GEMAS: Geochemical distribution of Mg in agricultural soil of Europe

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Abstract

Agricultural soil (Ap-horizon, 0–20 cm) samples were collected from 33 European countries as part of the GEMAS (GEochemical Mapping of Agricultural and grazing land Soil) soil-mapping project. The Mg data derived from total concentrations (XRF) and two acid digestion methods, *aqua regia* (AR) and Mobile Metal Ion (MMI®), were used to provide an overview of its spatial distribution in soil at the continental-scale. Magnesium is one of the most abundant elements in the Earth's crust and essential nutrient for plants and animals and its presence in soil is, therefore, important for soil quality evaluation.

In this study, the geochemical behaviour of Mg in European agricultural soil was investigated in relation to a variety of soil parent materials, climatic zones, and landscapes. The chemical composition of soil reflects mostly the primary mineralogy of the source bedrock, and the superimposed effects of pre- and post-depositional chemical weathering, controlled by element mobility and formation of secondary phases such as clays.

Low Mg concentrations in agricultural soil occur in regions with quartz-rich glacial sediments (Poland, Baltic States, N. Germany), and in soil developed on quartz-rich sandstone parent materials (e.g., central Sweden). High Mg concentrations occur in soil developed over mafic lithologies such as ophiolite belts and in carbonate-rich regions, including karst areas. The maximum extent of the last glaciation is well defined by a Mg concentration break, which is marked by low Mg concentrations in Fennoscandia and north-central Europe, and high Mg concentrations in Mediterranean region. Lithology of parent materials seems to play a key role in the Mg nutritional status of agricultural soil at the European scale. Influence from agricultural practice and use of fertilisers appears to be subordinate.

Comparison of the continental-scale spatial distribution of Mg in agricultural soil by using the results from three analytical methods (XRF, AR and MMI®) provides complementary information about Mg mobility and its residence time in soil. Thus, allowing evaluation of soil weathering grade and impact of land use exploitation.

Keywords: weathering, parent materials, mineralogy, total concentration, partial extraction

1 – Introduction

In total, 2108 samples of agricultural soil (Ap-horizon, 0–20 cm) were collected from 33 European countries (5.6 million km^2) as part of the GEMAS (GEochemical Mapping of Agricultural and grazing land Soil) project (Reimann *et al*., 2014a, b). The study area covers diverse groups of soil parent materials with a variable geological history, a wide range of climate zones, and many different landscapes. The chemical composition of soil is mostly controlled by the primary mineralogy of the source bedrock, the superimposed effects of the last glaciation, pre- and post-depositional chemical weathering, formation of secondary products such as clays, and element mobility (Négrel *et al*., 2015). All these factors contribute to the geographical variation in the continental-scale spatial distribution of elements (Reimann *et al*., 2014c; Ladenberger *et al*., 2015).

Magnesium is the eighth most abundant element in the upper continental crust (UCC) of the Earth, with an average elemental abundance of 14 955 mg/kg (Rudnick and Gao, 2003). Magnesium bearing minerals such as amphibole and pyroxene are common in mafic and ultramafic rocks, e.g., basalt and gabbro. In sedimentary rocks, the main Mg bearing minerals are carbonates, i.e., dolomite and magnesite. Magnesium is essential for all living organisms and is not toxic under normal circumstances. It is a key plant nutrient and essential for photosynthesis. It is used in industry (automotive, aircraft, train, laptop, mobile telephone, tablet), steel, titanium and zirconium production, pharmaceutical and agricultural chemical industries, and medical implants (Christie and Brathwaite, 2008). Magnesium may also be a preferred material in all light-weight vehicles, hydrogen storage and advanced battery technology. Currently, it is an essential alloying element in the aluminium industry. Magnesium may be recovered from various resources, such as dolomite and Mg-bearing evaporite minerals, Mg-bearing brines, and seawater (Christie and Brathwaite, 2008). All these resources are globally widespread and estimated to constitute billions of tonnes of Mg.

Thus, Mg resources are considered as enormous and unlimited. Magnesium's current criticality (i.e., economic importance versus supply risk; European Commission, 2017) is not based on lack of Mg raw materials in Europe, but rather on trade issues as the worldwide primary Mg production (around 878 Kt in 2016) is mainly supplied by China. However, the development of research and development technologies will increase the long-term demand worldwide.

Knowledge of the geochemical behaviour of this major element in the rock-soil cycle through weathering processes is important, both for recognising soil nutritional status and for targeting new Mg deposits. The GEMAS data set provides European-scale results for chemical elements (Reimann et al., 2014a, b), including several so-called high-tech materials, which are listed in the Critical Raw Materials list by the European Commission in 2017 (Scheib et al., 2012; Ladenberger et al., 2015; Négrel et al., 2016, 2019). In this study, geochemical data from the GEMAS project are used to (i) decipher the geochemical behaviour of Mg using low-sampling density geochemical mapping at the continental-scale, (ii) identify enriched and depleted regions of Mg, and (iii) interpret the Mg geochemical patterns to highlight the respective impacts of soil weathering stage and land use in relation to the different methods of analysis used, e.g., total analysis by X-ray Fluorescence (XRF), strong acid extraction by *aqua regia*, and weak extraction by MMI®.

2 - General setting

The GEMAS project (Reimann et al., 2014a, b) was carried out by the Geochemistry Expert Group of EuroGeoSurveys with funding by national Geological Surveys, collaborating Universities and Eurometaux (European Association of Metals). The project was managed by the Geological Survey of Norway. Soil samples from two land-use types (agricultural soil , n=2108; grazing land soil, n=2024) were collected in 33 European countries, covering an area

of about 5.6 million km^2 with an average density of 1 sample/2500 km^2 (Reimann et al., 2012a; 2014a, b). The countries covered are shown in Figure 1. The main objective of the pan-European project was to map the element variation in agricultural and grazing land soil, and to assess the impact of agricultural activities. Soil samples were not collected at known contaminated sites, in the immediate vicinity of industrial sites, power plants, railway lines, major roads, directly below high-power electric lines and near to pylons. The GEMAS *aqua regia* and XRF results were provided in a two-volume geochemical atlas (Reimann et al., 2014a, b), followed by a series of peer-review publications where detailed interpretation of the continental-scale distribution of single elements or related groups of elements or physical parameters of soil were presented, e.g., Reimann et al. (2012a; Pb), Ottesen et al. (2013; Hg), Tarvainen et al. (2013; As), Scheib et al. (2012; Nb), Sadeghi et al. (2013; Ce, La, Y), Ladenberger et al. (2015; In), Albanese et al. (2015; Cr, Ni, Co, Cu), Négrel et al. (2016, 2018a, b, 2019; - Ge, U-Th, Rb-Ga-Cs, Sc-W-Li), Fabian et al. (2014; pH), Birke et al. (2016, 2017; Cd), Jordan et al. (2018; Ni), Matschullat et al. (2018; C-N-S), Hoogewerff et al. (2019; Sr), Xu et al. (2019; pH, C).

3 – Material and methods

3.1. Sampling and sample preparation

Two land use soil types were collected from agricultural and grazing land, with a nominal sampling density of 1 sample per 2500 km^2 (Fig. 1b). Grazing land soil (Gr) was defined as 'land under permanent grass cover' and the sampling depth range was 0–10 cm according to REACH (Registration, Evaluation, Authorisation, and Restriction of Chemicals) regulation requirements (REACH, 2006). The agricultural soil (Ap) was collected from the ploughing layer of an arable field at a depth range of 0–20 cm, again according to REACH regulations. Each agricultural or grazing land soil sample (*ca*. 3.5 kg) corresponds to a composite of five sub-samples, taken from the corners and centre of a 10 × 10 m square. The total number of Ap

samples is 2108 and that of Gr 2024 samples. All soil samples for analysis and storage were prepared in a single facility (State Geological Institute of Dionyz Stur, Slovakia). Sample preparation involved air-drying at ambient temperature, sieving to <2 mm using a nylon screen, homogenising, and final splitting into 10 sub-samples (Mackovych and Lucivjansky, 2014). The analytical results for Ap and Gr samples are, with very few exceptions, highly comparable and, thus, the latter are not being further discussed in this study.

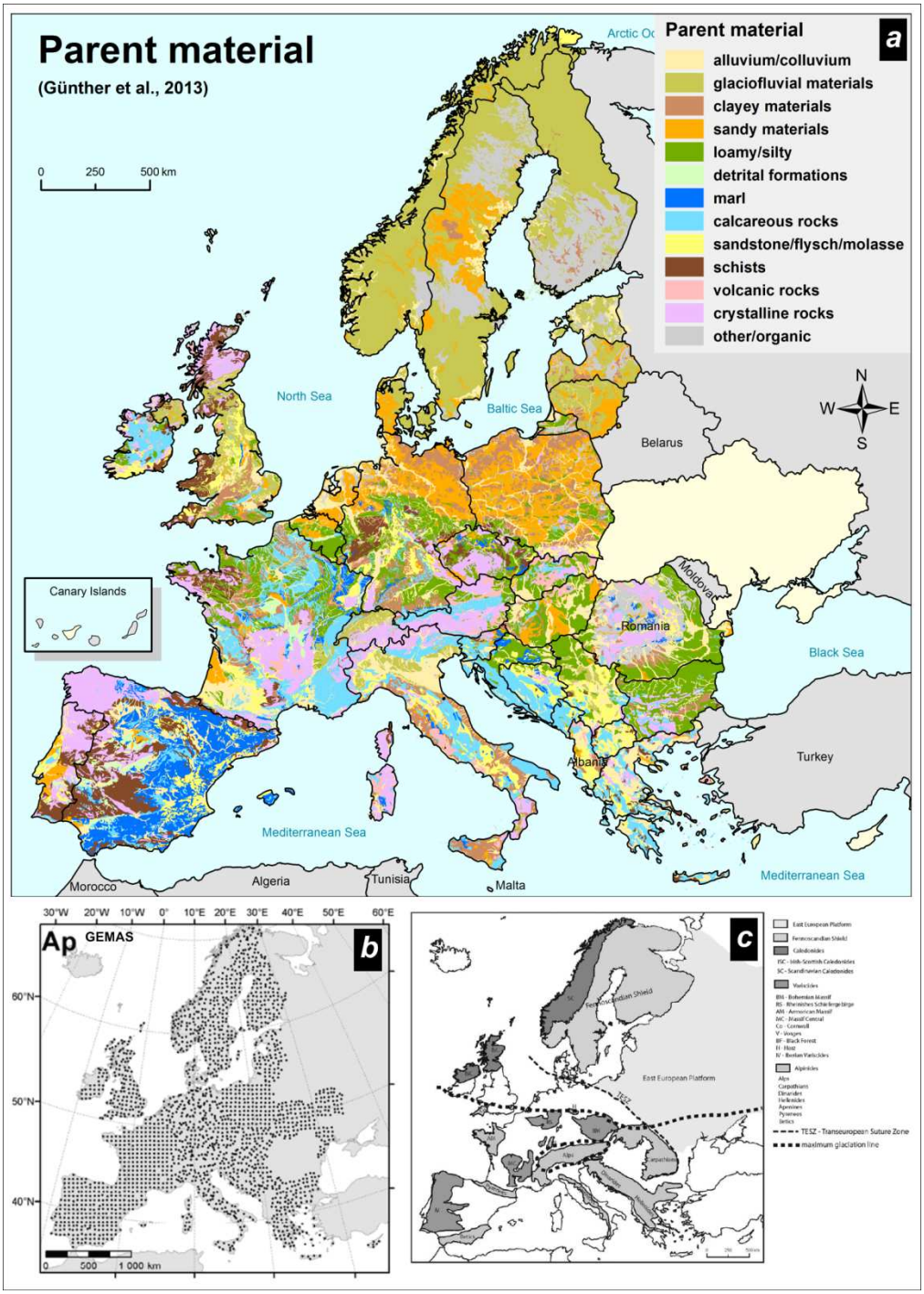


Figure 1. Modified from Négrel et al. (2015, Fig. 1, p.3). (a) Map of soil parent materials in Europe showing the distribution of various lithologies across the continent (modified from Gunther et al., 2013 and adapted from Négrel et al., 2015, Fig. 1, p.3). (b) Sample locations of the ploughed agricultural soil sample sites (dots); (Ap-samples, n=2108). Map projection: ETRS89 Lambert Azimuthal Equal-Area projection coordinate reference system, with central meridian at 10°. (c) Generalised geotectonic map of Europe with major lithotectonic units, Variscan and Alpine belts, Trans-European Suture Zone (TESZ) and the extension of maximum glaciation (modified from Reimann et al., 2012a, Fig. 1, p.198).

