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Effect of long-term fertilizer application in maize crop growing on chemical element leaching in Fluvisol

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Abstract. The study characterized the regime of nutrient leaching under different nitrogen and phosphorus supply of irrigated maize grown as monoculture on Fluvisol for the period 1999-2008 and additionally studied in the years 2009, 2010, and 2011. The aim of the study was to estimate the effect of long-term fertilizer application on the leaching of nutrients from the soil under maize grown as monoculture. The experiment design included four nitrogen fertilizer rates (B_1-control, B_5, B_4, B_3, B_2) calculated to compensate 50, 75, 100, and 125% from the plant N uptake, respectively. The field plots were equipped with lysimeters (at 50 and 100 cm depth) for studying the relationship between the applied fertilizer rates and the nutrient concentrations in the lysimetric water. The greatest nitrogen concentration in lysimetric water was observed under variant (B_3-N_{200} P_{150}) throughout the study period and the highest N losses were registered (36 kg ha^{-1}) in 2010 under the same treatment (B_3). A very good correlation was found between the N rates, calcium, and magnesium losses. Lysimetric water component compensation shows that agricultural activities have only influenced the speed of weathering and had no significant effect on the rates.

Keywords: fertilization, field experiment, lysimetric water, nutrients, chemical components

INTRODUCTION

The demand and food production is expected to increase in the next decades worldwide, which will put strong pressure on the environment due to the increasingly massive use of fertilizers. Soil fertility management have an influence not only on the quantity and quality of plant production but also on the agroecosystem. However, from the ecological point of view, the impact of the strength of anthropogenic load with nitrogen fertilizers can be assessed based on the established conditions for migration of chemical elements under one-meter soil layer. Many studies have documented that the chemical composition of lysimetric water depends on the natural conditions – geology and hydrology of the land, soil type and climatic conditions, the form and amount of fertilizer used, and the processes of weathering (Atanassov *et al*., 1985; Meissner *et al*., 2010; Stoichev, 1997; Stoichev *et al*., 1996; Zhao, 2010). It is estimated that the rate of weathering of various minerals is a function of export of dissolved chemical elements draining the soil profile and are determined by the mineral and chemical composition of soil forming rocks (Chadwick and Chorover, 2001; Taylor and Velbel, 1991; Yakubu and Ojanuga, 2013).

Some studies have been made on the climatic factors and changes that have a great impact on pedogenic weathering of minerals (White and Blum, 1995). Therefore (Atanassov, 1977), data on the content and migration of nutrients with infiltration water can provide objective information about the nature and trends in the weathering processes of soil minerals as a result of anthropogenic loading.

The aim of the study was to estimate the effect of long-term fertilizer application on leaching of selected components, including nutrients when maize is grown as monoculture.

MATERIAL AND METHODS

The field experiment was set up in 1972 at the experimental station of the N. Poushkarov Institute of Soil Science, Agrotechnology and Plant Protection in the village of Tsalpitsa, Southern Bulgaria (24°35'E, 42°14 N). The soil was classified as Alluvial-meadow soil (Koynov,

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T a b l e 1. Characteristics of the alluvial-meadow soil – Eutric Fluvisol

Horizons	Depth (cm)	pH_{H_2O}	Humus	Total N	C:N	$CaCO_3$ (%)	Sorption capacity (meq 100 g^{-1})	Particle size (mm)		
								2.0-0.02	0.02-0.002	< 0.002
			(%)						%	
A_{arable}	0-35	6.0	0.70	0.052	7.8	0.00	7.92	66.3	16.2	17.5
A_2	35-60	6.4	0.55	0.050	6.4	0.00	18.18	43.4	14.8	41.8
A_3C_1	60-87	6.5	0.42	0.042	5.8	0.00	22.77	33.5	20.6	45.9
C_2	87-118	6.5	0.38	0.030	7.5	0.00	23.11	31.4	29.6	39.0

According to Stoichev (1974, 1997).

1987), which corresponds to Eutric Fluvisol in the FAO classification WRBSR (FAO, 1998). The physico-chemical properties of the soil are presented in Table 1.

