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RATES OF LOSS OF CALCIUM FROM SCOTTISH CATCHMENTS MEASURED BY DIFFERENT METHODS

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Abstract: The rates of loss of calcium in eight Scottish catchments on four rock types have been calculated by three methods: (1) long-term rates from elemental depletion in soil profiles; (2) using the PROFILE model; (3) current rates from input-output budgets. The first two methods are soils based and yield rates which, with one exception, are lower than the current rates. Although comparisons of the values obtained by the three methods are complicated by the different assumptions inherent in the methods, the current rates are often an order of magnitude higher and presumably indicate sources of weatherable calcium-bearing minerals in the catchment outwith the soils.

Key words: catchments, weathering, soils, budgets, calcium, minerals.

Introduction

The rates of release of base cations from mineral weathering are important in relation to the acidification of soils as they have a major influence on whether a soil becomes acidified by internal processes and/or acidic inputs from the atmosphere (Reuss & Johnson 1985). The ability of soils to neutralize incoming acidity depends in the long term on the rates of release of these base cations by chemical weathering of the constituent minerals. Many investigations into soil and water acidification have been carried out on a catchment basis and in order to assess the sensitivity of catchments to acidification, it is necessary to obtain meaningful weathering rates so that these can be compared to the acidic atmospheric inputs. In addition, modelling catchment response requires an understanding of reaction mechanisms and reaction rates of silicate minerals related to the overall weathering rates in catchments.

There are several methods of calculating weathering rates and these have been summarized by Jacks (1990). They include long-term or historical rates averaged over hundreds or thousands of years, methods based on input-output budgets for catchments over a period of a few years, laboratory experiments extrapolated to the field, determination of strontium isotope ratios for estimation of the weathering rate for calcium (Jacks et al. 1989), and modelling approaches.

In a number of Scottish catchments, large discrepancies have been found in weathering rates for total base cations calculated by different methods (Bain & Langan 1995). This paper reports the differences in the weathering rates for calcium for which the discrepancy seems to be greatest.

Methods and materials

Sites, geology and soils

The eight catchments studied are from across Scotland from Halladale in the north to Galloway (Clauchrie and Cairnfore) in the south-west, with annual precipitation of 900–2800 mm and varying degrees of acid pollution. The catchments are developed on four different kinds of bedrock (andesite, granite, greywacke and schist) and the soils are mainly podzolic with some peaty gleys and brown forest soils.

Methods

So-called "long-term" weathering rates were calculated from chemical analyses of the soil horizons (< 2 mm) obtained by X-ray fluorescence spectrometry using the fused bead sample preparation method and interelement correction procedures of Norrish & Hutton (1969). Using the analyses, losses of base cations from the soil profiles were calculated from the amount of the base cations depleted relative to zirconium which is assumed to be a stable, immobile element (Bain et al. 1993). Initially, the losses were calculated for each horizon (using bulk density and thickness) and then the losses for all horizons in the profile were added together and divided by the age of the profile, assumed to be 10,000 years as all the soils are post-glacial in age, to give the average annual loss of each base cation. Details of the equations used in this calculation with an example are given in Bain et al. (1993). It is important to note that only soil profiles developed on uniform parent material can be included in the calculations by this method. Non-uniformity is evident as discontinuities in the profile, detected either in the field, or from the chemical and mineralogical analyses of the horizons.

Weathering rates were also calculated using the PROFILE model developed by Sverdrup & Warfvinge (1988) for this purpose and for calculating derived critical loads for soils and soil water. This multilayer steady-state model was the first to calculate weathering rates for soil profiles from independently measured soil properties such as mineralogy, surface area and bulk density for each horizon, and site measurements of precipitation, temperature and deposition.

Long-term weathering rates and those calculated from PROFILE were calculated for individual soil profiles. To obtain values for catchments, mean values were calculated for a number of soil profiles representative of the major soil groups in each catchment except for the two on greywacke which were calculated from one soil profile in each catchment.

So-called "current" weathering rates were calculated from input-output budgets in the catchments using analyses of weekly samples of bulk precipitation and streamwater taken over a period of two or three years. The amounts of calcium in the input were subtracted from those in the output, with a correction to make chloride conservative. This method is discussed in some detail in Hultberg (1985).

Results and discussion

The weathering rates for calcium calculated by all three methods for the eight catchments are listed in Table 1. Three main trends are very clear:

(1) the long-term rate is the lowest in every catchment;

(2) the PROFILE rate is always higher than the long-term rate;

(3) the current rate is the highest in every catchment, except for Halladale where it is the same as for PROFILE, and it is usually very much higher than both long-term and PROFILE rates.

In seven of these catchments, similar, but not identical, trends were noted by Bain & Langan (1995) for losses of total base cations (Ca+Mg+K+Na); the long-term rate was the lowest in five catchments, the PROFILE rate was always higher than the long-term rate, and the current rate was highest in the same five catchments as the long-term rate was the lowest. So the discrepancies noted by Bain & Langan (1995) between weathering rates for the sum of the base cations calculated from input-output budgets and those calculated from soil analyses are even greater when comparisons are made for calcium only.

