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GEMAS: Boron as a geochemical proxy for weathering of European agricultural soil

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ABSTRACT

About a century ago, B was recognised as an essential element for the normal growth of plants and terrestrial organisms. Limitations for plant development have been recognised in agricultural systems, particularly in highly weathered soil. Boron is rarely analysed in whole rock or soil analysis, as it requires specific analytical techniques. It is often determined, after partial extraction (aqua regia or Ca—Cl), usually on a limited number of samples. Many more questions than answers exist about the environmental behaviour of B.

We present B contents in agricultural soil samples (0–10 cm) collected in 33 European countries (5.6 million km^2) during the GEMAS (GEochemical Mapping of Agricultural and grazing land Soil) continental-scale project. The B content, determined by ICP-MS following hot aqua regia extraction, varies in European agricultural soil from 0.5 to 49 mg/kg (median 2.42 mg/kg, $n = 2108$), which is somewhat similar to total B estimates for the Upper Continental Crust (17–47 mg/kg). Its spatial distribution in agricultural soil shows a patchy pattern with low values in regions with granitic bedrock and high contents in soil formed over limestone and in volcanic areas.

Boron geochemical behaviour in soil is strongly dependent on other factors such as pH, CEC, presence of organic matter, clay and secondary oxides and hydroxides. Boron geochemical mapping at the continental scale in arable soil allows investigations of plant health, i.e., the beneficial and adverse effects due to the nutritional status of boron.

1. Introduction

Boron is an essential nutrient for plants with variable concentrations required for optimum growth (Kabata Pendias and Pendias, 2001; Brown et al., 2002; Kabata-Pendias and Mukherjee, 2007). In human health, there is only a narrow margin between boron deficiency and excess uptake leading to toxicity (Keren and Bingham, 1985; Kot, 2009). Boron deficiency in terrestrial plants has been reported in many countries and solutions are currently being actively sought (Shorrocks, 1997; Shireen et al., 2018; Brdar-Jokanović, 2020). This deficiency is the second most widespread micronutrient deficiency after zinc. It occurs when B leaches out of soil, particularly in humid regions, and in areas

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with sandy soil having a low organic matter content. Regions in north European countries and the Balkans are considered as endangered by B deficiency (Shorrocks, 1997). In contrast to B deficiency, soil B toxicity is less abundant and predominantly occurs in arid and semi-arid areas. Generally, soil with <0.5 mg/kg hot-water-extractable B is considered deficient (Yau et al., 1994; Alloway, 1995, 2008). According to Sun et al. (2019), 0.5–2.0 mg B/kg is the optimal soil B range, whereas lower (<0.5 mg B/kg) and higher (>3 mg B/kg) indicate deficiency and toxicity, respectively. Prolonged periods of drought and low soil temperature contribute to weak B uptake by plants, which results in B deficiency both in warm and cold climates. Soil with high B retention capacity is usually alkaline (high pH), and rich in clay, iron and aluminium oxides (Goldberg, 1997; Chen et al., 2009).

Boron in soil originates from the weathering of B-containing minerals from underlying rocks. The most common B-bearing minerals are hydrated borates, such as borax ($Na_2(B_4O_5(OH)_4)\cdot8H_2O$), kernite ($Na_2(B_4O_6(OH)_2)\cdot3H_2O$) and colemanite ($Ca(B_3O_4(OH)_3)\cdot H_2O$), which occur in evaporite deposits in closed basins in dry climates and are the major economical resource for boron (Boyle, 1974). These minerals are soluble and can be easily weathered. In Europe, however, B deposits are very rare and occur in Serbia (colemanite; Piskanja Boron, Jarandol Basin), and as by-products in Italy (geothermal brines; Bagnore, Larderello, Monte Gabbro, Piancastagnaio in Tuscany), and Germany (Stassfurt and Hamburg Salt Dome; Permian salt deposits) as evidenced by Cassard et al. (2012, 2015) and Demetriades and Reimann (2014). Another group of primary minerals containing B are tourmaline group minerals, which are complex borosilicate minerals resistant to weathering where the borate anion is a compound with Al, Fe, Mg, Na, Li and K, and are classified as gemstones occurring in a variety of colours. Other forms of B minerals such as borophosphates, borocarbonates and boroarsenates are rare. Among common rock-forming minerals, the highest B contents are observed in micas and serpentine. Clay minerals can have a high B content, e.g., illite, glauconite and montmorillonite. Iron oxides such as haematite and goethite may have high B concentrations, up to 300 mg/kg. Certain alkaline rocks (e.g., kimberlite, syenite) and volcanic rock varieties (rhyolite) can concentrate boron. Tourmaline occurs commonly in highly fractionated magmatic rocks and their fluid-altered products such as greisen. In metamorphic rocks, the highest B contents occur in mica and graphite schist (Wedepohl, 1978).

During weathering, B is mobile and goes into solution and its concentration is controlled by the presence of clay minerals onto which it can be adsorbed or incorporated into the illite structure. Clay and shale formed in saline lacustrine and marine environments can have high B contents (>2500 mg/kg; Wedepohl, 1978). Boron is enriched in saline groundwater, in oil-field water and in hydrothermal brines including hot springs in volcanic regions.

Boron is detected in all organisms and plants, as well as in ashes, wood and coal. Boron contents of 12,000 mg/kg have been observed in coal ash (Zubovic et al., 1967). The amount of B incorporated in organic matter seems to be higher than that in illite adsorbed from water. Boron is a fluid-mobile trace element and with few exceptions occurs always as the borate anion. Dissolved B can adsorb onto and desorb from the many different surfaces of soil particles like clays, Fe—Mn oxides or organic matter (Elrashidi and O'Connor, 1982; Goldberg, 1997; Padbhushan and Kumar, 2017; Van Eynde et al., 2020a, 2020b). Boron in soil available for plants occurs as boric acid and its direct source is usually decomposing organic matter.

Boron is an essential microelement for higher plants; it governs the productivity of both agriculture and forestry and its deficiency is widespread. Boron has a close affinity with calcium. Boron plays a significant role in plant cell division and shoot and root growth. Moreover, boron improves plant reproduction (e.g., pollination, flowering, seed production…). Another important role of boron is for the transport of sugars within the plant that are essential for photosynthesis. The visible B deficiency symptoms are the deformation of roots, buds, flowers, young leaves and fruits. In rare cases of B toxicity, the symptoms may vary from necrosis of plant organs to death of the whole plant. In animals, B helps to regulate the calcium release into the blood and enables the conversion of vitamin D into active form. The tendency of B accumulation in animal and vegetable tissues may present a potential health risk to those consuming food and water with high B content (Brown and Shelp, 1997; Pereira et al., 2021).

Compared to its natural origin, B is also released to a lesser extent, from human activities by the use of borate-containing fertilisers and herbicides, the burning of plant-based products such as wood, coal, or oil, and the release of waste from borate mining and processing (Woods, 1994). Boron also reaches the environment due to the use of borates and perborates in the home and industry, through leaching from treated wood or paper, and from sewage and sewage sludge disposal (Woods, 1994; EPA – OGWDW, 2008). Boron is also used in metallurgy for nuclear shields and in electronics, as well as for the production of aviation and rocket propellants (Streit, 1994).

