

Mobile Metal Ion[®] analysis of European agricultural soils: bioavailability, weathering, geogenic patterns and anthropogenic anomalies

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Abstract: Two thousand one hundred and eight agricultural soils (0–20 cm depth) collected at a density of one sample per 2500 km² under the auspices of the Geochemical Mapping of Agricultural Soils (GEMAS) project over most of the European continent have been analysed using the Mobile Metal Ion (MMI[®]) partial extraction technique with ICP-MS finish. For a number of elements, notably Ce, Ni, and Ca, coherent geogenic patterns have been observed which relate to underlying lithology. For Fe and Al, coherent patterns are also observed but the effects of weathering are evident, and provide a mechanism to explain the acidity of soils in high rainfall areas. Individual anomalies, many related to anthropogenic activity (mining, metallurgy, agriculture) have been observed for Ag, Au, Cu, Pb, Cd and Zn. Comparison of the results with aqua regia digestion and the equivalent National Geochemistry Survey of Australia (NGSA) provides insights into weathering processes and the concept of bioavailability.

Keywords: MMI[®] extraction, ICP-MS, geogenic patterns, anthropogenic anomalies, bioavailability, geochemical mapping, GEMAS

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Introduction

The Mobile Metal Ion (MMI[®]) technique is most often used on a prospect scale to identify sources of mineralization (Mann *et al.* 1998). However, recently some MMI[®] projects have been conducted at the regional and continental scale. The National Geochemical Survey of Australia (NGSA; see www.ga.gov.au/ngsa) was initiated in late 2006 by Geoscience Australia (Caritat *et al.* 2008; Caritat & Cooper 2011). The ultra-low density continental geochemical survey targeted transported regolith samples collected on the floodplains of large catchments, as much as possible. Because in many places the influence of aeolian material could not be avoided, this medium was more generally termed 'catchment outlet sediment' and was collected at the lower point of large catchments, be it near the catchment boundary or somewhere more central for internally draining catchments. Coverage of 81% of the Australian continent (>6 million km²) was achieved with some 1315 sites (including field duplicate sites) collected at an average sample density of 1 site/5200 km². The results of this study pertaining to nutrients were reported (Mann *et al.* 2012) but useful information, particularly relating to background and threshold levels for another 40 elements after MMI[®] extraction was also

obtained. Coherent regional patterns, some relating to lithology and weathering were clearly evident. Other anomalies relating to mineralization (e.g. for Au) and anthropogenic activities were also obtained (Mann *et al.* 2013). As a result, MMI[®] extraction was included in the GEMAS (GEOchemical Mapping of Agricultural Soils) European sampling project. Data in the form of kriged images were reported for some elements in Mann *et al.* (2014).

The reason for inclusion of MMI[®]-derived data into the GEMAS project was succinctly addressed in an early publication of GEMAS XRF and aqua regia data (Reimann *et al.* 2011). This report asked the question "what is the bioavailability of metals and other chemical elements in soil?" Clearly the restricted ability of XRF and aqua regia digestion to provide this information was apparent. The need to establish (where possible) natural background and to differentiate anthropogenic impact from geogenic background was well formulated, and a role for MMI[®] extraction and analysis in the project established.

Whilst MMI[®] extraction and analysis has a diagnostic response to lithology for some elements, principally Ce, Ni, Ca, Fe and Ti (Mann 2010), for a majority of elements including most base metals the highest response is to mineralisation and/or anthropogenic activities. The soil matrix is not dissolved, the analytes in solution being obtained from the portion of elements adsorbed (as ions) on the sur-

face of soil particles. Samples for MMI[®] analysis are normally taken from a depth of 10–25 cm in true soil (Mann *et al.* 2005), believed to be the zone of maximum evapo-transpiration in most soils. Given that soil pore waters also contain a number of inorganic and organic species capable of complexing metal (and non-metal) ions, while leaving the soil substrate relatively unaffected, MMI[®] analysis has the potential to provide a measure of bioavailability. Although bioavailability is relatively simple to parameterize under controlled simulated conditions, this is not true for field conditions (Iskander & Kirkham 2001). A number of factors, including the large number of elements, the range of soil types and the array of plant and animal species, make this a formidable task for partial digestion and extraction techniques. At best, bioavailability, when estimated by partial extraction (or digestion), is operationally defined, which means no two extractants will provide identical estimates.

A number of partial extraction chemicals have been used or have the potential to be used for assessment of bioavailability. Very few of these have the widespread elemental capability of the MMI[®] technique. Because of the inclusion into the extraction solution of a number of strong complexing agents, simultaneous analytical data can be obtained for base metals, transition metals, some precious metals, rare earth elements and some non-metals after MMI[®] extraction. Hall (1998) examines a number of reagents, in relation to their attack on specific soil phases and relevance to mineral exploration rather than agriculture or environmental monitoring. For example sodium acetate/acetic acid (NaOAc/HOAc) is a preferred reagent for dissolution of the carbonate phases, hydrogen peroxide (H₂O₂) or sodium hypochlorite (NaOCl) is used for selective dissolution of ‘soluble’ organics and hydroxylamine hydrochloride or Enzyme Leach is used for manganese oxide phases. Tamm’s reagent (ammonium oxalate in oxalic acid) and hydroxylamine hydrochloride are commonly used for release of elements attached to amorphous Fe oxide. The use of sodium pyrophosphate for treatment of humic substances and the issue of re-adsorption prior to analysis are also examined by Hall (1998). Magnesium and calcium chloride, sodium nitrate and ammonium nitrate provide unbuffered neutral salts for determination of many ‘exchangeable’ mobile species. An example of the application of calcium chloride (and sequential extraction) to Polish soils is given by Siebiel *et al.* (2006). Partial digestions have long been utilized in agriculture; individual techniques such as the Colwell method for P (Colwell 1967*a, b*) and the DTPA method for Cu, Fe, Mn, and Zn (Lindsay & Norvell 1978) have been designed to closely approximate the amount estimated to be obtained from a soil by plants by comparison with plant uptake studies (e.g. Podlesakova *et al.* 2001). The paper by Mann *et al.* (2012) indicated the correlation of values for MMI[®]-extractable nutrients with those from these techniques. Hall (1998) found that 1 M NH₄Cl and 0.1 M Na₄P₂O₇ extractions applied to chernozem and podzol soils on the Canadian prairies could be used to predict uptake of Cd in durum wheat, in contrast to a 1 M NH₄NO₃ extraction which suffered from severe problems of re-adsorption of elements during leaching.

Measurement of the bioavailable component in a soil is useful in assessing the environmental impact of anthropogenic activity. Ammonium acetate-EDTA (AA-EDTA) was used by Albanese (2008) in a classic study of urban geochemistry in a number of town-sites in Italy. Tarzia *et al.* (2002) used Pb isotope studies to distinguish between geogenic and anthropogenic lead contamination at a steelworks site near Naples whilst Cohen *et al.* (2012) used aqua regia extractable and total element geochemistry to attempt to distinguish between the effects of lithology and anthropogenic activity in Cyprus. They found that, for most elements, the soil geochemistry is dominated by parent lithology and subsequent regolith effects. Sajn (2005) used four-acid digestion of attic dust and soil to distinguish between natural and anthropogenic element sources in an old metallurgical area in Celje, Slovenia. A study utilising aqua regia digestion and ICP-MS analysis in Naples (Cicchella *et al.*

2005) was used to compile background and baseline data values of elements considered harmful to human health.

Strong acids dissolve soil phases and provide useful analytical data, but even more potentially useful information regarding bioavailability, mobility and chemical weathering is provided by ‘weak’ extraction solutions which contain strong complexing agents for elements. Mann (2010, p. 18) emphasizes that the distinction between a partial digestion and partial extraction is technically important and needs to be recognized. A *partial digestion* is one in which part of the soil matrix is dissolved (as opposed to conventional or total digestion where the entire soil sample is dissolved). A *partial extraction* attempts to dissolve or detach analytes from the soil matrix without dissolution of the matrix, thereby reducing background interference. The independent Canadian CAMIRO project (Hamilton *et al.* 2001) evaluated a number of partial digestions and extractions at Cross Lake in the Abitibi Belt of Canada. As reproduced by Mann (2010), it clearly shows the advantage of MMI[®] over aqua regia for detection of very low-level anomalies. In this case, Pb and Zn anomalies are located in exotic material (glacial till) over the Cross Lake volcanogenic massive sulphide mineralization *c.* 35 m below. Partial extraction geochemistry should also have useful application to the delineation of anthropogenic v. lithological anomalies.

Methods

Sampling

The GEMAS project was initiated by EuroGeoSurveys (EGS) geochemistry Group in 2008 and carried out in co-operation with financial support from Eurometaux, the European Association of Metals. Each member Geological Survey agreed in late 2007 to early 2008 to collect samples according to a jointly agreed field procedure. The sampling density was 1 per 2500 km². The whole territory was divided into 50 km × 50 km sampling cells, the countries were free to decide where within a cell to take the samples. Two types of sample were collected the ‘Gr’ sample from land under permanent grass cover (0–10 cm) and an ‘Ap’ sample from the ploughing layer of agricultural land at a depth of 0–20 cm. The MMI[®] extraction and subsequent ICP-MS analysis were undertaken only on the ‘Ap’ sample.

Sample analysis and quality control (QC)

Sample analysis was undertaken at the Toronto laboratory of SGS. Extracts were prepared using standard MMI[®] protocol; 50 g of sample were mixed with 50 ml of MMI-M solution and shaken for 30 mins. They were allowed to stand overnight before centrifuging for 10 mins at 8500 rpm, using a Sorvall Evolution RC (ThermoElemental Corporation). Extracts were analysed using a PerkinElmer NexION 300D ICP mass spectrometer fitted with a Universal Cell, by measuring them against calibration standards prepared in MMI-M matrix solution. Chromium, V and Se were measured in reaction mode using ammonia gas to remove matrix interferences. Sulphur was measured by a PerkinElmer Optima 4300DV ICP emission spectrometer using matrix matched standards. Laboratory internal quality control (QC) criteria included randomised duplicate analysis every 13 samples, plus blank and reference materials inserted every 46 analyses. The acceptance criteria were based on a limiting repeatability of 20%, and a lower level of detection of 2.5× the reporting limit for each analyte.

