Comments on the use of chemically based mixing models in glacier hydrology

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ABSTRACT. The assumptions involved in the use of chemically based mixing models for analysis of flow routing of meltwaters in glacierized basins are critically evaluated. The assumption that glacial drainage systems consist of only two primary flow components is arbitrary and must be supported by independent evidence. Recent studies of the processes by which meltwaters acquire solute indicate that the assumption that flow components have unique and constant chemical compositions is unlikely to be correct. Source-water composition and weathering potential will vary over the course of a melt season, and the extent of subglacial weathering is strongly dependent upon such factors as meltwater residence time and the availability of reactive sediment, both of which are known to vary on diurnal to seasonal time-scales. Mixing of flow components does not appear to be confined to the terminal regions of glaciers and is therefore unlikely to be conservative as assumed. A multi-parameter mixing model is applied to the analysis of data on the chemistry of waters sampled from boreholes drilled through Haut Glacier d'Arolla, Switzerland, to demonstrate the range of dissolved species for which the assumption of conservative mixing is violated. The consequences of this violation for quantitative hydrograph separation are shown to be highly significant. The utility of mixing models as a tool for the investigation of glacier hydrological systems is questionable and the results of previous studies are unreliable.

INTRODUCTION

A recurrent theme in research on glacier hydrology has been the use of measurements of meltwater quality to derive information about the character of subglacial and englacial drainage systems (Collins, 1978, 1979; Oerter and others, 1980; Collins and Young, 1981; Gurnell and Fenn, 1984; Sharp, 1991; Tranter and Raiswell, 1991; Lecce, 1993). One technique which has been widely adopted in these studies and used to make quantitative inferences about meltwater fluxes through the different elements of such drainage systems is the chemically based mixing model (Pinder and Jones, 1969). This technique is used to separate meltwater run-off hydrographs into components which allegedly arise from flow through two (or sometimes three) elements of the drainage system. The

technique makes a number of assumptions about the nature of englacial/subglacial drainage systems and the manner in which meltwaters acquire their solute load, most of which have not been tested in previous studies. Recent developments in our understanding of the nature and behaviour of glacier drainage systems (Nienow and others, in press), and of chemical weathering processes in glacial environments (Tranter and others, 1993), cast considerable doubt on the validity of these assumptions and thus on the application of the method. The purpose of this note is to draw attention to the nature of these assumptions, to present some of the data which challenge their validity and to examine their implications for quantitative hydrograph separation. It is prompted by a recent application of the mixing-model method (Lecce, 1993), which, like previous studies, draws conclusions

which we do not believe are sustainable in the light of the information presented.

ASSUMPTIONS OF CHEMICALLY BASED MIXING MODELS

Collins (1978, 1979) argued that a simple mixing model of the form:

$$Q_t C_t = Q_s C_s + Q_e C_e \qquad (1)$$

could be used to separate meltwater-discharge hydrographs into two flow components. Here Q refers to meltwater discharge and C to solute concentration. The subscripts t, s and e refer to the total flow, and to what Collins termed the "subglacial" and "englacial" components. Collins assumed that waters which pass more slowly through the system ("subglacial" waters) experience considerable enrichment as a result of contact with subglacial bedrock and finely comminuted rock debris. He also assumed that these two types of water mixed in a region close to the glacier snout, the *englacial* waters diluting the *subglacial* waters to produce bulk meltwaters with a chemical composition dependent upon the initial chemistries of the two components and their *mixing ratio* (the relative proportions of the two components in bulk waters). If the chemical composition of the components is known, the mixing-model equation can be rewritten to allow solution for the component discharges:

$$Q_s = [(C_t - C_e)/(C_s - C_e)] Q_t . \qquad (2)$$

Models of this form make a number of assumptions which we now examine.