3.2. Chemical analysis and quality control

The GEMAS project soil samples were analysed using total and partial extraction methods (for details refer to: Reimann et al., 2009, 2011, 2012b; Birke et al., 2014a). Two project reference materials, prepared in the same laboratory (State Geological Institute of Dionyz Stur, Slovakia), were used to monitor analytical performance (Demetriades et al., 2014; Reimann and Kriete, 2014).

Total concentrations of Mg were determined by XRF, and 7% of the results are below the detection limit of 302 mg/kg. In addition, two partial extractions were used, as described below.

Hot *aqua regia* digestion, representing a strong partial extraction and recommended in environmental and agricultural soil studies (e.g., Vercoutere et al., 1995; Santos and Alleoni, 2013; Sastre et al., 2002), was applied on the collected soil samples. It is stressed that residual elements not released by *aqua regia* digestion are mostly bound to silicate minerals, and are considered unimportant for estimating the mobility and behaviour of elements (Niskavaara et al., 1997; Chen and Ma, 2001).

A soil sample weight of 15 g of the <2 mm fraction was leached in 90 ml *aqua regia* (95°C, 1 hour), and then made-up to a final volume of 300 ml with 5% HCl. The supernatant solutions of over 5000 soil samples were analysed for 53 elements using a combination of Inductively Coupled Plasma Mass Spectrometry (ICP-AES) and Atomic Emission Spectrometry (ICP-MS) (ACME Laboratories in Vancouver, Canada; now Bureau Veritas Mineral Laboratories). Quality control was monitored using field duplicate-replicate splits, and matrix matched standards and reference materials. Only 5% of the agricultural soil samples have Mg concentrations below the detection limit of 50 mg/kg. The hot *aqua regia* digestion is able to extract elements adsorbed on clay minerals, dissolved Fe and Mn oxides and carbonate minerals, and can even dissolve some silicate phases (e.g., olivine, biotite,

176 pyroxene), while other silicates and oxides are only weakly to moderately dissolved (Dolezal
177 et al. 1968; Räisänen et al., 1992; Aatos et al., 1994; Snäll and Liljefors, 2000; Vilà and
178 Martínez-Lladó, 2015). Comparison of the *aqua regia* with the XRF data often provides an
179 insight to the host mineralogy for the element(s) being studied.

180 The Mobile Metal Ion (MMI®) method is a weak partial extraction technique
181 originally developed for mineral exploration (Mann et al., 1998), and was applied on the
182 agricultural soil samples (Ap) with the purpose of identifying those weakly adsorbed elements
183 that are bioavailable and may also be related to weathering processes and anthropogenic
184 factors (Mann et al., 2015; Sadeghi et al., 2015). The MMI® method, based on having a
185 number of strong ligands in a neutral to alkaline-buffered solution (Mann, 2010; Mann et al.,
186 2014a), enables ions that are weakly adsorbed onto soil particle surfaces to be brought into
187 solution for determination by ICP-MS (Mann et al., 2014b). This analytical method allows,
188 therefore, the evaluation of those elements that are mobile, and potentially bioavailable in soil
189 (e.g., Reimann et al., 2012a). The MMI® analytical method is a proprietary technique that
190 uses a high sample to solution ratio and a weak solution (MMI®-M) to extract only the more
191 accessible, or mobile metal ions. The Ap samples were analysed by MMI® extraction using a
192 50-g sample weight, which was shaken for 30 minutes in 50 ml of MMI®-M solution before
193 being centrifuged and the resultant leachate analysed by ICP-MS for 57 elements at SGS
194 Mineral Services in Toronto, Canada. Around 19% of the Ap samples have Mg concentrations
195 below the detection limit of 1 mg/kg.

196 A rigorous quality control (QC) procedure was part of the sampling and analytical
197 protocols of the GEMAS project (Reimann et al., 2009, 2011, 2012b; Demetriades et al.,
198 2014). The agricultural and grazing land soil samples were analysed in batches of twenty. In
199 each analytical batch were included one field duplicate, one analytical replicate of the field
200 duplicate and the project standard. An innovation of the GEMAS project was the calculation

of the practical detection limit (DL) of each determinand using the results of the project replicate samples through the estimation of regression line coefficients by the 'reduced major axis line' procedure (Demetriades, 2011). A detailed description of the analytical methods and quality control procedures are provided in the GEMAS project atlas (Birke et al., 2014a; Reimann and Kriete, 2014; Demetriades et al., 2014), and in three technical reports (Reimann et al., 2009, 2011, 2012b). Quality control procedures for the MMI® extraction method for the entire Ap data set are described in Reimann et al. (2012b) and Mann et al. (2014a, b). Only the data obtained for the Ap soil samples will be considered hereafter.

3.3 Data treatment

Geochemical data are a classical example of compositional data, element concentrations reported in wt % or mg/kg sum up to a constant and are thus not free to vary. The information value of such data generally lies in the ratios between the variables (Beus and Grigorian, 1977; Reimann et al., 2012a). Compositional data do not plot in classical Euclidean space, but they have their own geometry, the Aitchison simplex (Aitchison, 1986; Buccianti et al., 2006; Pawlowsky-Glahn and Buccianti, 2011). Thus, only order statistics should be used in the processing of geochemical data, noting that percentiles are unchanged under log-transformation. This is not the case, however, under a log-ratio-transformation.

The coloured surface map of each determinand was produced by kriging, based on a careful variogram analysis (Filzmoser et al., 2014). Kriging was used to interpolate values of each determinand from the irregularly distributed sampling sites to a regular grid and into unsampled space. Comparison with black and white point source maps has shown that the kriged maps reflect the spatial structure of the data very well (Reimann et al., 2014c). Class limits, used for the colour maps are based on percentiles (5, 25, 50, 75, 90 and 95). Maps displayed hereafter (Figs. 7-9) were produced in Esri's ArcGIS software.

Ten geological parent material subgroups were constructed for processing the Ap soil data set (Birke et al., 2014b): (1) alk: alkaline rocks; (2) chalk: calcareous rocks; (3) granite: plutonic felsic rocks; (4) green: greenstone, basalt, mafic bedrocks; (5) loess: loess; (6) org: organic soil; (7) other: unclassified bedrocks; (8) prec: predominantly Precambrian bedrocks (granitic gneiss); (9) quartz: soil developed on coarse-grained sandy deposits (e.g., the end moraines of the last glaciation), and (10) schist: schist. In addition, the relative proportions of six major lithological types were recalculated for the GEMAS project area (Reimann et al., 2012c), based on the global rock lithology presented by Amiotte-Suchet et al. (2003). Among these major lithologies, plutonic and metamorphic rocks (39%) and shale (37%) dominate; carbonate rocks (14%) and sand-sandstone (9.5%) are significant, whereas felsic volcanic rocks and basalt (0.5% each) play a subordinate role.

4 – Results and Discussion

4.1 Mg concentrations in agricultural soil

The minimum, median and maximum concentrations of Mg delivered by the GEMAS project, using the three analytical methods (XRF, AR and MMI® extractions), are provided in Table 1 together with the detection limit (DL) and percentage of samples under DL.

Table 1. Basic statistical parameters for Mg in European agricultural (Ap) soil samples determined by different analytical methods.

Method	N	DL	%<DL	Minimum	Median	Maximum
		mg/kg		mg/kg	mg/kg	mg/kg
XRF	2108	302	7	<302	5488	126368
AR	2108	50	5	<50	2860	116908

MMI	2108	1	19	<1	52	>500*

*upper detection limit of Mg in the MMI® extraction is 500 mg/kg

The boxplots comparing the Mg results of Ap soil samples clearly show the differences between the three analytical techniques (Fig. 2). They display a number of upper and lower outliers (only lower outliers for the MMI® data), which are, however, not far away from the main body of data (note the log-scale used). There is no significant overlap between the main body of the XRF, AR and MMI® data. The 95% confidence interval on the median, displayed by the notches, shows that there is no overlap, suggesting that there is a distinct difference at the 5% significance level among the Ap XRF, AR and MMI® data sets of Mg.

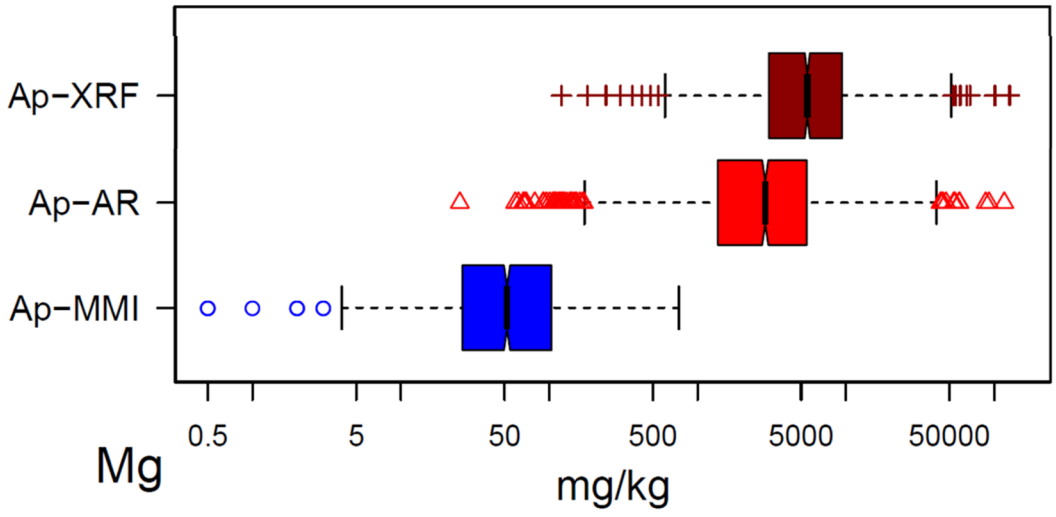


Figure 2. Boxplot comparison of Mg concentrations in European Ap soil samples determined by XRF, aqua regia and MMI®. Refer to Table 1 for the basic statistical parameters.

