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Comparing results from two continental geochemical surveys to world soil composition and deriving Predicted Empirical Global Soil (PEGS2) reference values

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ABSTRACT

Analytical data for 10 major oxides (Al_2O_3, CaO, Fe_2O_3, K_2O, MgO, MnO, Na_2O, P_2O_5, SiO_2 and TiO_2), 16 total trace elements (As, Ba, Ce, Co, Cr, Ga, Nb, Ni, Pb, Rb, Sr, Th, V, Y, Zn and Zr), 14 aqua regia extracted elements (Ag, As, Bi, Cd, Ce, Co, Cs, Cu, Fe, La, Li, Mn, Mo and Pb), Loss On Ignition (LOI) and pH from 3526 soil samples from two continents (Australia and Europe) are presented and compared to (1) the composition of the upper continental crust, (2) published world soil average values, and (3) data from other continental-scale soil surveys. It can be demonstrated that average upper continental crust values do not provide reliable estimates for natural concentrations of elements in soils. For many elements there exist substantial differences between published world soil averages and the median concentrations observed on two continents. Direct comparison with other continental datasets is hampered by the fact that often mean, instead of the statistically more robust median, is reported. Using a database of the worldwide distribution of lithological units, it can be demonstrated that lithology is a poor predictor of soil chemistry. Climate-related processes such as glaciation and weathering are strong modifiers of the geochemical signature inherited from bedrock during pedogenesis. To overcome existing shortcomings of predicted global or world soil geochemical reference values, we propose Preliminary Empirical Global Soil reference values based on analytical results of a representative number of soil samples from two continents (PEGS2).

1. Introduction

The Earth's surface is the interface between the geosphere, pedosphere, biosphere, hydrosphere and atmosphere, and supports human, animal and plant life. This “Critical Zone” hosts a multitude of physical, chemical and biological processes active over a range of spatial and temporal scales; these impact mass and energy exchanges governing processes as varied and crucial as soil formation, plant growth, water storage, nutrients cycling, metal and radionuclide transport, etc. (Brantley et al., 2007). This interface is under growing stress as the world's population continues to grow and with it the demand for food, water, energy and raw materials. Therefore, improving our understanding of the chemical composition and variability of soils at the continental, and ultimately global, scale is both important and pressing.

Many researchers have attempted to estimate the average chemical composition and natural variation of element concentrations in “world soils” (e.g., Bowen, 1979; Kabata-Pendias, 2001; Kabata-Pendias and Pendias, 1984; Koljonen, 1992; Rauch, 2011; Vinogradov, 1954). The values provided are based on data from existing soil surveys in different parts of the world often combined with estimates about the geochemical composition of the Earth's crust. In this approach, the empirical data usually come from surveys covering relatively small areas and with rather few samples (Bowen, 1979;

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Kabata-Pendias, 2001; Vinogradov, 1954). It is debatable how representative these values are of real soils from large and varied regions, whole continents, or indeed all continents. In addition, the samples behind the estimates often were analysed at different times, in different laboratories and using different analytical techniques, and are thus scarcely comparable.

Though this approach may still be useful to obtain reasonable estimates of the total concentrations of *major* elements, it is questionable whether it provides reliable values for *trace* elements. Furthermore, in environmental sciences it is not always realised that the average world soil or continental crust values provided in the literature are based on *total* concentrations, while soil guidance values or action levels are generally defined for element concentrations in *aqua regia extractions* (ISO, 1995; USEPA, 1996). For instance aqua regia extraction is widely used and is recommended for the analysis of solid materials in Europe (e.g., BBodSchV, 1999; Hjelmar and Holm, 1999; Langenkamp et al., 2001; REACH, 2008; Rodríguez Martín et al., 2006; Twardowska, 2004) and in Asia (Jung and Osako, 2009; Oh et al., 2010, 2011), and of sampling media for mineral exploration in Australia (e.g., Hamlyn, 2011). Reliable values for trace element concentrations in aqua regia extraction at the continental-scale have, until now, not been available, but must be expected, for some elements at least, to be very different from the total concentrations. This is because aqua regia only has a limited effect on minerals such as phlogopite (Mg-rich mica), dioctahedral mica (muscovite, sericite), quartz, feldspar, plagioclase, amphibole, barite, cassiterite, chromite, gahnite, garnet, ilmenite, monazite, rutile, sphene and zircon (Chen and Ma, 2001; Dolezal et al., 1968; Foster, 1973; Hamlyn, 2011; Klassen, 2001; Räisänen et al., 1992; Ryan et al., 2002; Tarvainen, 1995).

Here, new soil data collected and analysed to consistent protocols from two continents, one in the northern hemisphere (Europe) and one in the southern hemisphere (Australia), are presented and compared. The data come from continental-scale geochemical mapping programmes where a large number of samples were collected according to detailed and documented protocols, and analysed following a tight external quality control scheme. Internal project analytical standards were exchanged between the two projects and they, as well as international Certified Reference Materials, were analysed with the same techniques to guarantee comparability of analytical results between the two continents and estimation of bias, as outlined in Reimann et al. (2012).

