Human- and Climate- Induced Changes in the Surface Stream Activity Affecting the Element Cycling

Tomáš NAVRÁTIL[1,2], Petr SKŘIVAN[1] and Daniela FOTTOVÁ[3]

[1] *Geological Institute, Academy of Science, Rozvojová 135, 160 00 Praha 6, Czech Republic.*
[2] *Charles University Prague, Faculty of Science, Albertov 6, 120 00 Praha 2, Czech Republic.*
[3] *Geological Survey, Klárov 3,118 21 Praha 1, Czech Republic.*

ABSTRACT. Fluctuations in the content of reactive atmospheric trace gases, caused by natural (geologic) and anthropogenic impact, strongly affect the migration characteristics of elements in the environment. Changes of CO_2, SO_2 and NO_x contents in the atmosphere result in the changes of the precipitation pH. Such variations strongly affect the forms and distribution of chemical elements between the solid and liquid phase in soils and in surface water sediments. Recent pronounced decrease in deposition of atmospheric S compounds, induced by the desulfurization of coal power plant flue gases results in gradual decrease of H^+ input. This change of input is followed by surface stream pH increase.
More than 10 years of monitoring the bulk chemistry, trace element content and pH in waters draining the experimental catchment Lesni potok (Kostelec n. Č. lesy region, central Bohemia) has demonstrated considerable variations of the stream chemistry dependent on the pH and on amount of atmospheric precipitation. Results of the acidification experiment may contribute to the understanding of past geochemical development of the Earth's surface.

KEY WORDS: acid deposition, water chemistry, element mobility, pH, precipitation.

Introduction

Pre-industrial concentration of carbon dioxide, the essential natural acidifier of the Earth's atmosphere, fluctuated in the past 1.6×10^5 years between 170 and 280 ppmv. Recent (1996) concentration of atmospheric CO_2 is 360 ppmv (Houghton et al., 1996) and is steadily rising (by 1.8 ppmv or 0.5% annually). The acidifying effect of CO_2 follows from the formation of weak carbonic acid in aqueous solutions.

Concentration of carbon dioxide in soil and sediment atmosphere can reach much higher values. According to Norton and Henriksen (1983) the maximum pCO_2 in soils commonly reaches magnitudes by two orders higher than in the atmosphere. The soil water pH can be decreased down to 4.7 purely by the carbon dioxide impact. The decrease of pH is followed by more intensive weathering of the residual rock forming minerals and through shift in the cation exchange reactions. Subsequent degassing of water enriched in dissolved species of elements, takes place after its transport to the riparian zones and surface streams. Resulting increase of pH promotes the reverse precipitation- and adsorption reactions. $Al(OH)_3$ or other Al solid phase precipitation occurs, followed by decrease of numerous element concentration in solution. Pool of loosely bound elements that are absorbed on such solid phase is formed and can be readily mobilized by further acidification of the system. Such phenomenon can occur by (naturally or anthropogenically) enhanced input of protons, such as by the increased intensity or acidity of the precipitation.

The above described mechanisms results in increasing acidity of soils and surface water sediments, and in the shift of the adsorption/desorption equilibria of elements towards the dissolved species. To obtain new information about the gradual changes in partition of selected important elements (including Al) in a small surface stream after a marked change in the proton input, an artificial acidification experiment was performed at the experimental "Lesní potok" catchment. Recovery of the system after the reduction of the proton input was also an object of the field study.

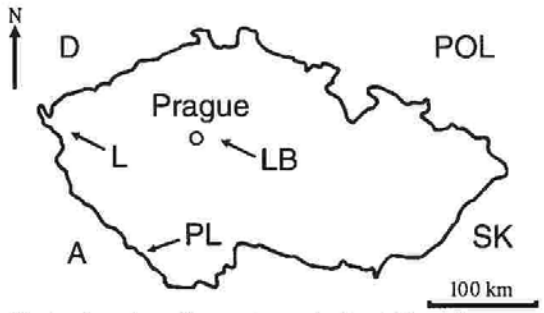

Fig. 1. Location of the catchment in Czech Republic.