The soil has coarse texture, low water holding capacity, and conditions for fast water movement downward the profile. The arable horizon is characterized by slightly acid soil reaction pH_{H_20} = 6.0, low humus and total nitrogen content, respectively 0.7 0 and 0.052%, and low cation exchange capacity in the plough soil layer. The agrochemical characteristics of the Alluvial Meadow soil are mineral nitrogen content – 21.25 mg kg^{-1} and available phosphorus and potassium – 7.50 and 10.20 mg 100 g^{-1}, respectively for the 0-30 cm layer.

The region belongs to the transition subzone between Moderate and Mediterranean Continental climate zones. According to the classification of the country thermal conditions, the experimental area belongs to temperate hot and dry zone (Levichanska, 1991). The region is characterized with the following mean annual climatic parameters: annual precipitation of 384, 655 and 443 mm in 2009, 2010, and 2011, respectively with the average annual air temperature 12.5-12.8°C.

The long-term field trial was set up with irrigated maize (*Zea mays* L., FAO group 500 and 700) grown as monoculture. The single-factor experiment included 4 levels of N fertilization including an unfertilized plot (B_1). In the optimum treatment (B_3), the rate was calculated for full compensation of the nitrogen uptake by the crop production. The rates for the other treatments were: 125, 75, and 50%, B_2, B_4, and B_5, respectively of the amounts of optimum treatment. The scheme of the field experiment and the principle of determination of fertilizer rates are described in more detail by Stoichev (1997). The average rates of fertilization with nitrogen and phosphorus for the two periods 1999-2008 and 2009-2011 were B_1-N_0P_0, B_2-$N_{250}P_{187}$, B_3-$N_{200}P_{150}$, B_4-$N_{150}P_{112}$, and B_5-$N_{100}P_{75}$ kg ha^{-1}. Nitrogen fertilizers were applied as ammonium nitrate – 2/3 of the rate was spread before sowing, and 1/3 – in spring. Phosphorous fertilizer was applied as super phosphate each year before planting. Potassium fertilizer was applied at the beginning of the field trial, but not thereafter. Soil management practices and other agrotechnical inputs were applied according to the standard technology for the crop growing.

Modified Ebermayer-Shilova lysimeters (0.11 m^2) (Stoichev, 1974) were installed at 1 m below the soil surface to collect leachate from the soil profile, under three replications of treatments B_1, B_5, and B_3. The contact trays of the lysimeters were cut into the soil profile without disturbing the overlaying soil layers. They were made of PVC and filled with polyethylene grains to ensure good contact between soil and lysimeters and good infiltration. Leachates were collected monthly from the plastic containers (5.0 l) at the bottom outlet of each lysimeters and analysed for nitrates and other components. The pH values and chemical composition (NO_3-N, Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^-, Cl^-, SO_4^{2-}, SiO_2) of lysimetric water and precipitation were determined using the following methods: pH – potentiometrically (Arinushkina, 1970); nitrogen content, sulphates and Silicate was measured by 'Spectroquant Pharo 100'; potassium and sodium were determined by a flame photometer, calcium and magnesium – by atomic absorption spectrometry – AAS (Page *et al*., 1982), hydrocarbonate by titration with 0.02M H_2SO_4 to pH 4.4, and chlorine by the Moor method (Arinushkina, 1970).

Lysimetric water analysis was used to assess the effect of agricultural activities on primary material weathering. The approach used to analyse the weathering process involves a charge-based compensation of lysimetric water anions and cations (Garels and Makkensi, 1974). The compensating procedure begins with subtracting ions introduced via precipitation. Na^+ was used for compensation of Cl^{-1}. Nitrate ions were compensated mainly by Ca^{2+} and Mg^{2+}. Compensating amounts were distributed according to the share of the elements in lysimetric water. The SO_4^{2-} concentration was compensated by the same cations and the amounts used for compensation were determined by

Table 2. Chemical composition of lysimetric water (mg l^{-1}) under 0-50 and 0-100 cm soil layer for the period of 1999-2008