Two drainage components

An immediate problem concerns the definition of the flow components. Collins envisaged two principal drainage routeways through a glacier — a system of major channels which allows rapid transit and isolates waters from potential solute sources, and a system which permits much slower transit and brings waters into contact with solute sources. The first he defined as the "englacial" component, even though it was said to drain via a system which includes "arterial conduits located at the bed" (Collins, 1979, p. 349), and the second as the "subglacial" component, which was said to drain via "channels which may be moraine-walled or cut in bedrock, and in which sediment transport occurs" (Collins, 1979, p. 349). This use of the terms "subglacial" and "englacial" to describe the flow components is misleading, since both can apparently drain through channels located at the glacier bed. The actual basis for distinguishing between the two components is the residence time of meltwaters at the glacier bed rather than their location or morphology. In this sense, it would seem more logical to differentiate the components using terms such as *delayed flow* and *quick flow* (cf. Tranter and others, 1993). Nevertheless, we retain Collins' terminology for the purposes of the present discussion.

Collins' definition of the hydrological pathways followed by the two components is vague, since ice-walled conduits at the glacier bed will presumably also have bedrock or morainic floors, and it is not clear why, given the definitions presented, the two pathways would result in systematic variations in residence time within the glacier. Equally, whilst it is clear that Collins envisaged the source of "englacial" waters to be surface melting, it is not clear what source he envisaged for "subglacial" waters. The source would presumably be surface melt, internal/subglacial melt or ground water. Which of these is actually the source has major implications for flux magnitudes, patterns of flux variation in time and component chemistries. A more rigorous definition of the morphology of the hydrological pathways followed by the two flow components is required if the results of mixing-model calculations are to be interpreted. Theoretical analyses of glacier hydrology now identify at least seven possible components to subglacial and englacial drainage systems. These include englacial conduits, subglacial water films (Weertman, 1972), R-channels incised upwards into the glacier sole (Röthlisberger, 1972), Nye channels incised into bedrock (Nye, 1973), linked-cavity systems (Walder, 1986), permeable subglacial sediments (Shoemaker, 1986) and broad canals incised into the surface of such sediments (Walder and Fowler, 1994). Given this diversity, it seems arbitrary and unreasonable simply to assume that the drainage system of a given glacier contains only two (or perhaps three) primary components. There is clearly a need for applications of the mixing-model technique to be supported by independent evidence (such as is provided by *intensive* dye-tracing or borehole-based studies) for the character of the subglacial drainage system.

Where multiple components do exist within a drainage system, it is important to understand how they are arranged in space and how they are interconnected. Failure of the drainage sytem to conform to the assumption that the hydrological pathways represented in the mixing model are arranged in such a way that mixing is confined to the terminal regions of the glacier has important hydrochemical implications. Where two distinct drainage pathways do exist, field evidence suggests that the slower one may be located up-glacier of the faster, so that "subglacial" waters actually pass along the same path as "englacial" waters in the lower glacier (Humphrey and others, 1986; Nienow and others, in press). If this is so, there would be considerable scope for continued chemical evolution of the combined waters after mixing. Such evolution would violate the assumption of conservative mixing (all solute transported by the bulk meltwaters is derived directly from the flow components) made by mixing models (see below).

Where mixing models have been applied to the interpretation of run-off data collected over whole melt seasons (Gurnell and Fenn, 1984), or large parts thereof, the use of a model with a single form is tantamount to assuming that the structure of the drainage system is constant over time. This assumption is directly contradicted by the results of dye-tracing studies which indicate significant changes in drainage-system structure over individual melt seasons (Willis and others, 1990; Hock and Hooke, 1993; Nienow, 1994). Since these structural changes are often manifested most clearly by changes in

meltwater residence time, they have profound implications for the processes and magnitude of solute acquisition by meltwaters, and thus for the assumption made in most mixing-model studies that component chemistries are unique and constant over time (see below).