Experimental

The forested catchment area Lesní potok (LP) with bedrock of the Říčany granite is situated in central Bohemia, approx. 30 km SE from Prague (Fig. 1). Catchment area is 0.765 km². Maximum elevation is 500 m a.s.l., the Thomson weir (in the northern part of the catchment) is 406 m a.s.l. The mean (past 10years) annual precipitation is 592.8 mm and the mean temperature is 7.3 °C.

Bulk atmospheric precipitation sampling in an open place occurred monthly since 1989 at the experimental station of the Faculty of Forestry, the Czech Agricultural University (locality "Truba") 5.5 km northeast from the catchment (Skřivan et al., 1995). Surface water of a small brook draining the catchment was sampled at least monthly since 1989 (Skřivan et al., 1993).

The experimental acidification of the Lesní potok stream was accomplished on July 13th and 14th, 1999 in Lesní potok catchment. The mean stream discharge was 1.7 $l.s^{-1}$. The stream water was continuously acidified with diluted hydrochloric acid (anal. grade) for 8,5 hours. Samples of water for chemical analyses and for the pH- measurements were collected 70 m (site I) and 127 m (site II) downstream. The stream bed is dominated by sand, gravel and in settling parts also by humic sediments.

The pH was measured in 30 min. intervals, 10 samples of water were taken for the bulk- and trace element analyses throughout the experiment. During the experiment 130.13 g of HCl was added to the stream with total 52,450 liters of water output.

Results and discussion

Initial pH, prior to the acidification, was 5.01 pH just below the weir decreased down to 4.11. The supplied 3.57 moles of H^+ were almost completely consumed by ion exchange in the first stream section. The pH at site I increased up to 4.97. This increase shows high buffering capacity of the stream bed. Changes of pH during the acidification and the recovery of the stream are displayed on the Fig. 2.

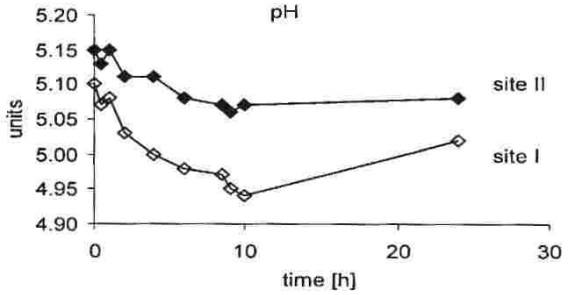

Fig. 2. Changes of pH concentration during the acidification experiment.

Data concerning the proton input and output and the mean annual concentrations of Al, Be, Mg, Ca, K and Mn in surface stream throughout the last 6 years are summarized in the Table 1. Intensified input of protons into the soils and weathering products of the granite bedrock affects the acidity of the surface stream. Resulting low pH of surface water determines the speciation of dissolved elements and affects the adsortion/desorption equilibria between the liquid and solid phases. Decreasing input of H^+ due to desulfurization of the power plants flue gases causes increase of surface water pH and decreasing concentrations of all presented cations.

Hydrol.	Precipitation		Discharge		Mean annual concentration mg L^{-1} (Al, Be µg L^{-1})						
year	mm	pH	mm	pH	Be	Al	Mg	Ca	Na	K	Mn
1994	637.3	4.11	121.6	4.37	9.03	1067	7.9	20.3	7.7	1.6	237
1995	771.0	4.23	127.4	4.75	9.62	1157	8.9	24.6	8.5	1.3	280
1996	592.8	4.23	146.3	4.78	9.21	1121	8.8	22.6	8.1	1.5	291
1997	609.2	4.30	97.3	4.89	6.00	912	6.9	16.1	7.6	1.0	222
1998	586.2	4.45	20.7	5.20	3.79	588	3.7	9.1	8.5	0.6	155
1999	457.1	4.47	94.8	4.92	4.92	836	7.2	16.3	7.9	1.1	130

Tab. 1. Lesní potok catchment: pH, input and output of water, discharge weighted mean concentration of elements in surface stream.

