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A water-leach procedure for estimating bioaccessibility of elements in soils from transects across the United States and Canada

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ABSTRACT

An objective of the North American Soil Geochemical Landscapes Project is to provide relevant data concerning bioaccessible concentrations of elements in soil to government and other institutions undertaking environmental studies. A protocol was developed that employs a 1-g soil sample agitated overnight with 40 mL of reverse-osmosis de-ionized water for 20 h, and determination of 63 elements following three steps of centrifugation by inductively coupled plasma–atomic emission spectrometry and inductively coupled plasma–mass spectrometry the following day. Statistical summaries are presented for those 48 elements (Ag, Al, As, B, Ba, Be, Br, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Ho, I, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Pr, Rb, Re, S, Sb, Si, Sm, Sn, Sr, Tb, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr, and pH) for which <20% of their data were reported as below the detection limit. The resulting data set contains analyses for 161 A-horizon soils collected along two transects, one along the 38th parallel across the USA and the other from northern Manitoba to the USA–Mexico border. The spatial distribution of three selected elements (Ca, Cu, and Pb) along the two transects is discussed in this paper both as absolute amounts liberated by the leach and expressed as a percentage of the total, or near-total, amounts determined for the elements. The Ca data reflect broad trends in soil parent materials, their weathering, and subsequent soil development. Calcium concentrations are generally found to be lower in the older soils of the eastern USA. The Cu data are higher in the eastern half of the USA, correlating with soil organic C, with which it is sequestered. The Pb data exhibit little regional variability due to natural sources, but are influenced by anthropogenic sources. Based on the Pb results, the percentage water-extractable data demonstrate promise as a tool for identifying anthropogenic components. The soil–water partition (distribution) coefficients, K_ds (L/kg), were determined and their relevance to estimating bioaccessible amounts of elements to soil fauna and flora is discussed. Finally, a possible link between W concentrations in human urine and water-extractable W levels in Nevada soils is discussed.

1. Introduction

Traditionally, regional-, national-, and international-scale geochemical surveys involving soils or stream sediments as sample media have been undertaken using analytical methods yielding total, near-total, or total recoverable concentrations of the elements analysed (Webb et al., 1978; Shacklette and Boerngen, 1984; McGrath and Loveland, 1992; Salminen et al., 2005; Xie et al., 2008). Recommendations for global-scale geochemical mapping (Darnley et al., 1995) also involve determinations of the total element content of the sample media. However, these procedures overestimate the amount of an element that might be easily accessible via solubilization to fauna or flora supported by the medium analysed. The issue of bioaccessibility is of increasing importance as data from regional-, national-, and international-scale geochemical surveys are being more widely used to support environmental and human health exposure and risk assessments, and the development of risk management strategies (Amini et al., 2005; Rapant et al., 2008).

In 2004, the US Geological Survey (USGS), the Geological Survey of Canada (GSC), and the Mexican Geological Survey initiated pilot studies in preparation for the soil geochemical survey of North America (the North American Soil Geochemical Landscapes Project) (Smith et al., 2009). The purpose of the continental-scale project is to establish baseline levels for the geochemistry of North American soils to support a variety of environmental risk assessment and management tasks being undertaken by government and other organizations. A workshop in 2003 was convened with the purpose of recommending sampling and analytical protocols for the North American project (USGS, 2003). In addition to total analyses, the workshop participants recognized the importance of estimating the bioaccessible fraction of elements in soil and recommended that one or more methods should be tested during the pilot phase of the project. In light of the presence of a wide variety of possible extractions to estimate the bioaccessible amounts of the elements in soils, with varying applicability to different soil

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types and environmental conditions, the consensus was to develop a simple water-leach as one of these methods. Another method recommended for testing involves an *in vitro* extraction using a simulated human gastric fluid and is discussed by Morman et al. (2009).

The pilot phase of the project consisted, in part, of sampling soils along two transects across the USA and Canada (Smith et al., 2009). A north-to-south transect extended from northern Manitoba to the US–Mexico border near El Paso, Texas. A west-to-east transect followed the 38th parallel from just north of San Francisco, California to the Virginia shore. A- and C-horizon soils and a surficial sample from a depth of 0–5 cm were collected at approximately 40-km intervals from 220 sites along these transects. Three bulk A-horizon soils from the transect field work were used to develop the water-leach protocol that was then applied to all the soil A-horizon transect samples.

This report describes the development work that led to the selection of a water-leach protocol to determine the amount of elements that may be in bioaccessible, i.e., easily leachable, forms to biota. The estimation of bioaccessibility, a laboratory chemical procedure, attempts to estimate the amount of an element that is available to cross an organism's cellular membrane from the environment, if the organism has access to the element (Semple et al., 2004). Traditional "near-total" hot acid extractions, by releasing metals strongly bound to soil minerals and organic matter, and "total" analytical methods, such as instrumental neutron activation analysis, overestimate the amount of elements in the soil that could cause a biological effect. Therefore, weaker extractions are needed to estimate bioaccessible amounts of elements in soils. Such knowledge is essential for properly informing risk assessments, and to assist in planning risk management, and remediation activities. In soil science, ecotoxicological and site remediation studies, a soil–water partition or distribution coefficient (K_d) is often used to model the amount of a trace element that may partition into soil pore water and to estimate bioaccessible amounts (Lee et al., 1996; Janssen et al., 1997; Sauvé et al., 2000). The results of applying the selected protocol to the A-horizon soils from the two continental-scale transects are described and discussed, together with the estimation of K_d values.