Laboratory-independent, external QC for the GEMAS project started during the sampling campaign: a field duplicate was collected at each 20th sample site (Reimann *et al.* 2011, 2012). During sample preparation an analytical replicate sample was prepared of each field duplicate. Finally, all samples were randomized and standard samples were also hidden between the real samples so that the laboratory could recognize neither the standards nor the analytical duplicates. When the analytical results were received standard,

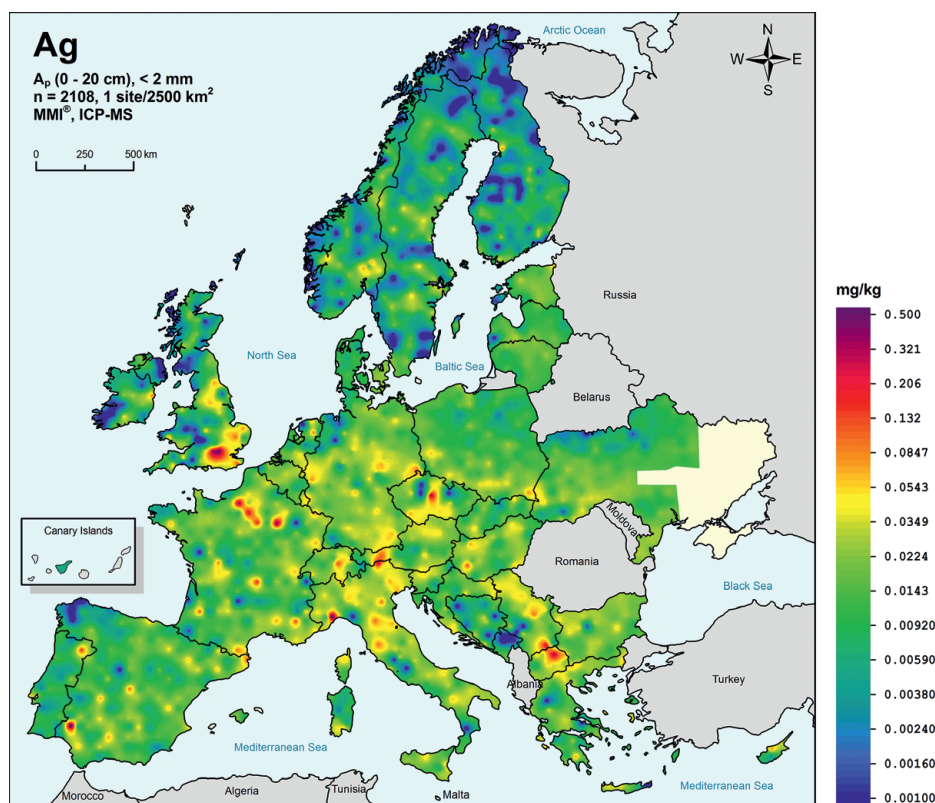


Figure 1. Colour surface map for Ag in European soils after MMI® extraction and ICP-MS analysis.

field duplicate and analytical replicate results were retrieved from the data set and X-charts and ‘Thompson and Howarth’ plots were prepared (Reimann *et al.* 2012). Precision was calculated based on the field duplicates, and an unbalanced analysis of variance (ANOVA) was carried out to estimate the suitability of the data for the construction of geochemical maps. The QC results suggest that the following elements can be mapped: Ag, Al, As, Au, Ba, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Hg, In, K, La, Li, Mg, Mn, Mo, Nb, Nd, Ni, P, Pb, Pr, Rb, S, Sb, Sc, Sm, Sn, Sr, Ta, Tb, Th, Ti, Tl, U, V, W, Y, Yb, Zn, Zr (Reimann *et al.* 2012).

Data analysis

Kriging is the recommended approach for generating raster maps from point source data (Reimann 2005) and this method was used to present maps in the GEMAS Atlas (Reimann *et al.* 2014a, b). In the present document coloured surface maps were generated from gridded data; kriging was used to convert the values from the irregularly distributed sampling sites to a regular grid for representation of the geochemical data on a map. A variogram analysis was then made to compile the parameters of the kriging function. The values at the points of the resulting regular grid were classified into 72 separate classes for each element. Areas of the same class were then formed and given the same colour on the element map. In this way both anomalously high (and low) values and the distribution of local and regional background values can be easily visualized. (Note: 1 mg/kg = 1 ppm (part per million) = 1000 ppb (parts per billion)).

Results

Continental-scale mapping of selected elements after MMI® extraction

Colour surface maps for some selected elements after MMI® extraction and ICP-MS analysis are presented in alphabetical order of their chemical symbols. Geochemical patterns and anomalies in soils essentially arise from three sources: (a) lithology; (b) mineralization; and (c) anthropogenic activities. The latter can be related

to agriculture, metallurgical processes or waste disposal whilst the former two can be influenced by weathering processes. The maps, plotted in Lambert Equal Area coordinates, will be investigated with all of these factors in mind.

The colour surface map for Ag (Fig. 1) shows the site with highest MMI® Ag (1.34 mg/kg) in European Ap soils is 80 km NW of Seville and 40 km NW of the Rio Tinto mining area in southern Spain. The Rio Tinto area is famous for rich concentrations of Cu, Ag and Mn which were exploited from the Bronze Age up until a few decades ago. The study of the Corta Lago site (Bronze Age to the second century AD) by Anguilano (2012) using XRD, XRF and ICP-MS (for Pb isotopes) interestingly found metallurgical processes centred on the mineral jarosite (which contained 1% Pb) and more akin to Fe than to Ag. Coincidentally the anomalous soil site, which is in a wooded area has high concentrations of Cu (1.55 mg/kg), Mn (35.8 mg/kg) and Pb (9.88 mg/kg), suggesting a nearby source with a similar style of mineralization. The Seine Valley of France has a number of sites with high values for Ag, the highest being 0.629 mg/kg. The median for Ag is 0.014 mg/kg or 14 ppb. Silver was the basis of the currency for the Roman Empire; the high values possibly reflect the re-distribution which has occurred after many centuries of metallurgical processing and usage.

The colour surface map for Au (Fig. 2) displays the highest value for MMI® Au (0.0237 mg/kg), in a field in northeastern Portugal. It is 8.6 km SE of Mirandela, a gold mining area since Roman times. The same soil sample has the highest value of all Ap samples for As of 0.530 mg/kg, probably indicating the association of Au with arsenopyrite. Whilst it is unlikely that this soil anomaly relates directly to this source, it is feasible that it relates to a similar style of mineralization (not necessarily economic) closer to the sample site in the same geological terrain, terrain which is unlikely to have this level of Au (or As) as uniform background. The second highest Au value in European Ap soils (0.0144 mg/kg) is from a field 1.8 km SE of Bujanovic in SE Serbia. Petkovic (2009) identifies three areas of archaeological interest in Eastern Serbia, all related to Roman mining and metallurgical activity, principally involving Au, Ag, Cu, Fe and Pb.

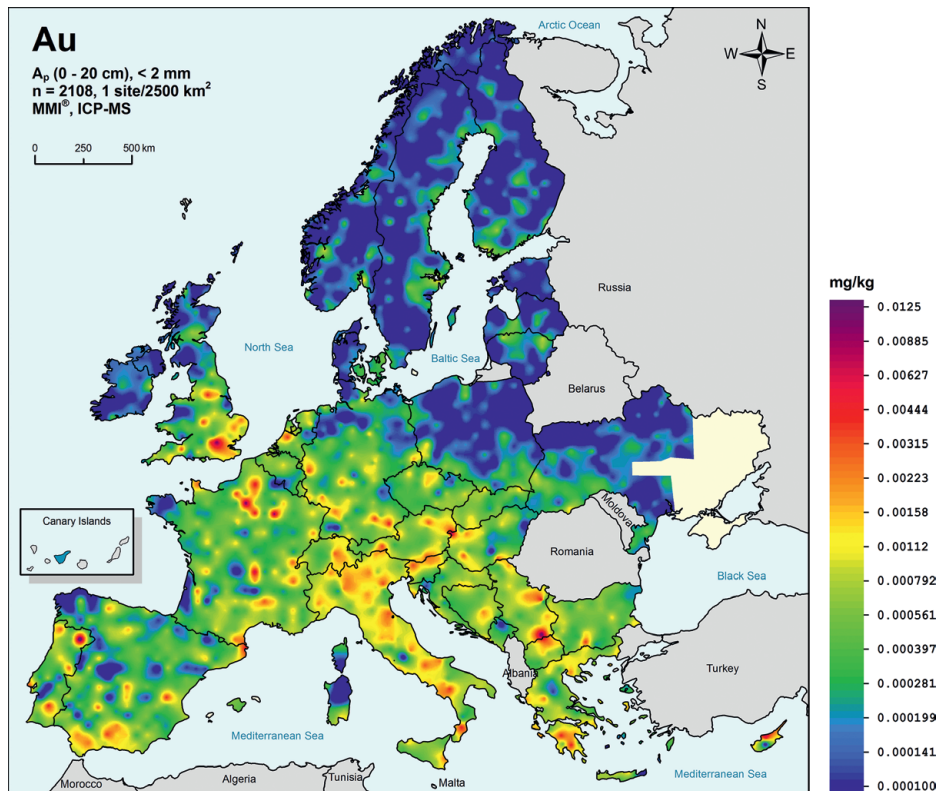


Figure 2. Colour surface map for Au in European soils after MMI[®] extraction and ICP-MS analysis.