Compared to the UCC total Mg average (14,955 mg/kg) by Rudnick and Gao (2003), the median Mg concentration (5488 mg/kg), measured by XRF, is substantially lower in the European agricultural soil samples (ratio median Ap/UCC = 0.367). This may suggest a possible overestimation of the UCC Mg value in previous calculations, or it may also be an indication of an overall depletion/removal of this important plant nutrient in agricultural soil.

The combination plot histogram - density trace - one-dimensional scattergram - boxplot (Fig. 3) shows the Mg univariate data distribution. The one-dimensional scattergram and boxplot highlight the existence of a substantial number of outliers in the Mg distribution. The density trace and histogram are overall symmetrical in the log-scale.

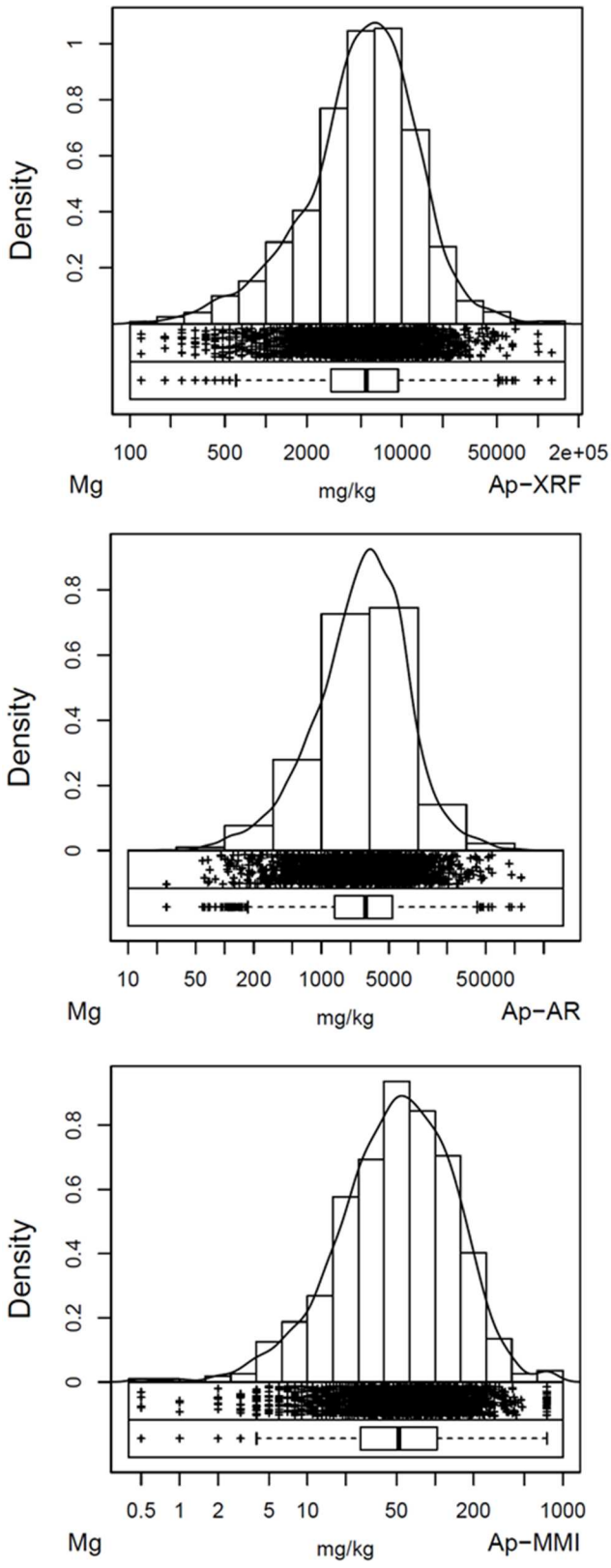


Figure 3. Combination plot of histogram, density trace, one-dimensional scatter-diagram and boxplot of the Mg distribution in European Ap soil samples determined by XRF (a), and ICP-AES/MS after an aqua regia (b), and MMI® extraction (c). Note in the density trace the upper limit of 500 mg in the MMI® extraction.

4.2 Spatial distribution of Mg in Ap soil

The maps of Mg determined by XRF, and ICP-AES/MS following *aqua regia* and MMI® extractions are presented in Figures 6, 7 and 8. Although the map of total Mg concentrations determined by XRF (Fig. 6) shows considerably higher concentrations (median 5488 mg/kg) in soil than the map of *aqua regia* extraction (median 2860 mg/kg), with average Mg extractability of 55% (Reimann et al., 2011), the overall continental-scale spatial distribution is quite similar.

The two classical maps of Mg arising from the *aqua regia* extraction and XRF (Figs. 6 and 7) show unusually low Mg concentrations over the coarse-grained sediments of the last glaciation in central-northern Europe. This is due to the mineralogical composition of these glacial sands, which consist almost exclusively of quartz (SiO_2) (Zeeberg, 1998; Reimann et al., 2012c; Scheib et al., 2014). The southern limit of the last glaciation is thus still visible as a Mg concentration break on both maps. The median Mg concentrations between northern and southern Europe are different by a factor of 2.4 (1500 *vs.* 3600 mg/kg, respectively), and are not as contrasted as for many other elements determined on the GEMAS project soil samples (Reimann et al., 2014c). For *aqua regia* extractable Mg concentrations in the agricultural soil of European countries, the highest Mg median value is in Cyprus (8785 mg/kg), followed by Montenegro (8098 mg/kg) and the Hellenic Republic (Hellas) (7845 mg/kg), countries with known ophiolite complexes (mafic and ultramafic intrusions). The lowest median value occurs in Poland (716 mg/kg); whereas, areas underlain by limestone (e.g., eastern and southern Spain), dolomite (Alps) and mafic-ultramafic rocks (e.g., Hellas, Norway and Finland) appear as large Mg anomalies on the map. Further, clay-rich soil such as the Central Scandinavian Clay Belt (central Sweden) is also visible as a Mg anomaly on the maps (Figures 6-8).One of the principal differences between XRF and AR geochemical maps is the intensity difference of Mg anomalies in Fennoscandia, which may indicate the widespread

occurrence of yet unweathered Mg-silicates in northern Europe that do not dissolve in *aqua regia*.

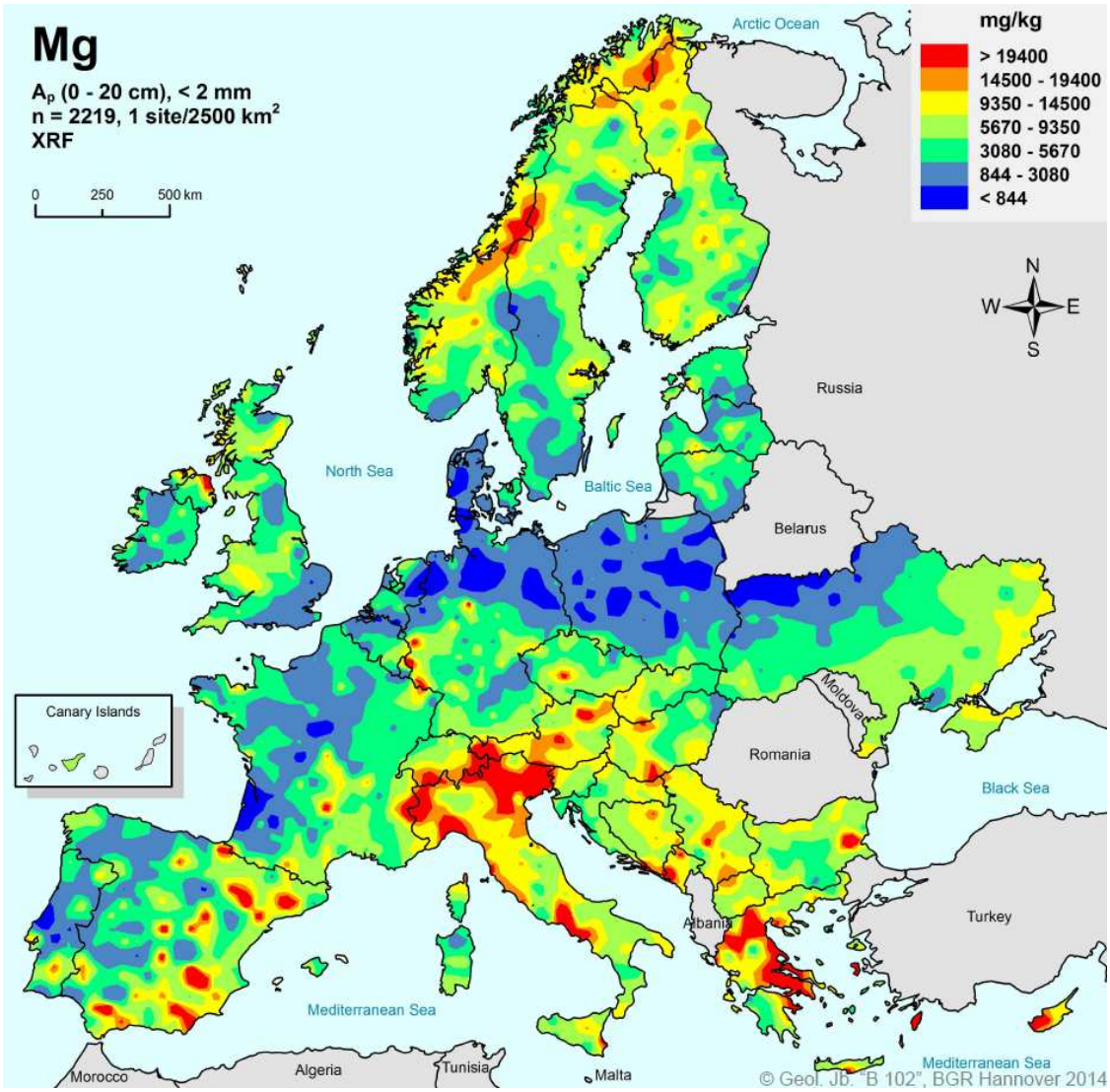


Figure 6. Geochemical map for Mg total concentrations in ploughed agricultural soil (Ap, n=2108) (XRF results). Interpolation by kriging, range = 1 000 km, and search radius = 300 km (from Reimann et al., 2014c, Fig. 11.34.5, p.300).

