivity (McDaniel et al., 2008; Rockefeller et al., 2004). Therefore, the fragipan plays an important role in water flow pathway formation during rainfall and snowmelt events (Gburek et al., 2006; McDaniel et al., 2008; Miller et al., 1971; Needelman et al., 2004; Rockefeller et al., 2004). As soil potassium is lost and then washed into streams, the concentration of

K^+ in stream water increases with increasing discharge (Edwards, 1973; Elsenbeer et al., 1995a; Evans and Davies, 1998; Foster, 1978; Siwek et al., 2011).

Relationships between stream water K^+ concentration and discharge often take the form of a hysteresis, which means that the K^+ concentration is different for the rising limb and the falling limb of the hydrograph (Evans and Davies, 1998; Foster, 1978; Holz, 2010; Siwek et al., 2017). Analysis of hysteresis direction and size provides useful insight into identifying pathways and sources of solutes in catchments (Butturini et al., 2006; Evans and Davies, 1998; Lloyd et al., 2016; Outram et al., 2014; Siwek et al., 2013). We used this method in our earlier research work (Siwek et al., 2017) conducted in three out of the four catchments examined in the present study. We have shown that throughflow and sometimes also overland flow are two main sources of K^+ in stream water during events. Our findings suggest that the pool of K^+ in soils plays the most important role in K^+ influx to streams via throughflow – due to soil flushing, and overland flow – due to soil erosion. In the present study, we aim to describe the role of exchangeable K^+ concentrations in soil profiles along a transect in determining stream water K^+ concentrations during events. We make an attempt to answer the following three research questions:

1. What is the linkage between the concentration of exchangeable K^+ in fragipan soils in catchments with different land use and stream water K^+ concentrations during events of different type?
2. What is the role of each studied soil horizon in K^+ influx to streams during events?
3. What is the role of soils on hillslopes and in riparian areas in K^+ influx to streams during events?

Most researchers focus on changes in the K^+ concentration during stormflow events (Caissie et al., 1996; Elsenbeer et al., 1995a, b; Foster, 1978; Hill, 1993; Ladouche et al., 2001; Sandén et al., 1997), but there still is a lack of research for other types of events. Our study takes into account all the event types observed in the Carpathian Foothills in southern Poland (Bryndal, 2015). Event categories are based on specific factors that initiate increases in discharge as well as specific conditions during events: events caused by rainfall, and events caused by melting snow and rain falling on snow. Other key criteria include differences in rainfall duration: events caused by short rainfall (storms) lasting between several hours and a dozen hours (R_s), and events caused by long-lasting rainfall generated by atmospheric fronts hovering over a geographic area for several days (R_p). Snowmelt events and rain-on-snow events, hereafter called snowmelt events, were distinguished based on the soil being frozen (S_f) or not frozen (S_u).

MATERIALS AND METHODS

Study area

The study area is located along the northern edge of the Carpathian Foothills in southern Poland. The studied catchment is called the Stara Rzeka catchment (22.22 km^2), and it is characterized by mixed land use (Table 1). Three different subcatchments were identified: Leśny Potok (woodland, 0.48 km^2), Kubaleniec (agricultural – traditional type, 1.03 km^2), and Dworski Potok (experimental agriculture, 0.29 km^2) (Fig. 1). The geomorphologic characteristics of the studied catchments are listed in Table 1.

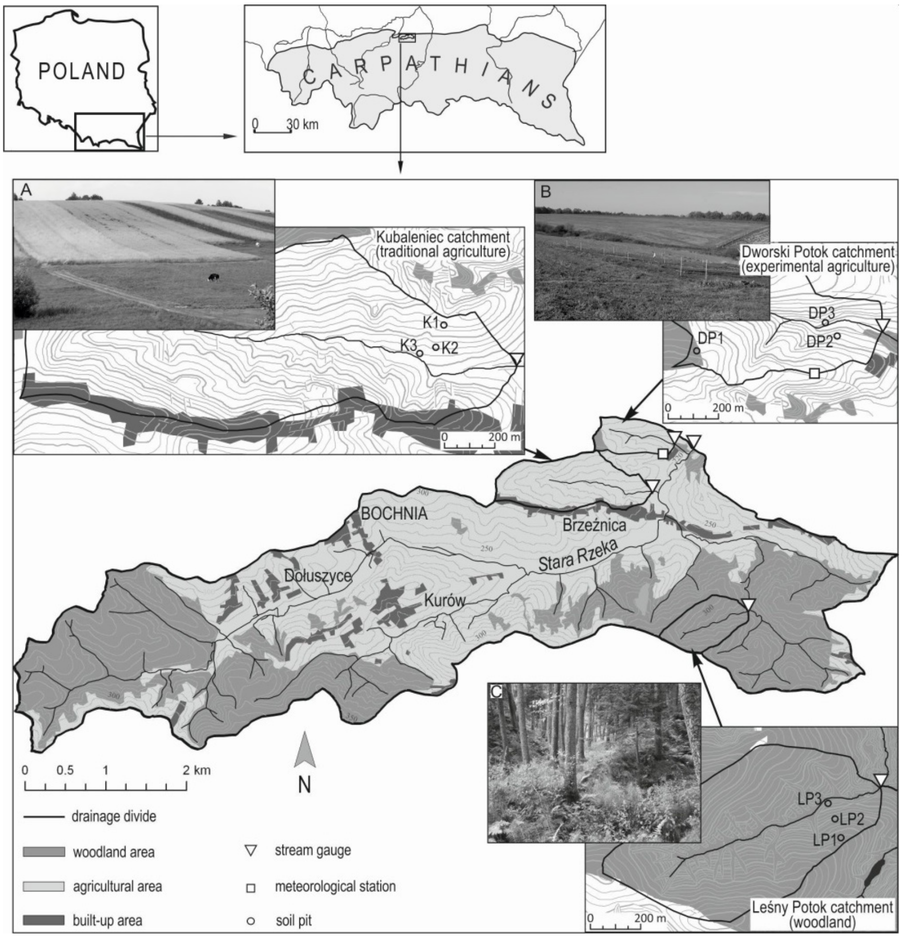

Fig. 1. Location of the study area.

Table 1. Environmental characteristic of the studied catchments.

Catchment characteristics	Stara Rzeka	Leśny Potok	Kubaleniec	Dworski Potok
Area (km^2)[a]	22.22	0.48	1.03	0.29
Elevation (m a.s.l)[a]	217–362	257–342	223–296	227–275
Inclination of slopes (^{o})[a]	2–10 in northern part, 10–35 in southern part	2–10 (60% of slopes), 10–35 (40% of slopes)	2–10 (85% of slopes), 10–35 (10% of slopes)	2–10 (80% of slopes), 10–35 (15% of slopes)
Hillslope length (m)	< 800	< 350	< 500	< 400
Width of the valley floor (m)[b]	50–250	6–22	10–60	5–50
Land use[a]	woodland (42%), arable land (36%), grassland (15%), orchards (2.5%), built-up areas (4.5%)	woodland (99%), arable land, grassland, and built-up areas (1%)	arable land (69.5%), grassland (20%), orchards (5%), built-up areas (5%), woodland (0.5%)	woodland (3.5%), arable land (80%), grassland (16.5%)

[a] – according to Święchowicz and Michno (2005)
[b] – according to Siwek et al. (2011)

The area's multi-year (1994–2016 hydrologic years) average annual air temperature is 8.9°C, average annual precipitation equals 720 mm, and average annual runoff depth in the Stara Rzeka catchment is 230 mm. The hydrologic regime of the Stara Rzeka, based on data from the 1994–2004 hydrologic years, is characterized by two periods of high flow. The first period is driven by the melting of snow and rain falling on snow (February–April), while the second period is driven by rainfall (June–July).

The geology of the study area consists primarily of Carpathian flysch (i.e. interbedded sandstone and shale) (Olewicz, 1973). The entire catchment is lined with loess-like deposits in excess of 10 meters in thickness at certain locations. This deposit serves as the parent material for Luvisols and Retisols (Albeluvisols) with a fragipan (Skiba et al., 1998; Szymański et al., 2011, 2012). The studied soils are usually characterized by silt loam texture, acidic or slightly acidic pH, lack of coarse rock fragments (i.e. fraction > 2 mm) and absence of carbonate (Szymański et al., 2011, 2012). A characteristic feature of the studied soils is the occurrence of the fragipan, which constitutes the uppermost part of the illuvial Bt horizon (Szymański et al., 2011, 2012). The fragipan has a much higher bulk density and lower porosity than overlying soil horizons due to much higher clay content (Szymański et al., 2011, 2012). Therefore, the macroporosity of the fragipan is very low (Klimek, 2005). The fragipan horizon is continuous in the studied catchments; however, its thickness and depth of its occurrence in the soil profile are variable (especially in agricultural catchments) due to soil erosion (Klimek, 2005; Skiba et al., 1998). The thickest fragipan and deepest occurrence of its top part are usually noted at the summits of hills and in foothill areas, while the thinnest and shallowest presence of the fragipan top is usually encountered in the steepest parts of hillslopes.

More than 99% of the Leśny Potok sub-catchment consists of woodland areas (Table 1, Fig. 1). The forest is mostly composed of beech (*Fagus sylvatica* L.) and fir (*Abies alba* Mill.). The catchment consists of a flat-bottomed valley characterized by high soil moisture and frequently populated with alder (*Alnus incana* L.). It also features many steep-sided V-shaped valleys forming deep-cutting badlands.