Boron behaviour in soil has been the subject of many studies as well as debates for decades (Berger and Truog, 1945; Singh, 1964; Okazaki and Chao, 1968; Elrashidi and O'Connor, 1982; Bussetti et al., 1995; Goldberg, 1997; Kabata-Pendias and Mukherjee, 2007; Padbhushan and Kumar, 2017; Pereira et al., 2021). Boron has also been studied in water either in groundwater (Casanova et al., 2005; Gonfiantini and Pennisi, 2006; Giménez and Morell, 2008) or in surface water, often using B isotopes (Chetelat et al., 2009; Guinoiseau et al., 2018). Here we present the spatial distribution and geochemical behaviour of B in agricultural soil at the European scale using the GEMAS data sets. The Geochemical Mapping of Agricultural and grazing land Soil project (GEMAS) focused on the mapping of the background element variation in soil at the European scale. Soil samples were collected by the Geochemistry Expert Group of EuroGeoSurveys, over an area of 5.6 million km^2 in 33 European countries (Reimann et al., 2012a, 2014a, 2014b) and the project was carried out in cooperation with the European Association of Metals (Eurometaux).

Reimann et al. (2016) discussed the use of low sampling densities (1 site/100 to 1 site/18000 km^2) for providing sufficient information for decision-making, rather than the costly and time-consuming very high-density sampling (100 s to 1000s of samples/km^2) employed for geochemical exploration or environmental monitoring. Their argument was based on the results of previous studies using low sampling density geochemical mapping at regional to continental scales (Garrett and Nichol, 1967; Armour-Brown and Nichol, 1970; Garrett et al., 2008; Smith and Reimann, 2008; Cicchella et al., 2013; Birke et al., 2015). The aim of this paper is to investigate the spatial distribution of hot aqua regia extractable B in European agricultural soil with a specific focus on topsoil (Ap horizon) derived or developed on various parent materials, using the GEMAS database (Reimann et al., 2014a, 2014b).

The B availability in hot aqua regia extraction is assumed to be low in relation to B-bearing minerals and their resistance to the leaching solution according to the fractionation tests carried out in some Saskatchewan soils (Raza et al., 2002). Generally, up to 10 % of B is adsorbed by soil particles (Padbhushan and Kumar, 2017).

Boron is a critical micronutrient of major importance in plant growth, as it is used in relatively small quantities in plants and is necessary for plants to complete their life cycle. Because B is a mobile nutrient within soil, improving knowledge of its cycle in soil, in connection with geology and considering the continental-scale approach, is a current challenge to take up, the objective of this study.

2. Materials and methods

The GEMAS project (Reimann et al., 2014a, 2014b) was conducted by the EuroGeoSurveys Geochemistry Expert Group in partnership with the European Association of Metals (Eurometaux). This project took advantage of the achievements of the first geochemical mapping survey at the European continental-scale, i.e., the Geochemical Atlas of Europe of the Forum of European Geological Surveys (FOREGS), the forerunner

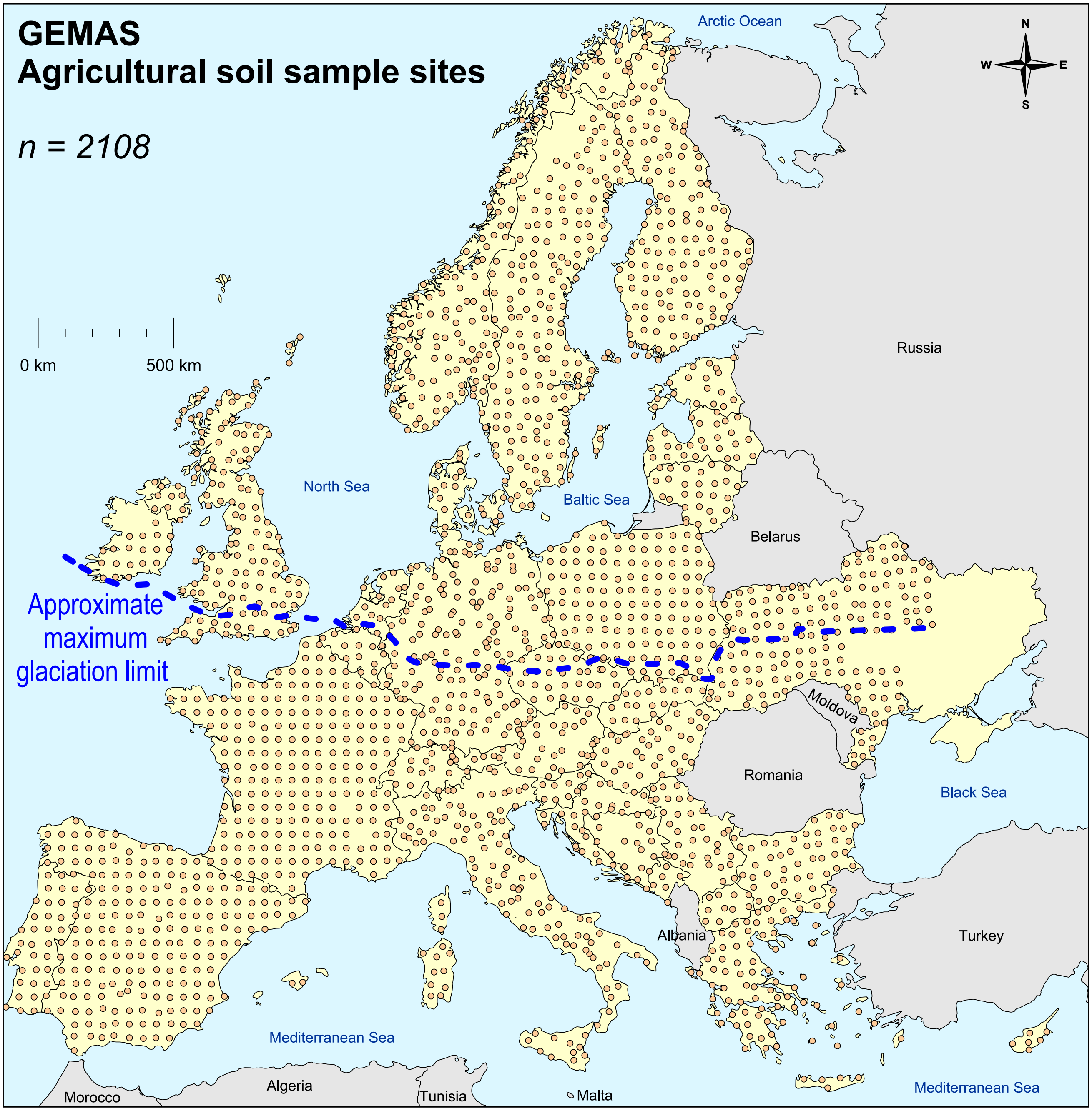

Fig. 1. Sample locations (dots) of the ploughed agricultural soil (Ap-samples; $n = 2108$ – without the 110 East Ukraine samples) and the approximate maximum extension of glaciation. Map projection: Lambert Azimuthal Equal Area (ETRS_1989_LAEA), with central meridian at 10°. Plotted with Golden Software's Surfer version 28 and modified from Négrel et al., 2021).