Chemical composition (mg l^{-1})	Rates of fertilization					
	B_1		B_3		B_5	
	0-50 cm	0-100 cm	0-50 cm	0-100 cm	0-50 cm	0-100 cm
pH	7.85	7.6	7.4	7.3	7.65	7.7
K^+	1.66	1.28	2.12	2.03	2.27	1.86
Na^+	16.52	16.68	17.85	15.6	18.14	17.99
Ca^{2+}	50.30	44.32	65.15	56.65	69.10	66.37
Mg^{2+}	17.32	14.76	16.45	18.62	16.69	17.50
NO_3^-N	6.16	6.73	31.01	33.74	22.40	26.22
HCO_3^-	114.51	93.36	61.89	71.30	102.42	91.75
Cl^-	19.64	18.94	20.79	20.91	25.53	24.51

the ratio of these elements regarding SO_4^{2-}. Calcium compensates phosphorus. After compensation of $H_2PO_4^-$, the remaining Ca^{2+} and Mg^{2+} were bound by HCO_3^-. After full compensation of the compounds, the ratio of the residual concentrations of SiO_2: HCO_3^- and $\sum(K^+ + Na^+)$ in the lysimetric water was determined and the chemical nature of the weathering process was defined.

RESULTS AND DISCUSSION

A continuous anthropogenic impact on the soil, especially when growing intensive crops, has a considerable influence on its quality and environmental functions. The liquid phase of the soil first accepts all anthropogenic impacts, accumulates residual effects, and stores the information of the quality and strength of the influence. It is known that the liquid phase of the soil reacts very quickly and accurately reflects anthropogenic loadings applied on it. According to some researchers (Atanassov, 1977), the ionic composition of the leachate reflects pedogenic weathering of the mineral fraction of the soil. In this context, water could be regarded as 'filtrates' of weathering. When comparing the values of the mineral composition of Fluvisol with the ionic composition of the lysimetric water obtained, it is possible to determine the impact of the anthropogenic loading on the direction of the processes of pedogenic weathering. For this purpose, the system of estimates offered by Garels and Mackenzie (1974) was used. Following this system of the SiO_2 residue in the drainage flow, it is possible to determine the type of changes in the mineral part of the soil. It was found that SiO_2, as part of sesquioxides and various ratios between them, can provide important information about the crystalline and amphoteric components of the soil clay fraction, which on the other hand, determines the weathering of clay minerals.

The main source of base cations is via processes of weathering of silicates and the input from precipitation and irrigation, and very small amounts are added *via* fertilizers as well. We used the methodology for lysimetric water analysis and the compensation procedure as a study tool to estimate the effect of agricultural practices on the weathering process. This does not mean that no transformation occurs in the reference system (Meisinger and Randall, 1991; Ranger and Turpault, 1999). In this particular study, the steady-state situation was defined with respect to long-term N sources and sinks within the different N treatments.

The genesis of the lysimetric water is established on the basis of the mineral and chemical composition of this soil (Atanassov, 1977; Stoichev, 1974). If we assume that lysimetric water does not contain carbonates, the source of Ca^{2+}, Mg^{2+}, Na^+, and K^+ in the waters are silicate and alum silicates in the soil (Table 2). As a result of the reaction between the soil minerals, water, and CO_2 in the lysimetric water, SiO_2 and cations were released in the water. The presence of SiO_2 in the lysimetric water comes from the decomposition of the silicates. Data on the mineral composition of the studied soil (Behar *et al.*, 1988) show that SiO_2 in the solution is mainly a product of feldspar decomposition. The sources of NO_3^- and SO_4^{2-} ions in the lysimetric water have biological origin (biochemical processes in the soil) or were introduced via rainfall and fertilization. An increase in SO_4^{2-} as a result of mineral weathering cannot be expected in this soil. The other cations in the lysimetric water (K^+ and Na^+) and SiO_2 originate from the weathering of feldspars. If we assume that transformation of the feldspars to kaolinite occurs in accordance with the reaction:

$$2NaAlSi_3O_8+2CO_2+3H_2O=Al_2Si_2O_5(OH)_4+2Na^+ +2HCO_3^- +4SiO_2,$$

T a b l e 3. Balance of the components in lysimetic waters for the period of 1999-2008