The Kubaleniec catchment is a typical Carpathian Foothills agricultural catchment featuring a foothills landscape divided into many long plots of land (<1 ha) running from the summits of hills towards valley floors. In the spring and autumn, its agricultural fields are fertilized to a great extent with various organic fertilizers. This is a catchment with traditional agriculture characterized by the employment of both animals and machines and production geared towards personal consumption. Most of the catchment consists of arable land, meadows, and pastures (Table 1).

The Dworski Potok catchment is not a typical foothills agricultural catchment due to the presence of experimental agriculture in the area. The entire catchment is essentially one large farm operated by Jagiellonian University. Most of the catchment (80%) consists of arable land (Table 1). The mean application of potassium on arable land in the Dworski Potok catchment is many times greater (104.8 kg K_2O/ha/year in 2002–2004) than the average for the Małopolska region of Poland (19.7 kg K_2O /ha/year; GUS, 2012), where the study area is located. No organic fertilizers were used.

Field methods, laboratory and statistical analysis

Stream water samples were collected in the hydrologic years 1997 and 2002–2004 at four gauging sites in the Stara Rzeka, Leśny Potok, Kubaleniec, and Dworski Potok catchments (Fig. 1). A total of 40 events of different type were monitored in the study (Table 2). Tables 2 and 3 show selected data on hydrometeorologic conditions causing the analyzed events – described also by Siwek et al. (2011, 2013, 2017). Data were obtained from a meteorologic station located in the Dworski Potok catchment (Fig. 1). Air temperature was measured three times per day (6:00, 12:00, 18:00 GMT) using a KWT mercury thermometer. Soil temperature at depths of 5, 10, 20, 50, and 100 cm was measured three times per day (6:00, 12:00, 18:00 GMT) using a ground mercury thermometer (KWT) placed in a tube and removed for measurement outside. The soil temperature just immediately before the event and average soil temperature during the event were determined individually for each catchment because some of the events began and ended on the same days but at different times during the day in the studied catchments. Precipitation was measured using a Hellmann-type rain gauge and a pluviograph, except in the winter.

Water samples were obtained at time intervals varying between several minutes and several hours – depending on changes in stream discharge and event duration. Overland flow was observed visually during the studied events, and water samples were collected during selected events at ungauged sites using plastic pipes to avoid collection of the soil material. Overland flow sampling sites were representative of different land use types: arable land, meadows, forest paths. The obtained water samples were filtered through SARTORIUS SFCA filters (0.45 μm), and the concentration of K^+ in water was measured using a JENWAY PFP flame photometer. The accuracy of the method and detection limit of K^+ in water equaled ±2% and 0.2 mg/L, respectively.

Table 2. Hydrometeorological characteristics of analyzed events (R_s – storm rainfall events, R_p – prolonged rainfall events, S_f – snowmelt events with the soil frozen, S_u – snowmelt events with the soil unfrozen, n.d. – no pluviograph data in winter).

Catchment	Time	Event type	Event duration	Mean air temperature		Amount of precipitation		Rainfall		Specific runoff	
				[ºC]		[mm]		duration	intensity	baseflow	max.
			[day]	7 days prior event	during event	7 days prior event	during event	[h]	[mm/h]	$[\mathrm{dm}^3\cdot\mathrm{s}^{-1}\cdot\mathrm{km}^{-2}]$	
Leśny Potok (woodland)	January 14–16. 2003	S_f	2	–10.2	3.6	5.5	0.5	n.d.	n.d.	0.9	7.3
	March 9–15. 2003	S_f	5	–2.3	4.2	0.0	25.5	n.d.	n.d.	2.6	156.9
	July 10–11. 2003	R_s	1	16.9	15.1	11.1	8.1	2.2	3.7	2.9	16.7
	January 12–15. 2004	S_u	3	–8.2	2.8	6.2	6.4	n.d.	n.d.	0.9	4.6
	June 20–21. 2004	R_s	1	16.1	14.2	15.9	6.9	1.8	3.9	2.2	13.8
	July 27–31. 2004	R_p	5	22.8	15.2	20.3	110.6	50.3	2.2	3.1	402.1
Kubaleniec (agricultural)	July 15–16. 2002	R_s	1	21.7	21.3	0.1	3.9	0.8	4.6	0.0	0.6
	July 16–17. 2002	R_s	1	21.8	21.8	3.9	40.4	4.6	8.8	0.1	235.2
	August 12–17. 2002	R_p	5	19.7	18.6	4.8	43.3	11.8	3.7	0.0	50.0
	October 17–19. 2002	R_p	3	6.4	9.8	22.1	20.4	13.3	1.5	4.6	79.3
	January 14–16. 2003	S_f	2	–10.2	3.6	5.5	0.5	n.d.	n.d.	1.8	72.8
	March 9–15. 2003	S_f	6	–2.3	4.2	0.0	25.5	n.d.	n.d.	4.6	228.8
	January 12–16. 2004	S_u	4	–8.2	2.8	6.2	6.4	n.d.	n.d.	0.8	10.5
	February 1–9. 2004	S_u	9	–4.8	7.5	1.6	17.0	n.d.	n.d.	0.6	12.8
	March 10–19. 2004	S_u	8	–2.8	7.3	2.6	0.2	n.d.	n.d.	2.4	77.9
	March 25–31. 2004	S_u	6	11.0	3.2	10.8	29.5	n.d.	n.d.	5.6	80.4
	July 27–August 1. 2004	R_p	6	22.8	15.7	20.3	110.6	50.3	2.2	0.1	103.1
Dworski Potok (agricultural)	July 4–5 1997	R_s	1	21.4	16.9	40.9	10.1	1.8	5.5	1.0	17.5
	July 5–12 1997	R_p	7	20.3	16.6	51.0	94.8	27.9	3.4	17.6	840.7
	July 18–24 1997	R_p	6	15.9	15.7	22.1	59.1	38.0	1.6	22.0	248.0
	July 16–17. 2002	R_s	1	21.8	21.8	3.9	40.4	5.2	7.7	0.1	803.3
	August 12–17. 2002	R_p	5	19.7	18.4	4.8	43.3	11.8	3.7	0.2	27.8
	October 17–19. 2002	R_p	3	6.4	9.8	22.1	20.4	13.3	1.5	3.0	47.9
	March 9–15. 2003	S_f	6	–2.3	4.2	0.0	25.5	n.d.	n.d.	8.5	284.9
	January 13–16. 2004	S_u	3	–8.2	2.6	6.2	6.4	n.d.	n.d.	1.6	6.9
	February 1–10. 2004	S_u	9	–4.8	7.5	1.6	17.0	n.d.	n.d.	n.d.	11.3
	March 10–20. 2004	S_u	9	–2.8	7.8	2.6	2.6	n.d.	n.d.	2.5	67.9
	July 26–31. 2004	R_p	5	22.8	16.0	20.3	110.6	50.3	2.2	0.0	100.8
Stara Rzeka (mixed)	July 15–16. 2002	R_s	1	21.7	21.3	0.1	3.8	0.8	4.6	0.5	10.0
	July 16–17. 2002	R_s	1	21.8	21.8	3.9	40.4	5.2	7.7	0.8	184.4
	August 12–17. 2002	R_p	5	19.7	18.4	4.8	43.3	11.8	3.7	0.5	19.4
	October 17–19. 2002	R_p	3	6.4	9.8	22.1	20.4	13.3	1.5	3.6	64.8
	January 14–16. 2003	S_f	2	–10.2	3.6	5.5	0.5	n.d.	n.d.	1.0	80.5
	March 9–15. 2003	S_f	6	–2.3	4.2	0.0	25.5	n.d.	n.d.	3.1	334.3
	January 12–16. 2004	S_u	4	–8.2	2.6	6.2	6.4	n.d.	n.d.	1.0	8.5
	February 1–10. 2004	S_u	10	–4.8	7.5	1.6	17.0	n.d.	n.d.	1.2	17.7
	March 10–20. 2004	S_u	9	–2.8	7.8	2.6	2.6	n.d.	n.d.	3.0	45.6
	March 25–31. 2004	S_u	6	11.0	3.8	10.8	29.5	n.d.	n.d.	6.0	47.0
	July 23–24. 2004	R_s	1	21.7	19.7	4.9	19.8	2.1	9.5	0.3	13.0
	July 26–August 1. 2004	R_p	6	22.8	16.0	20.3	110.6	50.3	2.2	0.7	200.7

Discharge was determined at gauging sites based on continuous measurement of water levels (float-type recorder – until May 2003) and at 10-minute intervals (pressure-type water level sensors – after May 2003). A compound rectangular weir was installed at the Stara Rzeka gauging site, while compound sharp-crested weirs (90º and ¼ 90º) were installed at the Leśny Potok, Kubaleniec, and Dworski Potok gauging sites. Stream discharge was measured using volumetric gauging (for discharge up to 20 L/s) and current metering (for discharge exceeding 20 L/s). Rating curves produced using a procedure by Wanielista et al. (1997) and Dingman (2002) were used to calculate discharge. Extrapolation was used to extend rating curves for data from the Kubaleniec and Dworski Potok gauging sites; however, the extrapolation never exceeded 10% of measured water stages.