of EuroGeoSurveys (Salminen et al., 1998, 2005; De Vos et al., 2006). Fig. 1 shows the distribution of GEMAS project agricultural soil samples in 33 European countries, covering about 5.6 million km^2 (Reimann et al., 2012a, 2014a, 2014b) for mapping the geochemical background variation of major and trace elements. To achieve this objective, the soil sampling avoided known contaminated sites, the immediate vicinity of industry or power plants, villages, towns, cities, railway lines or major roads. The two types of soil samples have been collected at an average density of 1 site per 2500 km^2 (Fig. 1). Grazing land soil (Gr; 0–10 cm depth; $N = 2024$ samples) has been defined as land under permanent grass cover, and agricultural soil (Ap; 0–20 cm depth; $N = 2108$ samples) refers to the ploughing layer of an agricultural arable field. At each sample site, a composite sample (ca 3.5 kg) was generated from five sub-samples collected from the corners and centre of a 10 × 10 m square.

Sample preparation (air-drying; sieving to <2 mm using a nylon screen; homogenisation and splitting to 10 sub-samples) was carried out at the State Geological Institute of Dionyz Stur (Slovakia). Boron was determined following a hot aqua regia (AR) extraction by inductively coupled plasma-mass spectrometry (ICP-MS) at Bureau Veritas Mineral Laboratories in Vancouver, Canada (Reimann et al., 2012a; Birke et al., 2014). The applied analytical extraction protocol to the soil samples, prior to their analysis, was a 15 g aliquot of the unmilled <2 mm fraction, leached in 90 ml of aqua regia for one hour at 95 °C, and then made up to a final volume of 300 ml with 5 % HCl. The analytical and external quality control protocol is described by Reimann et al. (2009, 2011, 2012c), Birke et al. (2014) and Demetriades et al. (2014); in each batch

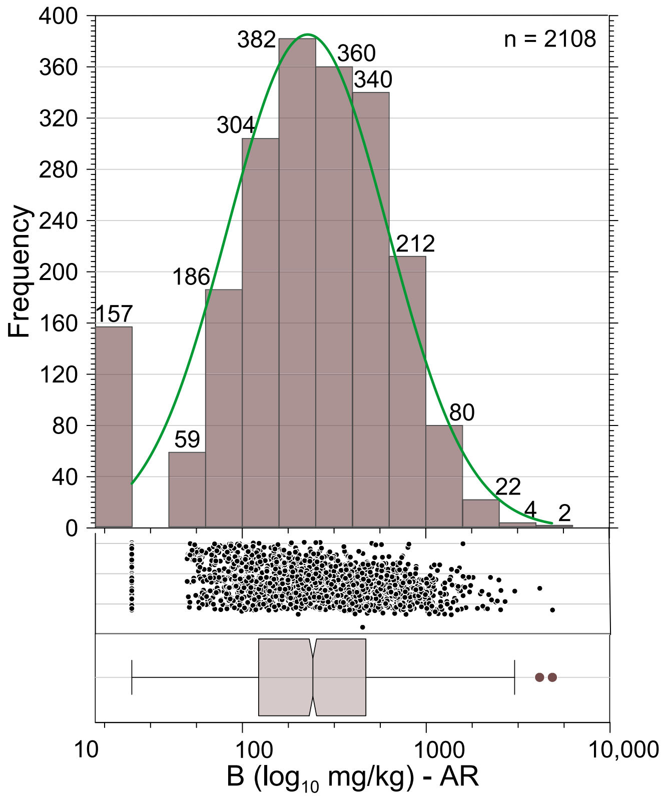

Fig. 2. A combined plot of histogram, density trace, one-dimensional scattergram and boxplot of B statistical distribution in European Ap samples following a hot AR extraction. Scale linear $\log_{10}$. Plotted with Golden Software's Grapher version 24.

of 20 samples, one replicate of the field duplicate and one project standard were inserted.

The practical detection limit was estimated from the uncensored results of project replicate samples by calculating regression line coefficients with the 'reduced major axis line' procedure (Demetriades, 2011; Demetriades et al., 2022) and the value for B is 0.76 mg/kg, with an analytical precision at ±14 % at the 95 % confidence interval (Reimann et al., 2009). The unbalanced analysis of variance (ANOVA) has given the following results for the geochemical (natural), sampling (site) and analytical variance: 87 %, 0.0 %, 13 %, respectively (Reimann et al., 2009; Demetriades et al., 2014). The generated geochemical data set is compositional as element contents are reported in wt% or mg/kg sum up to a constant and are thus not free to vary (Reimann et al., 2012d). Compositional data plot in the Aitchison simplex (Aitchison, 1986; Buccianti et al., 2006; Pawlowsky-Glahn and Buccianti, 2011) and only order statistics should be used in the statistical processing of geochemical data. The colour surface maps were produced by kriging, based on a careful variogram analysis (Filzmoser et al., 2014). Kriging was used to interpolate values from the irregularly distributed sampling sites into unsampled space to generate a regular grid. Class boundaries for the colour surface maps are based on percentiles (5, 25, 50, 75, 90 and 95).

3. Results

3.1. Boron contents in agricultural soil

The range of aqua regia extractable B contents in GEMAS Ap soil samples is from <0.5 to 49 mg/kg, with 7 % of the values being below the detection limit (0.8 mg/kg) and a median value of 2.4 mg/kg. In Gr soil samples, the range is similar, from <0.5 to 41 mg/kg, with 7 % of the values being below the detection limit and a median value of 2.6 mg/kg. The Ap soil median value of 2.4 mg/kg is several times lower than the value estimated for the Upper Continental Crust (UCC); the value itself varies depending on different studies, e.g., from 17 to 47 mg/kg as given by Rudnick and Gao (2003) and Hu and Gao (2008), respectively, indicating poor extractability of B in acid-leach methods. Compared to the estimated total B average in UCC, the AR extractable values reported here are exceptionally low with a ratio GEMAS Ap soil/UCC between 0.142 and 0.051. This very low ratio range is observed because most of the B in nature is bound in AR-insoluble minerals, like tourmaline (silicate mineral group containing 2.8 to 3.6 % B; Slack and Trumbull, 2011; Wimmer et al., 2015), and some micas. Soluble evaporitic B minerals are rare in Europe. Tourmaline as the main B-bearing phase occurs in granitic and metamorphic rocks (schist and marble), and as resistant to weathering heavy minerals can be found in sedimentary rocks such as sandstone, siltstone, mudstone and conglomerate. Additionally, from the analytical point of view, B can also be partly volatilised and lost during hot aqua regia acid extraction (Reimann et al., 2009).

