EPISODIC VARIATION IN STREAMWATER CHEMISTRY AT BIRKENES, SOUTHERNMOST NORWAY: EVIDENCE FOR THE IMPORTANCE OF WATER FLOW PATHS


ABSTRACT
We have investigated changes in stream and soil water chemistry and water table variations in the Birkenes catchment, southernmost Norway, during autumn rainfall and spring snowmelt episodes. Labile monomeric aluminium [Al\textsubscript{1}] concentrations in streamwater exhibited variable response to episodic increases in discharge. During events preceded by extended periods of low flow, episodic discharge coincided with large increases in [Al\textsubscript{1}]. Wet conditions were characterised by high but generally decreasing [Al\textsubscript{1}] sometimes with drops in concentration close to discharge peaks. Streamwater was saturated with respect to synthetic gibbsite at baseflow, but consistently undersaturated during wet periods. Water table measurements in piezometers situated in a subcatchment at Birkenes suggested generally higher interception of soil layers as the autumn rain season progressed. In some piezometers, later storms (when streamwater [Al\textsubscript{1}] decreased) resulted in interception of organic horizons which were not intercepted during earlier storms (when [Al\textsubscript{1}] increased). These data support the hypothesis that streamwater [Al\textsubscript{1}] is controlled primarily by changes in water flow path during high discharge episodes.

INTRODUCTION

Acid deposition is thought to cause a decrease in alkalinity and pH of surface waters in acid sensitive areas and also an increase in aluminium mobilization from watershed soils. Resulting elevated H\textsuperscript{+} and aluminium concentrations in lakes and streams have been linked with fish kills and toxicity to other aquatic biota (Leivestad et al. 1975, Baker and Schofield 1982, Henriksen et al. 1984). Aqueous aluminium and hydrogen ions are particularly elevated during periods of
Piezometer Results

Data from four representative piezometers are presented in Figure 4. Despite considerable variability in response, there was a consistent trend of rise in water table for 6 out of 7 piezometers with sustained water table between events. Of the remaining 7 piezometers, situated in upland hillside areas, 2 never gave water and 5 dried out completely between events (e.g. 8, Figure 4). In piezometer 6, situated in a deep boggy area adjacent to the stream, the water table intercepted organic deposits throughout the study period and rose steadily during that time, but showed no episodic response. This suggests that water moving through this area contributes less to episodic discharge than to baseflow. The water table rise caused interception of the organic horizon at four additional sites during the last event (piezometer 6, 14, Figure 4). During the first event none of these 4 piezometers responded by intercepting the organic horizon, but two did so in each of the second and third events.

Hydrological Implications

These data allow us to draw some conclusions regarding the influence of hydrology on episodic discharge chemistry. First, some areas of the hillslope probably contribute disproportionately to episodic runoff. Secondly, later events tended to cause interception of higher, organic soil layers. This was most pronounced for the last event, which was both preceded by the wettest conditions and was also the largest event of those studied. Soil solution (lysimeter) Studies at Birkenes have indicated a general trend of increasing Al concentration with increasing depth during both autumn and spring, although variability is high (Sullivan et al. 1986a, 1987a). These data therefore support the hypothesis of streamwater [Al] being determined largely by flowpath of soil water through various soil horizons. The hypothesis is consistent with the observed decreasing trend of [Al] in streamwater during the wet period of the autumn 1986 and with the episodic drop in [Al] at the last event (Figure 2).

We earlier suggested (Sullivan et al. 1986a, 1987a) that aluminium chemistry in streamwater was likely regulated by residence time of water in contact with soil, changes in flow paths during episodes, and/or redisolution of aluminium which accumulated in soil pores when water evaporated during dry periods. Soil water at Birkenes showed little temporal variation in concentrations of H and aluminium species despite sampling under widely varying hydrological conditions in both autumn and spring (Sullivan et al. 1987a). It is therefore un-
likely that either residence time or redissolution of aluminium in soil pores is the major controlling factor.

In a recent report, Henriksen et al. (1987) have found rapid release of aluminium from stream substrate and moss with artificial acidification of a tributary to the river Vikedal in western Norway. They attributed this release to dissolution of Al-hydroxides which had precipitated from aluminium-rich groundwater losing CO₂ in the stream resulting in increased pH. This phenomenon is probably of less importance in streams such as Birkenes which are chronically acidic. The Vikedal tributary generally shows pH variations of 5.0 - 6.0 (Henriksen et al. 1987), while Birkenes stream values are typically 4.2 - 5.2. Furthermore, Henriksen et al. acidified the tributary to as low as pH = 3.6 at 5 m below the point of acid addition, representing 241 µeq L⁻¹ of H⁺ above the stream's normal maximum. It is therefore difficult to equate the resulting Al pulse with snowmelt/rainfall episodic processes. If streamwater Al dissolution were important at Birkenes we would expect to see low flow and rising limb hydrograph Al concentrations in equilibrium with an aluminium hydroxide phase such as amorphous or micro-crystalline gibbsite. Figures 2 and 3 indicate low-flow saturation with respect to synthetic gibbsite, but streamwater remains well undersaturated with respect to other aluminium hydroxide mineral phases.

In summary, the piezometer data presented in this paper support the hypothesis of water flow path as the major determinant of streamwater [Al] at Birkenes. Other processes which could be important in regulating episodic streamwater Al chemistry appear to be of less significance at this catchment.

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high runoff such as autumn rain and spring snowmelt (Driscoll et al. 1980, Christophersen et al. 1982, Neal et al. 1986). Early life stages of fish are often present during these high discharge periods and appear to be especially sensitive to Al toxicity (Baker and Schofield 1982).