Three representative soil pits (arranged in catena) were excavated under dry antecedent soil conditions in the late spring (May and June, 2013) in each studied sub-catchment (Fig. 1). Soil profiles were described and classified according to the WRB system (IUSS Working Group WRB, 2015). Soil samples were collected from every mineral horizon. The samples were air dried, crushed, and sieved using a 2 mm sieve. The fine earth material (< 2 mm) was used to determine the texture, exchangeable K^+ concentration, soil pH, and soil organic carbon (SOC) content. The sand fraction (2.0–0.05 mm) was determined by means of wet sieving, while the silt fraction (0.05–0.002 mm) and clay fraction (< 0.002 mm) were determined using a hydrometer (Gee and Bauder, 1986). The exchangeable K^+ concentration was measured using flame atomic absorption spectrometry (FAAS) following extraction with 1M ammonium acetate at pH = 7 (Sumner and Miller, 1996). The accuracy of the method and detection limit of exchangeable K^+ equaled ±13% and 0.0013 $\mathrm{cmol_c}$/kg, respectively. Soil pH was measured in deionized water using a 1:2.5 soil/water ratio (Thomas, 1996). SOC content was determined by dry combustion using a Vario Micro Cube CHNS elemental analyzer, as all the studied soils did not contain carbonates. Soil saturated hydraulic conductivity (K_{sat}) of soil horizons was calculated using pedotransfer functions proposed by Saxton et al. (1986) included in SPAW model (Saxton and Rawls, 2006).

Information on the size and direction of K^+ hystereses in Leśny Potok, Kubaleniec, and Stara Rzeka was obtained from Siwek et al. (2017). We used a method we had used in Siwek et al. (2017) to calculate hysteresis parameters for Dworski Potok. This method is based on the range between average residuals from regression analysis for the rising and falling limbs ($|\bar{e}_r| + |\bar{e}_f|$). The larger the range, the wider the hysteresis. The direction of K^+ hystereses was determined using the relationship between average residuals for the rising limb ($\bar{e}_r$) and for the falling limb ($\bar{e}_f$). Clockwise hystereses were determined when $\bar{e}_r > \bar{e}_f$ while counterclockwise hystereses were determined when $\bar{e}_r < \bar{e}_f$. The direction of each hysteresis was additionally verified via visual inspection. While the Siwek et al. (2017) method yielded unambiguous results (either clockwise or counterclockwise), visual

Table 3. Soil temperature at different depth just before and during analyzed events (R_s – storm rainfall events. R_p – prolonged rainfall events. S_f – snowmelt events with the soil frozen. S_u – snowmelt events with the soil unfrozen. n.d. – no data).

Catchment	Time*	Event type	Ground temperature [ºC]									
			Just before the event					During event (mean)				
			5	10	20	50	100	5	10	20	50	100
			[cm]									
Leśny Potok (woodland)	January 14–16. 2003	S_f	–0.7	n.d.	–0.8	0.1	2.3	–0.2	n.d.	–0.5	0.1	2.3
	March 9–15. 2003	S_f	0.1	n.d.	–0.3	0.4	1.7	1.5	0.9	–0.1	0.4	1.6
	July 10–11. 2003	R_s	16.0	16.4	17.2	17.4	16.6	17.0	17.1	17.4	17.3	16.6
	January 12–15. 2004	S_u	–0.2	–0.3	0.0	1.6	3.5	–0.1	–0.2	0.0	1.4	3.2
	June 20–21. 2004	R_s	18.3	17.3	17.2	16.8	14.6	17.3	17.7	17.7	16.7	14.7
	July 27–31. 2004	R_p	22.4	21.5	20.4	19.7	17.8	15.9	16.0	16.3	17.4	17.4
Kubaleniec (agricultural)	July 15–16. 2002	R_s	28.2	26.3	22.7	20.8	18.5	25.1	25.4	23.2	21.0	18.5
	July 16–17. 2002	R_s	25.5	25.5	24.1	21.1	18.5	23.3	23.4	22.9	21.2	18.6
	August 13–17. 2002	R_p	17.8	18.5	19.9	20.5	19.1	19.5	19.4	18.9	19.4	18.9
	October 17–19. 2002	R_p	8.7	9.1	9.9	10.4	11.5	8.9	9.5	10.4	11.0	11.6
	January 14–16. 2003	S_f	–1.4	n.d.	–1.0	0.1	2.3	–0.2	n.d.	–0.5	0.1	2.3
	March 9–15. 2003	S_f	–0.5	n.d.	–0.4	0.3	1.7	1.4	0.8	–0.2	0.4	1.6
	January 12–16. 2004	S_u	–0.2	–0.3	0.0	1.6	3.5	–0.1	–0.2	0.0	1.5	3.3
	February 1–9. 2004	S_u	0.2	–0.1	0.0	1.2	2.7	4.6	4.2	3.2	3.1	3.2
	March 10–19. 2004	S_u	–0.2	–0.1	0.4	1.3	2.6	2.4	2.3	2.2	2.0	2.6
	March 25–31. 2004	S_u	5.5	6.0	7.0	6.6	5.3	1.5	1.7	2.7	4.4	5.1
	July 27–August 1. 2004	R_p	18.2	18.6	19.4	19.9	17.7	15.9	16.2	16.6	17.6	17.4
Dworski Potok (agricultural)	July 4–5. 1997	R_s	23.4	23.3	21.7	17.6	15.9	n.d.	n.d.	n.d.	n.d.	n.d.
	July 5–12. 1997	R_p	19.0	19.4	19.5	17.9	16.1	18.5	18.3	18.1	17.5	16.1
	July 18–24. 1997	R_p	15.8	16.6	17.1	17.4	16.2	16.1	16.6	16.8	17.2	16.2
	July 16–17. 2002	R_s	25.5	25.5	24.1	21.1	18.5	23.8	24.0	23.1	21.2	18.6
	August 13–17. 2002	R_p	17.8	18.5	19.9	20.5	19.1	19.7	19.7	18.9	19.4	18.9
	October 17–19. 2002	R_p	8.7	9.1	9.9	10.4	11.5	9.4	9.8	10.5	11.0	11.6
	March 9–15. 2003	S_f	–0.5	n.d.	–0.4	0.3	1.7	1.2	0.8	–0.2	0.4	1.6
	January 13–16. 2004	S_u	–0.2	–0.3	0.0	1.5	3.4	–0.1	–0.1	0.0	1.4	3.2
	February 1–10. 2004	S_u	2.1	1.1	0.1	1.5	2.7	4.8	4.3	3.2	3.1	3.2
	March 10–20. 2004	S_u	–0.2	–0.1	0.4	1.3	2.6	2.4	2.3	2.2	2.0	2.6
	July 26–31. 2004	R_p	22.4	21.5	20.4	19.7	17.8	16.08	16.2	16.7	18.0	17.5
Stara Rzeka (mixed)	July 15–16. 2002	R_s	28.2	26.3	22.7	20.8	18.5	24.9	25.2	23.2	21.0	18.5
	July 16–17. 2002	R_s	25.5	25.5	24.1	21.1	18.5	23.8	24.0	23.1	21.2	18.6
	August 13–17. 2002	R_p	17.8	18.5	19.9	20.5	19.1	19.5	19.4	18.9	19.4	18.9
	October 17–19. 2002	R_p	8.7	9.1	9.9	10.4	11.5	9.4	9.8	10.5	11.0	11.6
	January 14–16. 2003	S_f	–1.4	n.d.	–1.0	0.1	2.3	–0.2	n.d.	–0.5	0.1	2.3
	March 9–15. 2003	S_f	–0.5	n.d.	–0.4	0.3	1.7	1.2	0.6	–0.2	0.4	1.6
	January 12–16. 2004	S_u	–0.3	–0.4	0.0	1.6	3.5	–0.1	–0.2	0.0	1.5	3.3
	February 1–10. 2004	S_u	0.7	–0.1	0.0	1.2	2.8	4.8	4.3	3.2	3.1	3.2
	March 10–20. 2004	S_u	–0.2	–0.1	0.4	1.3	2.6	2.4	2.3	2.2	2.0	2.6
	March 25–April 3. 2004	S_u	5.5	6.0	7.0	6.6	5.3	3.1	3.0	3.0	4.4	5.1
	July 23–24. 2004	R_s	20.9	21.2	22.1	20.7	17.3	21.7	21.9	21.9	20.4	17.5
	July 26–August 1. 2004	R_p	22.4	21.5	20.4	19.7	17.8	16.0	16.2	16.7	17.7	17.4

inspection indicated that changes in the K^+ concentration were complex and unclear in the case of a few select events in the present study.

The determination of a direct link between the soil exchangeable K^+ concentration and stream water K^+ concentration was only possible for rainfall floods featuring dry antecedent conditions, as these were the conditions under which soil samples were collected. As it was not possible to make a direct comparison of the K^+ concentration in streams (mg/L) with the soil exchangeable K^+ concentration ($cmol_c$/kg), normalized values of stream water K^+ concentration and exchangeable K^+ concentration for soil profiles situated along a transect (hillslope – riparian area) in particular catchments were generated using Min-Max scaling normalization method (Jayalakshmi and Santhakumaran, 2011). The normalization yielded values ranging from –1 (minimum concentration) to +1 (maximum concentration) in particular catchments. The purpose of this procedure was to identify source areas of K^+ in each studied catchment. It was assumed that stream water K^+ concentrations during events are determined by variable influx of K^+ from soil horizons found on hillslopes (above the poorly permeable fragipan horizon) and in riparian areas. This means that the highest normalized K^+ concentrations in streams (+1) were associated with K^+ influx from areas with the highest normalized concentration of soil exchangeable K^+ (+1), while the lowest normalized K^+ concentrations in streams (–1) were associated with K^+ influx from areas with the lowest normalized K^+ concentration in soils (–1).