Hereafter, only the aqua regia extractable B data obtained for the Ap soil samples (ploughing layer of agricultural arable fields) will be considered because of the very few differences observed with the Gr soil samples (land under permanent grass cover). The combination plot histogram - density trace - one-dimensional scattergram - boxplot displays the B univariate statistical data distribution in Ap soil (Fig. 2). The detection limit problem at the lower end is obvious, and the existence of only very few outliers in the B statistical distribution is highlighted. The main body of the Ap B data is approximately symmetrical in the log-scale, and a bimodal distribution is indicated by the histogram.

3.2. Comparison of B boxplots for the AR extraction with assigned bedrock categories

The geochemical mapping of chemical elements determined on the GEMAS soil samples often evidenced a link between the element spatial distribution and the lithology of the underlying bedrock (Scheib et al., 2012; Ladenberger et al., 2013; Négrel et al., 2015, 2018a, 2019). In all geochemical maps, a geological separation is obvious between northern Europe, marked by the predominance of old crystalline (>1 billion years) and metamorphic rocks, and the rest of Europe with younger magmatic rocks (<1 billion years to recent) and large sedimentary basins. However, when generalising European bedrock geology, there are two major problems to be recognised: (i) too many small units are often defined on geological maps impeding a reasonable subgrouping of samples that are large enough for meaningful statistical comparison, and (ii) a geological map shows age relations whereas lithology is more appropriate for geochemical applications.

The soil parent material map of Europe (Fig. 3) is dominated by magmatic and metamorphic rocks (39 %), and shale (37 %); carbonate rocks (14 %) and sand-sandstones (9.5 %) are abundant, whereas felsic volcanic rocks and basalt (0.5 % each, respectively) play a subordinate role (Amiotte Suchet et al., 2003; Caritat et al., 2012). Based on these assumptions, a series of ten lithological parent material categories were defined for the Ap soil samples (Reimann and Caritat, 2012a; Reimann et al., 2012a). They consist of alkaline rock ('*Alk*'); carbonate rock ('*Calcar*'); granitic bedrock ('*Granite*'); greenstone ('*Green*'); mafic bedrocks ('*Basalt*'); loess ('*Loess*'); organic soil ('*Org*'); predominantly Precambrian gneiss and granitic bedrock ('*Prec*'); soil developed on coarse-grained sandy deposits, e.g., the end moraines of the last glaciation ('*Quartz*'), and schist ('*Schist*'); the remaining unclassified bedrock is defined as '*Other*'. These pre-defined 10 parent material subgroups were used to plot the B results as boxplots in Fig. 4.

Soil developed on or derived from carbonate ('*Calcar*') and alkaline ('*Alk*') parent materials shows the highest B median values. While the silicate-derived soil (e.g., '*Prec*', '*Granite*', '*Schist*' and '*Quartz*' parent materials subgroups) has the lowest median value confirming that initial B content in soil depends on parent material and the degree of

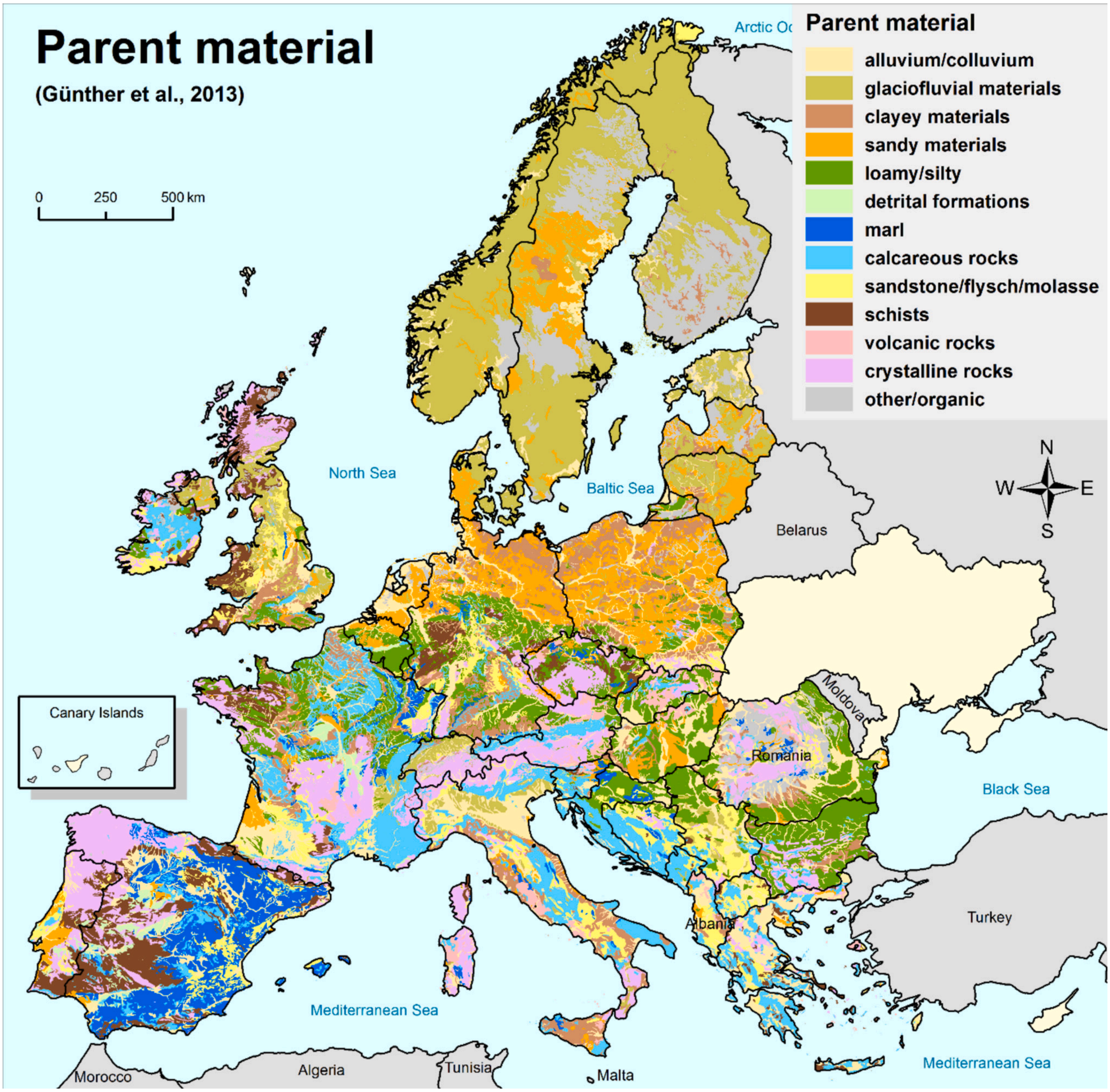

Fig. 3. Map of parent materials in Europe showing the distribution of various lithologies across the continent, modified from Günther et al. (2013) and adapted from Négrel et al. (2015). Plotted with Esri's ArcGIS version 10.6.1.

weathering (Biggar and Fireman, 1960; Padbhushan and Kumar, 2015). This can be compared with the mean values for total B content for the main lithological end-members defined by Parker (1967). Mafic and alkaline rocks display the lowest B mean content, 5 and 9 mg/kg, respectively, followed by granite with a mean value of 9 mg/kg, carbonate rocks and sandstone have intermediate mean values of 20 and 35 mg/kg, respectively, and the highest B mean contents are in shale (100 mg/kg) and clay (230 mg/kg).