Several researchers have suggested that hydrological factors such as flow path and contact time with mineral soil may be important in regulating surface water chemistry (Rosenqvist 1978, Seip 1980, Chen et al. 1984). Thus, the role of hydrology in influencing surface water chemistry has been recognized, but the quantitative importance of hydrologic processes in episodic acidification is largely unknown.

We have investigated changes in stream and soil water concentrations of $\text{H}^+$, Al-species and other important parameters in response to high discharge episodes at the Birkenes catchment since autumn 1984 (Sullivan et al. 1986a, 1987a, 1987b). The purpose of this paper is to summarize our findings to date regarding episodic changes in stream and soil water chemistry, and to report preliminary results of our investigations on groundwater table fluctuations during autumn rain-fall events. Based on earlier studies, the working hypothesis was that observed declines in inorganic monomeric aluminium concentrations in streamwater during later autumn events occurred because proportionately more water flowed through upper, organic horizons which contained less inorganic aluminium.

SITE DESCRIPTION

Birkenes is a small (0.41 km$^2$) forested catchment with shallow podzolic soils on granitic bedrock. It is situated 30 km north of Kristiansand in southernmost Norway and receives an atmospheric deposition loading of nearly 7 g SO$_4^{2-}$ m$^{-2}$ yr$^{-1}$ (Christophersen and Wright 1981). Streamwater is chronically acidic with a volume-weighted mean pH in the main brook of 4.5.

METHODS

Stream and lysimeter samples were collected during high discharge autumn (1984-85) and spring (1985-86) seasons. Meltwater and snow core samples were also collected in spring. Analyses of pH, conductivity and aluminium were accomplished immediately at an on-site field laboratory. Aluminium fraction concentrations were measured using the Barnes/Driscoll method (Barnes 1975, Driscoll 1984) at ambient temperature. Speciation of the labile (mainly inorganic) monomeric aluminium fraction was done with the ALCHEMI computer program (Schecher and

A subcatchment in the Birkenes watershed was instrumented with 14 piezometers (Figure 1) to record changes in the groundwater table level during storm events in the autumn of 1986. We wished to determine if a different flowpath, as evidenced by different soil horizons being intercepted by the saturated zone, could account for the differences in streamwater chemistry observed between initial and later events.

The piezometers were constructed of PVC tubing which was slotted up to 15 cm over the bottom. Conical tips were cemented on the lower end, and the tops were capped with a removable PVC cover; a small hole was drilled into the tube below the cap to allow equilibration with atmospheric pressure. The piezometers were hand augered into place and the holes were backfilled with extracted material and tamped at the surface to prevent water from running down the sides of the tube. The levels of the different soil horizons were measured before the piezometers were installed.

Figure 1. Map of the Birkenes catchment showing main brook sampling station (BIE01) and piezometer locations.
Four piezometers were placed along a transect adjacent to the stream just above the valley floor (8 10-13). The others were installed at suitable places along three approximate transects up the hillslopes. Piezometer 8 14 was placed in a 2 m deep boggy area close to the stream (Figure 1). Sites were selected to be as nearly planar as possible.

The interior of each piezometer was equipped with a clean polystyrene tube containing a styrofoam float which would rise to the surface and adhere to the walls of the tube if the water level dropped. These "maximum rise indicators" also provided a back-up to our manual monitoring program. Frequency of measurement was approximately every two hours during the rising limb of the hydrograph and less frequently as it declined. Precision of water depth measurements was approximately ± 1 cm.

RESULTS AND DISCUSSION

Chemical trends

During both autumn rain and spring snowmelt episodes the patterns of stream response were similar for most chemical components for all the five field seasons studied. Variations in discharge and concentrations of H⁺ and labile monomeric (mainly inorganic) aluminium ([Al⁺⁺]) for the main brook (G101) for autumn and spring of 1986 are presented in Figures 2 and 3; results for previous years are given elsewhere (Sullivan et al. 1986a, 1987a, 1987b). Hydrogen ion, nonlabile monomeric (mainly organically complexed) aluminium, and total organic carbon increased with episodic discharge while basic cations and total fluoride decreased. Cation and anion sums decreased during most of the snowmelt. Patterns for [Al⁺⁺] however, were more variable. The first episodes following extended baseflow periods resulted in large pulses of [Al⁺⁺] during both autumn and spring events. As autumn rain and spring snowmelt seasons progressed, [Al⁺⁺], though remaining high, followed a generally decreasing trend, sometimes with drops in concentration close to discharge peaks. The three major tributaries to the main brook followed similar patterns, although absolute concentrations varied somewhat among the four sites.
Figure 2. Autumn 1986 stream discharge, concentrations of $\text{H}^+$ and $\text{Al}^{3+}$ and saturation indices (SI) for synthetic gibbsite (SSG) and microcrystalline gibbsite (SMG) at BIE01. Sampling points for $\text{H}^+$ and $\text{Al}^{3+}$ are indicated on time axis. SI's have only been computed for samples with complete analyses. ($SI = \log \left(\frac{[\text{Al}^{3+}][\text{H}^+]}{K_{\text{slo}}}\right)$ where $K_{\text{slo}}$ is the gibbsite solubility product at the appropriate temperature). The largest peak in the hydrograph on 28-29 Oct. was not sampled.
Figure 3. Spring 1986 stream discharge, $H^+$ and $Al_{i}$ concentrations and saturation indices. Cfr. Fig. 2.
Figure 4. Stream discharge and water table height at four selected piezometers during the autumn 1986. Organic horizons are indicated as hatched areas to the right.