Although the PROFILE rates are considerably higher than the long-term rates, they are of the same magnitude, but the current rates in four catchments (Cairnfore, Clauchrie, Glensaugh and Sourhope) are an order of magnitude higher than both long-term and PROFILE rates. From a similar comparison of long-term weathering rates and recent weathering rates based on input-output budgets in a granitic catchment in the Adirondacks, April et al. (1986) suggested that the three times higher current rate of weathering may reflect a recent adjustment for higher hydrogen ion fluxes due to acid deposition. Kirkwood & Nesbitt (1991) also postulated increased inputs of anthropogenic acids as a possible reason for present-day cationic fluxes being double those averaged over the age of soils in a catchment at Plastic Lake, Ontario. By the same reasoning, it would appear from Table 1 that all the Scottish catchments have become more acidic in recent times, with the possible exception of Halladale.

Comparisons of this nature, however, are complicated by the nature of the calculations by the three methods. The long-term and PROFILE rates are calculated from a few individual soil profiles which are intended to be representative of the whole catchment, but spatial variability is largely overlooked. The long-term rate calculation assumes the C horizon to be the unweathered parent material, yet corrosion features can be seen on oligoclase grains from the C horizon soils in the Mharcaidh catchment (Bain et al. 1994). Furthermore, the long-term rate is an average annual loss over 10,000 years and may not reflect the present-day rate of loss. It is quite likely, therefore, that the methods based on soil analyses, i.e. the long-term and PROFILE rates, underestimate the present-day loss of calcium.

Current weathering rates, on the other hand, are based on samples taken over a period of only 2–3 years which may not be representative of a longer period. They include calcium removed from the entire catchment including the bedrock and are influenced by the presence of weatherable minerals along hydrologic pathways, many of which occur beneath the soil. As Velbel (1993) has pointed out, vein or grain-boundary calcite may occur in rocks beneath soil profiles completely depleted in carbonate but such subsoil calcite could easily supply calcium to stream solute loads. Mass balance studies are limited in their ability to document the sources of leaching losses which may be derived from atmospheric inputs, mineral weathering reactions, or decreases in ecosystem pools, including biomass, and the soil cation exchange complex. Nevertheless, Velbel concluded that weathering rates determined from solute budgets are more relevant than those determined from soils in relation to understanding the effects of acid deposition on surface water quality in that the streams integrate better the processes in the whole catchments.

Current weathering rates include losses from exchangeable cation pools and Bailey et al. (1996) in a study of calcium inputs and transport in a base-poor forest ecosystem as interpreted by strontium isotopes, suggested that determination of weathering by a mass balance approach, assuming steady state ecosystem storage, sub-

Table 1: Rates of loss of calcium (meq m^{-2} a^{-1}) calculated by three methods (long-term, PROFILE and current).

Catchment	Bedrock	Long-term	PROFILE	Current
Cairnfore	Greywacke	1	12	138
Chon	Schist	2	13	23
Clauchrie	Greywacke	1	11	105
Glensaugh	Schist	2	13	112
Halladale	Granite	<1	8	8
Kelty	Schist	1	6	11
Mharcaidh	Granite	2	9	26
Sourhope	Andesite	1	19	374

stantially overestimates weathering inputs and may ignore ecologically significant losses of basic cations from available pools.

There does not appear to be any particular relationship between the rock type in each catchment and the discrepancy between long-term and current weathering rates. The content of calcium in greywacke, schist, granite and andesite varies in amount and is mostly present in plagioclase feldspars although small amounts are present in other silicate minerals such as hornblende and epidote. The weatherability of each rock type depends not only on mineralogy, but also on the texture of the rocks, including the presence of fractures and microcracks, and the ease with which percolating waters can gain access to the more weatherable phases. The discrepancies between rates of loss of calcium derived from soil data and those derived from input-output budgets is the result of the interplay of a number of factors and it is not clear to what extent the rock type influences the discrepancies.

The greatest discrepancy between current and long-term weathering rates in the eight catchments studied occurs at Sourhope where these losses are 374 and 1 meq m^{-2} a^{-1}, respectively. From a study of $^{87}Sr/^{86}Sr$ ratios in rainwater, streamwater and the soils in this catchment, Bain & Bacon (1994) found that a very low $^{87}Sr/^{86}Sr$ ratio in the streamwater seemed to indicate that the main source of strontium in the stream was due to weathering of plagioclase feldspar. However, losses of calcium from plagioclase in the soil are reflected in the long-term rate, so clearly the source of calcium in the stream cannot simply be from plagioclase in the soils and presumably is due to a mineral phase containing non-radiogenic strontium present in the bedrock. Detailed studies of calcium-bearing minerals in the soils and bedrock are required and these are on-going.

Conclusions

In eight catchments on four different rock types, the rates of loss of calcium calculated from input-output budgets are almost always higher than the rates of loss calculated from soil analyses, and in four instances are an order of magnitude higher. Although comparisons of the rates calculated by these methods are difficult because of differences in the assumptions inherent in the methods, the magnitudes of the discrepancies are such that they must indicate that these catchments have become acidified in recent times, and that some of the calcium in the streams originates from calcium-bearing minerals in the catchment outwith the soils.

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