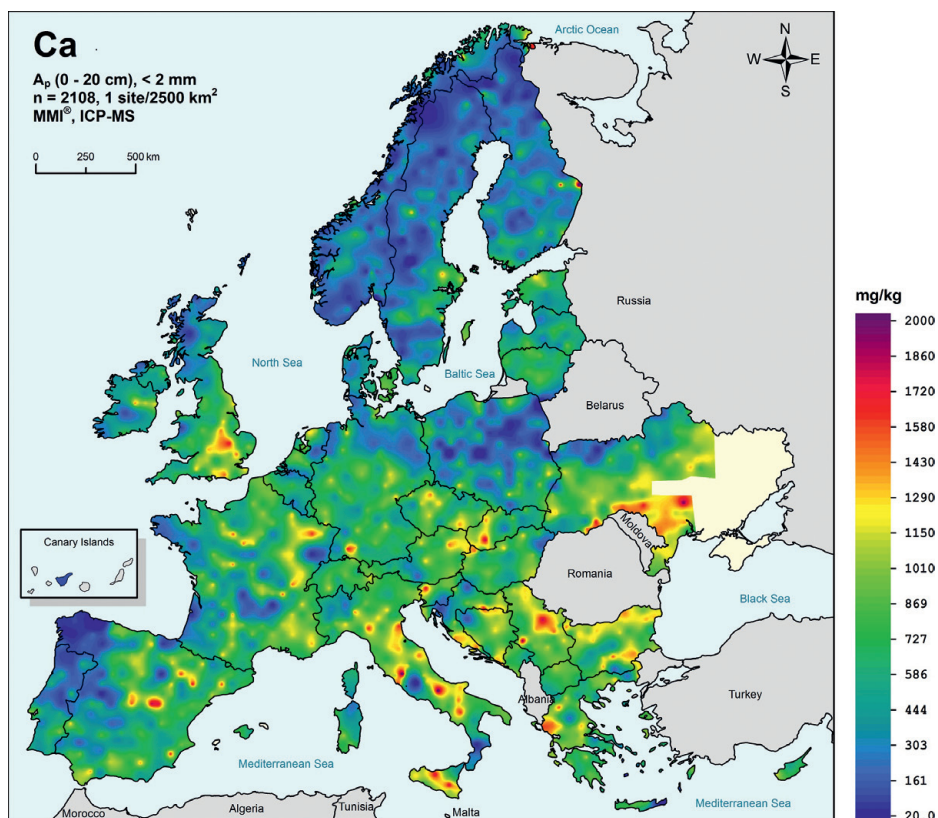


Figure 3. Colour surface map for Ca in European soils after MMI[®] extraction and ICP-MS analysis.

This field site also shows anomalous levels of Ag (0.265 mg/kg), Cu (4.23 mg/kg) and Pb (3.45 mg/kg), again suggesting comparable mineralogy. It is interesting that the next two highest MMI[®] Au values (0.0121 and 0.0114 mg/kg Au, respectively) are within 20 km of Paris and London, respectively, and clearly related to contamination rather than mineralization. Whilst there is Au mineralization in the Fennoscandian Shield, the MMI[®]

anomalies in this region are not as pronounced; Au after aqua regia digestion shows a similar pattern (Reimann *et al.* 2014a). The reasons for this are not yet fully understood, but possibilities include site proximity, the influence of soil age, weathering, the extent of glaciation, pH, the amount of dispersion during mining and metallurgical activities or distribution through usage. The highest MMI[®] Au value (19.8 ppb) in the equivalent Australian

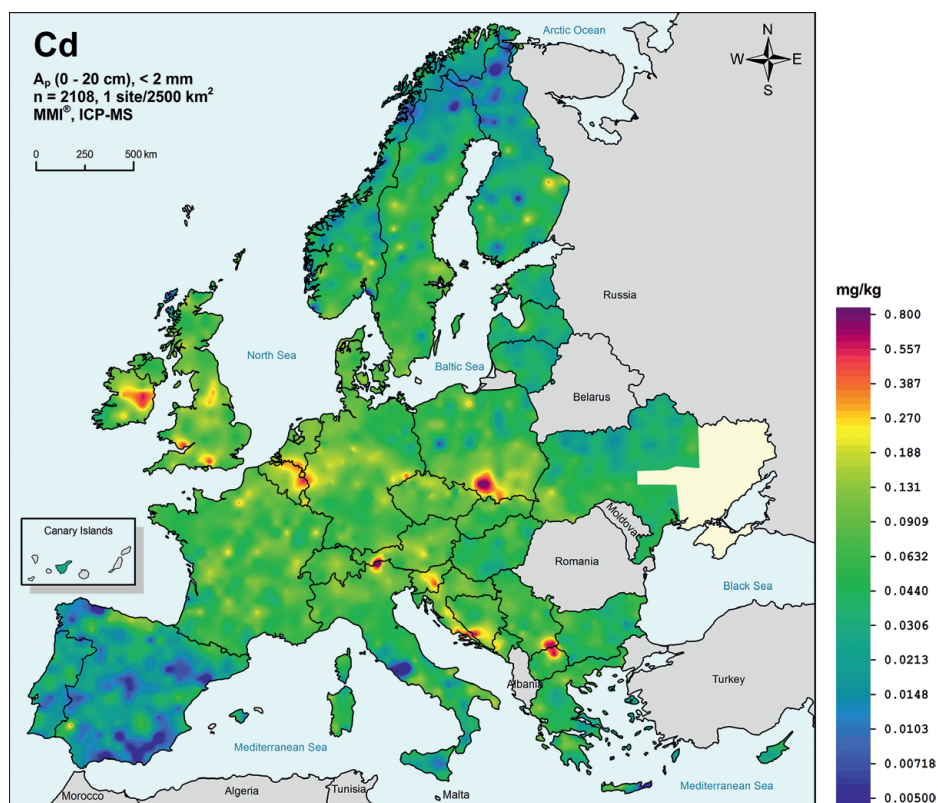


Figure 4. Colour surface map for Cd in European soils after MMI® extraction and ICP-MS analysis.

(NGSA) survey (Mann *et al.* 2013) was from an overbank sediment of the Burdekin River near Ayr in Queensland.

The colour surface map for Ca (Fig. 3) shows soil locations with MMI® Ca values of >1150 mg/kg highlighted in orange and red. In Australia the 800 mg/kg level of MMI® Ca has been linked to soils containing carbonate material (Mann *et al.* 2012). In the present case, the possibility that Ca is also reflective of naturally occurring gypsum, or gypsum or lime which has been added to ameliorate the soil, must also be kept in mind. Carbonate can be derived from primary carbonates (including dolomite), but may also, in arid and semi-arid areas, be derived from secondary carbonate, particularly if basic or ultrabasic rock types are actively weathering. In the present case, high Ca is most prevalent in southern Europe, but it is also apparent that sedimentary carbonates are contributing to high Ca soil values in the eastern UK, Sweden, Finland, and parts of France, Germany, Poland, Estonia, Lithuania the island of Oslund (Sweden) and the Ukraine. Predictably, from a climatic point of view, the concentrations of Ca in agricultural soil are greater the further the sampling point is to the SE in Europe. This is the area of lowest rainfall, and greatest evaporation, conditions which favor the accumulation of calcium carbonate in the soil.

The colour surface map for Cd is shown in Figure 4. The median for Cd is 0.055 mg/kg with a maximum value of 2.811 mg/kg in a field close to the border between Italy and Austria. This site also shows anomalous levels of Ag (0.315 mg/kg), Pb (7.37 mg/kg) and Zn (26.4 mg/kg), probably related to local mining activity; sphalerite usually contains high levels of Cd. The industrial area along the border of Belgium, The Netherlands and Germany also exhibits red and orange hues indicative of high values for Cd. This industrial area also has soils anomalous in Zn. In general, however, the broad distribution of high values for Cd over central Europe (as shown in yellow hues) is reflective of the use of phosphate fertilizer, which, if derived from guano inevitably contains high levels of Cd derived from the marine food chain. The change from green to blue hues in the Cd map across the border of France with Spain suggests different levels of fertilizer application in those two countries. It will be seen in the case of Cu, this also relates to application of fungicides to vineyards.

Cerium, being an element with large ionic radius, is excluded from mafic melts. It is an element which often relates closely to granitoid lithology (Mann 2010). The high values of Ce, shown in Figure 5 in red and orange, coincide with the granitoids of the Fennoscandian Shield, The Dalradian Belt of Western Scotland and Ireland, the Massif Central of France, the Galician area of northern Spain and Portugal as well as areas in Corsica, Sardinia and parts of eastern Europe. A number of other rare earth elements and yttrium and scandium show similar patterns.

The distribution pattern for Cu (Fig. 6) shows a number of interesting features. Regionally high values of Cu associated with ophiolite and ultrabasic lithology are evident in northern Italy, Slovenia, Bosnia-Herzegovina and Greece. Most of the highest individual Cu values are, however, associated with the vineyards of France and Italy where 'Bordeaux mixture' is used as a fungicide. The highest value of MMI® Cu, 62.1 mg/kg, occurs 20 km south of Bordeaux in a vineyard soil. The second highest value (58.8 mg/kg) for MMI® Cu in A_p soil is attributable to a field in Galicia, NW Spain. This has been a copper mining district since the Bronze Age, and accordingly high Cu soil values in this geological terrain cannot be automatically attributed to spraying with copper fungicide. The third highest Cu value of 58.6 mg/kg and 'still extreme' by normal MMI® standards is from a vineyard soil 20 km NE of Montpellier in SE France, whilst the fourth highest Cu value is from a vineyard in the Alsace region of NE France. The soil value for MMI® Cu for the latter is 56.7 mg/kg Cu. A value of 51.9 mg/kg Cu is registered from yet another wine growing district, the Beaujolais, c. 25 km NW of Lyon in central France, and the value of 46.9 mg/kg Cu from a soil in the recently expanded Languedoc Roussillon wine growing district of southern France indicates that high values of MMI® Cu are widespread throughout most wine-growing districts of France. It is surprising to find that Cu values are comparatively low in the vineyards of Spain, immediately to the south; instead they appear to have a number of high values of S in soil. Sulphur is also used as a fungicide, particularly in vineyards.