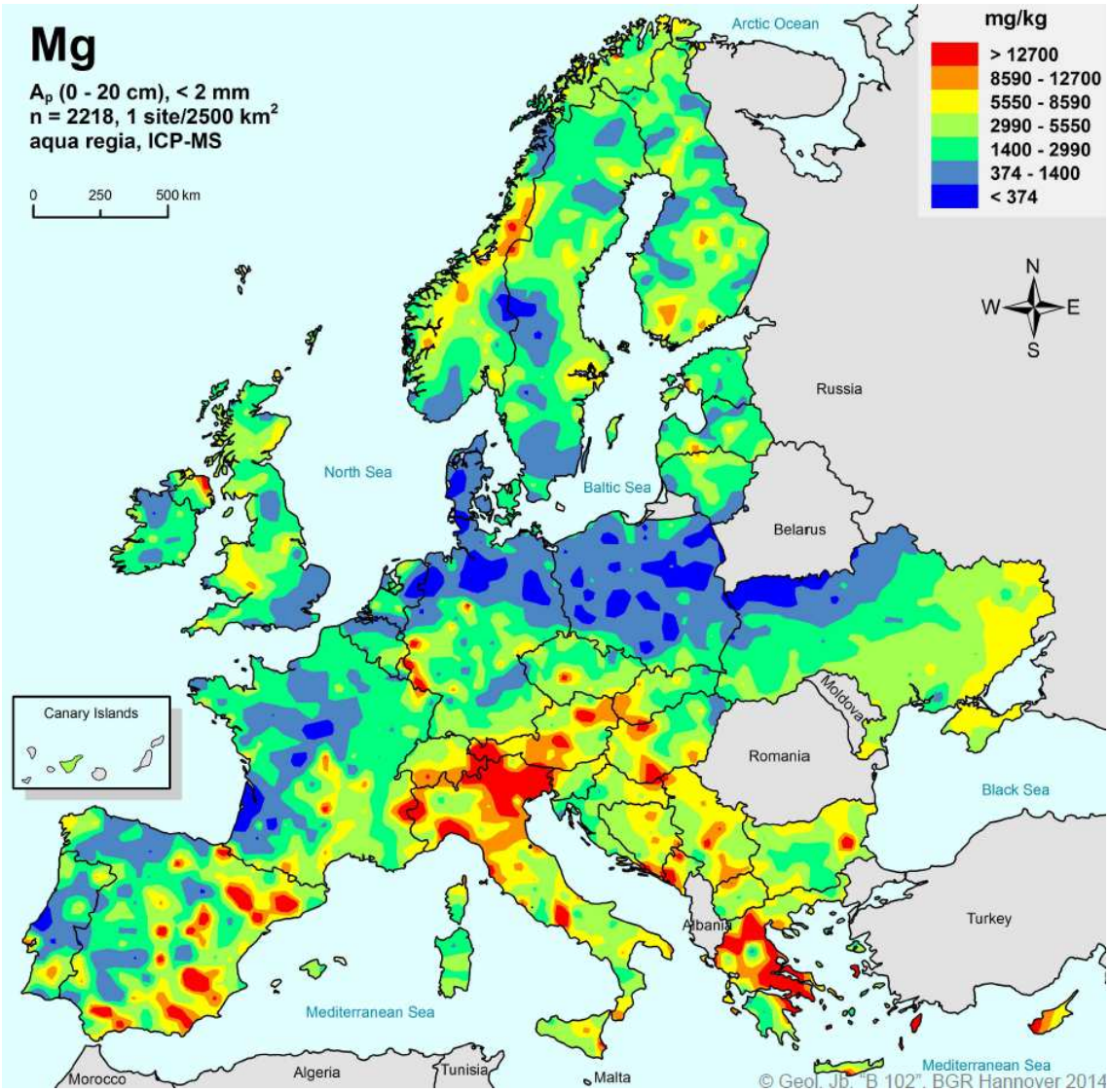


Figure 7. Geochemical map for aqua regia extractable Mg concentrations in ploughed agricultural soil (Ap, n=2108). Interpolation by kriging, range = 1 000 km, and search radius = 300 km (from Reimann et al., 2014c, Fig. 11.34.5, p.299).

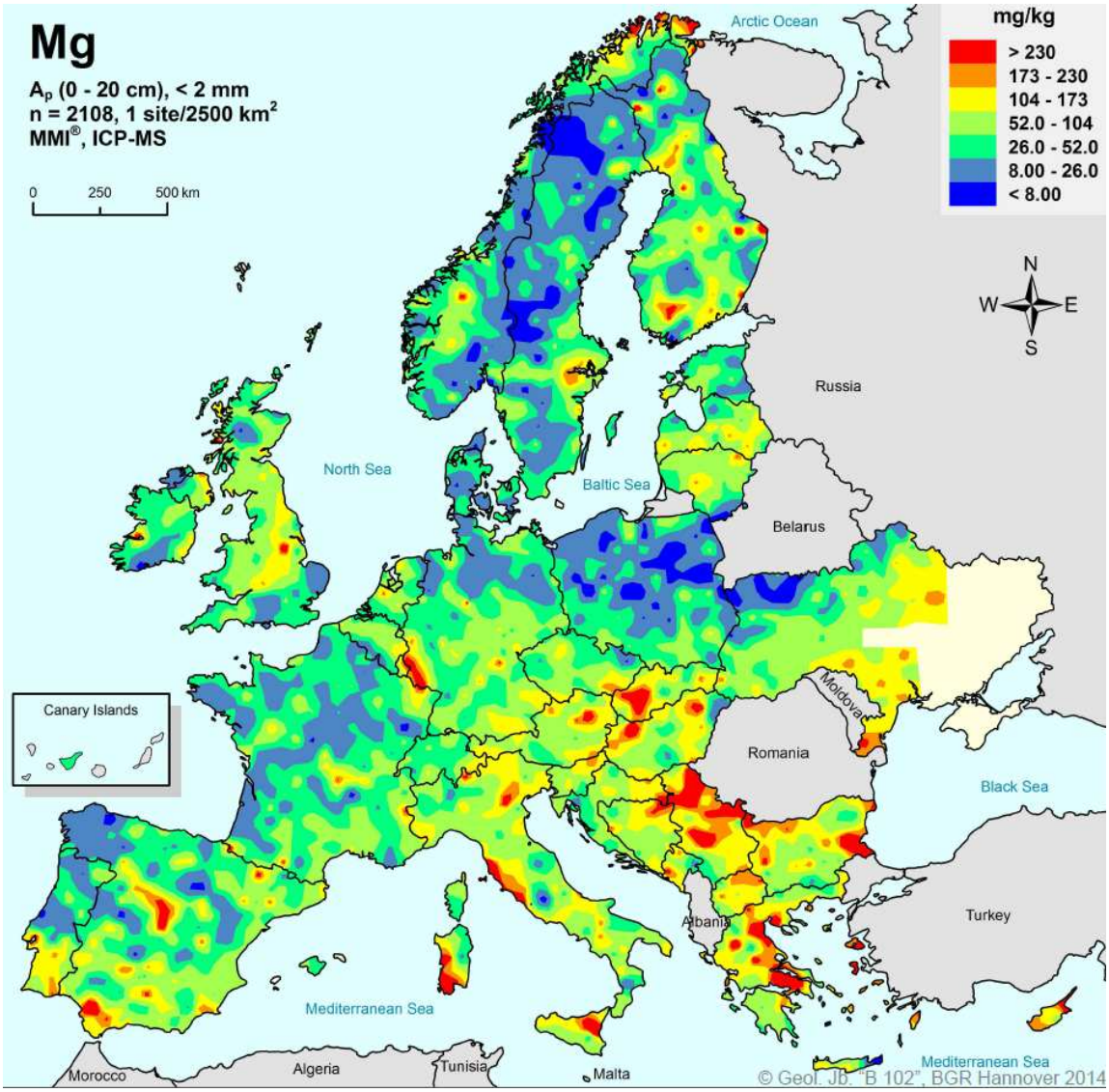
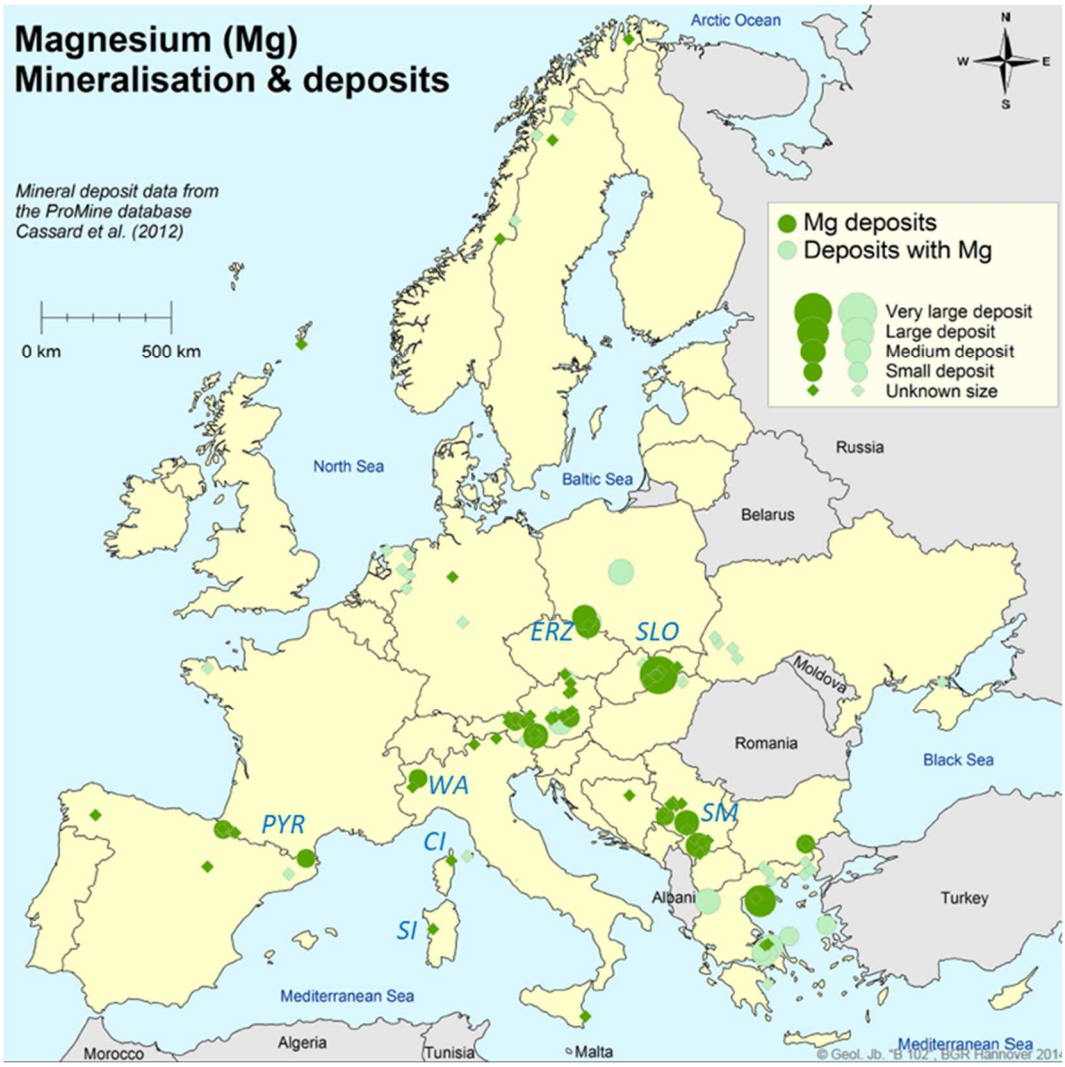


Figure 8. Geochemical map for MMI® extractable Mg concentrations in ploughed agricultural soil (Ap, n=2108). Interpolation by kriging, range = 1 000 km, and search radius = 300 km (from Reimann et al., 2014a, Figure on accompanying DVD).