Moreover, the plot of lithological parent material subgroups (Fig. 4) must be used with care, as in addition to lithology there are other changes from north to south in Europe that should be considered. Climate has a strong influence on soil geochemistry (Reimann et al., 2014a, 2014b; Zhang et al., 2020) and, therefore, contributes to a north-south imprint on the data showing that B values are significantly higher in the soil samples from southern Europe (e.g., median: 3 mg/kg) compared to those in northern Europe (e.g., median: 1.9 mg/kg). Temperature can affect soil chemical reaction rates, and B adsorption capability increases with increasing soil temperature, particularly under dry and hot weather conditions (Goldberg et al., 1993a; Adcock et al., 2007). Further, other soil factors (e.g., pH, organic matter, moisture, texture) affect the B availability in soil (Barber, 1995; Takkar, 1996; Jones Jr., 2008; Shafig et al., 2008).

4. Discussion

4.1. Spatial distribution of boron in European soil

The geochemical map of AR extractable B of agricultural soil samples (Fig. 5) shows unexpected patterns with patchy anomalies and a large variation at the regional scale. High B contents are observed over most of the known limestone-chalk (carbonate) areas, not only in the south (eastern and southern Spain, Italy with Sicily, Provence-Alpes-Cote-

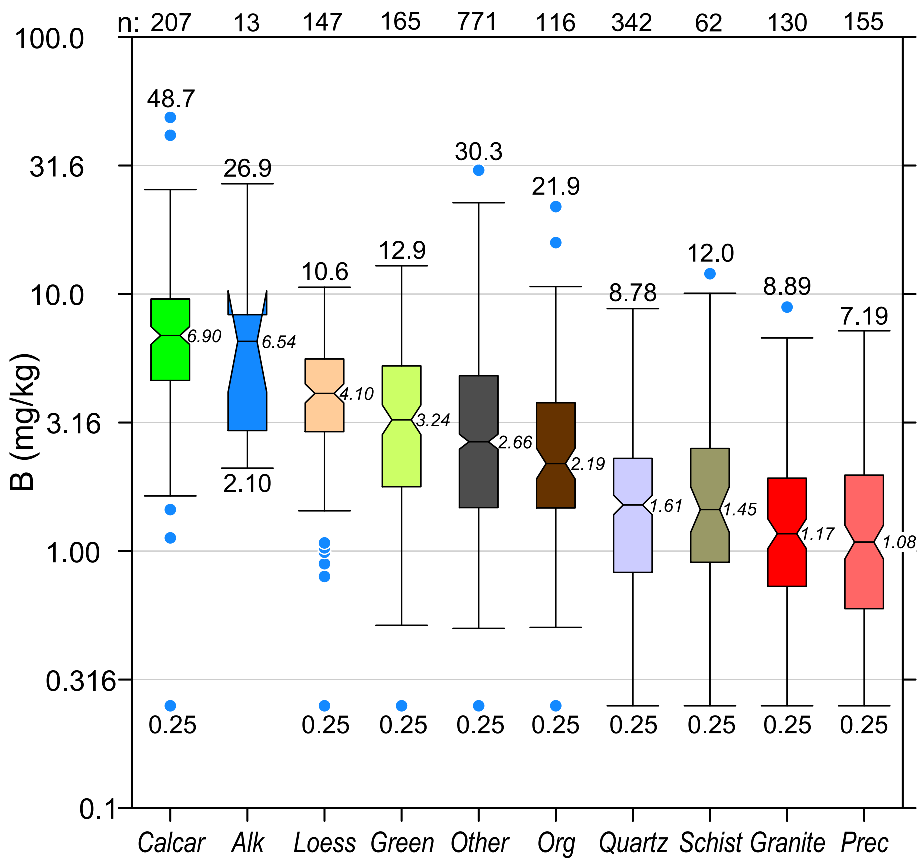

Fig. 4. Boxplots showing the statistical distribution of hot aqua regia extractable B contents in European Ap soil samples. Data are classified according to the lithological parent material subgroups 'Calcar' (carbonate rocks), 'Alk' (alkaline rocks), 'Loess', 'Green' (greenstone or ultramafic rocks), 'Other', 'Org' (organic soil), 'Quartz' (soil developed on coarse-grained sandy deposits), 'Schist', 'Granite' and 'Prec' (Precambrian gneiss) (Reimann et al., 2012a, 2012b). Y-axis linear $\log_{10}$ scale. Plotted with Golden Software's Grapher version 24. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

d'Azur in France, Cyprus and Hellenic islands), but also in northern Europe, e.g., in southern and central England, on the islands of Gotland and Öland in Sweden and along the coast of Estonia. Agricultural soil samples with high B concentrations in north-eastern and central Germany, north-eastern France, as well as in central Europe (Slovakia, Hungary) can be explained by the presence of limestone lithologies. Jurassic limestone seems to be particularly enriched in boron. The classical principal component analysis (PCA) of the Ap samples (Table 4; Birke et al., 2017) revealed one principal component (PC) with high positive loads for soil pH, associated with B and Ca (PC 5: pH_{CaCl2}-B-Ca). Elevated and anomalous positive PC scores of PC 5 confirm the distribution of anomalous AR extractable B in soil originating from carbonate parent materials. Some of the B anomalies are clearly related to areas with young and recent volcanic activity (e.g., in Italy). Shale (especially black shale) and marine clayey sediments are another source of elevated B contents in soil; for example, in central Sweden (postglacial marine clay, black shale), Estonia (black shale), and England (mudstone, clay). Apart from the specific bedrock and alkaline soil pH, in southern Europe and the Mediterranean region, high B concentrations in soil prevail due to warm climate and low precipitation rates.

Low B contents occur mainly in soil formed on granitic bedrocks and their metamorphic counterparts (e.g., most of Scandinavia, western Scotland, western Spain, north Portugal, Corsica, northern Sardinia, Rhodope Mountains in southern Bulgaria-northern Hellenic Republic), sandy deposits (Aquitanian Basin and part of the Paris Basin in France), sandy coarse-grained sediments of the last glaciation (Fig. 3; Poland and northern Germany). The overall spatial distribution patterns of B in soil are strongly governed by B extractability in hot aqua regia, resulting in higher contents in soil originating from carbonate-dominated parent materials, which have a few times higher extractability than silicate minerals, major host for B in crystalline rocks. It is expected that a map of total concentrations would give a different picture. The hot aqua regia extractable B contents provide more usable information about its occurrence in the surficial environment and possibly can be used as a guide for the nutrient status, although hot water extractions have been tested as more appropriate (Raza et al., 2002).