The colour surface map for Fe (Fig. 7) shows a very clear demarcation between northern and southern Europe. The highest

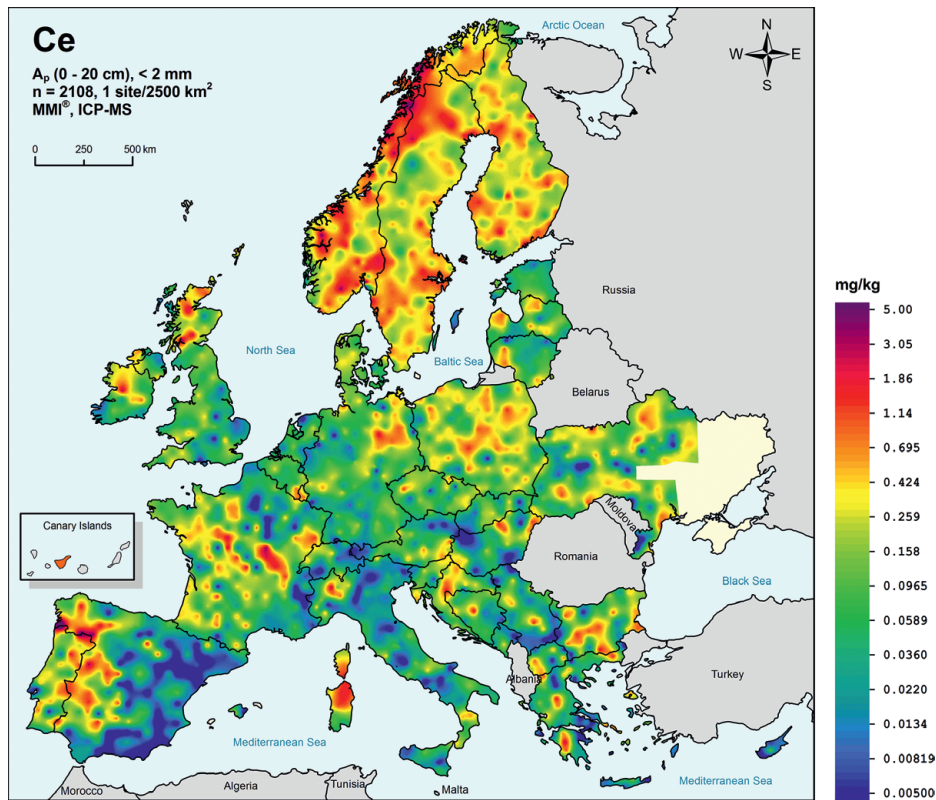


Figure 5. Colour surface map for Ce in European soils after MMI[®] extraction and ICP-MS analysis.

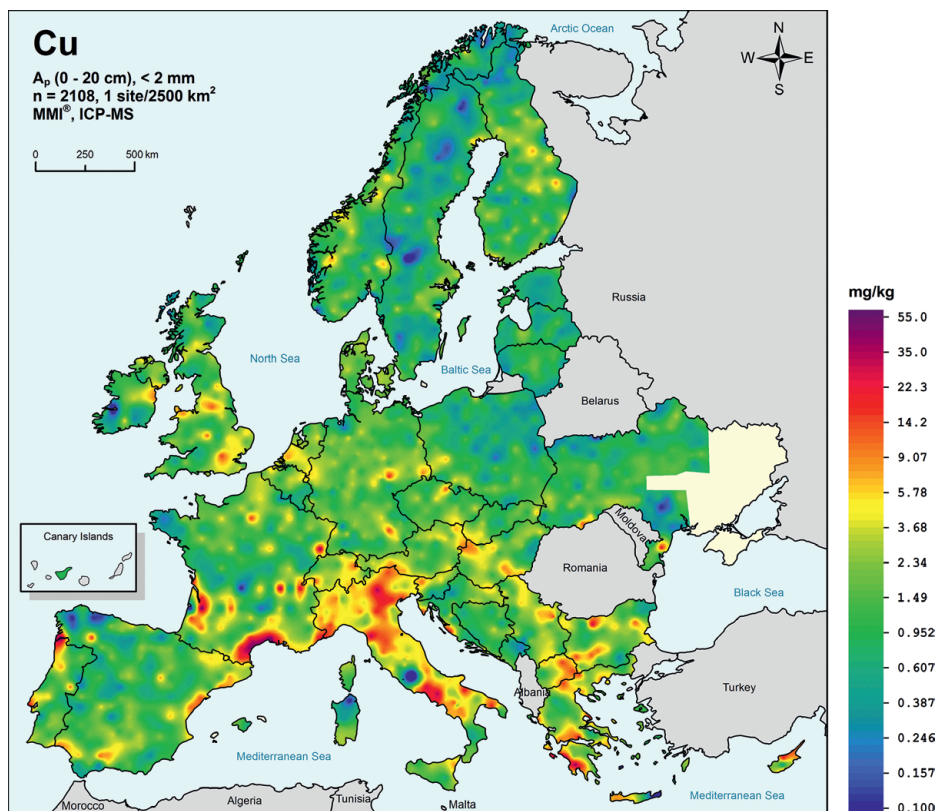


Figure 6. Colour surface map for Cu in European soils after MMI[®] extraction and ICP-MS analysis.

value for MMI[®] Fe (2201 mg/kg) is just 60 km east of Kiruna and 70 km NW of Malmberget, both large underground iron ore mining centres in northern Sweden but in this region there are a number of soils with high values of Fe, Ti and V. It is again unlikely that the anomalous value registered in such a distant agricultural soil is directly related to either of these two sources. It is,

however, almost certain that the soil anomaly is related to similar mineralization. The dominant mineral source of Fe here is magnetite, and weathering magnetite is known to produce MMI[®] signatures for Fe, Ti and V. The values in this soil sample are also anomalous in Ti (0.896 mg/kg) and V (0.242 mg/kg). Shown in Figure 7 is a widespread regional distribution for mobile Fe,

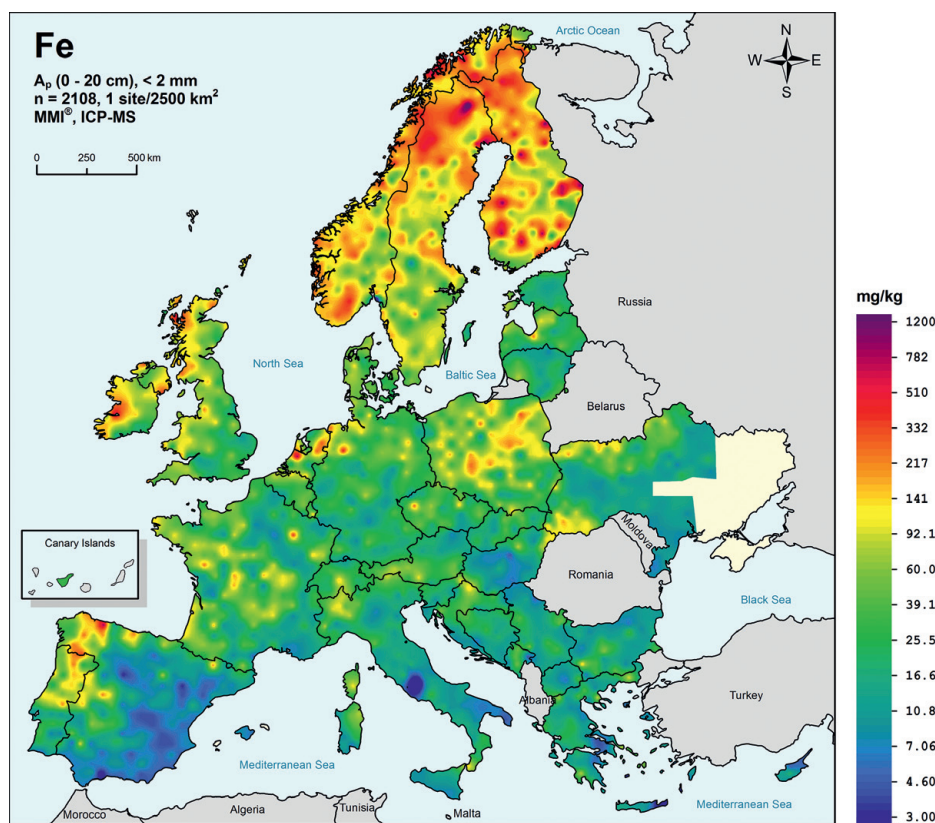


Figure 7. Colour surface map for Fe in European soils after MMI® extraction and ICP-MS analysis.

throughout not just the Fennoscandian Shield, but NW UK, Spain and Portugal, Ireland and Poland. The Fe distribution in Europe appears to have a relationship to high rainfall; highest precipitation is in Scandinavia and the west coasts of Ireland, the UK, Spain, Portugal, Slovenia, Croatia, and Bosnia and Herzegovina.

Highest values for MMI® Ni occur in SE Europe in an area dominated by ophiolites and ultramafic rocks. Nickel in soils after MMI® extraction and analysis has previously been shown to be diagnostic for ultramafic rocks at the 2 mg/kg level (Mann 2010) in soils and Figure 8 clearly shows large regions with Ni values in soils above this level. The highest value is 30.11 mg/kg for an agricultural field in Greece. Some sediments in the eastern UK and eastern Europe also show high levels of Ni.

