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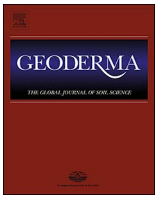

Comparison of measured (XRPD) and modeled (A2M) soil mineralogies: A study of some Swedish forest soils in the context of weathering rate predictions

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ABSTRACT

Quantitative soil mineralogy has been identified as a key factor influencing PROFILE weathering estimates, and is often calculated with normative methods, such as the “Analysis to Mineralogy” (‘A2M’) model. In Sweden and other countries, there is a large request for accurate base cation weathering estimates in order to establish how sustainable harvest of biomass should be performed in the future. However, there is a lack of knowledge around the accuracy of the arithmetic mean output of A2M estimates, the most common A2M solution used in weathering studies. To our knowledge, a thorough investigation of how A2M input data affect the arithmetic mean output (center of gravity of the A2M solution space) is missing.

In this study, the indirect geochemical normative method (A2M) was compared with a direct x-ray powder diffraction method (XRPD) to quantify soil mineralogy at two sites and 8 soil profiles, at a 10 cm depth interval. We explored the hypothesis that normative calculations performed with A2M produce an output in closer agreement with the mineralogy obtained from XRPD, if site specific mineralogical input data are used rather than regional data. Site-specific mineralogical input data consisted of mineral stoichiometry data measured by electron microprobe analysis (EMPA) and mineral identity determined by XRPD, whereas regional mineral input data were based on previously reported data on mineral stoichiometry and mineral identity, derived from three geological regions in Sweden.

The results from this comparison showed that the site-specific approach yielded relatively low average biases and root mean square errors (RMSE) for most minerals, with the exception of quartz (Average bias of − 4.8 wt%, RMSE of 5.3 wt%) at the Asa site. The regional approach yielded deviating results for K-feldspar and dioctahedral mica, with high average biases and RMSE for dioctahedral mica (Asa: 7.8 wt%, 9.0 wt%; Flakaliden: 12.8 wt%, 15.5 wt%) and for K-feldspar (Asa: − 5.2 wt%, 6.1 wt%; Flakaliden: − 5.6 wt%, 6.7 wt%). The results from this study were supported by a close agreement between measured geochemistry and normalized geochemistry derived from a back calculation of the XRPD mineralogy (i.e. mineral budgeting).

In conclusion, our findings suggest that A2M results in combination with site-specific mineralogical input data are improved independent of study site and soil profile. However, for future weathering studies it might be beneficial to find constraints of how to select a solution from the entire A2M solution space which is in better agreement with the XRPD mineralogy.

1. Introduction

Minerals are fundamental components of soils, and chemical weathering of minerals is the ultimate source of most nutrients in soils. Consequently, the accurate assessment of soil mineralogy is central to the estimation and modelling of weathering responses in soils (Hodson et al., 1996; Holmqvist et al., 2003; Jönsson et al., 1995). In particular, there is an increasing need for accurate estimates of weathering rates to

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assess the sustainability of increased biomass harvest in managed forests. For example, harvesting of above-ground logging residues (slash) and stumps for energy production means a higher export of base cations in harvested biomass from forest sites than stem-only harvest, causing soil acidification and depletions of base cations in the soil (e.g. Aherne et al., 2008, 2012; Löfgren et al., 2017; Thiffault et al., 2011). The capacity of weathering to compensate for losses of mineral nutrients and to buffer the concomitant soil acidification is of great importance for the long-term sustainability of these systems. However, weathering estimates are burdened with large uncertainties (Futter et al., 2012; Hodson et al., 1996).

The PROFILE model (Sverdrup and Warfvinge, 1993, 1995; Warfvinge and Sverdrup, 1995) is one model that has been widely used to assess weathering. Amongst other inputs, it requires information on the composition and the content of the various different minerals in the soil. Indeed, previous applications of the PROFILE model in Europe or Sweden have often been restricted by the unavailability of mineralogical data for single study sites (Koseva et al., 2010).

The accurate determination of the mineralogical composition of a soil sample is not a trivial matter (Amonette and Zelazny, 1994). It is obvious, however, that errors and uncertainties in determining the mineralogical composition of a soil sample will necessarily lead to errors and uncertainties in estimating the ability of weathering to mitigate changes in soil. For instance, small errors in the amount of epidote, hornblende and plagioclase minerals can potentially affect calculated base cation release rates significantly in applications of the PROFILE model (Sverdrup and Warfvinge, 1993).

There are a variety of direct methods for the determination of the quantitative mineralogical composition of samples such as soils, including thermal analysis, X-ray powder diffraction (XRPD) and optical and magnetic methods (Amonette and Zelazny, 1994; Zevin and Kimmel, 1995). Modern methods of direct quantitative mineralogical analysis by XRPD are capable of a level of accuracy that is appropriate and useful for various quantitative applications in soil studies (Hillier, 1999, 2002; Omotoso et al., 2006). In particular full pattern fitting methods that use prior measured XRPD patterns, or calculated XRPD patterns, to fit the measured diffraction pattern, have matured as a powerful approach that can be readily applied to soils and other clay bearing samples (Chipera and Bish, 2002, 2013; Eberl, 2003). In blind round robin tests, results may be compared to the 'true' mineralogical compositions in well-defined samples in order to evaluate method uncertainty (Kleeberg, 2005; McCarty, 2002; Omotoso et al., 2006). When applied to real samples, where the true composition is unknown, geochemical cross validation (e.g. the mineralogical budgeting approach (Andrist-Rangel et al., 2006)), is about the only approach that may be used to make some independent assessment of the likely accuracy achieved.

