

Weathering and pedogenesis at the watershed scale: Some recent lessons from studies of acid-deposition effects

M.A. Velbel

Department of Geological Sciences, Michigan State University, East Lansing, MI 48824-1115, USA

(Received March 1, 1993; revised and accepted March 30, 1993)

Mineral-weathering reactions are fundamental processes in the interaction of acid precipitation with susceptible landscapes. Landscapes underlain by crystalline silicate bedrock are the most sensitive to acidification, because the silicate minerals of which these rock types are composed react only slowly with through-going solutions. Consequently, silicate mineral-water interactions do not occur quickly enough to neutralize the added acidity or to contribute base cations and acid-neutralizing capacity to the soil exchange complex and natural waters (e.g., Johnson et al., 1972; Johnson, 1979, 1984). Thus, the weathering rates of bedrock minerals are fundamental controls on landscape and surface water acidification (Bricker and Rice, 1989; Turner et al., 1990).

Geochemical mass balance (input-output budgeting) is commonly used to calculate mineral weathering rates, especially in small watersheds. Small watersheds are hydrologically and topographically well-defined drainage basins, for which inputs, outputs, and internal properties (e.g., rock type, soil type, vegetation type) can be characterized with relative ease. Small watersheds are easily studied in terms of hydrologic and geochemical dynamics, and are a unit appropriate for studying regional (bio)geochemical processes at natural space and time scales (as opposed to simulations of such processes in the laboratory). Weathering rates of individual minerals

in watershed mass-balance studies are determined by solving a system of simultaneous linear equations with constant (stoichiometric) coefficients. Biomass effects can be incorporated where appropriate (Taylor and Velbel, 1991).

Weathering rates determined from biogeochemical mass-balance calculations conform closely to other quantitative methods of studying landscape processes, including laboratory kinetic studies and ecological studies of nutrient cycling. The stoichiometrically specific mass-balance method permits comparison of field rates for the weathering of individual minerals with rates determined in laboratory experiments. Relative rates (rate ratios) calculated by the geochemical mass-balance method (including the terms for botanical uptake) compare most favorably with relative rates determined in laboratory kinetic studies of mineral weathering (Velbel, 1985, 1992, 1993). The geochemical mass-balance results for one southern Appalachian hardwood forest watershed (W18, U.S. Forest Service Coweeta Hydrologic Laboratory, Franklin, North Carolina, U.S.A.) compare favorably with previously published botanical nutrient-cycling studies of the same watershed (Taylor and Velbel, 1991).

Several long-standing questions regarding geochemical mass balance can be addressed with results from acid-rain studies. Cation ex-

change has long been regarded as an important but overlooked (or deliberately neglected) factor in geochemical mass-balance calculations of weathering rates. The minimal contribution of cation exchange to watershed solute budgets cannot be proven, but is strongly suggested by the fact that rates calculated by the geochemical mass-balance method give relative rates (rate ratios) which compare most favorably with relative rates determined in laboratory kinetic studies of mineral weathering (Velbel, 1985, 1992, 1993). As Taylor and Velbel (1991) show, contributions to elemental fluxes from botanical factors (which were not accounted for in most previous mass balances) have large effects on the calculated weathering rates of some minerals, and almost no effect on others. Unless the "extraneous" source(s) such as cation exchange contribute to all major elements in the same proportions as does weathering, such inputs would distort the calculated weathering rates of different minerals to different degrees, modifying the rate ratios. This is not observed (Velbel, 1985, 1992, 1993). Furthermore, one recent highly detailed model of surface water acidification of another southern Appalachian watershed [White Oak Run (WOR), Virginia; SWAS/MAGIC model; Cosby et al., 1985a, b, c] strongly suggests that cation exchange does not contribute to solute fluxes to an extent sufficient to affect calculation of weathering rates by mass balance. The "calibrated" weathering rates in the MAGIC model for WOR (fluxes from primary minerals required to make the model predict stream chemistry) are essentially identical to stream outputs. In other words, cation exchange is a negligible influence on solute output, and estimating weathering rates from output alone, without accounting for cation exchange, would have minimal effect on weathering rates calculated from solute mass balance and mineral-weathering stoichiometries alone.

Numerous recent studies in glaciated landscapes of North America and Scandinavia

compared present-day (short-term) weathering rates (from solute budgets) with long-term weathering rates determined from mineral and/or elemental depletion in weathering profiles on glacial parent materials of known age. Such studies invariably find higher present-day rates, and generally conclude that the higher rates are a consequence of recent environmental acidification. However, because the residual solids which are the basis of the long-term estimate are time-integrated accumulations of weathering products, it may be inappropriate to compare (instantaneous) short-term rates from solute input-output budgets with long-term rates from bulk profile chemistry. In the simplest case, bulk solid-phase profile chemistry represents total, time-integrated, cumulative weathering losses, averaged over the life of the profile. These must equal *time-averaged* solute losses (total removal by solution over the life of the profile, e.g., thousands of years or more), but not necessarily the instantaneous solute losses (those measured by solute fluxes over short periods of record, e.g., decades or less). Short-term budgets represent only a small portion of the profile's life, a portion possibly not representative of the entire life of the profile, but directly related to those weathering reactions taking place during the period of solute sampling.

There is another limitation to such comparisons. The long-term rate measures only material removed from the soil, whereas the input-output rate represents element removal from the entire watershed (including weathering of bedrock beneath the soil). Elemental fluxes released by weathering of the deeper material contribute to the solute fluxes, but not to losses estimated from the soil-profile measurements alone. Solute budgets are influenced by the presence of weatherable minerals along hydrologic flowpaths, many of which occur beneath the soil profiles in which the profile's mineral/element depletion is measured. For instance, vein or grain-boundary calcite may occur rocks beneath soil profiles completely

depleted in carbonate. Such "subsoil" calcite could easily supply Ca and HCO_3^- to stream solute loads. Since the purpose of research on acid-deposition effects is to understand the effect of weathering on surface water quality, *not* on soil genesis, the rates determined from solute budgets are *more* relevant — the streams (and their compositions, fluxes, and budgets) have "seen" *every* relevant reactant mineral, including those weathering below the soil. Perhaps it is the soils which inadequately represent the material with which the water comes into contact along deeper flowpaths. Thus, there are disparities in *both* the time-scales over which the two methods "measure" rates, *and* the volume fraction of the regolith being sampled. Soils better integrate time; solute budgets better integrate space.

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