One might expect the areas with highest P to be those which are most intensively cultivated (Fig. 9). However, the influence of lithology, particularly on the Fennoscandian Shield which is rich in apatite also seems to have an influence on P distribution. There is an operating apatite mine at Siilinjärvi in Finland. The highest value for P, 188 mg/kg, is, however, from an agricultural field in Germany and clearly occurs as a result of fertilizer addition to the soil.

The highest value for Pb in this survey of 58.3 mg/kg occurs west of Chesterfield in Derbyshire in the UK (Fig. 10). Not only is this a lead mining district, it is an area where Pb has been smelted and processed over many centuries. The name Chesterfield stems from the Roman words 'Caester' meaning fort and 'Feld' meaning grazing land. A number of lead roofing companies operate in the area today. This level of Pb in the soil, which is one of the highest ever recorded by the MMI® technique, is hard to reconcile with just sub-surface weathering mineralization, given the district's history. The second highest Pb value of 18.9 mg/kg is from a field 25 km south of Amsterdam and 20 km west of Utrecht, and unlikely to have mineralization as a direct source. As indicated by the median of 0.33 mg/kg, Pb values are not normally recorded at ppm levels by this technique.

High values for Pb are evident over various geological substrates, suggesting some at least may be related to anthropological (waste disposal) activities.

The colour surface map for Zn (Fig. 11) displays a zone with high Zn along the border of Belgium with The Netherlands and Germany; this region is the home for several zinc smelters. Other zinc anomalies, not all related to smelting, are evident on the Fennoscandian Shield, and in northern Spain, southern France, northern Italy and southern Poland. Zinc also is an essential nutrient and often added to soil as a trace element supplement. The highest value for MMI® Zn (36.3 mg/kg) is from a soil on a farm on the Isle of Mull off the coast of western Scotland. The Cd concentration in this soil is a relatively modest 0.123 mg/kg, suggesting weathering sphalerite is not a direct source in this case.

Relevant GEMAS maps for rainfall, pH and aqua regia Fe

Several other GEMAS maps are pertinent to the discussion of the above results. They have been obtained by the GEMAS Project Team and are published elsewhere (Fabian *et al.* 2014; Reimann *et al.* 2014a, b). The first of these is the map for rainfall (Fig. 12). It is clear from this map that highest rainfall is on the western coasts of Scandinavia, the UK, Spain, Portugal, Italy, and in Austria, Slovenia and Greece. Evaporation, another important climatic factor, in general follows latitude; it is lowest at higher latitudes and increases, in many cases to exceed rainfall on an annual basis, toward lower latitudes. These are the conditions which favor retention of calcium carbonate in the regolith, as evidenced in the calcium distribution map (Fig. 3), which also, of course, reflects the lithological importance of sedimentary carbonate in some higher latitude situations. The high rainfall zones in Figure 12 coincidentally show some similarities to the west coast areas with predominantly granitoid rocks (e.g. Fig. 4); there is no apparent link but the potential exists for biased

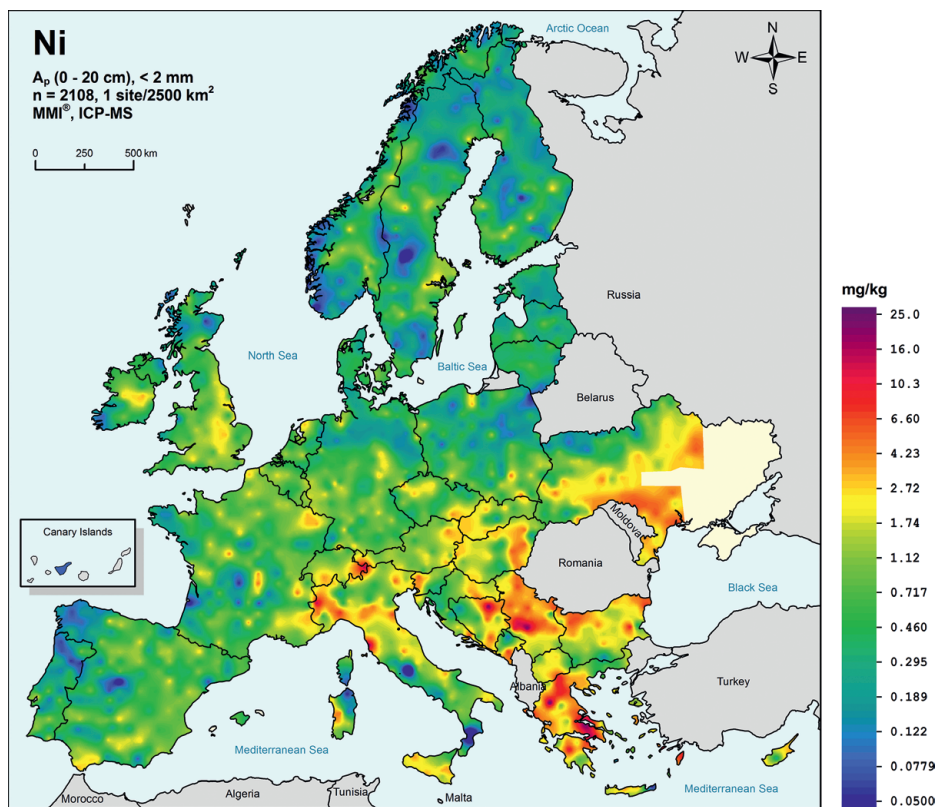


Figure 8. Colour surface map for Ni in European soils after MMI® extraction and ICP-MS analysis.

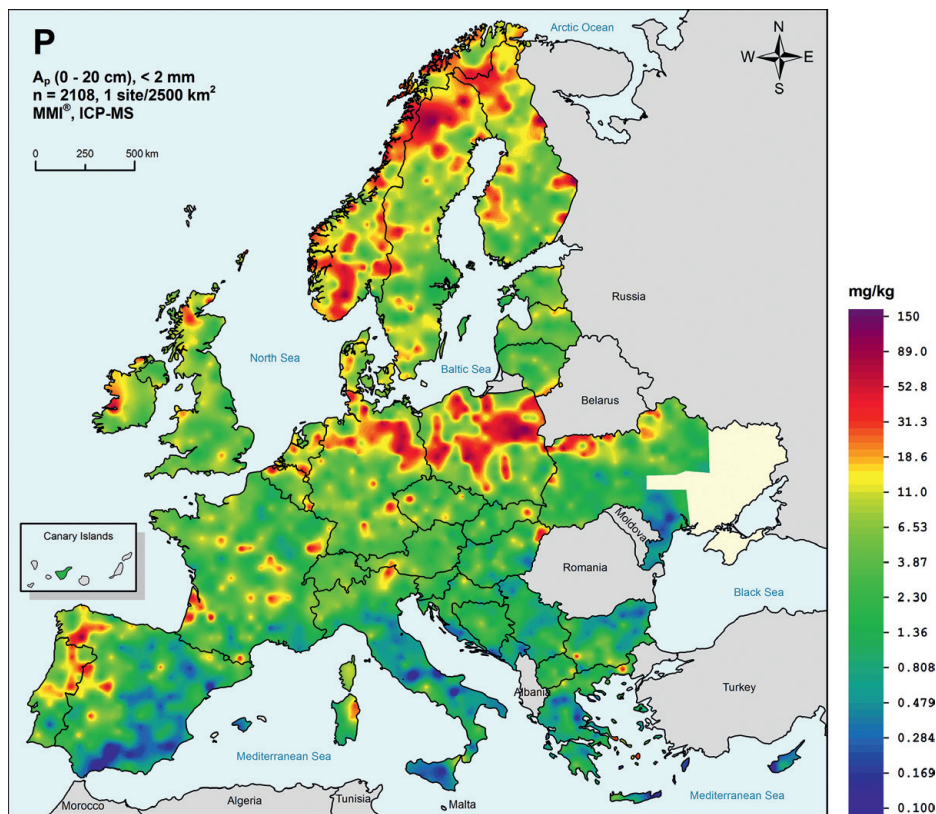


Figure 9. Colour surface map for P in European soils after MMI® extraction and ICP-MS analysis.

interpretation when comparing element distributions with that for rainfall. However, a causative link can be established between high rainfall, mobile Fe and low pH, which is illustrated in Figure 13.

Figure 13 shows high soil pH is common in the areas with low rainfall and high evaporation in southern and eastern Europe and

evidenced in the Ca map (Fig. 5). Low pH is predominant in the high rainfall areas of the western coasts of Scandinavia, the UK, Spain and Portugal. Iron is believed to be the principal causative agent; whilst common in soils throughout Europe it is particularly mobile in this same area (Fig. 7).