There are also so called normative methods of determining soil mineralogy, based on the bulk geochemical composition of a soil (Cohen and Ward, 1991; Paktunc, 1998, 2001; Posch and Kurz, 2007; Räisänen et al., 1995). The main advantage of these indirect methods is that accurate chemical analysis is a relatively straightforward routine technique that can be determined rapidly on large numbers of samples. However, normative methods based on geochemical analyses also require information on both the available minerals in the soil and their stoichiometry, i.e. chemical compositions. The accuracy of such information will have a significant impact on the certainty in normative mineralogy determination. One such normative method, the "Analysis to Mineralogy" ('A2M') model of Posch and Kurz (2007) has been widely used to estimate soil mineralogical compositions across sites and regions for use as input to weathering models in Europe, Canada and the U.S. (Akselsson et al., 2007; Koseva et al., 2010; Phillips and Watmough, 2012; Stendahl et al., 2013; Watmough et al., 2014; Yu et al., 2016). Yet, there are few examples where the accuracy of these mineralogical data is discussed or evaluated (Akselsson et al., 2006; Posch and Kurz, 2007; Warfvinge and Sverdrup, 1995), despite the fact that it may have obvious consequences for uncertainty of weathering estimates. For a soil sample with known total elemental composition and a pre-defined list of possible minerals along with their known or assumed stoichiometry, A2M calculates a range of possible mineralogical compositions for the soil sample. The 'arithmetic mean' of all extreme mineral compositions (i.e. the center of gravity of the A2M solution space) that is calculated by A2M for each sample has often been used as input for weathering calculations, although as emphasized by Posch and Kurz (2007) all solutions of the A2M model are equally probable. One example of how a normative method for determination of mineralogy at the local scale was combined with the available mineralogy at the regional scale was demonstrated by Warfvinge and Sverdrup (1995). They determined weathering rates on a national scale in Sweden with PROFILE applying the so called 'Bern' model (Akselsson et al., 2006; Kurz, 1998), a predecessor of A2M. To define available mineralogy, Swedish soils were classified into 4 'norm' mineralogical provinces (Warfvinge and Sverdrup, 1995). Soil mineralogy at the local scale was determined as output from the normative model for samples in any of the four provinces based on the geochemical analysis of the local soil sample, a defined list of minerals for that province and a corresponding province specific list of the chemical compositions of each mineral, as input to the normative model. The province specific lists of minerals and the judgements with respect to the compositions of the different minerals were based on a synthesis of expert knowledge.

Similar to this, a limited setup of mineral stoichiometries are typically assumed in recent applications of A2M in weathering studies as input to the PROFILE model (Johnson et al., 2015; Phillips and Watmough, 2012; Stendahl et al., 2013; Watmough et al., 2014), although many minerals show extensive variability in their chemical composition (e.g. > 80 individual mineral species have been identified within the amphibole group). It can also be assumed that the composition of some minerals belonging to mineral groups, e.g. 'plagioclase feldspars', that exhibit extensive solid solution will vary between soils derived from different parent materials. Thus, it remains largely unknown as to whether or not using methods like microprobe analysis (e.g. electron microprobe methods (Reed, 2005)), or other methods to constrain mineralogical compositions, may improve the accuracy of normative A2M mineralogy.

In this study, we compared mineralogical compositions of soils determined directly using a quantitative mineralogical method (XRPD) with mineralogical compositions determined using an indirect geochemical normative method (A2M). Samples for this study were collected from podzolised till soils from 8 soil profiles at two forest sites in northern and southern Sweden, respectively, where further understanding of the ability of weathering to supply nutrients is required.

The primary objective of this study was to evaluate the performance of the A2M model in producing accurate mineralogy from its arithmetic mean solutions based on the use of regional mineral input data, as well as site specific data, in comparison to XRPD determined mineralogy as the reference. It was hypothesized that normative calculations performed with A2M produce an output in closer agreement with the mineralogy obtained from XRPD, if site specific mineralogical data are used rather than regional data.

In order to validate the use of the XRPD analyses as a reference to the normative method, a mineralogical budgeting approach (Andrist-Rangel et al., 2006) was applied to test if the XRPD determined mineralogy, in combination with mineral compositions, correctly predicted the measured bulk geochemistry of the soil samples.

2. Materials and methods

2.1. Study sites

Soil samples from two forest sites with Norway spruce were selected for the study, Asa in southern and Flakaliden in northern Sweden (Supplementary Table 1). The sites have been used for long-term field