Unique component chemistries

In most applications of the mixing model published to date (e.g. Collins, 1978, 1979; Gurnell and Fenn, 1984), it has been assumed that the chemical composition of the "subglacial" and "englacial" components is constant, and that variations in bulk meltwater chemistry reflect variations in the mixing ratio of the two components (an exception to this is the work of Tranter and Raiswell (1991)). Collins (1979) justified this assumption on the grounds that (a) the drainage pathways followed by "englacial" waters are essentially free of solute sources, and (b) that solute acquisition in the pathways followed by "subglacial" waters is sufficiently rapid to bring them to a uniform equilibrium concentration. Neither argument is convincing. Collins' "englacial" waters are derived largely from melting of surface snow and ice. It is well known that impurities held within a snowpack are not released in meltwater at a uniform concentration corresponding to their bulk concentration within the snow, but that they are released at significantly higher concentrations within the first meltwater produced (Johannessen and others, 1977). The chemistry of such waters will therefore vary over a melt season in response to this leaching effect. Seasonal changes in the acidity of source waters will also impact on their ability to acquire solute by weathering of subglacial sediment, as demonstrated by laboratory weathering experiments (Brown and others, in press).

Experimental studies of solute acquisition from glacial flour by dilute aqueous solutions (Tranter and others, 1989; Brown and others, in press) indicate that, although rates of acquisition decrease exponentially over time, they are nevertheless still significant after periods of time comparable with meltwater residence times in glaciers indicated by dye-tracing experiments (Collins, 1982; Burkimsher, 1983; Seaberg and others, 1988; Willis and others, 1990; Fountain, 1993; Hock and Hooke, 1993; Nienow, 1994). Thus, if meltwaters come into contact with suspended sediment or other rock material during their transit through a glacier, they are likely to experience significant enrichment in solutes. Since both residence time and suspended-sediment concentration vary with meltwater discharge (Burkimsher, 1983; Gurnell, 1987), the degree of enrichment is likely to vary over time, producing variations in meltwater chemistry which are not directly attributable to the mixing ratio (Brown and others, 1994). The kinetics of the weathering processes are such that the impact of such variations on solute acquisition will be greatest in major subglacial channels where significant suspended-sediment transport occurs. When dilute waters are placed in contact with suspended sediment, solute-acquisition rates are initially rapid but they decline exponentially over time (Brown and others, in press). Thus, a given change in water–sediment contact time will have maximum impact on solute acquisition when the average contact time is short. Dye-tracing studies indicate that this is usually the case in major subglacial channels.

The consequence of assuming constant-component chemistries, when these are in fact variable, is that variations in component chemistry will be expressed as variations in the mixing ratio in the mixing-model results. For instance, increased solute concentrations in bulk waters, such as occur under recession-flow conditions, would normally be interpreted as resulting from an increased proportion of "subglacial" waters in bulk run-off. In reality, they may be at least partly attributable to "subglacial" waters becoming more concentrated over time as discharges decrease and residence times consequently increase. If such artefacts, which may involve both the magnitude of the component discharges and their pattern of variation over time, are to be avoided, it is necessary to determine accurately the chemistries of the components and their temporal variability. Tranter and Raiswell (1991) suggested a method for doing this using measurements of the properties of bulk meltwaters, but direct measurements in the subglacial environment would be preferable.

A further problem with the assumption of constant meltwater chemistry relates to the choice of appropriate concentration values for each component. Various suggestions have been made concerning which values should be used. For the "englacial" component, these include the concentration of a species in supraglacial waters and the minimum concentration in bulk meltwaters recorded during a melt season. For the "subglacial" component, they include the concentration in ground-water springs, winter base flow or summer recession flows (see Fenn (1987) for a review). Each of these possibilities will result in a different value for the component chemistry, which will affect both the magnitude and temporal pattern of flow calculated for each component (Brown and Tranter, 1990). Higher values of C_s and/or C_e will reduce Q_s, though the effect of varying C_e is less marked because C_e occurs on both sides of Equation (2). Choice of an appropriate value for C_e is, however, critical at times when Q_e comprises the majority of bulk meltwaters. We have particular concerns about the use of maximum and minimum solute concentrations in bulk run-off to characterize the compositions of the flow components because, during the summer of 1993, we regularly sampled waters from the base of boreholes at Haut Glacier d'Arolla, Switzerland, which were up to three times more concentrated than any which drained from the glacier during that melt season.