RESULTS

Soils: saturated hydraulic conductivity (K_{sat}) and exchangeable K^+ concentration

The hillslopes of all the studied catchments are covered with fragipan soils: Fragic Retisols and Fragic Luvisols. These soils are characterized by a very low K_{sat} of the fragipan horizon due to high clay content (Table 4, Fig. 2). In the woodland Leśny Potok catchment, the fragipan occurs at depths between 40 and 50 cm. In the agricultural Kubaleniec and Dworski Potok catchments, the fragipan occurs at much smaller depths atop hills and at greater depths at lower parts of slopes. The soil horizons E and A found above the fragipan are characterized by a much higher K_{sat} value than the fragipan (Table 4). Reductic Gleysols occur in the riparian areas of all the studied catchments normally exhibiting a higher K_{sat} than soils found on hillslopes (Table 4).

Table 4. Measured soil texture (according to United States Department of Agriculture) and predicted soil saturated hydraulic conductivity (*K_{sat}*) in the studied catchments (n.a. – not analyzed).

Leśny Potok (woodland)				Kubaleniec (agricultural)				Dworski Potok (agricultural)			
Horizon	Depth [cm]	Texture	K_{sat} [mm/h]	Horizon	Depth [cm]	Texture	K_{sat} [mm/h]	Horizon	Depth [cm]	Texture	K_{sat} [mm/h]
LP1 Dystric Stagnic Glossic Fragic Retisol (Siltic, Cutanic, Densic)				K1 Stagnic Fragic Luvisol (Siltic, Cutanic, Densic)				DP1 Dystric Stagnic Glossic Fragic Retisol (Siltic, Cutanic, Densic)			
Ol	0–2	n.a.	n.a.	Ap1	0–6	Silt loam	11.7	Ol	0-2	n.a.	n.a.
Ah	2–5	Silt loam	63.0	Ap2	6–17	Silt loam	9.8	Ah	2–5	Silt loam	233.5
AE	5–13	Silt loam	16.9	Btx1	17–40	Silt loam	4.3	E	5–22	Silt loam	12.3
Eg	13–37	Silt loam	8.3	Btx2	40–75	Silt loam	4.9	Eg	22–37	Silt loam	11.9
Btx1	37–80	Silt loam	3.3	BCg1	75–110	Silt loam	4.7	Btx1	37–62	Silt loam	6.3
Btx2	80–115	Silt loam	3.3	BCg2	110–150	Silt loam	4.3	Btx2	62–87	Silt loam	3.4
2C	115–150	Sandy loam	36.2					Btg	87–142	Silt loam	5.5
								BCg	142–180	Silt loam	6.1
LP2 Dystric Stagnic Glossic Fragic Retisol (Siltic, Cutanic, Densic)				K2 Gleyic Fragic Luvisol (Siltic, Colluvic, Cutanic)				DP2 Stagnic Glossic Fragic Retisol (Siltic, Cutanic, Densic)			
Ol	0–2	n.a.	n.a	Ap1	0–20	Silt loam	18.2	Ap1	0–11	Silt loam	18.7
Ah	2–6	Silt loam	59.2	Ap2	20–35	Silt loam	18.6	Ap2	11–25	Silt loam	12.8
AE	6–13	Silt loam	15.1	Ab	35–55	Silt loam	13.6	Eg1	25–50	Silt loam	10.1
E	13–35	Silt loam	9.5	Egb	55–80	Silt loam	9.9	Eg2	50–70	Silt loam	12.3
Eg	35–50	Silt loam	5.0	Btxb1	80–90	Silt loam	7.3	Btx1	70–110	Silt loam	5.1
Btx1	50–95	Silt loam	3.4	Btxb2	90–110	Silt loam	5.4	Btx2	110–160	Silt loam	6.5
Btx2	95–125	Silt loam	3.1	BCgb	110–130	Silt loam	4.6				
BCg	125–180	Silt loam	3.9								
2C	180–200	Loam	8.1								
LP3 Dystric Fluvic Reductic Gleysol (Abruptic)				K3 Dystric Reductic Gleysol (Siltic)				DP3 Dystric Reductic Gleysols (Siltic, Colluvic)			
Ol	0–1	n.a.	n.a.	Ol	0–2	n.a.	n.a.	Ol	0–2	n.a.	
A1	1–6	Silt loam	47.4	Ag1	2–8	Silt loam	59.9	Ag1	2–18	Silt loam	32.3
C	6–17	Silt loam	21.8	Ag2	8–17	Silt loam	18.3	Ag2	18–23	Silt loam	51.1
2A2	17–20	Loam	104.7	Cg1	17–47	Silt loam	8.8	Ag3	23–30	Silt loam	40.9
2ACg1	20–30	Loam	38.0	Cg2	47–73	Silt loam	7.9	Cg	30–60	Silt loam	15.9
3Cg1	30–40	Silt loam	8.6	Cg3	73–95	Silt loam	11.1				
4Cg2	40–57	Loam	40.0								
4Cg3	57–75	Loam	34.3								
5Cg4	75–81	Loamy fine sand	77.8								
6Cg5	81–90	Sandy loam	45.3								
7Cg6	90–115	Loam	35.2								
8ACg2	115–150	Silt loam	24.3								

In the studied agricultural catchments, soils found on hillslopes were characterized by a much higher exchangeable K^+ concentration than soils found in riparian areas, while in the woodland catchment the concentrations of K^+ were similar (Fig. 2). The exchangeable K^+ concentration in hillslope soils in the woodland Leśny Potok catchment was highest in the fragipan horizon (Fig. 2A). Topsoil Ah horizons also had a relatively large concentration of exchangeable K^+. The lowest exchangeable K^+ concentration was determined in E horizons. In the hillslope soils of the agricultural catchments of Dworski Potok and Kubaleniec, the highest exchangeable K^+ concentrations were detected in soil horizons found above the fragipan – in topsoil A horizons as well as shallow-lying E horizons (Figs. 2 – B and C). The exchangeable K^+ concentration in horizons found above the fragipan (A, E) in agricultural catchments was three to four times higher than that in the same horizons in woodland areas while in the fragipan and in horizons below the fragipan it was similar.

Stream water: K^+ concentration during events

The concentration of K^+ increased with increasing stream discharge in all four studied streams. During storm events, long-lasting rainfall events, and snowmelt events with the soil not frozen, the concentration of K^+ at a given specific runoff was three to four times higher in streams draining the agricultural catchments of Kubaleniec and Dworski Potok and the mixed-use catchment of Stara Rzeka than in the stream draining the studied woodland catchment (Fig. 3). During snowmelt events with frozen soils, the concentrations of K^+ in the studied agricultural catchments and mixed-use catchment were much lower than those during all other types of events (Fig. 3). These low concentrations were only slightly higher than K^+ concentrations measured in the stream draining the woodland catchment (Fig. 3).

Changes in K^+ concentration in stream water during most of the studied events took the form of a hysteresis (Table 5). In the woodland catchment during most events clockwise hystereses were noted. This means higher K^+ concentrations for the rising limb versus the falling limb of the hydrograph. In the agricultural catchments and the mixed-use catchment, the direction of the K^+ hysteresis varied between events. Clockwise hystereses were generated for storm events under wet antecedent conditions and long-lasting events produced by heavy rainfall with a high intensity. Counterclockwise hystereses were generated for storm events preceded by a rain-free period of several days and for long-lasting rainfall events produced by rainfall of high volume and low intensity. During snowmelt events with the soil frozen and soil not frozen, most hystereses assumed a counterclockwise direction for streams draining agricultural and mixed-use catchments. Changes in the K^+ concentration were quite complex (unclear) for several events, especially those occurring in the agricultural Dworski Potok catchment and mixed-use Stara Rzeka catchment (Table 5). During storm events and long-lasting rainfall events, stream water K^+ hystereses for the woodland catchment were much more narrow than those for the studied agricultural catchments and mixed-use catchment. These narrow patterns are reflected in smaller ranges between average residuals from regression