Mobile Metal Ion analysis of European Soils

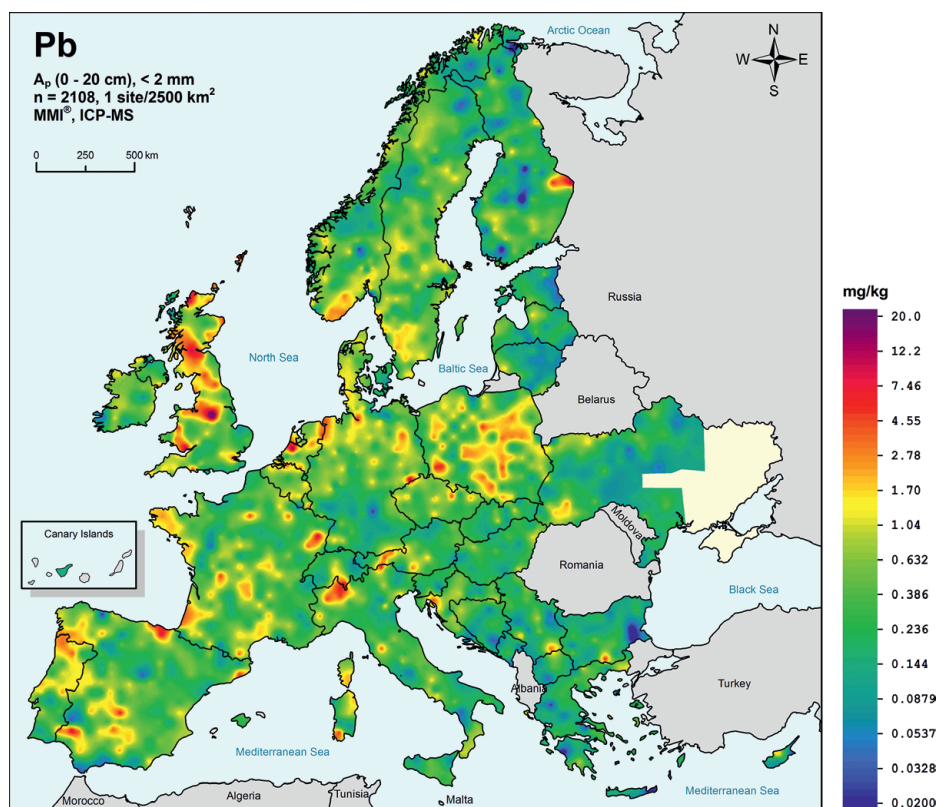


Figure 10. Colour surface map for Pb in European soils after MMI[®] extraction and ICP-MS analysis.

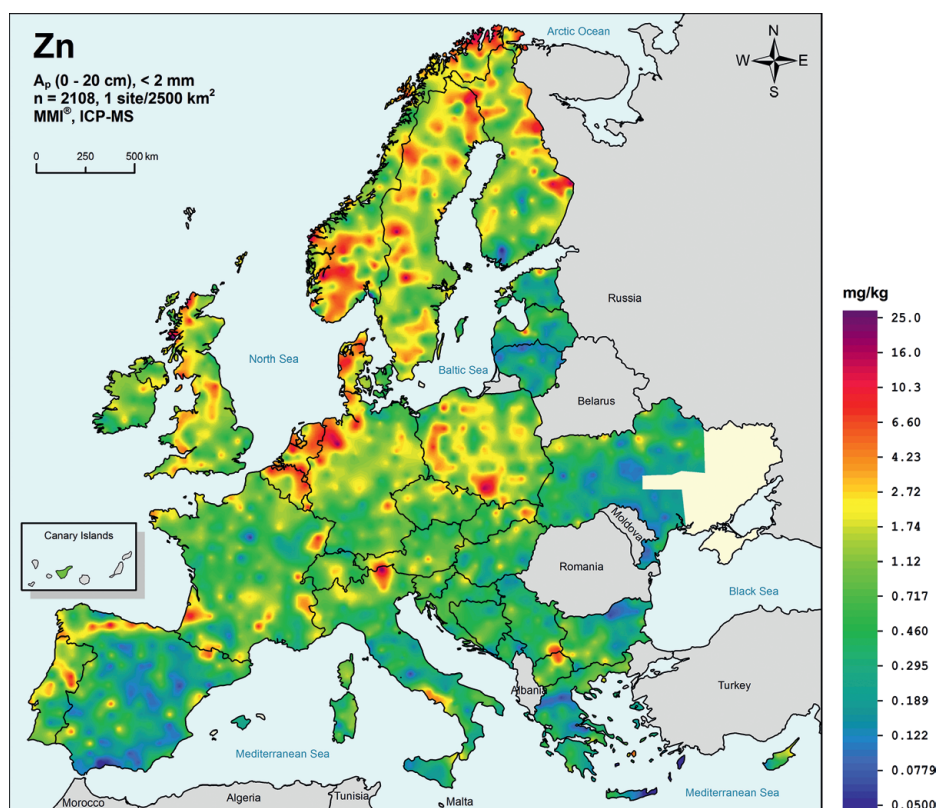
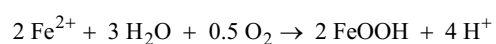


Figure 11. Colour surface map for Zn in European soils after MMI[®] extraction and ICP-MS analysis.

In actively weathering profiles, Fe is released into solution as Fe²⁺ at the weathering interface, and subsequently oxidized to Fe oxide/oxyhydroxide, commonly goethite (FeOOH). The oxidation and immobilization of soluble Fe²⁺ according to the reaction:



has been referred to (Mann 1983) as ferrollysis (oxidation and hydrolysis of Fe). Importantly, whenever and wherever oxidation of one mole of Fe occurs by this process, two moles of acid (H⁺) are produced.

It is of note that total Fe is not highest in the areas where highest Fe is recorded by the MMI[®] technique. Figure 14 shows the

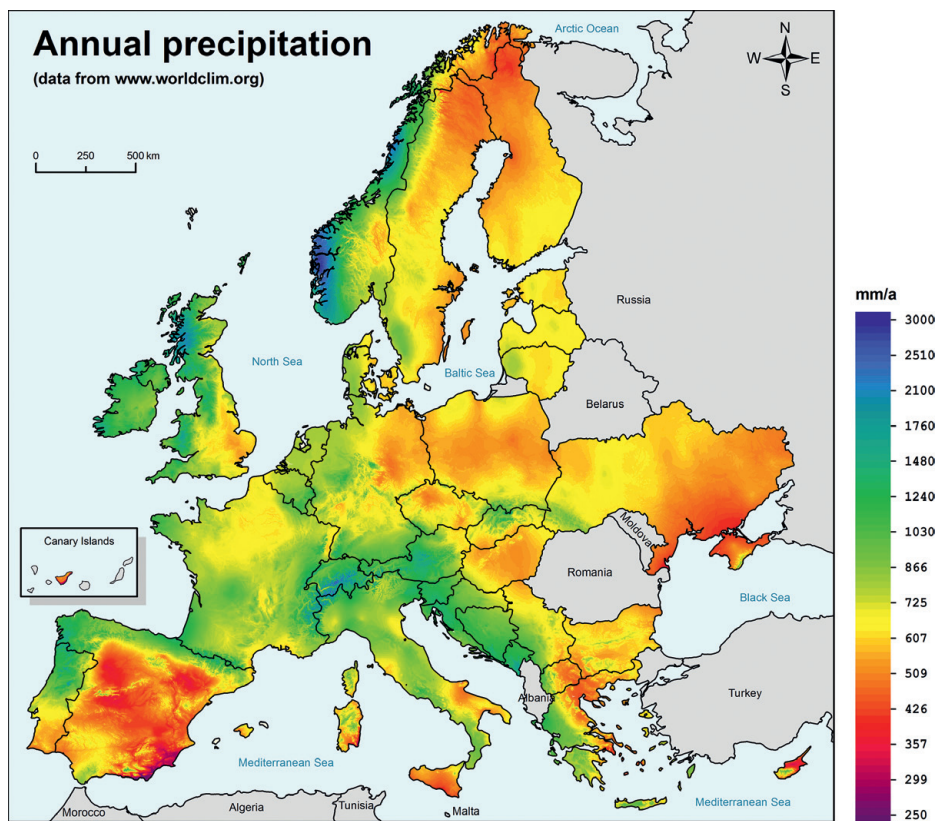


Figure 12. Colour surface map for European rainfall.

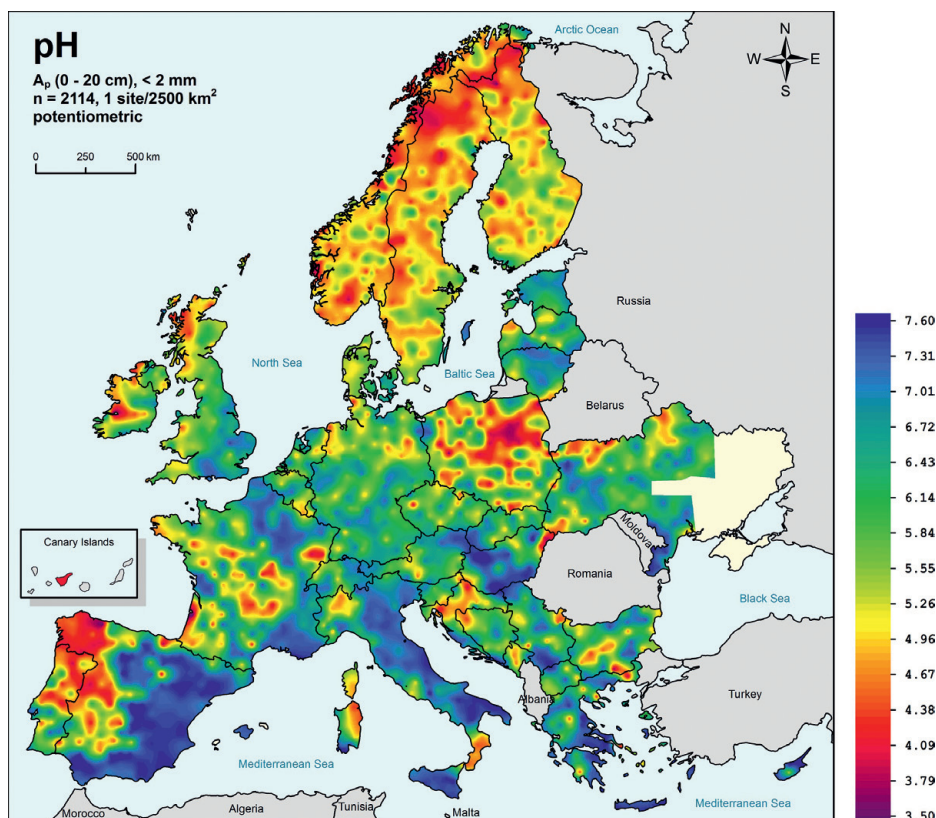


Figure 13. Colour surface map for pH in European Soils.

