



## Geochemical fingerprinting and source discrimination of agricultural soils at continental scale



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### ABSTRACT

2108 agricultural soil samples (Ap-horizon, 0–20 cm) were collected in Europe (33 countries, area 5.6 million km<sup>2</sup>) as part of the recently completed GEMAS (GEOchemical Mapping of Agricultural and grazing land Soil) soil mapping project. GEMAS soil data have been used to provide a general view of element origin and mobility with a main focus on source parent material (and source rocks) at the continental scale, either by reference to average crustal abundances or to normalized patterns of element mobility during weathering processes. The survey area covers a large territory with diverse types of soil parent materials, with distinct geological history and a wide range of climate zones, and landscapes.

To normalize the chemical composition of European agricultural soil, mean values and standard deviation of the selected elements have been compared to model compositions of the upper continental crust (UCC) and mean European river suspended sediment. Some elements are enriched relative to the UCC (Al, P, Pb, Zr,) whereas others, such as Mg, Na and Sr are depleted. The concept of the UCC extended normalization pattern has been applied to selected elements. The mean values of Rb, K, Y, Ti, Al, Si, Zr, Ce and Fe are very similar to the values from the UCC model, even when standard deviations indicate slight enrichment or depletion. Zirconium has the best fit to the UCC model using both mean value and standard deviation. Lead and Cr are enriched in European soil when compared to the UCC model, but their standard deviation values span a large, particularly towards very low values, which can be interpreted as a lithological effect.

GEMAS soil data have been normalized to Al and Na, taking into account the main lithologies of the UCC, in order to discriminate provenance sources. Additionally, sodium normalization highlights variations related to the soluble and insoluble behavior of some elements (e.g., K, Rb versus Ti, Al, Si, V, Y, Zr, Ba, and La, respectively), their reactivity (e.g. Fe, Mn, Zn) and association with carbonates (e.g., Ca and Sr). Maps of Europe showing the spatial distribution of normalized compositions and element ratios reveal difficulties with the use of classical element ratios because of the large lithological differences in compositions of soil parent material. The ratio maps and color composite images extracted from the GEMAS data can help to discriminate the main lithologies in Europe at the regional scale but need to be used with caution due to the complexity of superimposed processes responsible for the soil chemical composition.

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### 1. Introduction

The interaction between water and rocks at the Earth's surface consumes atmospheric CO<sub>2</sub>, releases the most soluble ions and leads to the formation of soils and sediments (Amiotte Suchet et al., 2003). The mineralogy, particle size and elemental composition of soil and sediment are related to the nature of the parent rock material and the degree to which this material has been weathered (summary in Jain and Sharma, 2001). Chemical weathering of the Earth's surface results in a large loss of the most soluble elements, whereas the least soluble ones essentially remain in situ (Gaillardet et al., 1999). Weathering

stages of soils and sediments are usually evaluated by comparing their chemistry and mineralogy with the chemistry and mineralogy of their parent material. This may be quantitatively estimated by some weathering indicators such as enrichment factors (Nesbitt, 1979; Chester et al., 1985; Goldstein and Jacobsen, 1988), indices of geochemical maturity, such as the resistate index (corresponding to the ratio of  $\text{SiO}_2$  over  $\text{CaO} + \text{K}_2\text{O} + \text{Na}_2\text{O} + \text{MgO}$ ), the hydrolyzate index (corresponding to the ratio of  $\text{Al}_2\text{O}_3$  in clays over  $\text{Al}_2\text{O}_3$  in sand) and the oxidate index (corresponding to the ratio of  $\text{Fe}_2\text{O}_3$  in clays over  $\text{Fe}_2\text{O}_3$  in sand) of maturity (Wakatsuki et al., 1977). The concentration of a resistant component (often Si or Al) relative to the more mobile alkaline (Na and K) and alkaline earth (Ca and Mg) components determines the Chemical Index of Alteration (CIA) (Nesbitt and Young, 1982; Gallet et al., 1998; Schucknecht et al., 2012). The CIA ( $[\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O})] \times 100$ ) is based on the transformation of feldspar into clay during weathering where the major element oxides are given in molecular proportions and  $\text{CaO}^*$  represents the CaO content of silicate minerals only (review in Bahlburg and Dobrzinski, 2011). At river catchment scale, one way to understand the chemical composition of the soils or the sediments developed from the same parent lithology is to normalize each chemical species in sediment or soil by the average value of the same species in the parent material (Dennen and Anderson, 1962; Cullers et al., 1988; Négrel, 2006). This methodology has also been applied to weathering profiles (Nesbitt et al., 1980).

Using soil and sediment geochemistry, many researchers have attempted to estimate weathering and denudation rates of continents, recycling of continental crust and anthropogenic influence, (Huanghe: Yang et al., 2004; Ganges–Brahmaputra: Stummeyer et al., 2002; Congo: Gaillardet et al., 1995; Dupré et al., 1996; large river systems: Gaillardet et al., 1999; Viers et al., 2009; loess: Gallet et al., 1998; world soils: de Caritat et al., 2012; Schucknecht et al., 2012; regional soils: Rawlins et al., 2003). A similar approach in sedimentary basin studies provided information about weathering history, composition, and tectonic setting of the continental crust (Roser and Korsch, 1986; Raza et al., 2012).