Table 1 also demonstrates that Be, Al, Mg and Ca possess strong dependence of their concentration in surface stream on the pH. Labile forms of these elements are present in the weathered rock material (partly as hydrated oxides, in the structures of secondary clay minerals or adsorbed on oxyhydroxides or bound to organic matter). No dependence on the pH was observed for Na (owing to its sources), for Mn (which is strongly metabolised and dependent on the Eh).

Nevertheless, output of mobile elements such as Be, Mg, Ca and Mn through surface stream strongly exceeds their input by bulk precipitation. This is evident from the Table 2, which displays these two dominant fluxes of the above mentioned elements in past 6 water years. Summarized values show distinct sequence of decreasing mobility of elements in a row Be>> Mg> Ca> Na> Al> Mn> K. It must be stressed that the sequence represents their apparent mobility, as it is affected by several factors: Be, Mg, Ca, Al are released into the surface stream mainly from their loosely bound forms in the weathered material. Na, on the other hand, comes from the atmospheric precipitation and directly from the hydrolysis of crystalline phases (feldspars). The output of Mn is affected by its strong metabolic cycling in the vegetation and by strong dependence of its mobility on Eh of the particular system.

		Flux of elements: Be in µg.m^{-2}.$year^{-1}$, other elements in mg.m^{-2}.$year^{-1}$							
year	flux	Be	Al	Na	Mg	Ca	K	Mn	H^+
1994	input	33.40	35.56	116.10	43.80	341.00	112.00	14.00	69.81
	output	732.29	129.83	938.71	960.35	2478.60	197.58	15.90	4.76
	out/in	21.92	3.65	8.09	21.93	7.27	1.76	1.14	0.07
1995	input	39.90	43.01	177.90	42.40	231.00	198.00	13.10	42.32
	output	1172.19	141.00	1039.40	1090.20	3009.90	165.20	34.10	4.08
	out/in	29.38	3.28	5.84	25.71	13.03	0.83	2.60	0.10
1996	input	20.00	47.98	156.23	47.90	313.00	92.40	12.40	40.09
	output	1360.82	166.00	1211.00	1300.50	3352.40	223.00	42.90	2.45
	out/in	68.04	3.46	7.75	27.15	10.71	2.41	3.46	0.06
1997	input	15.80	58.00	207.03	45.90	289.00	147.00	12.10	36.31
	output	584.90	89.00	743.09	674.52	1564.90	99.20	21.60	1.25
	out/in	37.02	1.53	3.59	14.70	5.41	0.67	1.79	0.03
1998	input	14.00	55.15	162.70	37.80	285.00	165.00	23.40	13.19
	output	80.76	12.20	176.42	76.82	189.00	13.60	3.20	0.13
	out/in	5.77	0.22	1.08	2.03	0.66	0.08	0.14	0.01
1999	input	4.08	16.61	153.05	31.95	186.11	90.70	10.80	17.79
	output	466.89	79.28	752.67	685.14	1553.97	106.60	12.40	0.98
	out/in	114.35	4.77	4.92	21.44	8.35	1.18	1.15	0.05
average	input	21.20	42.72	162.17	41.62	274.19	134.19	14.30	36.58
	output	732.97	102.89	810.21	797.92	2024.79	134.18	21.68	2.27
	out/in	46.08	2.82	5.21	18.83	7.57	1.16	1.71	0.054

Tab. 2. Annual (water year) input of selected elements through bulk precipitation.

Table 2 shows also strong retention of H^+, which is caused by its substitution or ion exchange for cations in the weathered rock residues. The same characteristic changes of the cation exchange for H^+ are observed directly in the surface stream during the experimental acidification of water.