The map of Mg results from MMI® extraction on Ap soil samples (Fig. 8) shows rather complementary pattern in comparison to both the *aqua regia* (Fig. 7) and XRF (Fig. 6) geochemical maps. The features shared by all three maps are: (1) the southern limit of the last glaciation; (2) the major Mg anomalies appear to be related to the occurrence of mafic-ultramafic rocks (intrusive and volcanic) and dolomite or dolomitic limestone; (3) regions with silica-rich loose sandy deposits and granitic bedrock are usually outlined by low Mg content in soil, and (4) low pH facilitating Mg removal from soil may contribute to low Mg

anomalies irrespectively of the underlying bedrock, e.g., in central Sweden, in northern-central Europe and NW Spain. However, apart from many similarities, some interesting differences can also be observed. In northern Fennoscandia, high Mg content in soil, caused by Palaeoproterozoic greenstone belts and Caledonian mafic and ultramafic rocks, are well outlined on the XRF Mg map. In comparison, on the *aqua regia* Mg map these features are shown with a decreasing intensity to disappear completely on the MMI® map. There are possibly two reasons for this geochemical behaviour of Mg; either Mg is hosted by resistant silicate minerals which have a limited dissolution in these acids, or low soil pH effectively removes weakly bound Mg from soil particles resulting in very low Mg content in acid extractions. Another interesting example can be observed in Sardinia, where the Mg MMI® map has a very contrasting pattern, with high concentrations in the south-western and low in the north-eastern parts of the island, features that are not visible on either the XRF or AR maps. In this case, the distinct contrast is most likely caused by a lithology difference, i.e., occurrence of a low Mg granite in the NE, and Mg enriched sedimentary rocks, especially limestone and dolomite, in the SW.



345

346 *Figure 9. Distribution of Mg-bearing ore deposits in Europe (based on the ProMine Mineral*
347 *Database; Cassard et al., 2012, 2015; Demetriades and Reimann, 2014). Abbreviations of*
348 *mineralised districts: CI: Corsica Island; ERZ: Erzgebirge (Ore Mts.); PYR: Pyrenees; SI:*
349 *Sardinia Island; SM: Serbo-Macedonian ore district; SLO: Slovakia; WA: Western Alps.*
350

351 The geographical distribution of the Mg deposits in Europe is shown in Figure 9. Most
352 important Mg mineral resources are hosted by ultramafic lithologies and their
353 weathering/alteration products (magnesite), carbonate rocks (dolomite) and chemical deposits
354 (carnallite) as given by Cassard et al. (2012, 2015). The classification of Mg deposits on the
355 ProMine map (Figure 9) is based on threshold values for Mg in metric tonnes (t): class A for
356 super-large deposits (100,000,000 t), class B for large deposits (10,000,000 t), class C for
357 medium deposits (1,000,000 t), and class D for small deposits (100,000). Many of the
358 magnesium deposits are represented by magnesite and contact metamorphic deposits of

359 brucite along granite-dolomite contacts. Magnesite in the Caledonides, Hellas and Italy are
360 associated with the ultramafic parts of ophiolites (Pohl, 1990). Magnesia can be also produced
361 from surface or subterranean brines (Christie and Brathwaite, 2008). Natural magnesite occurs
362 in few large, high grade (70-90% $MgCO_3$) and a large number of small, lower grade (>12%
363 $MgCO_3$) deposits either as crystalline or amorphous phases. Crystalline deposits of magnesite
364 occur in Austria and Spain, whereas amorphous magnesite deposits are known in Austria and
365 Hellas (Christie and Brathwaite, 2008). The correlation between the location of Mg deposits
366 and Mg anomalies in agricultural soil is relatively good, if a rather random distribution of Mg
367 deposits across the continent is considered. The XRF Mg anomalies correlate well with Mg
368 deposits in Central Caledonides (Sweden and Norway), northernmost Norway and Finland, in
369 Austria and in the Alps (Italy, Austria), Balkan region and Hellas, SE Sicily, N Corsica and N
370 Spain (Pyrenees and its foreland). *Aqua regia* extractable Mg anomalies largely follow XRF
371 results (due to relatively high Mg extractability). The MMI® Mg results in agricultural soil
372 display additional anomalies, which follow ProMine Mg deposits in SW Sardinia and
373 Hellenic island of Lesbos in the eastern Aegean Sea. In contrast to XRF and AR data, MMI®
374 results do not show high Mg concentrations in Central Caledonides of Norway and Sweden.
375 This phenomenon can be related to climate, dry conditions with low precipitation in an
376 environment with presumable alkaline soil (>7 pH) in the Mediterranean region, and high
377 precipitation combined with acidic soil (<6 pH) and rapid wash-out in the mountain region of
378 the Scandinavian Caledonides.
379
380 **4.3. The role of parent material on Mg variation in soil at the European scale**
381 The chemical composition of sediments and soil represents, to a large extent, the primary
382 mineralogy of the source bedrock, the effects of pre- and post-depositional chemical
383 weathering, formation of secondary products such as clays, and element mobility, either by
384 leaching or mineral sorting with superimposed effects of glaciation. Therefore, Mg in soil,

like Al and K, is often retained in weathering soil profiles, compared to Na and Ca, which are rapidly leached as dissolved ions. Liming and use of Mg fertilisers are the main anthropogenic interferences on natural Mg-cycles.

To evaluate the input from parent materials and chemical weathering trends, ternary plots of carefully selected parameters can be used (e.g., Kasanzu et al., 2008; Négrel et al., 2015). Comparison of Ca, Na and Mg total XRF and AR contents in Ap soil samples (Fig. 10a and b) allows discrimination between carbonate and silicate parent materials including various siliciclastic components (low Ca granite, sandstone and ultramafic rocks). XRF results (Fig. 10a) show that soil chemical composition is scattered between three extreme end-members, defined by mafic-ultramafic rocks, carbonates (limestone) and low Ca granite variation. The carbonate-rich soil forms a distinct group on the diagram, while soil developed on silicate parent materials has a rather large spread with predominance of felsic source rocks (towards low Mg composition), and deviates from typical UCC end-members (Fig. 10a).

The *aqua regia* results of Ca-Mg-Na in Figure 10b show a trend dominated by the correlation between Mg and Ca, while Na is exceptionally low. This pattern might be simply the result of a difference between extractability of Ca, Mg and Na, with the first two being highly soluble in AR, while Na has low extractability. This would indicate that the pattern is not related to the type of source parent materials.

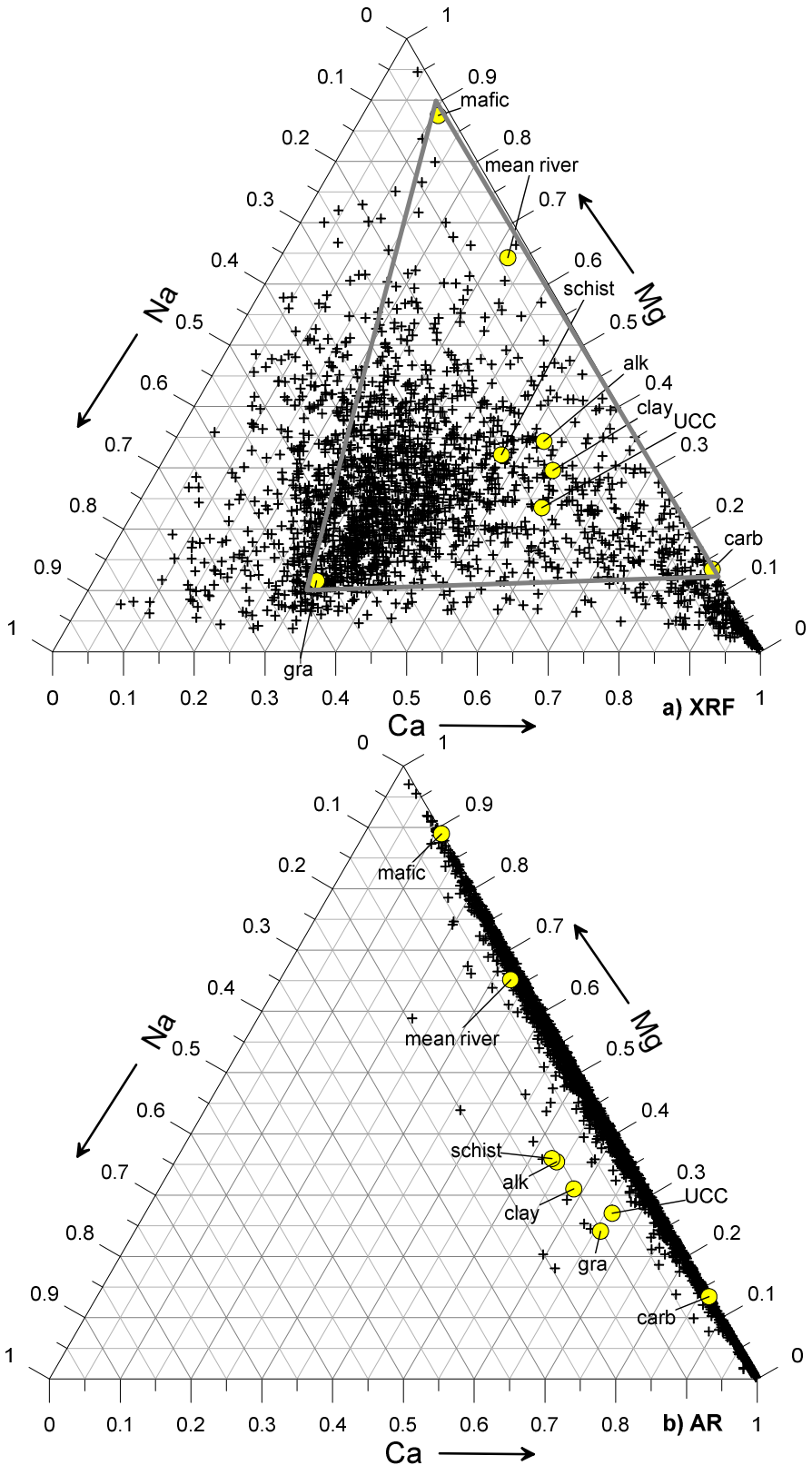
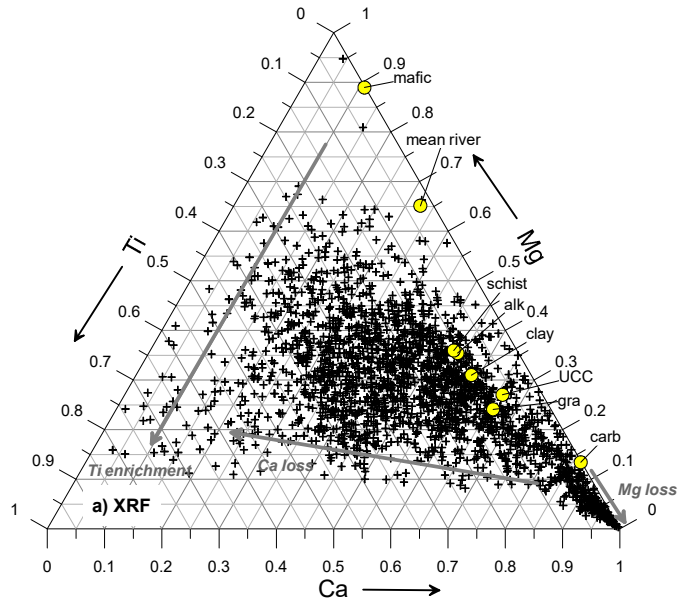