Ions	Contents of the components (meq l^{-1})		Difference (2-3)	Anions + compensating cations (meq l^{-1})					
	lysimetric waters	precipitations		Cl^-	NO_3^-	SO_4^{2-}	H_2PO_{4-}	HCO_3^-	Ratios SiO_2: HCO_3^-: ∑ (Na+K)
K^+	0.08	0.063	0.017	0.167	0.167	0.167	0.167	0.167	0.337
Na^+	0.724	0.072	0.652	0.170	0.170	0.170	0.170	0.170	
Ca^{2+}	2.865	0.351	2.514	2.514	1.084	0.846	0.776	0	
Mg^{2+}	1.359	0.153	1.206	1.206	1.206	0.786	0.614	0	
HCO_3	1.702	0.546	1.156	1.156	1.156	1.156	1.156	0.312	0.312
NO_3^-	1.780	0.254	1.526	1.526	0	0	0	0	
Cl^-	0.557	0.373	0.184	0	0	0	0	0	
SO_4^{2-}	0.928	0.467	0.461	0.461	0.461	0.461	0	0	
H_2PO_{4-}	0.070	0.010	0.600	0.060	0.060	0.600	0	0	
SiO_2	0.417	0.054	0.363	0.363	0.363	0.363	0.363	0.363	0.363
Total amount	10.412	2.343	12.755	–	–	–	–	–	
Compensated quantities	–	–	–	0.184	1.526	0.461	0.060	0.844	

for each HCO_3^- two moles of SiO_2 were formed, which was a very big amount to be compensated by the other ions in the lysimetric water. Otherwise, if the weathering of feldspars leads to formation of three-layer clay minerals (like montmorillonite) in accordance with the reaction:

$$2NaAlSi_3O_8 + 2CO_2 + 2H_2O = Al_2Si_4O_{10}(OH)_2 + 2Na^+ + 2HCO_3^- + 2SiO_2,$$

the ratio $SiO_2 : HCO_3^- : \sum (K^+ + Na^+) = 1:1:1$ is in full agreement with the compensated equivalents in the lysimetric water (Table 3) SiO_2: HCO_3^-: $\sum (K^+ + Na^+) = 0.363 :0.312: 0.337$. This suggests that the weathering of feldspars leads to the formation of three layer clay minerals (montmorillonite) (Atanassov, 1977).

The potassium content varies slightly for the all study periods (2009-2011) 0.90-5.87 mg l^{-1}. It was observed that the potassium content in lysimetric water was not substantially influenced by the fertilizer rates. The sodium content reaches the values of 23.44 mg l^{-1} (B_5-$N_{100}P_{75}$) in 2009 for 0-50 cm and 0-100 cm soil layer (Fig. 1a). The lowest values were observed in 2010 - 8.87 mg l^{-1} (Fig. 1b). The results show that in the lysimetric water, the cations of calcium dominate, which are indicative of Alluvial Meadow soil. When maize grew in 2010, the Ca^{2+} content reached the highest values of 103 mg l^{-1} (Fig. 1c). We established that the Mg^{2+} behaviour fully corresponds to that of calcium. The experimental data show that the nitrate nitrogen content varied in a very wide range from 3.28 to 73.7 mg l^{-1} in 2009 (Fig. 1a). The greatest nitrogen concentration in lysimetric water was observed under variants (B_3-$N_{200}P_{150}$) for all the study periods. The study results show that the hydrocarbonate content ranged from 69.6 to 208 mg l^{-1}.

It was found that the chemical composition of lysimetric water in the period of 2009-2011 was characterised by the same ratio of SiO_2: HCO_3^-: $\sum (K^+ + Na^+) = 0.363:0.307: 0.319 = 1:1:1$.