The geochemical map of AR extractable B (Fig. 5) reflects its natural sources, and its spatial distribution seems to be governed mainly by weathering type and degree, Quaternary history and the underlying parent materials. The role of mineralisation is considered minor because, according to the ProMine Mineral Database of the ore deposits in Europe (Cassard et al., 2012, 2015; Demetriades and Reimann, 2014; map not shown), primary (tourmaline) and secondary (sedimentary and evaporite deposits) B mineral deposits in Europe are rare and rather small. The low B content in soil of Northern Europe is possibly due to low soil pH and the resulting leaching can be discussed as a subset in Fennoscandian countries (Fig. 6). With the local class divisions, the B anomalies are better defined and can be easily explained by: (i) the presence of post-glacial clay in central Sweden and southern Finland (so-called Central Scandinavian Clay Belt; Ladenberger et al., 2013); (ii) the Palaeozoic limestone which occurs on Gotland, Öland and Scania, and (iii) the Palaeozoic alum shale occurring in southern Sweden, and in central Sweden by the Caledonian mountain front south-west of Östersund (Jämtland) as well as in the Oslo Graben.

The PCA results of the clr-transformed data (e.g. CoDA approach) also provided one PC that includes B (PC7: B-K-[-Mo, -U], Table 5, Birke

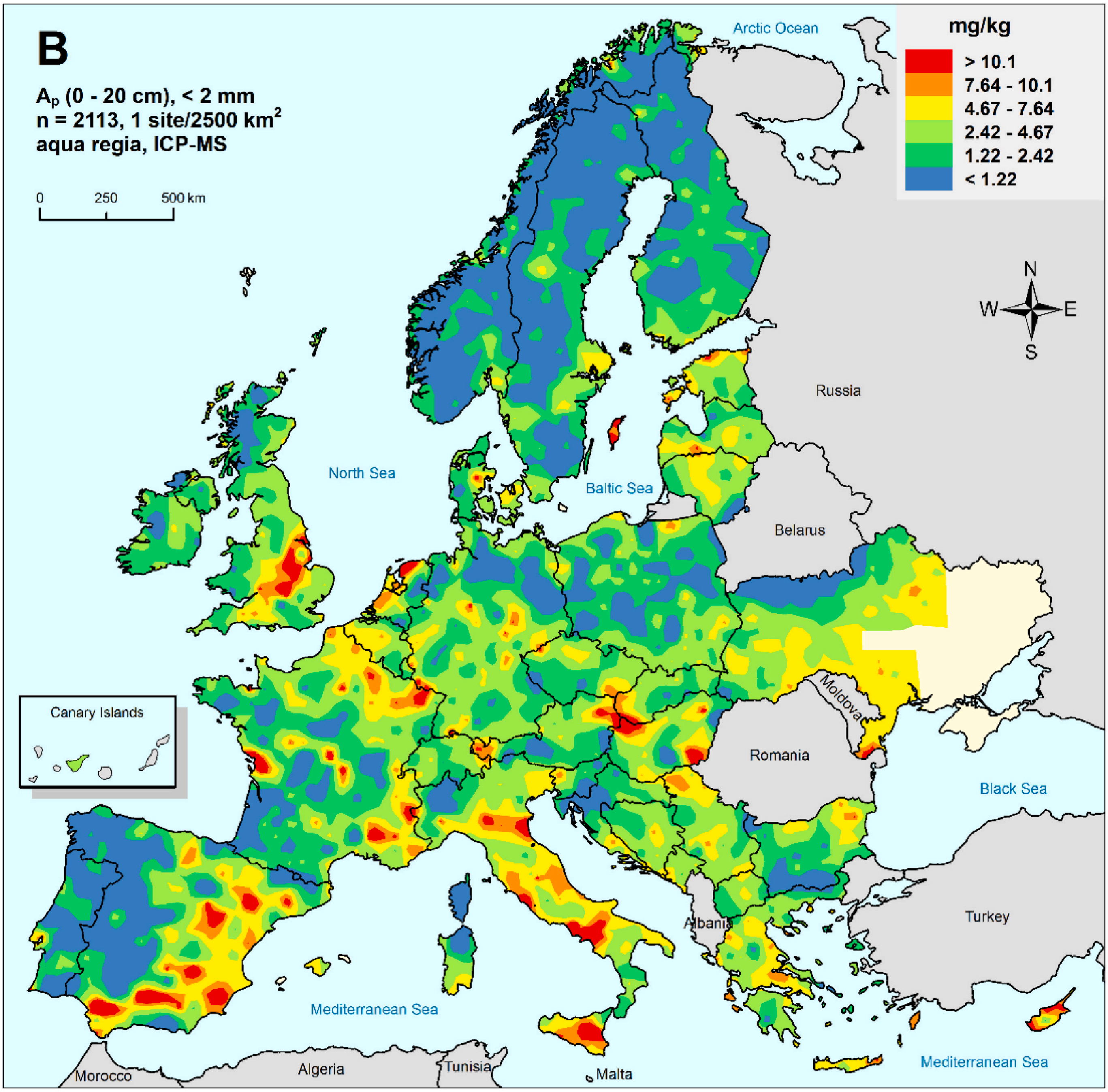

Fig. 5. Soil geochemical map of hot aqua regia extractable B contents for ploughed agricultural soil (Ap, n = 2113). Map plotting kriging parameters: cell size = 5000 m, search radius = 1,000,000 m. Plotted with Esri's ArcGIS version 10.3. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

et al., 2017) related to lithology (parent material). The PC 7 score anomalies can be mainly explained by geogenic sources (e.g., sandy sediments of the last glaciation in northern Germany and Poland; glaciofluvial material in the Baltics; carbonate lithologies in the United Kingdom, north-eastern France and eastern Hungary; the Central Scandinavian Clay Belt, see Fig. 5). Thus, B originating predominantly from geological formations and the observed spatial variation in agricultural soil depends on the lithology complemented by the AR extraction capacity, and the subsequent control by the prevailing secondary phases or processes (e.g., adsorption on clay particles and Fe—Al oxides, organic matter accumulation and low pH), as well as climate.

4.2. Role of weathering on boron behaviour

In addition to B, rubidium (Rb) and strontium (Sr) can be used as tracers for weathering (Négrel et al., 2018c). Mobile Sr is indicative of the weathering of both silicate and carbonate rocks, and relatively immobile Rb is a direct tracer of silicate weathering as it is essentially absent in carbonates (Rb = 3 mg/kg; Parker, 1967) compared to Sr (610 mg/kg; Parker, 1967). While Sr shows a strong affinity for Ca and in carbonate minerals, Rb, as a large +1-charged cation, substitutes for K in common aluminosilicate minerals such as micas and feldspar. The chemical weathering of the most commonly Sr-bearing phases from the silicate host rock, (e.g., the primary phases apatite, plagioclase, K-

