Abstract

Surface waters from crystalline areas are a significant easily accessible source of drinking water. However, these areas often experienced high loads of acids from atmospheric deposition over the last century. Degradation of soils and surface waters occurred subsequently, especially in areas built of rocks vulnerable to acidification. The main objectives were to quantify the role that groundwaters play during streamflow generation and to evaluate the rate that groundwaters control stream water chemistry. The present-day quality of groundwaters and surface waters was compared with the quality at the period of easing atmospheric deposition. Groundwater brings base cations released by bedrock weathering into streamflow enhancing streamwater alkalinity at all flow levels. During baseflow conditions, streamflow was predominantly supplied with groundwater from deeper fractured bedrock. However, groundwater runoff is supplemented by water from shallower catchment reservoirs (shallower fractured bedrock, soils and overland flow). Thus, the chemistry of baseflow is not as invariable as usually considered. The acid neutralizing capacity (ANC) of stream water was correlated with the amount of more acid waters. To the contrary, the pH of streamflow was stable during baseflow conditions. Alkaline groundwaters (positive ANC) consumed transient increase in H^+ ions in a process similar to titration and stabilized the pH of baseflow. H^+ concentrations started to increase when the volume of shallower waters exceeded deeper groundwaters. Then, groundwaters ceased to buffer an influx of acid waters resulting in episodic acidification. A moment when shallower waters started to dominate, groundwaters launched the transition from baseflow to stormflow conditions (episodic acidification). Acid groundwaters (negative ANC) are not able to consume H^+ ions from fluctuating shallow acidic waters, and baseflow pH fluctuated along with ANC. Hence, there is no sharp difference in acidity between baseflow and episodic acidification in such streams.

The pH of stormflow is controlled by the mixing rates. Streamflow H^+ usually increased 2 to 3 times during episodic acidification. Intensity of episodic acidification was dependent on the quantity and quality of deeper and shallower waters. Lithology primarily controlled the rate of groundwater runoff. Groundwaters supplied 40 to 50% of stormflow on gneiss and 25% on granitic bedrock. Thus, whereas episodic acidification on gneiss might not necessarily occur, granitic catchments surely experience high-intensity acidification. Alkaline bedrocks in connection with favorable factors controlling water/rock interaction (fracture zone density, geomorphology and catchment size) produce high ANC groundwaters. On the other hand, sulfates suppressing ANC displayed

declining concentrations in polluted stormflow and baseflow accompanied by increasing ANC. There is no doubt
that acidified ecosystems have started to recover.