Fe distribution in agricultural soils after aqua regia digestion and ICP-MS analysis.

Clearly there are a number of rock types throughout Europe with high Fe content which result in soils with high Fe content. It is only in the highest rainfall areas that mobility of Fe is a

maximum; this is purely a weathering phenomenon highlighted by the two different methods of analysis, digestion v. extraction, residual Fe v. actively weathering or 'mobile' Fe. The same phenomenon was observed in the equivalent Australian study (Mann *et al.* 2012) where the residual Fe of the Pilbara

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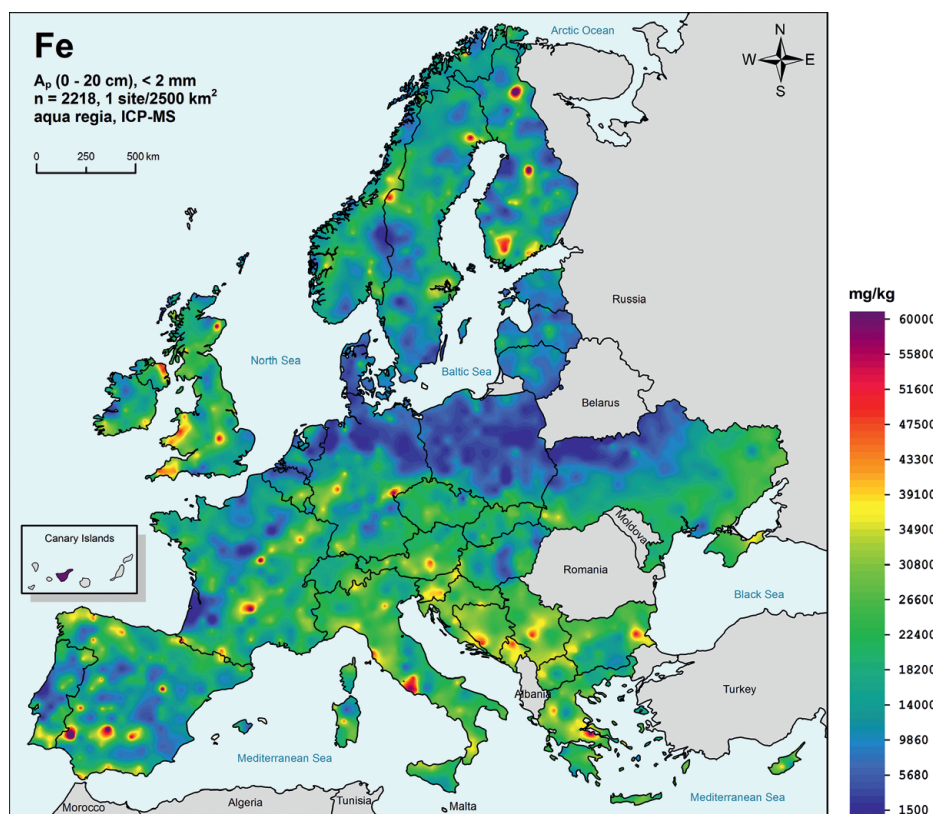


Figure 14. Colour surface map for Fe in agricultural soils after aqua regia digestion and ICP-MS analysis.

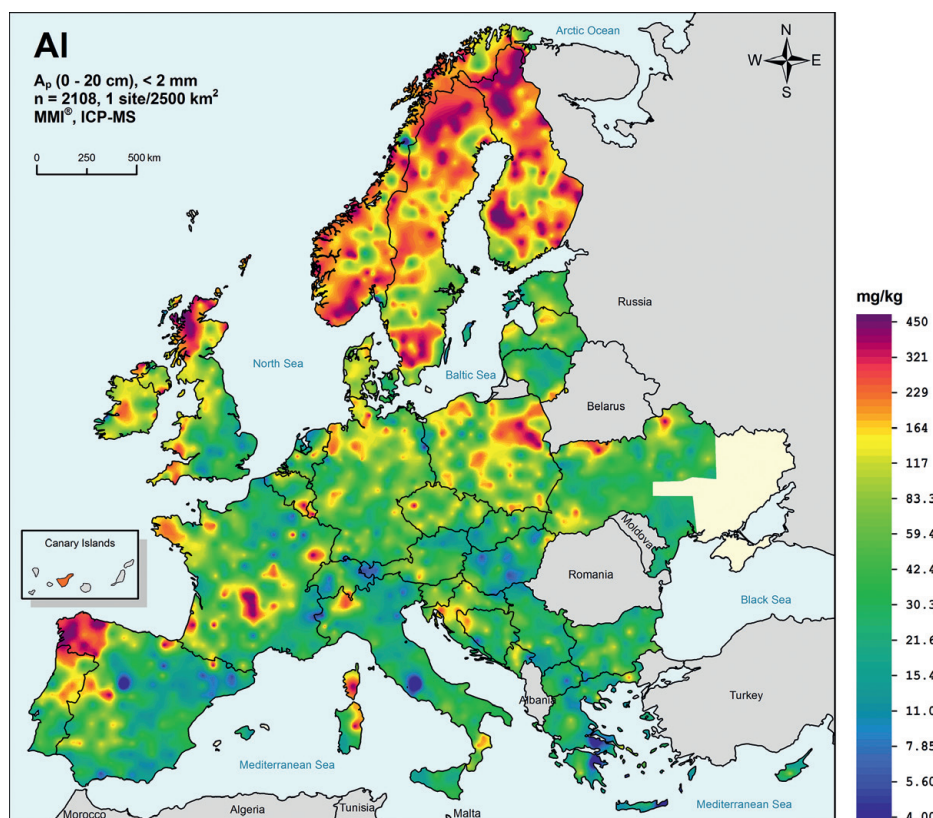


Figure 15. Colour surface map for Al in European soils after MMI[®] extraction and ICP-MS analysis.

did not feature as strongly in the MMI[®] Fe map as ‘mobile’ Fe of the east and south coasts, which incidentally are also areas of high rainfall and low pH and in some cases where lateritic and bauxitic processes are taking place.

Aluminium after MMI[®] extraction shows a similar distribution pattern in Europe to Fe as shown in Figure 15. In both of

these cases there is possibly a positive feedback mechanism operating; it is well known that Fe and Al are more soluble at low pH (Caritat *et al.* 2011). Any trivalent metal undergoing hydrolysis will produce acid, and because of the relatively high concentration of both of these elements in many rock types, acidity will be a consequence of rapid weathering. It is of note

that the MMI® extraction method is not implicated; it is buffered and contains a strong complexing agent for both of these elements which results in the capability of dissolving and holding in solution far higher concentrations of these elements at any pH than would be expected in the absence of strong ligands (e.g. see Mann 2010). The effects discussed here were first evidenced (Mann 1983) in salt lake solutions on the Yilgarn Block of Western Australia.

Comparison of MMI® results with aqua regia and XRF for European agricultural soils

Median values for MMI® extraction of the 2108 European soils (Table 1, column 2) range from 600 mg/kg for Ca to 0.0003 mg/kg for Au. Comparison values of the percentage extraction (Table 1, column 3) for MMI® v. aqua regia range from 36.8% for Ag to 0.04% for Ti and for MMI® v. XRF (Table 1, column 5) from 7.06% for Ca to 0.001% for Ti. One of the most interesting features of this table is the comparison of extraction % of elements in aqua regia v. XRF (column 4). The aqua regia digestion is far from 'total' for most elements; over half the elements in column 4 have an extraction efficiency of less than 50% v. XRF, yet it is still a very useful analytical method. All three analytical methods have their advantages and disadvantages (Mann *et al.* 2014) and potentially provide different information.

Correlation coefficients for elements after aqua regia digestion v. MMI® extraction (Table 1, column 6) are in most cases positive, and in many cases above 0.5. The most notable exceptions are Al, Fe, and Ga which have small negative correlations. Aluminium and Fe have both been mentioned above, and Ga is another Group 5 element with geochemical affinity to Al and a very low extraction % in MMI® solution.

Comparison of median values for MMI from the GEMAS and NGSa surveys

A similar continental survey, designated NGSa (National Geochemical Survey of Australia) incorporating the MMI® method was carried out on catchment outlet samples in Australia (Caritat & Cooper 2011). Detailed comparison of the median values for MMI® from the two surveys was presented in Mann *et al.* (2014). Table 2 summarizes the main findings of this comparison as a series of median ratios (column 4).

Most elements show slightly higher medians in European soils, with ratios in the range 1.0–2.0. Exceptions to this are four elements – K, Mg, Rb and Sr – which have higher median values in Australian soils. They are all elements which are predominant in the arid and semi-arid interior and favored by dry climatic conditions. Five elements – Al, Cd, Fe, Pb and Zn – have ratios greater than 5 and are considerably more concentrated in the mobile form in European soils. Two of these, Al and Fe have previously been mentioned in connection with the extensive high rainfall, low pH soils on the western coasts of Scandinavia, Ireland, the UK, Spain and Portugal. The other three, Cd, Pb and Zn possibly reflect greater anthropogenic activity in Europe. In connection with Cd, it is interesting that P also has significantly higher levels (ratio of 3.4) in European agricultural soils than in Australian catchment outlet sediments. This suggests that agriculture and not the metals industry or coal-fired power plants is the principal source behind enhanced MMI Cd concentration in European agricultural soils.