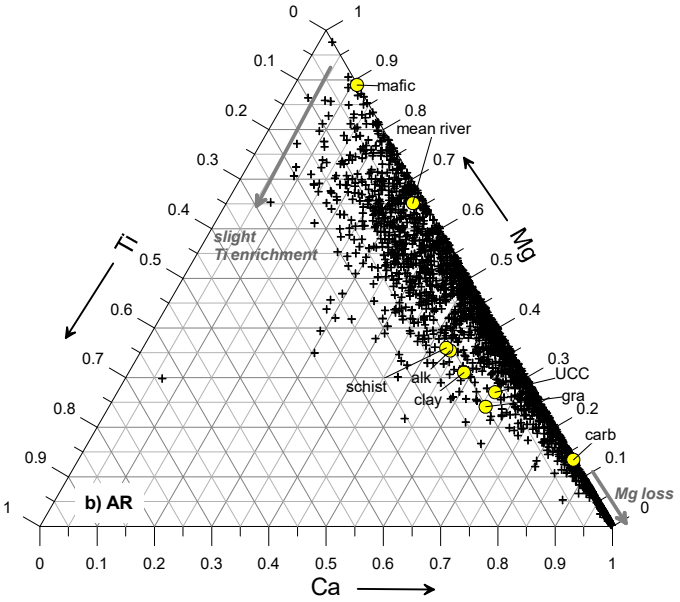
Figure 10. Ca–Mg–Na (in molecular proportions) distribution in GEMAS agricultural soil samples (black crosses), plotted together with bedrock and Upper Continental Crust (UCC) composition (yellow circles) according to Parker (1967) and Rudnick and Gao (2003), respectively. Calcium, Mg and Na Ap data from (a) XRF and (b) aqua regia.

A second ternary plot is the Ca, Mg and Ti association (Figure 11), using their contents in molecular proportions in the GEMAS Ap samples of the XRF (Fig. 11a) *aqua regia* (Fig. 11b) and MMI® (Fig. 11c) results. The GEMAS Ca, Mg and Ti Ap data are plotted together with the main lithological end-members taken from Parker (1967), e.g., plutonic and metamorphic rocks and shale, carbonate rocks and sand-sandstone, and the upper continental crust average from Rudnick and Gao (2003). Using Ti as an insoluble element allows discrimination compared to more soluble elements during weathering like Ca and Mg.

In Figure 11a representing the XRF total concentrations, the main spread of data along the Mg axis reflects the variation in Mg content between sedimentary end-member (carbonate and sandstone) and mafic (ultramafic rocks) end-member parent materials. The closeness of a soil sample approaching the 10% apex along the Mg axis is an indication of similarity to a lithological end-member, with additionally Mg loss during carbonate weathering. The arrowhead lines denote compositional trends of weathering of silicate and carbonate rock types. Increased weathering causes Ca loss and Ti enrichment. Both indices are a measure of the geochemical maturity of soil with respect to the weathering of underlying bedrock.

Figure 11b displays the *aqua regia* extraction results, where again the main spread of data along the Mg axis reflects the variation in Mg content between sedimentary end-member (carbonate and sandstone) and mafic (ultramafic rocks) end-member parent materials. The Mg loss during carbonate weathering is also marked. Increased weathering causes Ti enrichment, which is less marked in the *aqua regia* extraction as compared to the XRF analytical data. This is explained by the fact that Ti is not so soluble in *aqua regia*. Figure 10c, representing the MMI® extraction results, shows a completely different pattern, where there is no Ti enrichment, and Mg loss (e.g., less Mg complexation by the Mg-bearing phases like clays and organic matter brought into solution by the MMI® extraction).


Ti
Mg
Ca
mafic
mean river
schist
alk
clay
UCC
gra
carb
Ti enrichment
Ca loss
Mg loss
a) XRF


Ti
Mg
Ca
mafic
mean river
slight
Ti enrichment
schist
alk
clay
UCC
gra
carb
Mg loss
b) AR

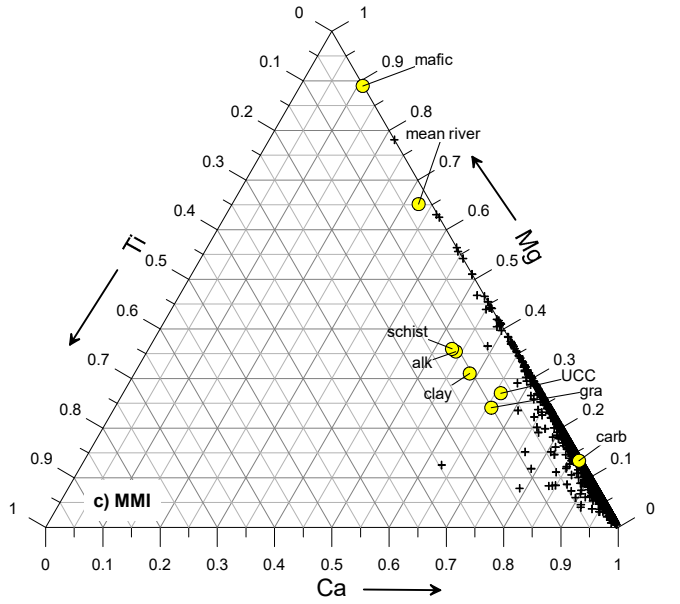

Ti
Mg
Ca
mafic
mean river
schist
alk
clay
UCC
gra
carb
c) MMI

Figure 11. Ca–Mg–Ti (in molecular proportions) distribution in GEMAS soil samples (black crosses), plotted together with bedrock and Upper Continental Crust (UCC) composition (yellow circles) according to Parker (1967) and Rudnick and Gao (2003), respectively. Grey arrowhead lines denote compositional weathering trends of silicate and carbonate rock types towards Ca loss and Ti enrichment. Calcium, Mg and Ti molecular proportions from (a) XRF total, (b) aqua regia extraction, and (c) MMI® extraction.

4.4 Soil classification based on geochemical signature of parent material

To classify the GEMAS soil parent materials the approach used by Caritat et al. (2012) was applied by calculating the relative proportions of five major lithological types. According to the global rock lithology model of Amiotte Suchet et al. (2003), the most common lithologies in Europe are (1) plutonic and metamorphic, (2) shale, and (3) carbonate rocks. Based on these assumption, Caritat et al. (2012) defined the source parent materials where plutonic and metamorphic rocks (39%) and shale (37%) are dominant; carbonate rocks (14%) and sand-sandstone (9.5%) are significant, whereas basalt and felsic volcanic rocks (0.5% each) play a subordinate role.

The Mg distribution is further depicted for chalk (carbonates) and granite, according to the geological parent material subgroups constructed for processing the Ap soil results from the GEMAS data set (Birke et al., 2014b). Figure 12a displays Mg and Al concentrations in the geological parent material subgroup *chalk* (carbonates) for *aqua regia* and MMI® extractions and total XRF contents. Magnesium and Al concentrations, determined by XRF and *aqua regia* extraction, partly overlap and there is a clear shift on the horizontal axis for the Al results reflecting major extractability difference between Mg and Al in *aqua regia* digestion (55% and 22%, respectively; Reimann et al., 2011). In general, the carbonate-rich soil seems to contain substantial amounts of (alumino-) silicate components, including heavy minerals, which are more resistant to the *aqua regia* extraction. It is worth noting that the agricultural soil samples have exclusively lower Mg and higher Al concentrations in both XRF and *aqua regia* extraction results than the value of the carbonate bedrock composition

461 from Parker (1967), which suggests that typical carbonate-rich soil contains more clay
462 weathering products, and Mg is usually one of the elements that is depleted in such soil,
463 possibly due to leaching. The difference in Mg and Al concentrations from the *aqua regia* and
464 MMI® extractions is around three orders of magnitude. Further, the data from the *aqua regia*
465 extraction plot mostly below the 1:1 line, while the majority of the XRF results fall below the
466 1:1 line, and those of the MMI® extraction are above the 1:1 line. These observations suggest
467 that Al in carbonates, apart from its occurrence in carbonates themselves, occurs also in
468 siliceous phases and clays, and can be brought into solution by the MMI® extraction in the
469 chalk (carbonates) subgroup.

470 Additionally, Figures 12b to 12d show measured values by XRF compared to those
471 determined after *aqua regia* extraction for Ca, Mg and Al; in all three diagrams, the carbonate
472 bedrock composition from Parker (1967) is plotted. The values of Ca_{XRF} versus Ca_{AR} in
473 Figure 12b plot along the 1:1 line, with most of the values falling above it, indicating that the
474 XRF results are slightly higher than the corresponding AR. Calcium extractability is 61% for
475 all Ap soil samples, implying that extractability can be even higher for the carbonate-rich soil
476 subgroup. This excellent linear correlation also suggests that almost all Ca in this subgroup is
477 easily leachable and, therefore, hosted in minerals which can be dissolved in stronger acids
478 with high efficiency. Only a slight enrichment of the values measured by XRF over the whole
479 measured range is observed. This enrichment reflects that there is a residual fraction of Ca,
480 which cannot be extracted by the *aqua regia* extraction, mostly occurring in the silicate-clay
481 fraction.

482 The Mg_{XRF} versus Mg_{AR} values shown in Figure 12c plot parallel to the 1:1 line but
483 offset towards the XRF side and, more pronouncedly, with respect to values <10,000 mg
484 Mg/kg, i.e., lower Mg concentrations measured by XRF are clearly higher than those
485 determined by AR. The highest Mg values, measured either by XRF or AR, are close to the

carbonate bedrock composition from Parker (1967). The deviation from the 1:1 line possibly indicates that Mg-rich parent materials have more mobile Mg available than parent materials with primordial low Mg content. The marked enrichment for low Mg values, determined by XRF, suggests either a higher clay content when Mg is less concentrated, or more magnesian carbonates in accordance with lower Ca concentrations.