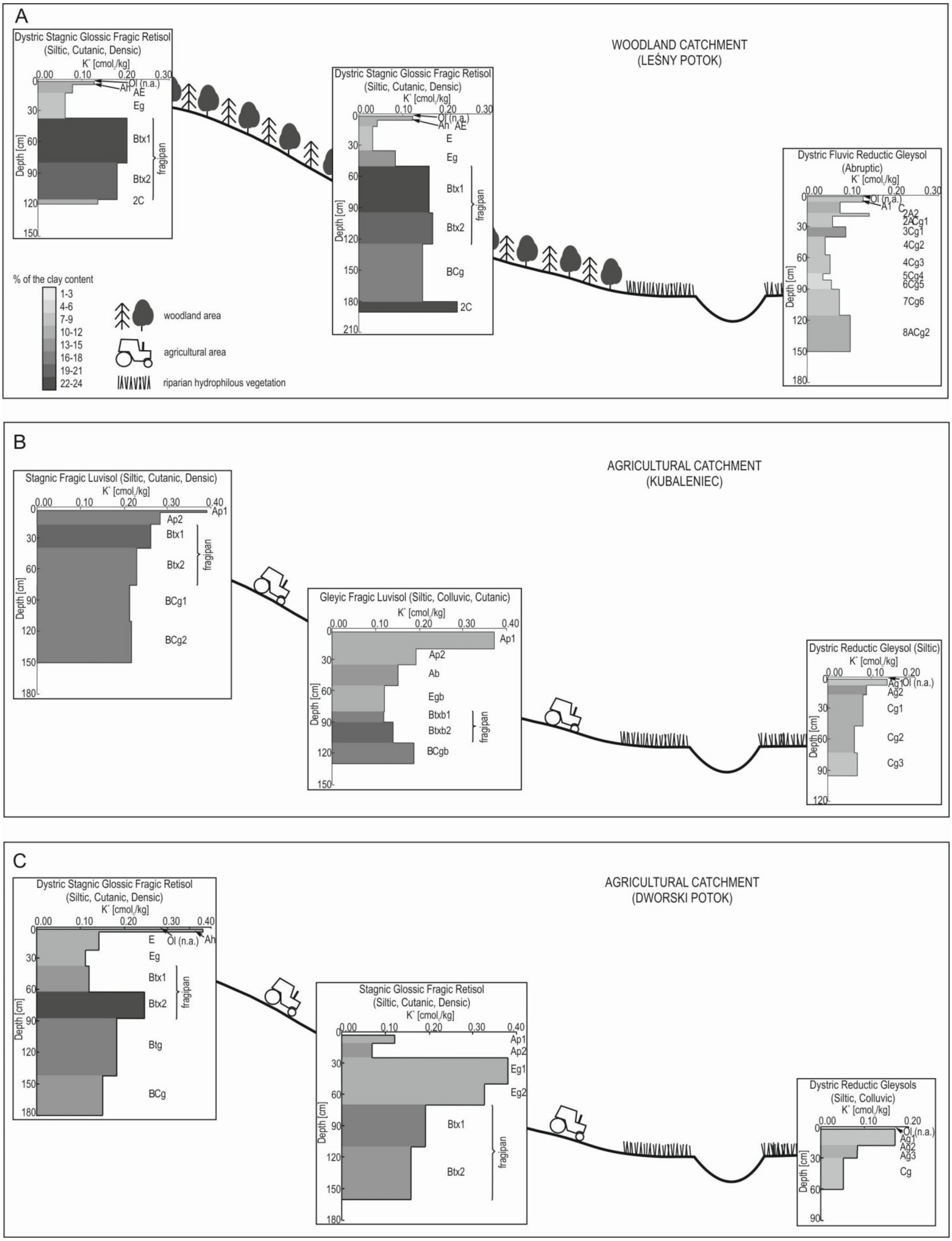

Fig. 2. Exchangeable K^+ concentration and clay content in soils of the studied catchments.

analysis for the rising limbs and falling limbs (example in Fig. 4; Table 5). During snowmelt events with the soil frozen and not frozen, stream water K^+ hysteresis loops were narrow for all the studied catchments (Table 5).

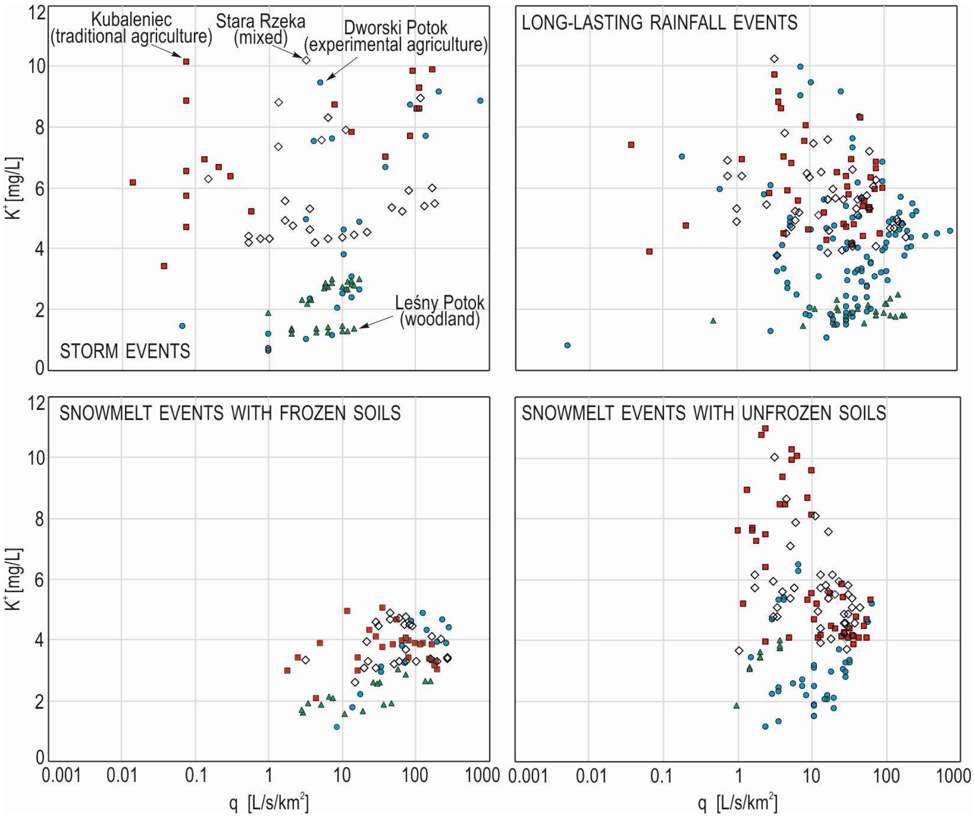

Fig. 3. Concentration of K$^+$ versus specific runoff in the streams studied for the different event types (filled triangle – Leśny Potok, filled square – Kubaleniec, filled circle – Dworski Potok, empty rhombus – Stara Rzeka).

Link between normalized soil exchangeable K$^+$ concentration and normalized stream water K$^+$ concentration – example of rainfall events under dry antecedent conditions

The link between the distribution of the K$^+$ concentration in soil profiles and changes in the stream water K$^+$ concentration during events may be a way for understanding the 3-dimensional pattern of K$^+$ delivery to streams. In the studied catchments analyses were possible only for rainfall events under dry antecedent conditions, as the soil samples were collected only in dry conditions.

In the woodland catchment the highest stream water K$^+$ concentration occurred during the rising limb of the hydrograph, while the highest soil exchangeable K$^+$ concentration occurred in upper soil horizons (Ah) on hillslopes and across valley bottoms (A). The lowest stream water K$^+$ concentration occurred during the falling limb, while the lowest soil exchangeable K$^+$ concentration occurred in E horizons on hillslopes and in the Cg horizon in the valley floor (Fig. 5A). This suggests that in this catchment the upper horizons of the soil profile on the studied hillslope as well as those found in the studied valley bottom may be responsible for the rapid influx of K$^+$ in the initial stages of the event.

In agricultural catchments, the lowest stream water K$^+$ concentration occurred during the rising hydrographs limbs. The lowest soil exchangeable K$^+$ concentration in these catchments occurred in all soil horizons at valley floor. The highest stream water K$^+$ concentration occurred during the falling limb. The highest soil exchangeable K$^+$ concentration occurred in soils found on the hillslope, both in the Ap and Eg horizons (Figs. 5 B and C). This suggests that the influx of K$^+$ from rich in K$^+$ soil layers found on hillslopes may be delayed and the valley bottom was crucial for K$^+$ delivery in the early stages of the event.

DISCUSSION

Link between soil exchangeable K$^+$ concentrations in catchments of different land use and stream water K$^+$ concentrations during events of different type

Our study has shown that the exchangeable K$^+$ concentration in upper soil horizons (above the fragipan) in agricultural areas is three to four times higher than that in the same horizons in woodland areas; this difference was not observed in the fragipan or the horizons below it. This results in a three to four times lower K$^+$ concentration in the stream draining the studied woodland catchment than that in streams draining the agricultural catchments during rainfall and snowmelt events with the soil not frozen. A notable exception consisted of snowmelt events with the soil frozen – during these types of events, the K$^+$ concentrations in streams draining catchments with agricultural land use were only slightly higher than those measured in the stream draining the woodland catchment. Hence, our study indicates that water flushing soil horizons above the poorly permeable fragipan (Ap, E) is a key source of K$^+$ in streams draining agricultural catchments. Vertical cracks were detected in the fragipan in the Stara Rzeka catchment (Szymański et. al., 2011); however, these usually did not run cross the fragipan horizon. Hence, it may be assumed that they do not significantly affect the circulation of water in the catchment. The identification of soil horizons contributing to streamflow supplements our earlier findings in Siwek et al. (2017) that the ability to flush K$^+$ out of soil is the most important factor controlling the influx of K$^+$ to streams during events. During events when flushing is impossible – during snowmelt events with frozen soils, the contribution of frozen Ap and E horizons to streamflow is strongly limited in agricultural catchments. Streams are fed mainly by melting snow water flowing on the frozen ground. Our findings are similar to those of Coles and McDonnell (2018),

Table 5. Size and direction of stream water K^+ hysteresis based on Siwek et al. (2017) method supported by visual inspection (R_s – storm rainfall floods; R_p – prolonged rainfall floods; S_f – snowmelt floods with the soil frozen; S_u –snowmelt floods with the soil unfrozen; N – number of samples; $\bar{e}_r$ – average values of residuals from regression analysis for rising limb; $\bar{e}_f$ – average values of residuals from regression analysis for falling limb; $|\bar{e}_r| + |\bar{e}_f|$ – sum of absolute values of $\bar{e}_r$ and $\bar{e}_f$).