Discussion

This survey has been conducted over a very large area: *c.* 50 degrees of longitude and 42 degrees of latitude. Such a large land area comprises many different geological terrains and climatic

Table 1. Median values, correlation and extraction percentages of MMI v. aqua regia (AR) and XRF

Element	Median MMI (mg/kg)	Extraction % MMI v. AR	Digestion % AR v. XRF	Extraction % MMI v. XRF	Correlation MMI v. AR
Ag	0.014	36.8	–	–	0.83
Al	62	0.56	22	0.11	–0.13
As	0.02	0.37	81	0.29	0.36
Au	0.0003	33.3	–	–	0.60
Ba	1.09	1.76	17	0.28	0.60
Bi	<0.001	–	–	–	0.41
Ca	600	19.8	61	7.06	0.26
Cd	0.054	30	–	–	0.84
Ce	0.135	0.48	53	0.23	0.20
Co	0.18	2.43	83	2.02	0.56
Cr	0.065	0.33	34	0.11	0.24
Cs	0.0007	0.06	23	0.01	0.38
Cu	1.34	9.24	115	10.3	0.68
Fe	31	0.18	72	0.13	–0.12
Ga	0.002	0.06	32	0.02	–0.12
Hg	<0.001	–	–	–	0.41
In	<0.0005	–	–	–	0.02
K	64.2	5.14	8	0.41	0.31
La	0.049	0.34	69	0.21	0.20
Li	0.0025	–	–	–	0.29
Mg	52	1.82	55	0.95	0.12
Mn	19.65	4.42	80	3.25	0.09
Mo	0.015	3.57	41	1.50	0.40
Nb	0.0009	0.19	4	0.007	0.25
Ni	0.652	4.44	79	3.26	0.69
P	4.1	0.63	83	0.52	0.05
Pb	0.32	2.03	77	1.52	0.77
Pd	<0.001	–	–	–	–
Pt	<0.001	–	–	–	–
Rb	0.069	0.48	21	0.09	0.48
S	24.2	11.7	–	–	0.55
Sb	0.002	0.86	9	0.08	0.48
Sc	0.016	0.74	29	0.20	0.15
Se	0.01	2.8	–	–	–
Sn	<0.001	–	–	–	0.45
Sr	1.675	9.25	19	1.66	0.58
Ta	<0.001	–	–	–	–
Te	<0.01	–	–	–	–
Th	0.0221	0.76	36	0.25	0.13
Ti	0.038	0.04	3	0.001	0.17
Tl	0.0006	0.50	–	–	–
U	0.084	10.9	38	5.60	0.72
V	0.027	0.11	40	0.04	0.05
W	0.001	1.37	3	0.04	–
Y	0.184	2.75	25	0.68	0.32
Zn	0.76	2.75	74	1.26	0.30
Zr	0.051	2.85	1	0.02	0.13

zones. The distribution of elements such as Ce (and the remainder of the lanthanides) in agricultural soils has been shown to be diagnostic of known granitoid terrain types, particularly in Scandinavia, the western UK, Ireland, Spain and Portugal, Corsica and Sardinia. Ophiolite suites of northern Italy, Slovenia and Greece have been portrayed by high MMI® Ni, Mg and Cu concentrations in the agricultural soils of these regions. Calcium has been seen to be indicative of primary and secondary carbonate in the soil, the latter where climate, and in particular the excess of evaporation over rainfall has played a part. Climate has also influenced to a very great extent the geogenic contributions of Fe and Al, which in turn are shown to produce acid during weathering, which has an effect on the mobility of many

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Table 2. Comparison of median values for MMI analysis in the GEMAS (European) and NGSA (Australian) continental studies for the elements deemed mutually consistent

Element	MEDIAN MMI GEMAS mg/kg (n=2108)	MEDIAN MMI NGSA mg/kg (n=1191)	Ratio GEMAS/ NGSA
Ag	0.014	0.005	2.8
Al	61	12	5.1
Au	0.0003	0.0002	1.5
Ba	1.09	0.87	1.3
Ca	600	390	1.5
Cd	0.054	0.005	10.8
Ce	0.135	0.101	1.3
Co	0.182	0.178	1.0
Cr	0.065	0.024	2.7
Cu	1.34	0.96	1.4
Dy	0.035	0.023	1.5
Er	0.0202	0.011	1.8
Eu	0.0075	0.007	1.1
Fe	31	4	7.8
Gd	0.036	0.029	1.2
K	64.2	82.2	0.8
La	0.049	0.027	1.8
Mg	52	140	0.4
Mn	19.6	3.99	4.9
Mo	0.015	0.007	2.1
Nd	0.102	0.092	1.1
Ni	0.652	0.411	1.6
P	4.1	1.2	3.4
Pb	0.32	0.04	8
Rb	0.069	0.107	0.6
Se	0.01	0.007	1.4
Sm	0.029	0.025	1.2
Sr	1.675	2.4	0.7
Th	0.0221	0.021	1.1
Ti	0.038	0.019	2
U	0.084	0.063	1.3
V	0.027	0.025	1.1
Y	0.184	0.098	1.9
Zn	0.76	0.12	6.3

elements. Anthropogenic contributions have been clearly identified by MMI[®] analysis of soils within the vineyards of France (for Cu), metallurgical sites for Pb (Chesterfield, England) and for soils located in known mining areas involving Ag and Au dating back to Roman times. In the case of Cd and P, the anthropogenic contribution of agriculture is clearly evident, whilst for Pb and Zn, disposal of wastes appears to be a contributing factor to some soil anomalies.

It is in the case of Fe, Al and to some extent other metals such as Ti, that the greatest difference between digestion and extraction techniques is made most evident. Clearly the distribution maps for these elements by aqua regia digestion and MMI[®] extraction are very different. We need to look carefully at the *modus operandi* of the techniques to comprehend the results. Aqua regia digests the products, the results of weathering as they eventuate in the soil, often in the case of Fe, Al and the REEs as sesquioxides. The MMI[®] technique measures the active, ongoing, indicators of weathering via the mobile or soluble species and/or recently adsorbed material *en route* to production of the final residual products in the regolith. For many other elements, the differences between techniques are not as great as they are for the resistate elements. For example, the strong multi-element anthropogenic anomalies in soils of the Seine and Thames valleys in the vicinity of Paris and London have been mentioned. The anomaly patterns after MMI[®] extraction and aqua regia digestion for Ag, Au, Cu and

Pb for these soils are very similar. In the case of strong robust soil anomalies, most soil analysis methods will produce anomalies, albeit at different concentrations levels; it is the signal to background contrast which defines the anomaly. It is in the case of more subtle anthropogenic anomalies where a technique such as MMI[®] might display its advantages as in the case of the weak anomalies for Pb and Zn related to mineralization at Cross Lake (Hamilton *et al.* 2001; Mann 2010).

It is apparent from Table 1 that the MMI[®] extraction technique liberates far less of each element from a soil than does strong acid digestion. In Mann *et al.* (2012), the values obtained from MMI[®] analysis of Australian soils were known to correlate well with values obtained by the partial extractions developed and used in agriculture (e.g. Colwell 1967a, b; Lindsay & Norvell 1978) to approximate plant requirements. It would appear that the values obtained by strong acid digestion of a soil are much higher than the values 'seen' by a plant in soil pore water. Tiller (1983) suggests that organic ligands, similar to those used in the DTPA method of Lindsay & Norvell (1978) and in MMI[®], are present in natural soils and complement inorganic complexes for these micronutrients. Concentrations of acetic acid and polybasic acids of up to 10⁻³ M and free amino acid concentrations of 10⁻⁴ M in bulk incubated soil solutions have been suggested. Hodgson *et al.* (1965) showed that Cu and Zn in soil solutions are present mainly as metal-organic complexes. The data from Table 2 show that for many elements median values for MMI[®] extraction from European agricultural soils and Australian catchment outlet sediments are very similar. Accordingly, it appears that as in the Australian case, in European soils MMI[®] extraction offers a good measure of 'bioavailability' for many elements (Ag and Au are two possible exceptions). For the nutrients, the values obtained in this large, encompassing survey may provide useful threshold levels for nutrients. Three categories 'low', 'normal' and 'high' can be identified for European agricultural purposes (Mann *et al.* 2014) for 10 of the most important nutrients. For MMI[®] Ca, the 'normal' range is 410–820 mg/kg, for Cu, 0.9–2 mg/kg, for Fe 18–63 mg/kg, for K 47–89 mg/kg, for Mg 34–82 mg/kg, for Mn 14–27 mg/kg, for Mo 0.01–0.02 mg/kg, for P 2.3–7.3 mg/kg, for S 20–31 mg/kg and for Zn 0.45–1.3 mg/kg. Clearly these values are based on a statistical evaluation of what the soils contain, not necessarily what plants require.

Conclusions

It is remarkable that such a widely spaced geochemistry program based on agricultural soils has identified many interesting and coherent, lithology-related patterns, and a number of anthropogenic anomalies. It must be remembered that the GEMAS project was designed to map the 'European background' of metal concentrations in agricultural soils and not to find mineralization or anthropogenic contamination. Using XRF total concentrations or the strong aqua regia digestion, European background was mapped; for these methods lithological contents and the broad geochemistry of geological terrains dominate the elemental maps. In contrast, in the maps based on the MMI[®] extraction we detect, in addition to lithology patterns, a number of mineralogical and anthropogenic anomalies. The iron ore province in Scandinavia, for example, is only evident in the MMI[®] maps (Fe, P, V) due to the sensitivity of the technique toward weathering magnetite. Examples of anthropogenic anomalies due to agricultural activities include the MMI[®] Cd anomalies in central Europe and the MMI[®] Cu anomalies in French vineyards. In all of these cases, recognition of these anomalies has been facilitated by the use of 72-colours surface maps.

It is easy to forget the contribution that advances in analytical technology, and in particular the exceedingly low lower levels of detection (LLDs) for many elements, has made to project such as

this. The continued use of, for example, ICP-MS technology, and the pursuit of even lower LLDs require samples to be presented in a uniform manner, from digestion and extraction procedures which allow intelligent geochemical interpretation to be made. In this survey MMI® has made such a contribution.

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