The geology, geomorphology and pedology of Europe and Australia are complex subjects worthy of detailed discussions far beyond what can be covered in a brief article. Nevertheless, the most salient and relevant characteristics of, and differences between, these two continents (or at least the large parts thereof under study here) are summarised in the following. Major geological provinces in Europe are, in decreasing order of prevalence, (1) extended continental crust, (2) shield, and (3) orogen; in Australia, they are (1) shield, (2) platform and (3) orogen (USGS, 2011). The most common lithologies in Europe are (1) plutonic and metamorphic, (2) shales, and (3) carbonate rocks; in Australia, they are (1) shales, (2) sand, and (3) plutonic and metamorphic rocks (Amiotte Suchet et al., 2003). Generally speaking, fresher rock exposures are more common in Europe, especially northern Europe, than in Australia, mainly because of the more recent last glaciation in Europe (Holocene, ca 20 ka) compared to Australia (Early Permian, ca 290 Ma), but also because Australia has remained tectonically relatively stable for tens or even possibly hundreds of millions of years allowing weathering under varying climates to affect surface materials both extensively and deeply in many places (BMR Palaeogeographic Group, 1990; Gale, 1992; Pillans, 2007; Veevers, 1984). Both continents span a range of present-day climate zones (Europe: from polar to arid, dominantly temperate; Australia from tropical to temperate, dominantly arid; Peel et al., 2007) and ecoregions (Europe: from tundra to Mediterranean forests, woodlands and scrub, dominantly temperate broadleaf and mixed forests; Australia from tropical and subtropical grasslands, savannas and shrublands to Mediterranean forests, woodlands and scrub, dominantly deserts and xeric shrublands; Olson et al., 2001). Soils vary enormously across such diverse settings (Europe: from spodosols dominating in the north, through alfisols in the centre, to inceptisols in the south; Australia from ultisols and inceptisols in the north, through vertisols, entisols and aridisols in the centre, to alfisols in the southeast and southwest; USDA, 2005). Given this range of conditions, and the differences between these two continents, it should be instructive to compare empirical soil geochemistry data from Europe and Australia with world soil reference values and investigate if any observed differences can be related back to these conditions.

Thus, the present study aims to address the following questions:

1. How do extensive and consistent empirical datasets from two new continental-scale surveys compare with world soil values?
2. Can lithology be used as a predictor of soil chemical composition?
3. Can this work covering two continents provide improved world soil reference values, including – for the first time – aqua regia extractable concentrations for several elements?
4. What is needed to obtain a robust estimate of global soil composition?

2. Methods

During the last four years, continental-scale geochemical surveys have been conducted in Europe and Australia covering 5.6 and 6.2 million km^2, respectively. These are the Geochemical Mapping of Agricultural Soils (GEMAS) and the National Geochemical Survey of Australia (NGSA; www.ga.gov.au/ngsa) projects, briefly described below. Average sampling densities were 1 site/2500 km^2 for GEMAS and 1 site/5200 km^2 for NGSA. The GEMAS project sampled agricultural soils (hereafter referred to as 'Ap' samples for A ploughed horizon), whereas the NGSA project focused on soils developed on catchment outlet sediments generally similar to floodplain sediments. The Ap samples from GEMAS (N = 2211) were taken as composites of 0 to 20 cm depth, air-dried and sieved to <2 mm using nylon mesh sieves. The NGSA samples considered here (N = 1315) are the Top Outlet Sediments (TOS) collected as composites from 0 to 10 cm depth, oven-dried at 40 °C and sieved to <2 mm (or 'coarse' as the project also used a <75 μm 'fine' fraction) using nylon mesh sieves (hereafter referred to as 'Tc' for TOS coarse). Details relating to survey design, sample collection, and preparation are found in EGS (2008) for GEMAS and in Caritat et al. (2009) and Lech et al. (2007) for NGSA.

In both projects, samples were analysed for an extensive suite of total and aqua regia soluble element contents, as well as for other parameters (Caritat and Cooper, 2011; Caritat et al., 2010; Reimann et al., 2009, 2011a). In both the GEMAS and NGSA projects, total major element contents were obtained by X-Ray Fluorescence (XRF) for Al_2O_3, CaO, Fe_2O_3, K_2O, MgO, MnO, Na_2O, P_2O_5, SiO_2 and TiO_2. Total trace element contents (As, Ba, Ce, Co, Cr, Ga, Nb, Ni, Pb, Rb, Sr, Th, V, Y, Zn and Zr) were determined by XRF for the GEMAS samples and by total digestion ($HF + HNO_3$ digestion of fused XRF bead) followed by ICP-MS analysis for the NGSA samples. The aqua regia extracted elements (Ag, As, Bi, Cd, Ce, Co, Cs, Cu, Fe, La, Li, Mn, Mo and Pb) were determined in both cases by a similar aqua regia digestion followed by ICP-MS analysis. Further details are provided in Reimann et al. (2012).

Early on, Internal Project Standards (IPSs) were exchanged between GEMAS and NGSA to allow demonstration of intercomparability between both geochemical datasets despite the minor differences in analytical protocols discussed above. These IPSs were (1) a representative agricultural soil 'GEMAS-Ap' and (2) a