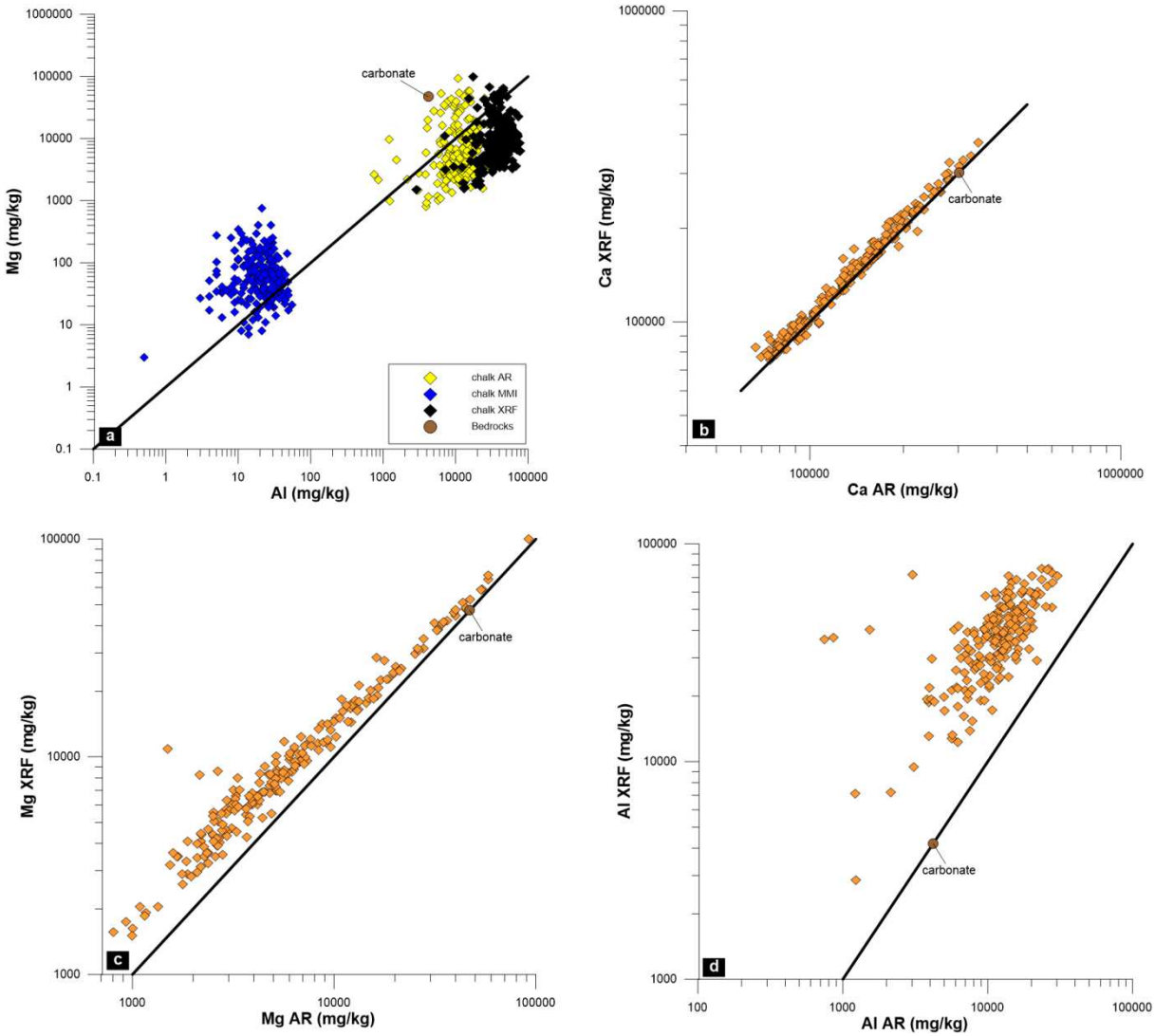


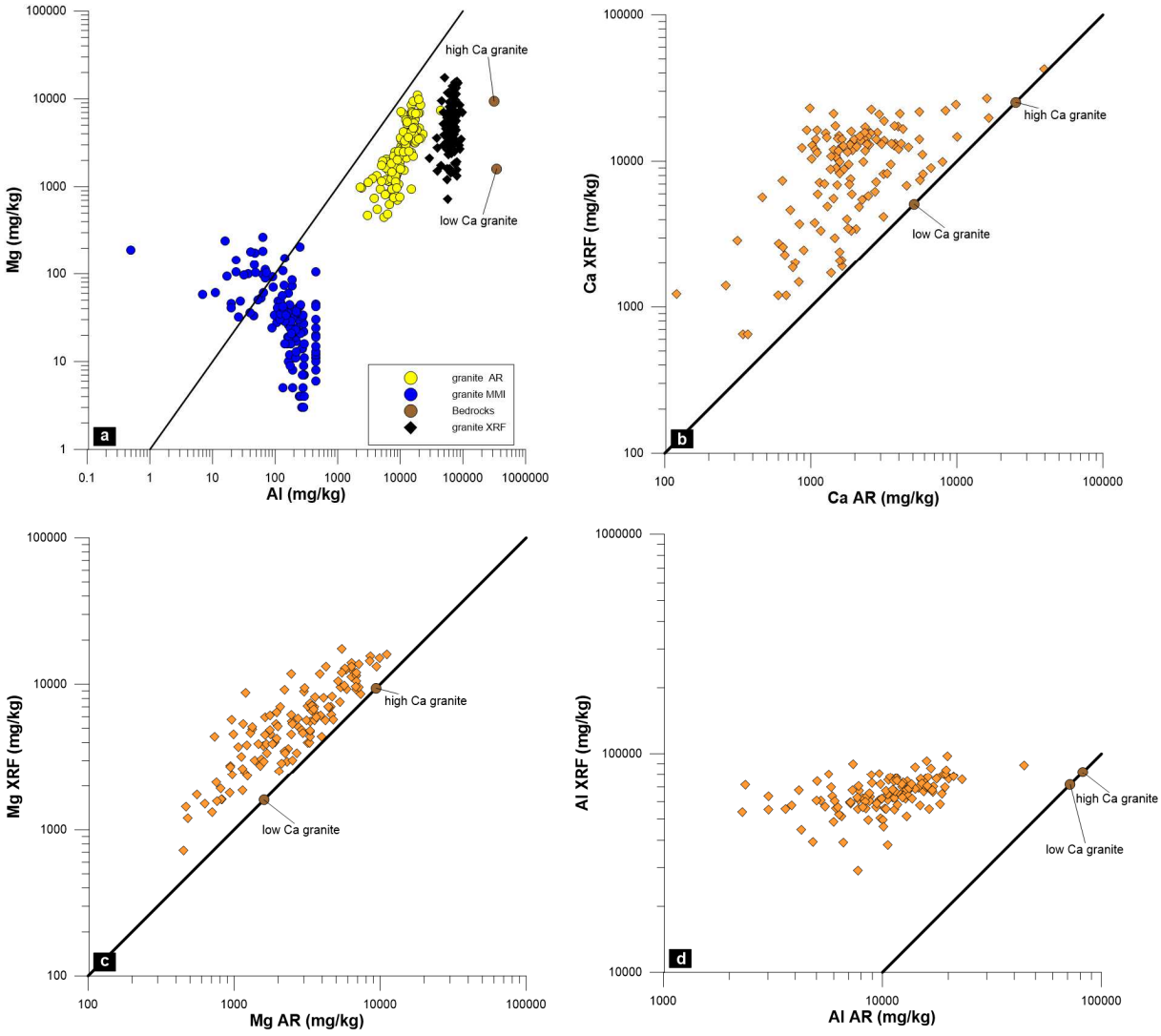
Figure 12. (a) Mg versus Al content in soil subgroup 'chalk' (carbonates) obtained by XRF (black), aqua regia (yellow) and MMI® (blue) extractions; Plots comparing XRF results with aqua regia extraction for Ca (b), Mg (c) and Al (d) in soil subgroup 'chalk'. Reference values of calcareous rock together with carbonate bedrock composition are from Parker (1967).

498 The comparison of Al_{XRF} versus Al_{AR} values in agricultural soil (Figure 12d) shows
499 two major features. First, the concentrations measured by XRF and AR in agricultural soil are
500 higher than the Al concentration in the carbonate bedrock composition as recorded by Parker
501 (1967). This reflects the capability of AR digestion to extract Al from the clay fraction in soil.
502 Secondly, the Al concentrations lie well above the 1:1 line and mainly reflect low Al *aqua*
503 *regia* extractability in soil (ca. 20%), with the XRF data showing substantially higher values
504 than AR results. This may have implications for the weathering patterns in carbonate-rich soil
505 where Mg is the mobile and Al the residual part, resulting in Mg depletion and Al enrichment
506 in agricultural soil. This feature can be observed in karst-rich areas in the Mediterranean
507 region.
508 To evaluate the major difference between carbonate-rich and silica-rich soil parent
509 materials in relation to Mg distribution, another subgroup parent material '*granite*' was
510 examined.
511 Figure 13 displays the Mg, Ca and Al concentrations in the geological parent material
512 subgroup '*granite*' for *aqua regia* and MMI® extractions and total XRF contents. The
513 '*granite*' subgroup has similar geochemical character as two other parent material subgroups:
514 Precambrian bedrock '*Prec*', predominantly consisting of granitic gneiss, and '*schist*'
515 subgroup, which will not be discussed here in detail.
516 The major difference between the '*chalk*' and '*granite*' subgroups observed on the
517 plots of Mg versus Al concentrations, determined by XRF and *aqua regia* extraction, do not
518 overlap in Figure 13a. In this case, the XRF concentrations are one order of magnitude higher
519 than those measured by *aqua regia*, suggesting that Mg in agricultural soil, developed over
520 silicate parent materials, is often hosted by minerals that are insensitive to *aqua regia*
521 digestion, for example, mafic silicate minerals such as olivine, pyroxene, amphibole and some
522 micas. The refractory heavy minerals (e.g., hornblende, tourmaline, staurolite) occurring in

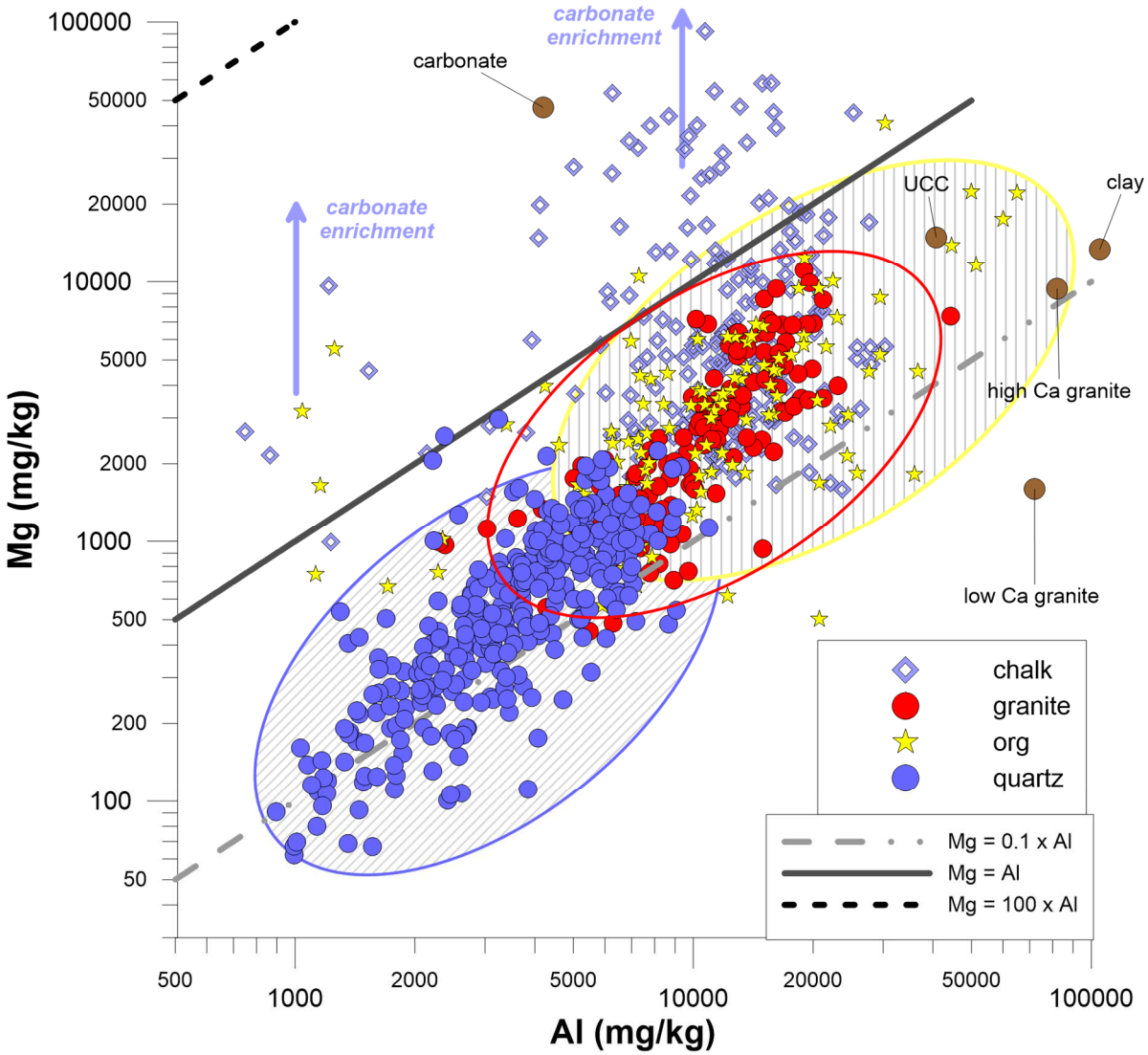
523 the sandy and quartz rich agricultural soil may host Mg to a minor extend, and other minerals
524 like feldspar having Mg within their structures must be considered too. Figure 13a shows that
525 there is no linear correlation between the Mg XRF and AR results. The variation in Mg
526 concentrations is much larger than Al, while the Al content is much higher in the '*granite*'
527 subgroup soil samples than Mg. This is an indication of the weathering status of the '*granite*'
528 subgroup soil, and infers a higher resistance of Al to weathering processes where a significant
529 amount of Al is held within secondary minerals like clays leading to its enrichment in this soil
530 type. While the higher mobility of Mg during weathering results in its removal from the
531 system, often in soluble form. The difference between Mg and Al concentrations from the
532 *aqua regia* and MMI® extractions is around three orders of magnitude. With the exception of
533 several samples plotting above the 1:1 line, reflecting a higher affinity of Mg for the hosting
534 phases (like clays and organic matter), most MMI® extraction results plot below the 1:1 line,
535 suggesting that the amount of organic matter is not sufficient to adsorb all Mg in the forms
536 made available by the MMI® extraction. It also indicates that in the part below the 1:1 line, Al
537 in the MMI® extraction occurs not only in siliceous phases but also in clays, which can be
538 brought into solution by the MMI® extraction. Thus, it is assumed that Al can be accessed by
539 living organisms via soil, plants and water, and thus it is potentially more bioavailable than
540 Mg for the parent material subgroup '*granite*'.