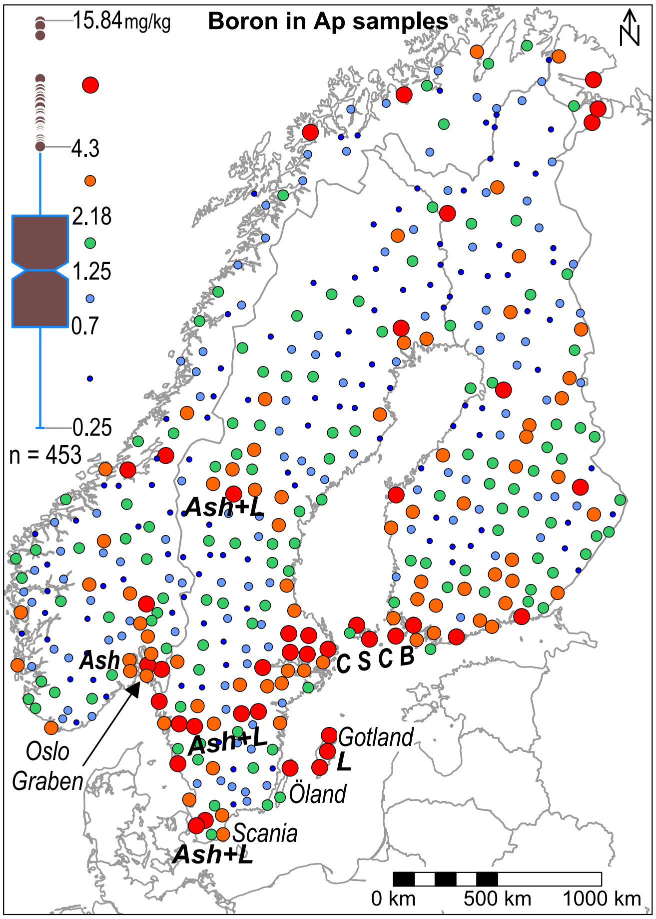

Fig. 6. Boron contents (in mg/kg, AR extraction) in agricultural soil of Norway, Sweden and Finland. The class division is based on a subset of the data (n = 453) defined by the boxplot. Ash = Alum shale; L = Limestone; CSCB = Central Scandinavian Clay Belt. Map plotted with Golden Software's Surfer version 28.

feldspar, biotite and muscovite) or their alteration products (epidote and clay minerals) control the Sr mass balance in a crystalline environment (Brantley et al., 1998; Négrel et al., 2018c). Further, Rb mobility in the environment is generally extremely low because after being released during weathering, it is strongly adsorbed by the clay fraction of soil, more than potassium (Goldschmidt, 1954; Wampler et al., 2012). Complementary to B, Rb—Sr can be used to evaluate the input from parent materials and chemical weathering trends in a ternary plot in molecular proportions in the GEMAS Ap samples using the AR results (Négrel et al., 2015, 2021).

Fig. 7 illustrates the Sr, Rb and B contents for the lithological parent material subgroups except the unclassified bedrock ('*Other*'). The GEMAS Ap data are plotted together with the mean value of the main lithological endmembers taken from Parker (1967), e.g., plutonic and metamorphic rocks, and shale, carbonate rocks and sand-sandstone, and the upper continental crust (UCC) average from Rudnick and Gao (2003). In Fig. 7, the main spread of data along the Rb axis (Négrel et al., 2018b) reflects the variation in Rb content between the sedimentary (carbonate) and mafic (ultramafic rocks) endmember parent materials (low Rb content) to granite (intermediate Rb content), both with high Sr and low B contents. The closeness of a soil sample approaching the 100 % apex along the Sr axis and 0 % along the Rb axis is an indication of similarity to the carbonate lithological endmember. The evolution along the Rb axis overpassing the granite lithological endmember is a measure of the geochemical maturity of soil with respect to the weathering of underlying parent materials, e.g., silicates endmember weathering and enrichment in Rb-bearing minerals resistant to weathering (K-feldspars, for example) as stated by Négrel et al. (2018b). The arrowhead line denotes compositional trends of weathering of the different rock types and increased weathering causes Sr loss and B enrichment, as well as variable Rb enrichment. The B enrichment is more marked in soil developed on coarse-grained sandy deposits, loess and granite, in relation to the presence of secondary phases as described hereafter.

4.3. Influence of secondary phases

4.3.1. General considerations for B behaviour in secondary phases

Boron adsorption in soil is mainly controlled by the presence of Al and clay minerals, as well as Fe-Al-Mn oxides and hydroxides (Sims and Bingham, 1967, 1968a, 1968b; Goldberg, 1997). Adsorption reactions (Goldberg, 1997; Van Eynde et al., 2020b) were described by empirical or phenomenological models (Langmuir or Freundlich equations, Keren equation), chemical surface complexation models (e.g., constant capacitance, triple-layer, surface charge variable surface potential). Boron is an essential micronutrient for plants, but the uptake is only related to B activity in soil aqueous solution and, thus, B adsorbed by soil particles is not perceived as toxic by plants. The control of B by secondary phases is important in terms of weathering and its circulation in the ecosystems. Boron adsorption on various Al and Fe oxide minerals, both crystalline and amorphous phases, has been previously evidenced (Fleming, 1980; Goldberg and Glaubig, 1985; Tamuli et al., 2017 and references therein; Kumari et al., 2017; Van Eynde et al., 2020a and references therein). Adsorption increases between pH 5.5 and 8.5, exhibiting a peak in the pH range of 8 to 10 and then decreases at pH >10 (Wear and Patterson, 1962; Goldberg and Glaubig, 1986). The magnitude of B adsorption is greater for amorphous materials and decreases with increasing crystallinity of the solid.

A second ternary plot is constrained for B (expressed as 1000B), Fe and Al association (Fig. 8), using their contents in molecular proportions in the GEMAS Ap samples, together with the main lithological endmembers from Parker (1967), i.e., plutonic and metamorphic rocks, and shale, carbonate rocks and sand-sandstone, and the UCC average from Rudnick and Gao (2003). Using Fe and Al as proxy, elements for the secondary phases allows discrimination compared to the more mobile element B during weathering and its control by the formation of secondary phases (Ataman, 1967). In Fig. 8, representing the AR results for B–Fe–Al, the main spread of data along the arrowhead line denotes compositional trends of increased control of B by clay minerals (as denoted by the lithological endmember clay) and Al oxides, mainly marked in soil developed on or derived from (i) carbonate rocks ('*Calcar*'), (ii) coarse-grained sandy deposits ('*Quartz*') and (iii) organic soil ('*Org*'). The role of Fe oxides is marked by a lower B enrichment than that observed for Al.

4.3.2. The clay content and role of the cation exchange capacity (CEC)

The European median of clay size particle content in the Ap soil samples is 15.2 % with the most striking pattern on the spatial repartition (Reimann et al., 2014a, 2014b) being the clear difference between northern (low-median clay of 8 %) and southern Europe (high-median clay of 18 %) with the content break occurring at the southern limit of the last glaciation (Fig. 1). This limit divides the young soil developed under cold to moderate climate in northern Europe – rich in organic matter and clay - from the much older and more weathered (mature) soil in west-central and southern Europe. These two domains may require a separate interpretation as internal variation is visible between the northern and southern domains.