Catchment	Time	Event type	N	Relation $\bar{e}_r$ to $\bar{e}_f$	Hysteresis size ($|\bar{e}_r| + |\bar{e}_f|$)	Hysteresis direction
Leśny Potok (woodland)	January 14–16. 2003	S_f	6	$\bar{e}_r > \bar{e}_f$	0.1	clockwise
	March 9–15. 2003	S_f	11	$\bar{e}_r > \bar{e}_f$	0.3	clockwise
	July 10–11. 2003	R_s	15	$\bar{e}_r > \bar{e}_f$	0.2	clockwise
	January 12–15. 2004	S_u	9	$\bar{e}_r < \bar{e}_f$	0.3	counterclockwise
	June 20–21. 2004	R_s	11	$\bar{e}_r > \bar{e}_f$	0.2	clockwise
	July 27–31. 2004	R_p	23	$\bar{e}_r > \bar{e}_f$	0.1	clockwise
Kubaleniec (agricultural)	July 15–16. 2002	R_s	10	$\bar{e}_r < \bar{e}_f$	1.1	counterclockwise
	July 16–17. 2002	R_s	10	$\bar{e}_r > \bar{e}_f$	0.6	clockwise
	August 12–17. 2002	R_p	10	$\bar{e}_r < \bar{e}_f$	0.8	counterclockwise
	October 17–19. 2002	R_p	9	$\bar{e}_r < \bar{e}_f$	0.7	counterclockwise
	January 14–16. 2003	S_f	11	$\bar{e}_r < \bar{e}_f$	0.8	counterclockwise
	March 9–15. 2003	S_f	16	$\bar{e}_r < \bar{e}_f$	0.5	counterclockwise
	January 12–16. 2004	S_u	11	$\bar{e}_r < \bar{e}_f$	1.5	counterclockwise
	February 1–9. 2004	S_u	9	$\bar{e}_r > \bar{e}_f$	0.2	unclear
	March 10–19. 2004	S_u	20	$\bar{e}_r < \bar{e}_f$	0.6	counterclockwise
	March 25–30. 2004	S_u	6	$\bar{e}_r > \bar{e}_f$	0.1	unclear
	July 27–August 1. 2004	R_p	20	$\bar{e}_r > \bar{e}_f$	1.2	clockwise
Dworski Potok (agricultural)	July 4–5 1997	R_s	17	$\bar{e}_r < \bar{e}_f$	4.4	counterclockwise
	July 5–12 1997	R_p	37	$\bar{e}_r > \bar{e}_f$	0.4	unclear
	July 18–24 1997	R_p	29	$\bar{e}_r > \bar{e}_f$	0.6	clockwise
	July 16–17. 2002	R_s	10	$\bar{e}_r < \bar{e}_f$	0.2	counterclockwise
	August 12–17. 2002	R_p	12	$\bar{e}_r > \bar{e}_f$	3.3	clockwise
	October 17–19. 2002	R_p	9	$\bar{e}_r > \bar{e}_f$	0.3	clockwise
	March 9–15. 2003	S_f	15	$\bar{e}_r < \bar{e}_f$	0.6	counterclockwise
	January 13–16. 2004	S_u	7	$\bar{e}_r < \bar{e}_f$	0.2	unclear
	February 1–10. 2004	S_u	9	$\bar{e}_r > \bar{e}_f$	0.2	unclear
	March 10–20. 2004	S_u	20	$\bar{e}_r < \bar{e}_f$	0.1	counterclockwise
	July 26– 31. 2004	R_p	14	$\bar{e}_r > \bar{e}_f$	0.8	clockwise
Stara Rzeka (mixed)	July 15–16. 2002	R_s	12	$\bar{e}_r < \bar{e}_f$	1.6	counterclockwise
	July 16–17. 2002	R_s	10	$\bar{e}_r > \bar{e}_f$	0.4	unclear
	August 12–17. 2002	R_p	11	$\bar{e}_r > \bar{e}_f$	0.8	clockwise
	October 17–19. 2002	R_p	9	$\bar{e}_r > \bar{e}_f$	0.3	unclear
	January 14–16. 2003	S_f	11	$\bar{e}_r < \bar{e}_f$	0.3	counterclockwise
	March 9–15. 2003	S_f	15	$\bar{e}_r > \bar{e}_f$	0.2	clockwise
	January 12–16. 2004	S_u	10	$\bar{e}_r > \bar{e}_f$	0.8	clockwise
	February 1–10. 2004	S_u	9	$\bar{e}_r < \bar{e}_f$	0.3	unclear
	March 10–20. 2004	S_u	20	$\bar{e}_r > \bar{e}_f$	1.0	clockwise
	March 25– 30. 2004	S_u	6	$\bar{e}_r > \bar{e}_f$	0.8	unclear
	July 23–25. 2004	R_s	7	$\bar{e}_r < \bar{e}_f$	0.9	counterclockwise
	July 26–August 1. 2004	R_p	22	$\bar{e}_r > \bar{e}_f$	0.6	clockwise

which were based on stable isotope analysis of meltwater on agricultural hillslopes of the northern Great Plains (Canada). They showed that during snowmelt season – over frozen ground – runoff water was actually event snowmelt water with limited mixing with pre-event soil water.

The role of particular soil horizons in K^+ influx to streams during events

Our research has shown that the time of influx of various doses of K^+ from particular soil horizons plays a substantial role in determining the stream water K^+ concentration during most events in the studied woodland catchment. This is due to the distinct vertical variation in exchangeable K^+ concentration in soil profiles on slopes. The concentration of K^+ in the stream draining the woodland catchment during most events was higher during the rising limb versus the falling limb of the hydrograph giving a clockwise hysteresis. Walling and Foster (1975) as well as Evans and Davies (1998) explained the same patterns of stream water K^+ concentration by a flushing of K^+ from the soil in the early stages of events and a gradual exhaustion of the K^+ supply in the soils. In our earlier work, Siwek et al. (2017), we found that flushing via throughflow plays a major role in the influx of K^+ from hillslopes to stream channels for all event types in the woodland catchment. Throughflow is triggered very quickly during events in the woodland catchment (Siwek et al., 2017). Here, we found that the flushing effect of K^+ may be reinforced by a rapid influx of water percolating through surface soil horizons (O, Ah) with a relatively high permeability, as shown by K_{sat} and high concentration of exchangeable K^+. After a certain period of time, water percolating through less permeable E horizons holding much less K^+ reaches the stream channel (Fig. 6). Moreover, our study suggests that preferential flow, most likely in the form of macropore flow, may play an important role in the rapid influx of water and K^+ during storm events in the studied woodland catchment. This idea is supported by a faster flow response to precipitation than what may be inferred from the hydraulic conductivity (K_{sat}) of horizons above the fragipan (Table 4). According to Alfaro et al. (2004b) and Bestland et al. (2009), preferential flow is a very important pathway of K^+ movement during events. Sidle et al. (2000) found that preferential flow may account for up to 25% of subsurface flow during large rainfall events in a woodland catchment in Japan; however, they found that preferential flow emerges during peak flow and the recession limb of hydrographs. Our findings suggest that preferential flow forms more rapidly and contributes to streamflow at the beginning of events.

The timing of K^+ influx from topsoil Ap horizons determines changes in stream water K^+ concentration during snowmelt events with frozen soils in agricultural catchments. At the beginning of each event of this type, streams are fed mainly by snowmelt water flowing across frozen soil surfaces. When snowmelt water comes into contact with thawing topsoil A horizons (rich in K^+), it becomes enriched in K^+ to a substantial extent. For example, during an event in March 2003 the K^+ concentration in overland flow (n = 15) ranged from 1.0 mg K^+/L at the beginning of the event when soils were entirely frozen to 4.2 mg K^+/L at peak flow when soils were partly not frozen. With gradual thawing of the soil, the rate of K^+ leaching increased. This resulted in higher stream water K^+ concentrations for the falling limb of the hydrograph compared with the rising limb giving a counterclockwise hysteresis (Fig. 7D).