The amount of nutrients leached out of the top one-meter soil profile (Table 4) was derived from the volume and element concentration of lysimetric water. The average amount of water leached out below 1 m ranged between 5 and 13% of the incoming water. Almost the whole amount of N leached was in the nitrate form. In all cases, fertilization had led to increasing N losses. During the study period of 2009-2011, the amount of N leached out from the control site was 10-20 times lower in comparison with fertilized treatments B_5 and B_3. The variation in nitrate

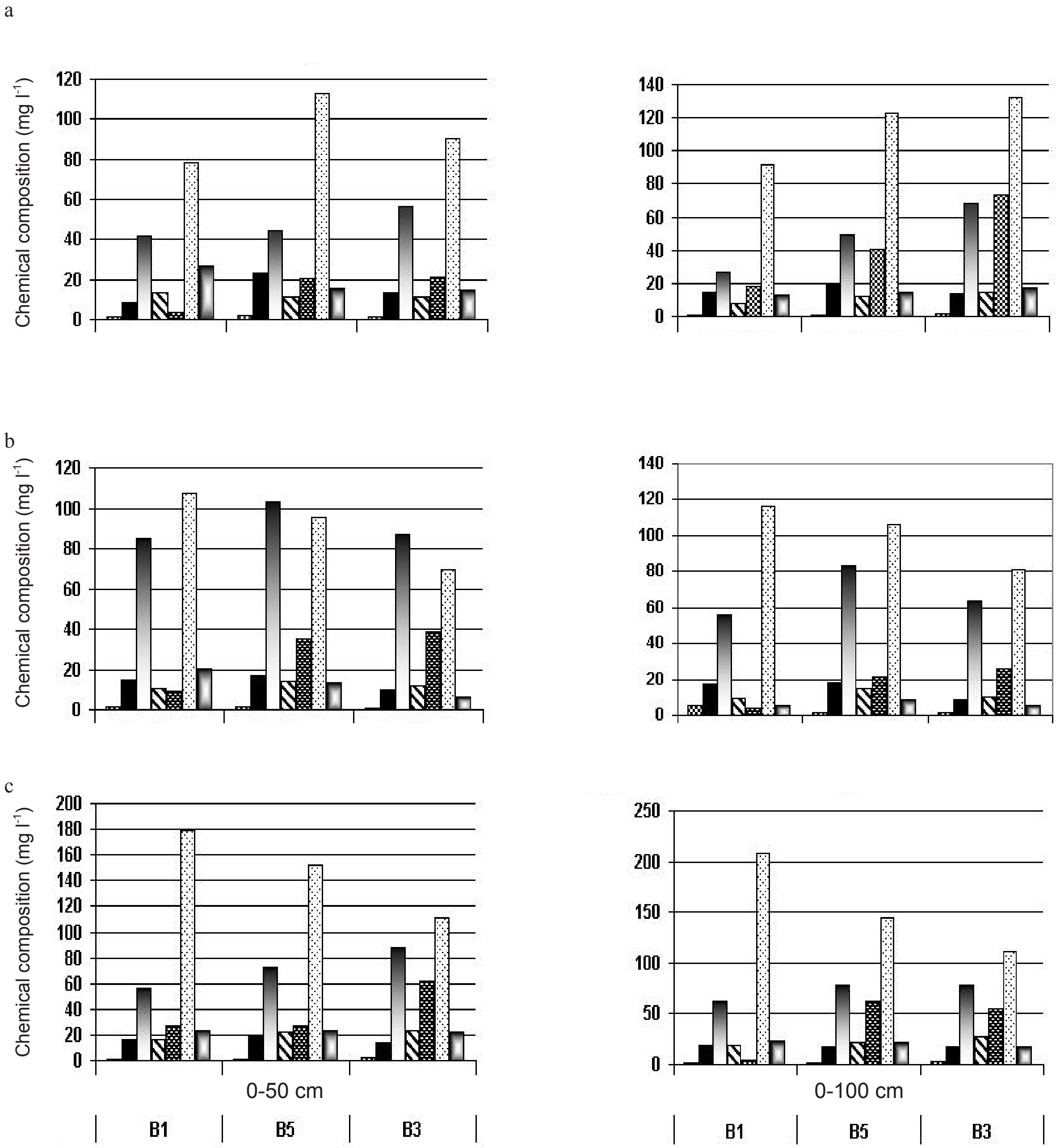

Fig. 1. Chemical composition of lysimetric waters under 0-50 and 0-100 cm soil layers in: a – 2009, b – 2010, c – 2011.