Fig. 2 shows gradual decrease of surface water pH on both sampling sites throughout the addition of acid. Course of the lines between 8.5 and 24 hours shows gradual recovery of the system, which is by far not completed. Changes in dissolved Al concentrations throughout the acidification and recovery are plotted on Fig. 3. Course of the curve emphasizes the fact that the extent of Al retention throughout the recovery period results in the decrease of concentrations even below the original value prior to the acidification.

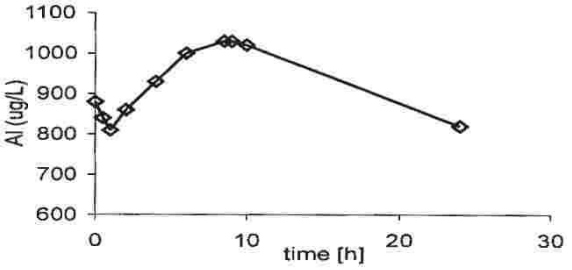

Fig.3. Changes of Al concentration during the acidification experiment.

Conclusions

Mobilization and transport of elements in surface streams is strongly affected by the precipitation- and consequently stream water pH. Six years of monitoring the precipitation- and surface discharge chemistry, as well as the experimental acidification of the monitored stream, proved the chemical fragility of acid soils where the H^+ input determinates the release of cations into the surface water. Metals Al and Be appeared as the most sensitive and mobile elements in acidified environment. Results prove importance of current processes such as desulphurisation.

Acknowledgements

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Late Pleistocene Pluvial Phase in Patagonia

Andrzej TATUR[1], Rodolfo del VALLE[2], Maria-Martha BIANCHI[3], Valeria OUTES[3] and Gustavo VILLAROSA[3]

[1] *Institute of Ecology, PAS, 05 092 Dziekanów Leśny, Poland*
[2] *Instituto Antartico Argentino, Buenos Aires, Cerrito 1248, Argentina*
[3] *PROGEBA, San Carlos de Bariloche, Argentina*

ABSTRACT: A large and deep lake occupied Maquinchao basin (41°S), probably between 13,200 years BP and 11,800 years BP during the great regional deglaciation, and was followed by shallow phase still lasting to about 11,000 years BP. Afterwards, recessive shoreline truncated formerly accumulated deposits during drying of the lake to more or less recent size about 8000 years BP. Presented chronology of events is based on TL dating, the comparison with record from sediments of Laguna Cari Laufquen Chica, and position of two dacite tephra horizons considered here as a regional stratigraphic markers (pre-dating and post-dating) bracketing the pluvial phase. Tephra markers were identified and dated in Andean Laguna El Trebol. Radiocarbon dating of sedimentary carbonates from paleolake suggests scenario about 4000 years older.

KEY WORDS: lakes, Late Pleistocene, climate changes, Patagonia.

Introduction

Several closed catchment areas with lakes in the lowest part occur in Patagonia Steppe. Large inland lake basins, like those from Patagonia, are primarily tectonic in origin. They are formed on long-lasting sags in cratonic areas, they persist for long periods of geological time, theirs margins fluctuate over hundreds of kilometres. Lakes with no surface outflow have shoreline extremely susceptible to fluctuations in water level as a response to the climate changes. This relationship is particularly clear in arid or semi-arid zones.

The last pluvial phase in Maquinchao basin (N-W Patagonia, near Inginiero Jacobacci, Fig. 1) followed by continuous trend of drying has happened after the last glacial maximum. The Size of Cari Laufquen Grande and Cari Laufquen Chica Lakes observed recently in the central part of Maquinchao basin, corresponds to vanishing stages of formerly much larger paleolake (Volkheimer, 1973). Laminated sediments accumulated during the onset of the last pluvial phase form "tercer nivel" of Coira (1979). Maquinchao River cut this "nivel" (Fig. 2).

Methods

Field investigations were carried out in years 1992–1999 by Argentine-Polish team, in the "Proyecto Pangea & Glopas" of IGCP Project 324 UNESCO, and in Argentine