Role of soils on hillslopes and in riparian areas in K^+ influx to streams during events

Our research has shown that the timing of the influx of various doses of K^+ from riparian areas and hillslopes plays a substantial role in determining the dynamics of stream water K^+ concentration during most events in agricultural catchments, except for snowmelt events with frozen soils. This is due to distinct differences in concentrations of exchangeable K^+ in soils in riparian areas and on hillslopes. The K^+ concentration measured in streams draining the studied agricultural catchments during small storm events (low precipitation of high intensity), preceded by long rain-free periods (dry antecedent soil conditions), was markedly lower during the rising limb versus the falling limb of the hydrograph. While discharge increased rapidly in response to rainfall, stream water K^+ concentrations remained low. The key question is: What is responsible for these differences in time response? Field observations have shown that overland flow plays a marginal role during these types of events due to the large water retention ability of soils. Therefore, an increase in discharge is caused by the arrival of throughflow. This prompts an important question: Wherefrom is the throughflow with such a low K^+ concentration arriving at the beginning of an event in agricultural catchments? In the Dworski Potok catchment

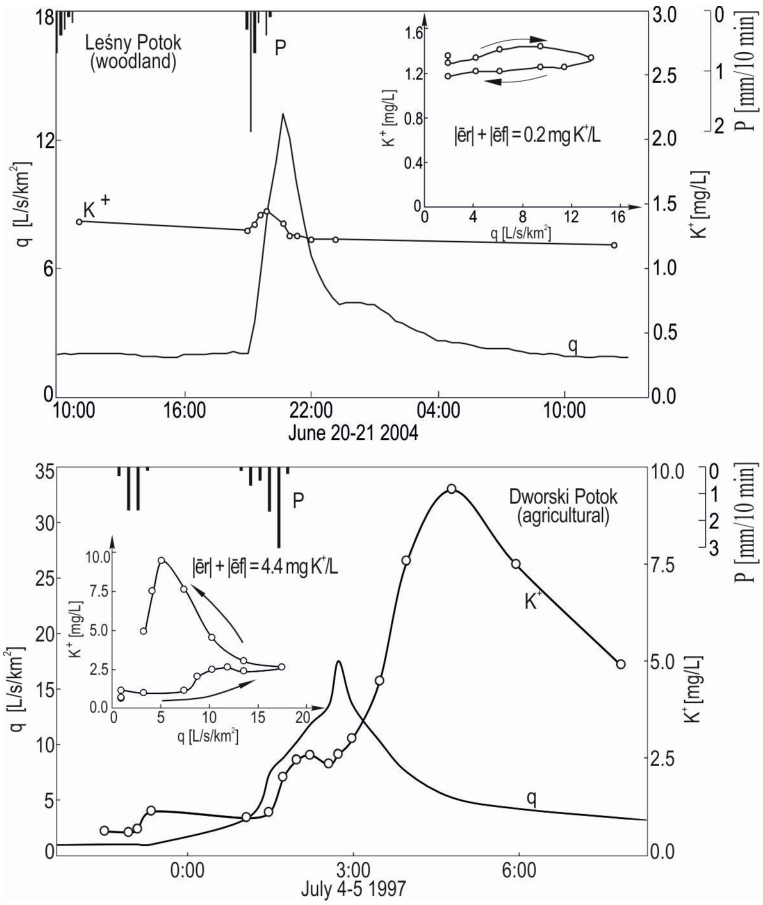

Fig. 4. Concentration of K^+ in streams draining woodland and agricultural catchments during storm events.

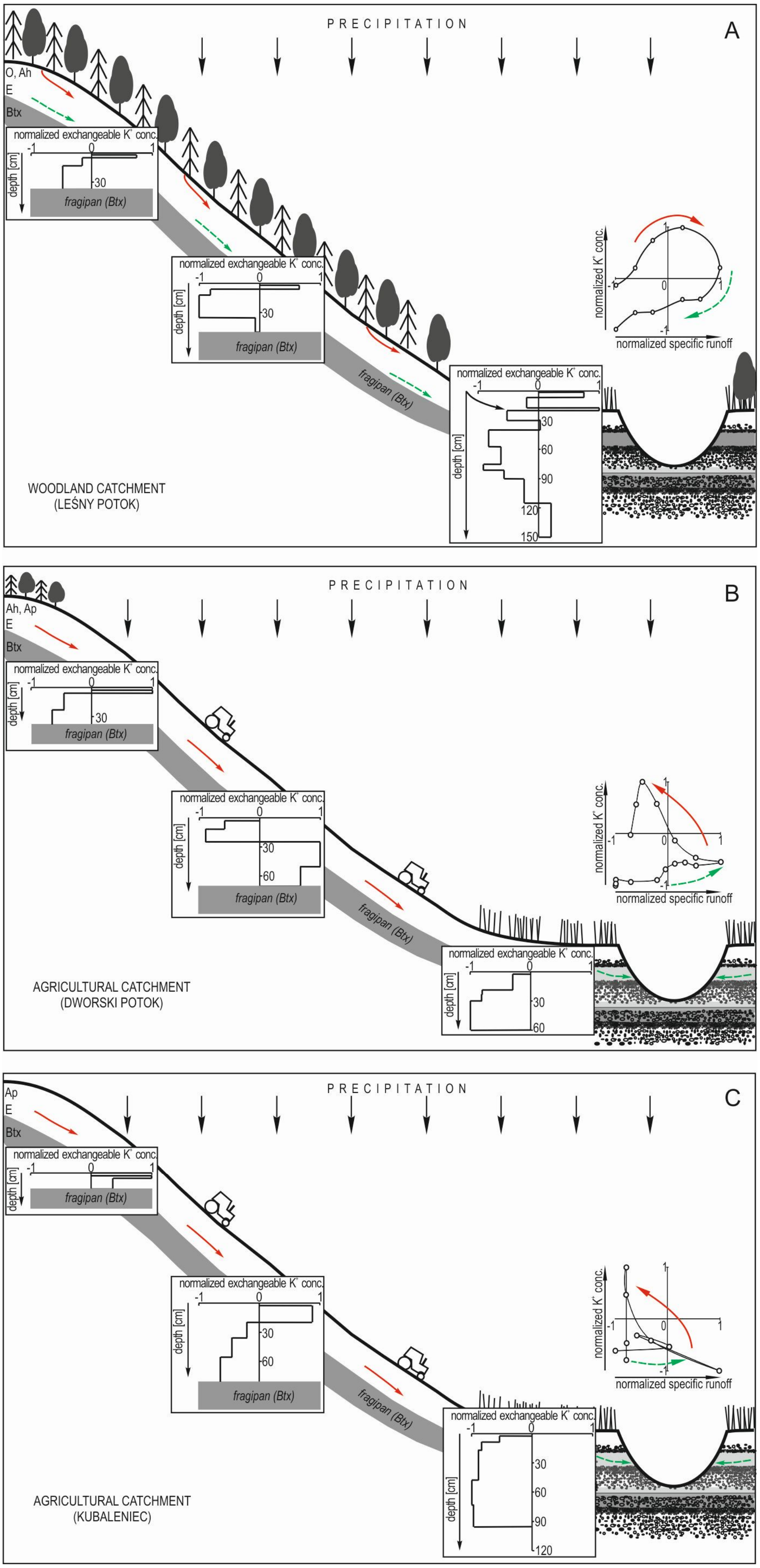

Fig. 5. Normalized values of soil exchangeable K$^+$ concentration (above fragipan) and stream water K$^+$ concentration – example of rainfall events under dry antecedent conditions.

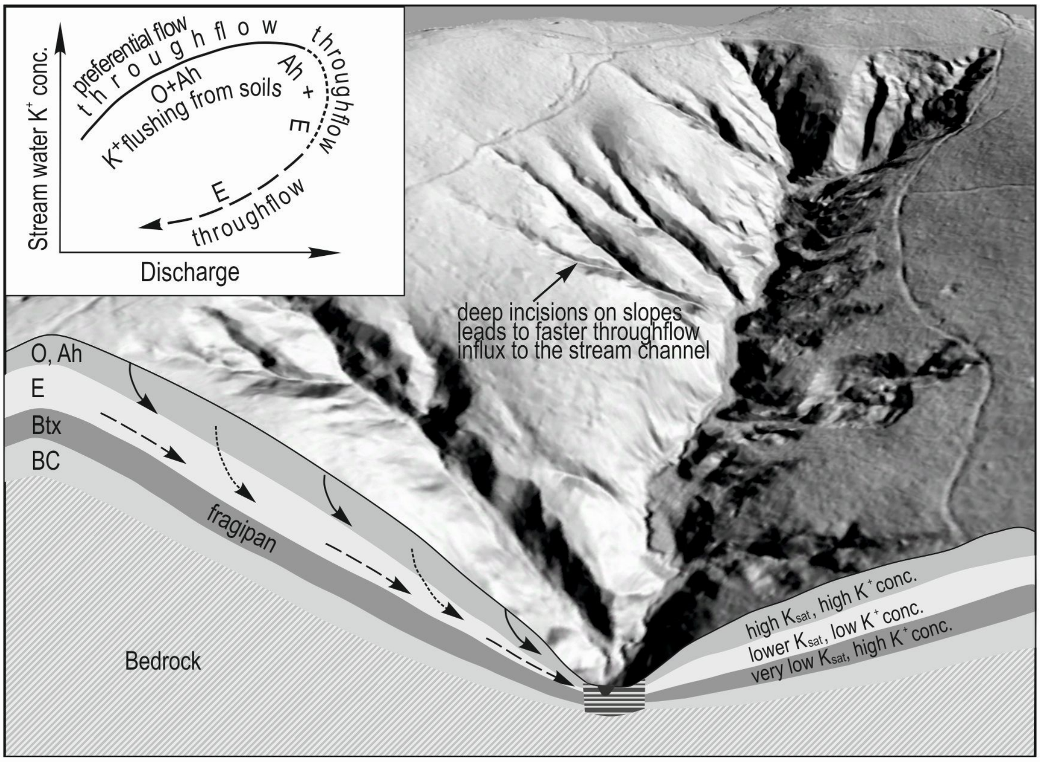

Fig. 6. Scheme of K^+ delivery to streams draining a woodland catchment during rainfall and snowmelt events (conceptual model).

