

Long-Term Acidification Resulting From Catchment Base Cation Depletion: Geochemical Theory and Field Observations

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Long-term monitoring data from Europe and North America show that since the late 1970's, sulfate deposition and runoff sulfate concentrations have declined significantly. This has led to expectations for rapid improvement in water quality in lakes and streams. However, in many cases water quality has improved much less rapidly than expected, or not at all, because decreases in runoff sulfate levels have been matched by declining base cation concentrations. Data from Hubbard Brook, Solling, and four Norwegian catchments illustrate the processes responsible for these base cation trends, and their implications for surface water quality.

Several lines of evidence support the hypothesis that exchangeable base cations are being depleted from catchment soils, at sites where mineral weathering rates are inherently low. The observed declines in base cation concentrations are larger than can be explained by simple equilibrium responses to declining acid loading. For example, when the effects of changes in acid anions are statistically removed, data from Birkenes (Norway) reveal a consistent long-term loss of $1.4 \pm 0.2 \mu\text{eq/L/yr Ca+Mg}$ from streamwater, throughout 17 years of record. At the Solling spruce forest (Germany), 19 years of monitoring data reveal an ongoing loss of $10.8 \pm 1.3 \mu\text{eq/L/yr Ca+Mg}$ from seepage water--again, after the effects of changes in acid loading have been removed.

Base cation concentrations are declining most rapidly at catchments subject to highly acidic deposition, which suggests that high acid loading has accelerated leaching of bases from catchment soils. The observed rates of decrease in runoff base cation concentrations are also quantitatively consistent with plausible rates of depletion of exchangeable bases. At Solling, where changes in exchangeable bases have been documented by repeated inventories over 22 years, the documented rates of soil base cation loss are consistent with the rates of change in seepage water base cation concentrations.

Simple geochemical formulas, with no adjustable coefficients, predict how base cation concentrations will respond to changes in acid loading and to depletion of exchangeable bases from catchments. These simple formulas show that although acid loading reductions have not been sufficient for sensitive catchments' water quality to recover, they have nonetheless prevented significant acidification, which would otherwise have occurred under constant acid deposition.

Halting depletion of exchangeable bases requires reducing acid deposition below the long-term critical load, which will be difficult to achieve at the most acid-sensitive sites. Reversing long-term acidification of soils requires replacing depleted exchangeable bases, which is ultimately limited by rates of mineral weathering and will require timescales of decades to centuries. By depleting exchangeable bases, acid deposition has altered the chemistry of catchments themselves, not just the chemistry of waters flowing from them. As a result, continued deposition reductions will be needed to avoid further acidification of

sensitive sites, and recovery from acidification will be slow.