Conservative mixing

As defined by Equation (1), the mixing model assumes that the mass of solutes transported by the two flow components remains unchanged after they mix. Collins (1979) defended this assumption on the grounds that sedimentary particles in suspension retain significant quantities of ions adsorbed to their surfaces after they exit from the glacier portal. This is said to imply that solution and surface exchange between suspended load and meltwaters play only a minor role in modifying the composition of meltwaters once flow is in large channels. This conclusion is, however, contradicted by the fact that

Table 1. *Chemical composition (mean and standard error of the mean) of the three water types sampled from boreholes at Haut Glacier d'Arolla, Switzerland, in 1992. Concentrations of cations and anions are measured in micro-equivalents per litre. EC_0 is the electrical conductivity of the waters at $0°C$ ($\mu S\,cm^{-1}$). SI_{cc} is the saturation index for calcite and $p(CO_2)$ is the partial pressure of carbon dioxide (atmospheres) with which the water appears to be in equilibrium. The latter two parameters are calculated from group mean data rather than individual sample analyses*

Species	Mode 1		Mode 2		Mode 3	
	Mean	S.E.	Mean	S.E.	Mean	S.E.
Ca^{2+}	10	4.3	183	16.4	815	10.4
Mg^{2+}	6	3.2	17	1.4	90	1.4
Na^+	4	1.1	10	2.0	15	0.2
K^+	2	0.5	13	3.7	16	0.2
HCO_3^-	9	17.1	166	26.7	596	10.0
Cl^-	4	1.0	4	0.7	5	0.3
NO_3^-	5	4.4	6	3.0	27	0.2
SO_4^{2-}	6	3.2	37	5.1	312	4.8
pH	6.4	0.1	8.5	0.6	7.5	0.1
EC_0	1.8	0.3	10.9	0.8	45.5	0.2
SI_{cc}	−6.22		−1.62		−1.47	
$-\log p$ (CO_2)	2.66		3.52		1.96	

bulk meltwaters are commonly undersaturated with respect to reactive minerals such as calcite (Raiswell, 1984; Brown and others, 1994), as are waters sampled at the glacier bed from boreholes (Table 1). In addition, laboratory weathering experiments involving suspended sediment which has passed through the drainage system of Haut Glacier d'Arolla (Brown and others, in press) show significant and continuing solute acquisition by deionized water placed in contact with sediment concentrations comparable to those recorded in melt streams over at least the first 3 h of contact (Fig. 1). Other experiments, which simulate the mixing of dilute and concentrated meltwaters, also reveal significant solute acquisition from suspended sediment after mixing (Tranter and others, 1989). If, as suggested earlier, mixing is not confined to the extreme terminal regions of the glacier, it is extremely unlikely to be conservative. Brown and others (in press) estimated that as much as 70% of the Ca^{2+} load transported by bulk meltwaters draining from Haut Glacier d'Arolla in August 1990 may have been acquired by post-mixing reactions.

To illustrate the significance of this point, we present the results of analyses of waters from 22 boreholes drilled through Haut Glacier d'Arolla in August–September 1992. Over 3000 measurements of electrical conductivity (EC) were made on these waters, and the resulting frequency distribution shows three clear modes. Samples of each water type were analyzed for their pH and major cation and anion composition (Table 1). The conven-