(experimental agriculture), this is particularly troubling, as the soil in the catchment receives a regular and high dose of mineral fertilizer. This problem we have solved via an analysis of the exchangeable K^+ concentration in selected soil horizons on hillslopes and across valley floors under dry antecedent conditions. While the exchangeable K^+ concentration in the upper soil horizons (above the nearly impermeable fragipan) on agricultural catchment slopes was high, the exchangeable K^+ concentration throughout the entire soil profiles in riparian areas was much lower. Hence, the deciding factor in low K^+ concentrations in stream water during the rising limb of the hydrograph was the arrival of alluvial waters from the immediate vicinity of the studied stream channels. Throughflow water from hillslopes would only arrive in the stream channel sometime later and provide a high dose of K^+ (Fig. 7A). Wide hysteresis loops for stream water K^+ concentrations indicate a large difference in the K^+ concentration between water from the riparian area and water from hillslopes in the studied agricultural catchments. Sidle et al. (2000) as well as McGlynn and McDonnell (2003) have shown that most of total storm runoff was generated in the riparian area during a small storm event when catchment soils are fairly dry. Furthermore, stream recharge originating in hillslope areas had played a marginal role. Sidle et al. (2000) have shown that 100% of runoff volume can be generated within the narrow riparian zone during small storm events. Our research has shown that hillslope water plays an important role in the runoff generation process and in K^+ influx to streams during late stages of storm events with dry antecedent conditions in agricultural catchments.

The situation was different in agricultural catchments during rainfall events (storm-driven and long-lasting rainfall), which occurred under moist soil conditions and were caused by high precipitation of high intensity. During such events the concentration of stream water K^+ during the rising limb of the hydrograph was higher than that during the falling limb (clockwise hysteresis). This suggests a higher K^+ concentration of water in the riparian area than that for hillslopes. Rainfall that preceded these types of events contributed moisture to the studied soils. Water from hillslopes with a higher concentration of K^+ reached the riparian area, filling the alluvial water reservoir. Therefore, the K^+ concentration measured in baseflow in the agricultural Kubaleniec and Dworski Potok catchments before an event with wet antecedent soil conditions was higher (4.6 mg K^+/L in both catchments) than that measured one day earlier during a rainfall event preceded by a long period with no rainfall (3.4 and 0.6 mg K^+/L, respectively). A gradual flushing of K^+ from Ap and E horizons of soils on hillslopes occurred during these types of events. Throughflow filling the riparian area and reaching the stream channel was characterized by an increasingly smaller K^+ concentration (Fig. 7B).

In agricultural catchments, during most snowmelt events with the soil not frozen, the concentration of stream water K^+ during the rising limb was lower than that during the falling limb (counterclockwise hysteresis). This indicates that the first water to reach the stream channel was water poor in K^+ from the riparian area, while the second influx of water consisted of throughflow rich in K^+ arriving from hillslopes (Fig. 7C). Hence, the K^+ supply mechanism during snowmelt events with the soil not frozen was similar to that during storm events with dry antecedent conditions. However, stream water K^+ hystereses during snowmelt events with the soil not frozen were more narrow than those produced for storm events. Given the higher moisture content of soils in the period preceding the event, some slope water was already available in the riparian area, which is confirmed by a higher K^+ concentration in baseflow during snowmelt events with the soil not frozen versus that for storm-driven events. In addition, water flowing down from hillslopes already contained less K^+ due to the pre-flushing of soils across hillslope areas. Field observations and changes in the concentration of other solutes such as PO_4^{3-} (Siwek et al., 2013) suggest that stream recharge during snowmelt events with the soil not frozen tends to occur via throughflow, while overland flow plays a marginal role.

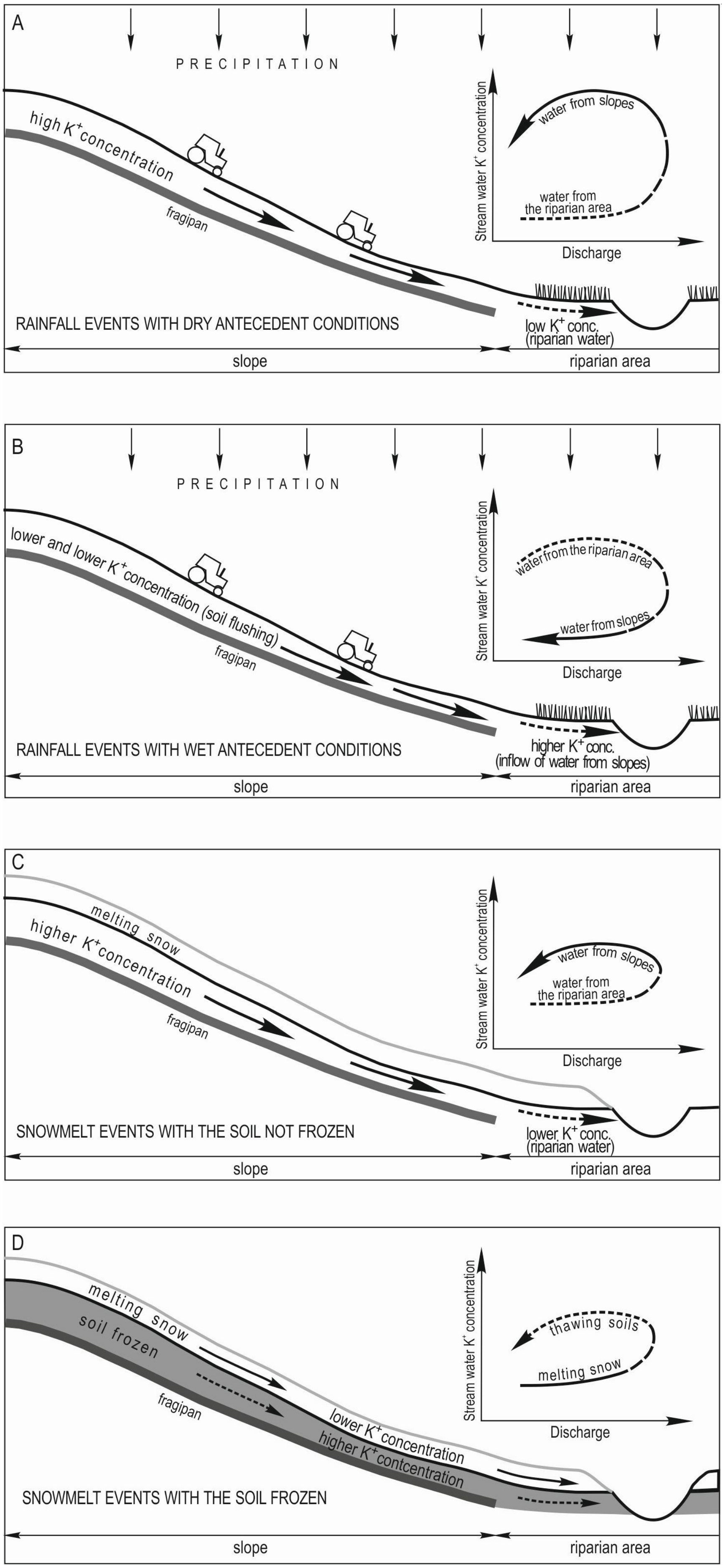

Fig. 7. Schemes of K^+ delivery to streams draining agricultural catchments during events of different type (conceptual models).

CONCLUSIONS

Data on exchangeable K^+ content in soil profiles and the hydrologic properties of soils (K_{sat}) in a catena-type spatial system (hillslope – riparian area) allow to yield new information on the role of particular soil horizons and the various contributing areas, such as hillslope or riparian areas, in K^+ delivery to stream channels draining woodland and agricultural catchments during events.

The upper A and E horizons occurring above the poorly permeable fragipan in soils located on hillslopes played a substantial role in water and K^+ supply to all studied streams during short and long lasting rainfall events, and snowmelt events with the soil not frozen. A higher exchangeable K^+ concentration in the upper soil horizons in the studied agricultural catchments compared with the woodland catchment resulted in a higher stream water K^+ concentration in agricultural catchments than in the woodland catchment. During snowmelt events with the soil frozen when upper soil horizons do not contribute to streamflow, K^+ concentrations were similarly low in all of the studied streams.

In the woodland catchment, a high variability in soil exchangeable K^+ concentrations and soil hydraulic conductivity (K_{sat}) in horizons above the fragipan determine the rate of influx of K^+ to stream channels during most events. Rapid flushing of K^+ from the topsoil Ah horizon with higher K_{sat} and higher exchangeable K^+ concentrations than in the lower-lying E horizon resulted in a higher concentration of stream water K^+ during the rising limb than during the falling limb of the hydrograph (clockwise hysteresis).

In the studied agricultural catchments, different concentrations of exchangeable K^+ in upper soil horizons (above fragipan) on hillslopes and in riparian areas resulted in different arrival times for water with different concentrations of K^+. The first water to reach the stream channel during most events is alluvial water from the riparian area and the second water is throughflow from hillslopes. Our research has shown, basing on the soil exchangeable K^+ concentration on hillslopes and in the riparian area, that during rainfall events with dry antecedent conditions, water in the riparian area is characterized by distinctly lower K^+ concentrations than water on hillslopes. The influx of water with different concentrations of K^+ results in a wide counterclockwise stream water K^+ hysteresis. A similar mechanism controlled the K^+ influx during snowmelt events with the soil not frozen in the study area. During rainfall events with wet antecedent conditions, stream water K^+ hystereses assumed a clockwise form, which suggests a higher K^+ concentration of water in the riparian area than that for slopes.

We believe that an interesting issue for further research would be to compare our findings with (i) temporal variations in the potassium concentration in soils under different meteorologic conditions, and (ii) hydrograph separation based on environmental tracers such as stable isotopes. These new studies might provide better insight into water flow pathways and K^+ influx to stream channels during events of different type.

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