2. Development of the water-leach procedure

Leaching with water, as distinct from other weak partial extractions, ensures the pH of the extraction is controlled to a large degree by the sample itself and results should reflect that portion of an element most likely to be mobile under ambient conditions. A leach formula approximating rainwater chemistry was not pursued because this composition varies significantly with location (e.g., high salt content in coastal regions, 'acidified-rain' in areas of high emissions from industry) and with climate and season. Furthermore, addition of ions such as Ca^{2+}, K^+, Na^+, Mg^{2+}, NO_3^-, NH_4^+, PO_4^{3-}, and SO_4^{2-} would preclude study of their extraction behaviour.

A sample weight to extractant ratio of 1 g soil per 40 mL extractant was selected, based on previous research (e.g., Hall et al., 1996a,b,c, 1998), as being optimum. Less volume of extractant per g of soil tends to create a less efficient extraction, and a larger volume of extractant impairs detection limits. Three bulk A-horizon soil samples selected by the USGS (30-2d1-A, 45-4d2-A, 46-2d1-2, referred to as 30, 45, and 46 in subsequent tables and figures) from the 2004 transect study and three GSC control samples (CR-Ap, CR-BR, and CR-MO7) were used to design and evaluate the leach (Table 1). These samples represent both glaciated and non-glaciated terrains east of the Rocky Mountains, and were derived from rocks ranging in age from Precambrian to Cretaceous. Both the effect of exposure time to the leach fluid and the number of centrifuging ± filtering steps involved were studied. Three protocols were tested, each using three different times of extraction (60, 240, and 1200 min). The 'basic' leach protocol, identified as 'CCC', is as follows:

1. Weigh out 1.000 g of each sample into new pre-cleaned (rinsed with reverse osmosis-deionised water, [RO-DI H_2O]) 50-mL polypropylene (PP) centrifuge tubes;
2. Add 40 mL of RO-DI H_2O to each sample and cap tightly. Shake by hand to suspend;
3. Shake samples horizontally for 60, 240, and 1200 min on a mechanical shaker @ 160 shakes/min;
4. Centrifuge samples for 10 min at a Relative Centrifugal Force (RCF) of 3230;
5. Decant supernatant into a new pre-cleaned 50-mL PP tube;
6. Decant an aliquot of ca. 5 mL that will be used for Br and I dilutions and pH;
7. Re-centrifuge the supernatant for 20 min at a RCF of 3230;
8. Dilute the sample twofold with 2% HNO_3 into a 15-mL PP centrifuge tube, mix by vortexing, and centrifuge immediately for 20 min at a RCF of 3610; and
9. Analyse by inductively coupled plasma–atomic emission spectrometry (ICP–AES) and inductively coupled plasma–mass spectrometry (ICP–MS) the same day.

Quality control of the experiments was monitored by the inclusion of blanks and standard solutions. There are no Standard Reference Materials (SRMs) for water-leaches of solid samples, so it was not possible to monitor the accuracy of such extractions.

2.1. Centrifuging and filtration steps to separate particulate and colloidal matter

Two variants on the CCC procedure were investigated to study the role of colloids in influencing the amounts of elements determined in the leach solutions. Firstly, following Step 7, the leach solution was filtered at 0.45 μm using a Sterivex® syringe capsule with Durapore membrane (Millipore® part number SVHV010RS). The filtrate was acidified by diluting twofold with 2% HNO_3 and analysed without a third centrifuging; this procedure was identified as 'CCF'. Secondly, commencing with the CCF protocol, a third centrifuging was carried out after acidification at a RCF of 3610 for 20 min; this procedure was identified as 'CCFC'. Each of these three procedures was applied to the six selected samples in triplicate and for each of the leaching times of 60, 240, and 1200 min. For the development of this component of the water-leach, only ICP–AES determinations were made for the following elements: Al, As, Ba, B, Be, Ca, Cd, Co, Cr, Cu, Fe, K, La, Mg, Mn, Na, Ni, P, Pb, S, Sb, Sc, Se, Si, Sr, Ti, V, Y, and Zn.

Results of this test for Ca, Na, and S (selected as they exhibit different characteristic behaviours) in four samples (30, 45, 46, and CR-Ap) are presented in Table 2. The concentration units in this table, and in all subsequent Tables and Figures, are reported as ppm (mg/kg) or ppb (μg/kg) of the elements in the solid sample. The immediate conclusion is that the reproducibility for each of these procedures for each time-sample combination is excellent, regardless of the fact that this is a weak partial extraction and the transect samples had been sieved to <2-mm only (CR-Ap had been further comminuted to <100 μm). Furthermore, there is no significant difference in results amongst the three procedures for any of the four (or six, others not shown) samples. There is little or no change in amounts extracted with time (60–1200 min, 1–20 h) for Na and S for all four. This is also true for Ca in samples 45 and 46, but there is a significant increase in Ca extracted with time for sample 30 (ca. 90 at 1 h to 200 ppm at 20 h) and CR-Ap (ca. 120 ppm at 1 h to 180 ppm at 20 h). Samples CR-BR and CR-MO7