tional mixing-model approach to glacier hydrology would make the assumption that waters of intermediate composition (mode 2) were produced by conservative mixing of more dilute (mode 1) and more concentrated (mode 3) waters. To determine whether our chemical data are consistent with this assumption, we used the multivariate mixing model SOLMINEQ88 (Kharaka and Barnes, 1973) to determine whether or not mixing was conservative for the full range of dissolved species analyzed. A mixture of nine parts mode 1 and one part mode 3 waters would have concentrations of Mg^{2+}, Cl^-, NO_3^- and SO_4^{2-} which are comparable with those of mode 2 waters. However, such a mixture would contain significantly less Ca^{2+}, K^+ and HCO_3^-, and have a lower pH, EC and calcite-saturation index, and higher $p(CO_2)$ than mode 2 waters. To reproduce these properties of mode 2 waters, it was necessary to simulate the dissolution of an additional $5 \times 10^{-5}\,mol\,l^{-1}$ of calcite and $8 \times 10^{-6}\,mol\,l^{-1}$ of potash feldspar in the mixture. This clearly indicates that, for many dissolved species, it would be incorrect to assume that mixing of dilute and
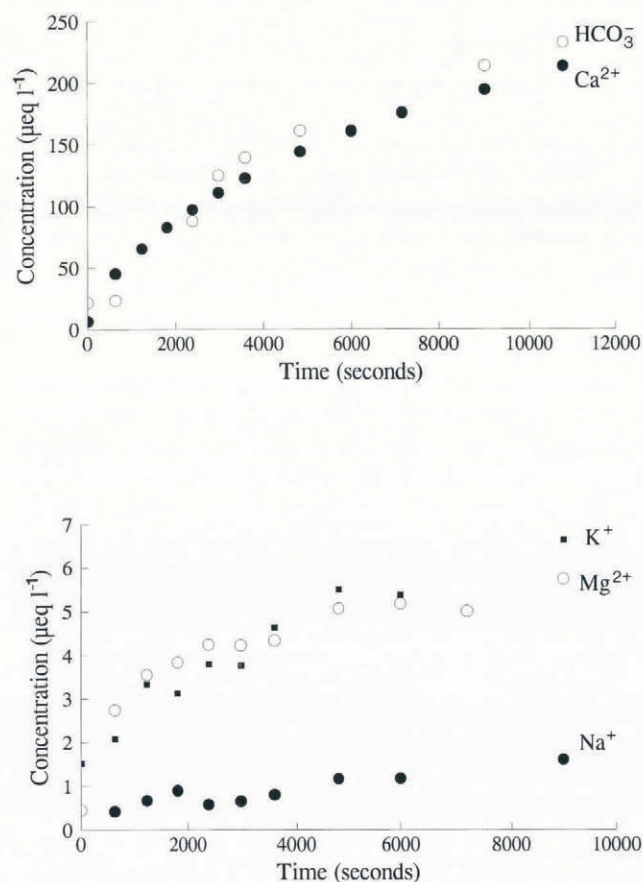

Fig. 1. *(a) Concentrations of Ca^{2+} and HCO_3^- as a function of time in a laboratory dissolution experiment using a water : rock ratio of $4\,g\,l^{-1}$. (b) Concentrations of Mg^{2+}, Na^+ and K^+ as a function of time in a laboratory dissolution experiment using a water : rock ratio of $4\,g\,l^{-1}$. The sediment used in the experiment was collected from the margins of the main meltwater stream draining from Haut Glacier d'Arolla; the solvent was deionized water left in free contact with the atmosphere and stirred continuously for the duration of the experiment.*

concentrated waters is conservative. It may also be the case that mode 2 waters are not, in any event, produced by mixing of mode 1 and mode 3 waters, but that the three water types evolve independently along different flow paths with different residence times.