leaching strongly depended on the precipitation and irrigation volume. The lowest N losses were registered in 2009 in treatment B with N leaching 0.2 kg ha^{-1}. The highest N losses were in the range from 36 and 25-26 kg ha^{-1} in 2010 and 2011 (Table 4). Expressed in mass, the leaching of Ca^{2+} was the highest. The annual average losses of Ca^{2+} ranged from 7.4 to 80.0 kg ha^{-1} depending on the N fertilizer rates. A very good correlation was found between the N rates and Ca^{2+} losses. Calcium leaching increased with the increasing N leaching rates. The same trend was observed in Mg^{2+} leaching but the absolute values were lower. Leaching of K^+ and Na^+ was not significantly affected by the fertilizer inputs. The migration of hydrocarbonates decreased with the increasing fertilizer rates, especially in 2011.

CONCLUSIONS

1. The studied Fluvisol has very high spatial heterogeneity due to the soil formation process and distribution of alluvial sediments through the soil profile and hence very high variation between leachate volumes was observed.

Table 4. Migration of chemical elements (kg ha^{-1}) with lysimetric water through 0-100 cm soil layer for the period of 2009-2011 (maize)

Treatment	Depth (cm)	pH	Migration of chemical elements (kg ha^{-1})								
			K^+	Na^+	Ca^{2+}	Mg^{2+}	$N\text{-}NO_3^-$	HCO_3^-	Cl^-	SiO_2	SO_4^{2-}
						2009					
B_1	0-50	7.90	0.5	5.7	8.9	2.7	0.2	27.1	5.8	–	–
	0-100	7.90	0.3	4.8	8.7	2.5	5.9	30.1	4.2	3.3	12.1
B_3	0-50	7.65	0.6	4.5	19.1	3.9	7.3	30.6	5.0	4.4	32.6
	0-100	7.75	0.5	4.9	23.6	5.2	25.5	44.8	6.1	3.6	35.6
B_5	0-50	7.85	0.3	3.9	7.4	1.9	3.4	18.8	2.5	1.9	16.5
	0-100	7.65	0.5	8.8	22.7	5.4	18.9	56.5	6.6	6.2	54.5
						2010					
B_1	0-50	8.00	3.2	3.8	21.8	2.8	2.3	27.6	5.2	–	16.9
	0-100	8.15	2.5	7.2	22.8	3.9	1.7	47.7	2.2	4.0	27.3
B_3	0-50	8.00	0.9	8.8	80.8	9.0	36.0	64.7	5.8	3.0	39.8
	0-100	7.90	1.0	10.0	52.4	8.2	21.4	66.9	4.3	8.2	45.5
B_5	0-50	8.00	1.0	1.0	78.7	0.9	26.7	72.8	10.1	3.1	77.8
	0-100	8.00	1.3	14.8	69.5	2.2	17.9	88.8	7.3	8.0	82.6
						2011					
B1	0-50	7.80	0.7	8.1	27.0	8.1	12.9	85.8	11.0	11.9	47.3
	0-100	8.15	0.7	6.5	21.7	6.5	1.3	72.1	8.1	7.6	42.2
B3	0-50	7.30	0.8	5.7	36.8	9.7	26.0	46.1	9.3	0.4	53.5
	0-100	7.40	1.3	8.3	36.7	2.7	25.8	52.8	8.2	8.0	42.4
B5	0-50	8.00	0.5	7.4	28.9	8.6	10.6	68.4	9.4	9.1	46.9
	0-100	7.80	0.2	3.6	16.1	4.4	12.7	29.6	4.4	4.5	23.0

2. The type of land-use and different fertilizer rates are among factors that influenced element leaching and losses.

3. By this compensating procedure, it was established that agricultural practices had influenced only the intensity of weathering but did not lead to significant changes in the geochemical nature of the process and weathering rates.

Conflict of interest: The Authors do not declare conflict of interest.

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