The aim of this paper is to present a combined approach for interpreting the large database on the major and trace element composition of European soils from the continental-scale GEMAS project (*Geochemical mapping of agricultural and grazing land soils of Europe*, Reimann et al., 2014a,b). Comparison with upper continental crust UCC, UCC extended normalized patterns, Al-normalized enrichment factors, Na normalized ratios, normalized composition maps of weathering indices has been applied to the dataset, which represents highly variable parent materials, climate conditions, and landscapes. We provide a continental scale view of element mobility by a combined approach that helps to verify the validity of widely used models and methods when applied to large-scale datasets.

## 2. The GEMAS project

The GEMAS project was carried out by the Geochemistry Expert Group of EuroGeoSurveys in cooperation with Eurometaux and managed by the Geological Survey of Norway NGU (Reimann et al., 2012a). Soil samples were collected in 33 European countries, covering an area of 5.6 million  $\text{km}^2$  (Reimann et al., 2011, 2012a). The survey area is shown in Fig. 1 with a grid representing a sample density of 1 site per 2500  $\text{km}^2$ . Two sample materials have been used in this survey: agricultural soil (Ap-horizon, 0–20 cm depth range) and grazing land soil (i.e., soil under permanent grass cover, 0–10 cm depth range).

This study focuses on the Ap-horizon (0–20 cm) of regularly plowed agricultural land. Sample collection followed a strict field manual protocol regarding the landscape and sample site location (EuroGeoSurveys

Geochemistry Working Group, 2008). As a main objective of the project was to detect and to map the natural element variation at the European scale, the soil samples were never taken at known contaminated sites, in the immediate vicinity of industry or power plants, near a railway line or a major road, directly below high electric power lines or close to pylons. Flat-lying arable land sites were selected wherever possible and landscape depressions were avoided. In addition, sampling was carried out at a time when fertilizers were not being used by landowners. A total of 2108 samples were analyzed and reported on (Reimann et al., 2014a).

## 3. Materials and methods

The methods for GEMAS sampling, sample preparation and analysis for major and trace elements were described in detail in Reimann et al. (2011, 2012a, 2014a) and Reimann and de Caritat (2005). All composite samples were collected as rather large (2–2.5 kg) samples from one large field, sieved to <2 mm, and milled to less than 63  $\mu\text{m}$ . Depending on LOI (with a threshold of 25%), two different types of fused disks were prepared and analyzed by wavelength dispersive X-ray fluorescence spectrometry (WD-XRF). Project standards and replicates of project samples were used to monitor trueness, repeatability and accuracy, detection limits and QC results and are discussed in detail in Reimann et al. (2011).

The classification of European soils is presented here in the form of descriptive elemental ratios or ternary plots, following the chemical classification presented by Garrels and Mackenzie (1971). We have then used the upper continental crust (UCC) model as a reference for investigating element mobility following Taylor et al. (1983), either by comparison with the UCC, or using the UCC extended normalized patterns. We therefore implemented the normalization of element concentrations to a background indicator as used by Nesbitt (1979), i.e. the Al-normalized enrichment factor, or the Na normalized ratios. Finally, the spatial distribution of weathering indices in soils have been displayed in a series of interpolated geochemical maps produced with Arcview GIS software using the inverse distance weighted (IDW) algorithm to generate a regular grid with a  $6 \times 6$  km cell size and a circular window with fixed radius of 150 km (Sadeghi et al., 2013).

## 4. Results

Total concentrations of  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , MnO, MgO, CaO,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{P}_2\text{O}_5$ , Cl, F, As, Ba, Bi, Ce, Co, Cr, Cs, Cu, Ga, Hf, La, Mo, Nb, Ni, Pb, Rb, Sb, Sc, Sn, Sr, Ta, Th, U, V, W, Y, Zn and Zr were determined by wavelength dispersive X-ray fluorescence spectrometry (WD-XRF). The whole GEMAS dataset is provided in a two-volume geochemical atlas (Reimann et al., 2014a, 2014b accompanied by a DVD containing all data and maps) where the XRF results are discussed in detail with respect to their spatial distribution on geochemical maps and their statistical parameters. In several earlier publications, the GEMAS XRF data have been used to discuss the mathematical nature of such datasets and have been compared to other continental-scale geochemical surveys (e.g., Reimann et al., 2012a; de Caritat et al., 2012; Reimann et al., 2012c). The regional distribution of single elements or related groups of elements was presented in e.g. Reimann et al. (2012b – Pb), Ottesen et al. (2013 – Hg), Tarvainen et al. (2013 – As), Sadeghi et al. (2013 Ce, La, Y).

In our study, only selected elements are presented with a focus on major elements and associated trace elements. In order to classify the GEMAS soil parent material, we follow the approach from de Caritat et al., 2012 who calculated the relative proportions of five major lithological types. According to the global rock lithology model of Amiotte

**Fig. 1** (a) Map of parent materials in Europe showing the distribution of various lithologies across the continent (modified from Günther et al., 2013). (b) Sample locations of the agricultural soil (Ap-samples) from the EuroGeoSurveys GEMAS Project ( $n = 2108$ ). (c) Generalized geological map of Europe with major lithotectonic units, Variscan and Alpine belts, Transeuropean Suture Zone (TESZ) and the extension of maximum glaciation (modified from Reimann et al., 2012b).

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