Nevertheless, it is useful for our present purposes to try to quantify the significance of violation of the assumption of conservative mixing. If we take the mean EC of mode 1 (C_e) and mode 3 (C_s) waters as a measure of their solute content (Table 1), and use Equation (1) to calculate the EC of mode 2 waters (C_t), we find that a 9:1 mixture of mode 1 (Q_e) and mode 3 (Q_s) waters would give $C_t = 6.3 \mu S\,cm^{-1}$. Mode 2 waters have a measured mean EC of $10.85 \mu S\,cm^{-1}$. If we then use this measured value as an estimate of C_t, and take the mean values for mode 1 and mode 3 waters as estimates of C_e and C_s, we can use Equation (2) to estimate Q_s. We obtain a value of 2.1 instead of the true value of 1. The results of similar calculations performed using concentrations of other dissolved species are presented in Table 2. Estimates of Q_s range from 1 (for SO_4^{2-}) to 7.9 (K^+), when the true value (assuming conservative mixing for SO_4^{2-}) is 1. Thus, even if one accepts the validity of the basic mixing-model approach to glacier hydrology, hydrograph separations which are based upon dissolved species for which mixing is non-conservative may be very seriously in error.

Most previous mixing-model studies have based separations on the EC of meltwaters (e.g. Collins, 1978, 1979; Gurnell and Fenn, 1984). The results presented above suggest that EC is not a conservative property of glacial meltwaters and that this practice is therefore unreliable. Better estimates are more likely to be obtained if separations are based upon measurements of the concentration of conservative species such as Mg^{2+}, SO_4^{2-}, Cl^- and NO_3^-. Of these species, Mg^{2+} and SO_4^{2-} are likely to be more useful than Cl^- and NO_3^- because the latter two species are normally derived primarily from the snowpack and will be preferentially leached from the catchment in the early part of the melt season (Tranter and others, 1993). This conclusion is consistent with the argument put forward by Tranter and Raiswell (1991) that SO_4^{2-} may be the best species to use for mixing-model calculations.

SUMMARY

The application of mixing models to the investigation of flow routing of meltwaters in glaciers demands:

(a) Independent confirmation that the number of flow components included in the mixing model is appropriate for the glacier in question.

(b) More rigorous definition of the hydrological pathways associated with each flow component, so that interpretation of mixing-model results can be facilitated.

(c) Confirmation that the flow components identified have unique chemistries and selection of appropriate values for these. If component chemistries are not unique, it is necessary to evaluate how they vary over time.

(d) Determination of an appropriate solute species on which to base hydrograph separations in order to minimize the impact of violating the assumption of conservative mixing. The commonly used parameter, EC, is not conservative and is therefore inappropriate for this purpose.

Table 2. Results of mixing-model calculations performed using water compositions equivalent to the mean composition of each of the three water types sampled from boreholes at Haut Glacier d'Arolla in 1992. Mode 2 concentration refers to the observed solute concentration ($\mu eq\,l^{-1}$) in waters of intermediate composition believed to form by mixing of dilute (mode 1) and concentrated (mode 3) waters with additional solute furnished by post-mixing reaction. Predicted C_t is the expected concentration of intermediate waters formed by mixing nine parts mode 1 with one part mode 3 waters with no post-mixing reaction. The percentage of solute derived by post-mixing reaction is given by: ((Mode 2 concentration − Predicted C_t) / Mode 2 concentration) × 100. Predicted Q_s refers to the estimate of Q_s that would be obtained using Equation (2) if $Q_t = 10$ and the measured mean compositions of the three borehole-water types given in Table 1 are used as estimates of C_e, C_t and C_s

Species	Mode 2 concentration	Predicted C_t	% solute from post-mixing reactions	Predicted Q_s
Ca^{2+}	183	90	51	2.1
Mg^{2+}	17	14	13	1.3
Na^+	10	5	51	5.5
K^+	13	3	73	7.9
HCO_3^-	166	68	59	2.7
Cl^-	4	4	0	0.0
NO_3^-	6	7	14	0.5
SO_4^{2-}	37	37	0	1.0
EC	11	6		2.1

At present, it is not clear that these requirements can actually be met and we therefore advocate restraint in the application of mixing models in glacier hydrology. We also believe that conclusions drawn from past applications are unreliable and that they do not provide a satisfactory basis for discussion of the functioning of glacier drainage systems.

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