541 Figures 13b-d compare XRF total concentrations with *aqua regia* extraction results for
542 Ca, Mg and Al in the '*granite*' subgroup. Comparison of Ca content in the soil subgroup
543 '*granite*' (Ca_{XRF} versus Ca_{AR}, Figure 13b) shows that all samples plot above the 1:1 line, and
544 they are partly in agreement with the values of low and high Ca granite bedrock composition
545 (Parker, 1967). The higher values, measured by XRF over the whole range, indicate that Ca is
546 located in mineral phases or their interfaces, which cannot be dissolved in strong acids like
547 *aqua regia*, and mostly remain in the silicate-clay fraction. The Mg_{XRF} versus Mg_{AR} values

(Figure 13c) show a more confined trend than for Ca and, with the exception of some outliers, are partly in agreement with the concentration range for granite bedrock composition from Parker (1967). The higher values, measured by XRF over the whole range, reflect the non-extractable Mg remaining in the silicate-clay fraction. The plot of Al_{XRF} versus Al_{AR} values (Figure 13d) is extremely controlled by low Al extractability, and XRF results are tenfold higher than the corresponding AR. Considering that feldspar is the most common Al host in soil developed on crystalline and felsic bedrocks, and it is difficult to dissolve in strong acids, the Al from AR originates most likely from more advanced weathering products such as clays.



559 *Figure 13. (a) Mg versus Al content in the soil subgroup 'granite' obtained by XRF (black),*
560 *aqua regia (yellow) and MMI® (blue) extractions. Plots comparing XRF results with aqua*
561 *regia extraction for Ca (b), Mg (c) and Al (d) in the soil subgroup 'granite'. Reference values*
562 *of high and low Ca granite bedrock composition are from Parker (1967).*
563
564 The solid phases commonly anticipated to dissolve, during sequential extraction,
565 according to the initial work of Tessier et al. (1979), are carbonates (exchangeable ions and
566 acid extractable), Fe–Mn-hydroxides (reducible), sulphides and organic matter (oxidisable).
567 The other phases, e.g., some silicates and well-crystallised oxides, are generally not extracted
568 by *aqua regia* (residual). Such sequential extraction is used for prediction of deficiency or
569 toxicity and assessment of soil trace element status in soil (Ure, 1996). The AR digestion has
570 the capability to extract elements from the clay fraction, as well as to dissolve Fe-Mn oxides
571 and carbonates and organic matter and is considered to assess the extent of element
572 concentration in a pseudo-total digestion (Ure, 1996). Strong acid digestions, such as *aqua*
573 *regia,* are commonly employed even though silicates and other refractory oxides are not
574 completely dissolved, the recovery is often >75% and never 100% (Chen and Ma, 2001).
575 Clay minerals may contain appreciable quantities of Mg either in inter lattice sites or
576 in exchange positions resulting from broken edges or unbalanced charges. Magnesium, like
577 Al, is especially common in montmorillonite, chlorites, and vermiculites (Kahle, 1965).
578 However, Al interlayers in soil, developed from silicate bedrocks (granite, gneiss and schist),
579 are more pronounced and stable than in soil derived from basaltic rock or limestone
580 (Sawhney, 1960). Mixed Mg-Al hydroxides occur frequently (Brown and Gastuche, 1967;
581 Mascolo and Marino, 1980), and both clay minerals and Al or Fe oxides/hydroxides can sorb
582 dissolved organic carbon (DOC). Surfaces of minerals in soil, capable of sorbing DOC, may
583 be distinguished into two dominant types: (1) surfaces of phyllosilicate clay minerals
584 containing cation exchange sites, and (2) surfaces on the external periphery of pedogenic
585 oxides/oxyhydroxides minerals (Kahle et al., 2004), with oxides usually being better sorbents
586 than phyllosilicate clay minerals (Jardine et al., 1989; Kaiser and Zech, 2000).



587

588 *Figure 14. Plot of Mg vs. Al contents in Ap soil samples for aqua regia extraction data for the*
589 *parent material subgroups 'chalk', 'granite', 'org' (organic soil), and 'quartz' (soil*
590 *developed on coarse-grained sandy deposits). The blue shaded field delineates quartz parent*
591 *material group; the yellow shaded area – the organic parent material soil group, and the red*
592 *ellipsoid – the granite parent material group.*
593

594 In Figure 14, the aqua regia Mg *vs.* Al concentrations in Ap soil samples were used for
595 the four parent material subgroups '*chalk*' (carbonates), '*granite*', organic soil subgroup (*org*)
596 and '*quartz*' (soil developed on coarse-grained sandy deposits). The first two subgroups
597 ('chalk' and 'granite') can help to investigate the role of organic residues in terms of sorption
598 with the subgroup organic soil (*org*), and the same role of clay minerals regarding soil

599 developed on coarse-grained sandy deposits, e.g., the moraines of the last glaciation, with the
600 subgroup '*quartz*' (Négrel et al., 2018a).

601 The *aqua regia* extraction results for the subgroups organic soil (*org*) and soil
602 developed on coarse-grained sandy deposits (*quartz*) plot below the Mg/Al 1:1 line, and
603 mostly above the 0.1 Mg/Al line. Both are marked by the hatched ellipses that, with the
604 exception of some outliers, encompass the majority of data. An enrichment of the Mg/Al ratio
605 for '*quartz*' can be observed together with enrichment for the highest Mg and Al
606 concentrations. For organic soil (*org*), the data of the *aqua regia* extraction show higher
607 concentration for Mg and Al in comparison to the range of subgroup '*quartz*', and an overlap
608 of the lower concentrations of the subgroup '*org*' with the higher values of subgroup '*quartz*'.
609 The range observed in the '*granite*' subgroup in Figure 14, has similar Mg and Al
610 concentrations as most of the '*organic*' soil samples, with the exception of some outliers. As
611 far as the role of organic residues in the '*granite*' subgroup, this can be interpreted as the
612 presence of Mg-Al rich mineral phases, most likely Al or Fe oxides/hydroxides. For the
613 '*granite*' subgroup, the importance of clay minerals and fine-grained hydroxides in the
614 geochemical cycles of Mg and Al in soil start from the clay end-member from Parker (1967),
615 and follow a downward trend along the Mg/Al 0.1 ratio line towards the lowermost values of
616 Mg and Al observed in the '*quartz*' subgroup. The role of clay minerals, thus, appears not so
617 important compared to that played by the organic residues in the '*granite*' subgroup, as the
618 highest Mg-Al concentrations for the '*quartz*' subgroup overlap with the lowest
619 concentrations observed in the '*granite*' subgroup.
620

621 # 5 – Conclusions

622

623 The GEMAS European agricultural soil results can be used to define the 'normal' Mg
624 concentration ranges (25^{th} to 75^{th} percentile of the distribution) in agricultural soil at the
625 European scale using three different analytical techniques. Normal total Mg concentrations
626 (XRF) range from 3015 - 9407 mg/kg. In an *aqua regia* extraction, they range from 1370 -
627 5447 mg/kg Mg. For the MMI® extraction, which comes closest to 'plant available' contents,
628 the normal range is from 26 to 103 mg/kg Mg.

629 Due to the importance of Mg for plants, the occurrence of unusually low
630 concentrations in agricultural soil is of more concern than the high concentration range. In
631 Europe, unusually low Mg concentrations in agricultural soil for both XRF and *aqua regia*
632 results are observed on top of the quartz-rich glacial sediments in north-central Europe
633 (Poland, Baltic States, N. Germany), and a sandstone unit at the Swedish/Norwegian border.
634 In contrast, unusually high Mg concentrations occur predominantly on top of known ophiolite
635 belts and carbonates (e.g., Hellas and eastern Spain, respectively). The maximum extent of the
636 last glaciation is visible on all three maps as a clear Mg concentration break. In the MMI®
637 extraction, a quite different pattern emerges. Large areas in Fennoscandia additionally show
638 low Mg concentrations, indicating that weathering and soil formation are still in a stage where
639 many Mg-bearing minerals are not easily dissolved. High concentrations in MMI® do still
640 predominantly occur on top of ophiolites, however, on a much more restricted scale than
641 observed for *aqua regia* available or total XRF concentrations. Thus, geology still plays the
642 key role in determining the distribution of Mg in agricultural soil at the European scale, while
643 agricultural practice and the use of fertilisers seem to play a subordinate role.

644 To better understand the factors that determine the availability of Mg, the *aqua regia*
645 and MMI® extraction results were studied in more detail on four different substrates (organic
646 soil, quartz-rich soil, soil developed on granite and soil on top of calcareous rocks). The

results highlight the importance of organic material, the presence of clay minerals (grain size distribution of soil) and fine-grained hydroxides for the observed element concentrations.

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