The B and clay contents are compared in Fig. 9a. The classical representation of clay (%) vs. B (mg/kg) contents shows the existence of heteroscedasticity in the data. To overcome this, the B contents are plotted on a logarithmic scale and the clay contents are expressed as a binary logit function, i.e., a logistic transformation according to log[P/(100-P)], where P is the clay content (Négrel et al., 2023). No clear trend is observed in Fig. 9a for all soil samples. However, a more visible

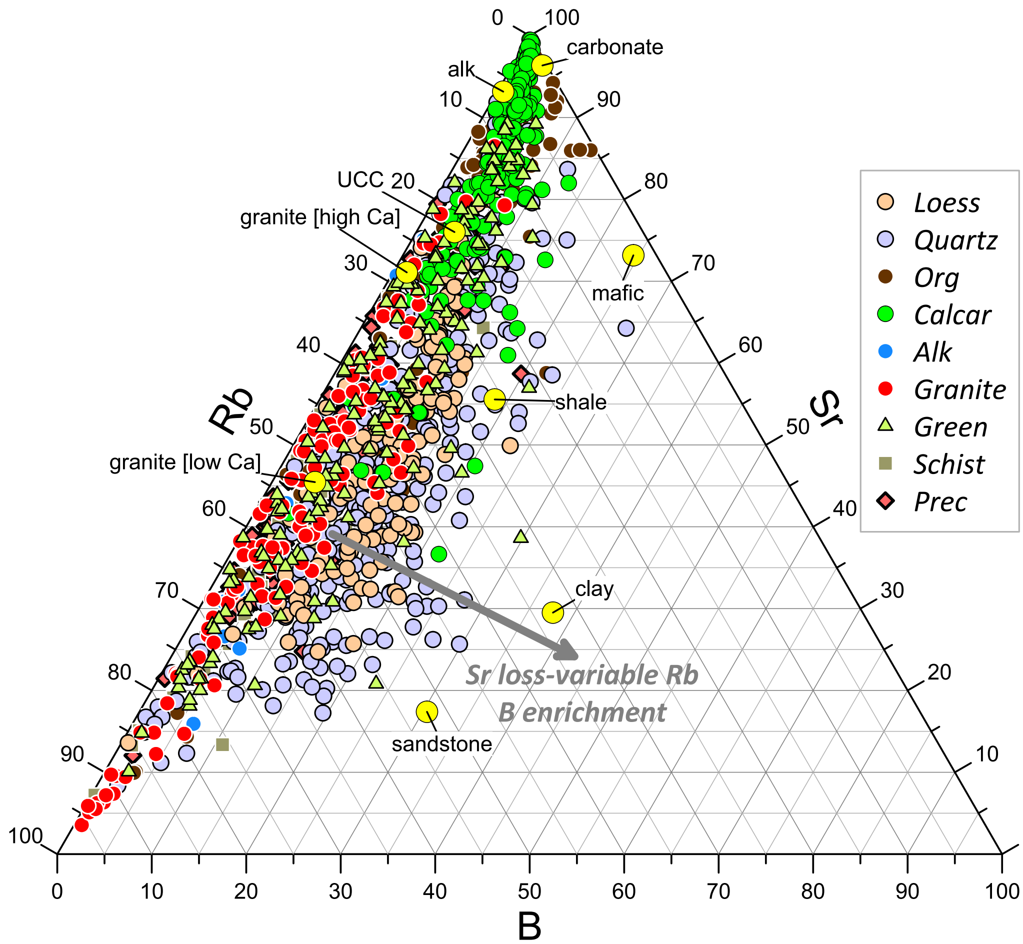

Fig. 7. Distribution of hot aqua regia extractable B–Sr–Rb contents (in molecular proportions) in the GEMAS Ap soil samples classified according to the lithological parent material subgroups plotted together with bedrock compositions (yellow circles) according to Parker (1967). The grey arrow denotes compositional weathering trends or enrichment/loss. Data are classified according to the lithological parent material subgroups 'Loess', 'Quartz' (soil developed on coarse-grained sandy deposits), 'Org' (organic soil), 'Calcar' (carbonate rocks), 'Alk' (alkaline rocks), 'Granite', 'Green' (greenstone or ultramafic rocks), 'Schist', 'Prec' (Precambrian gneiss) from Reimann et al. (2012a, 2012b). Plotted with Golden Software's Grapher version 24. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

set of trends occurs for soil developed on loess, carbonate rocks ('*Calcar*') and greenstone ('*Green*') as these parent materials are sources of clay overburden resulting from the weathering processes, especially in a warm and humid climate. The correlation between B and Al, with an R^2 of around 0.61, was earlier reported by Reimann et al. (2012a) and is not shown here. This correlation, although moderate, can be explained by the fact that kaolinite, the most aluminous mineral, hardly fixes large amounts of B compared to other minerals such as illite or chlorite (Hingston, 1964).

The cation exchange capacity (CEC) defines the relative ability of soil to store nutrients, particularly the cations through the maximum quantity of total cations that a soil is capable of holding at a given pH value. The CEC of a soil sample depends on its clay and humus contents, e.g., the higher the clay and/or humus content, the higher the CEC is. The clay type in the soil may also have a role in the CEC values. The median for CEC in Ap soil is 16.4 meq/100 g. Weathering intensity and climate may also impact the CEC value, as given by the clear difference in the Ap soil samples between northern (low CEC-median for the Ap samples 12 meq/100 g) and southern Europe (higher CEC-median for the Ap samples 19 meq/100 g); the values being higher in southern European soil samples. As for clays, the content break occurs at the southern limit of the last glaciation (Fig. 1), separating the young soil in northern Europe from the much older and more weathered soil in southern Europe. High CEC values are either due to soil rich in organic matter or clay. This can be further emphasised by comparing the B content with the CEC values for Ap soil in Fig. 9b, where the B – CEC relationship differs according to the lithological parent material subgroups. Low CEC values are often observed in soil developed on silicate bedrocks ('*Granite*', Precambrian gneisses '*Prec*') and soil developed on coarse-grained sandy deposits ('*Quartz*'), both with low clay and humus (e.g., organic matter) contents. Conversely, the highest B – CEC values are observed for carbonate-derived soil ('*Calcar*'), organic soil ('*Org*'), and '*Loess*', reflecting the high amount in clay and/or organic matter. The scatter of the B – CEC data in Fig. 9a mimics that of the B content vs. the clay content reflecting well the role of clay in the CEC.

Parfitt et al. (1995) reported a high CEC for smectite and the lowest for kaolinite. Goldberg et al. (1993b) showed that B adsorption on kaolinite increased within a range of pH from 3 to 6, with a peak between pH 6 and 8.5, and decreased from pH 8.5 to 11. For B adsorption on montmorillonite and soil, the adsorption maximum was located near pH 9. Results of their modelling suggested an inner-sphere adsorption mechanism for gibbsite and kaolinite, and an outer-sphere adsorption mechanism for montmorillonite. This reinforces the role of the cation exchange capacity of soil, e.g., the CEC value, as an important characteristic to assess B behaviour (Raza et al., 2002), and the degree of cation saturation influences the adsorption of B as shown in Fig. 9b.

Similar to kaolinite, B adsorption on the common Fe oxides increases from pH 3 to 6, with a peak between pH 6 and 8.5, and then decreases from pH 8.5 to 11 (Goldberg et al., 1993b), and the modelling suggests an inner-sphere adsorption mechanism for goethite. Recently, Van

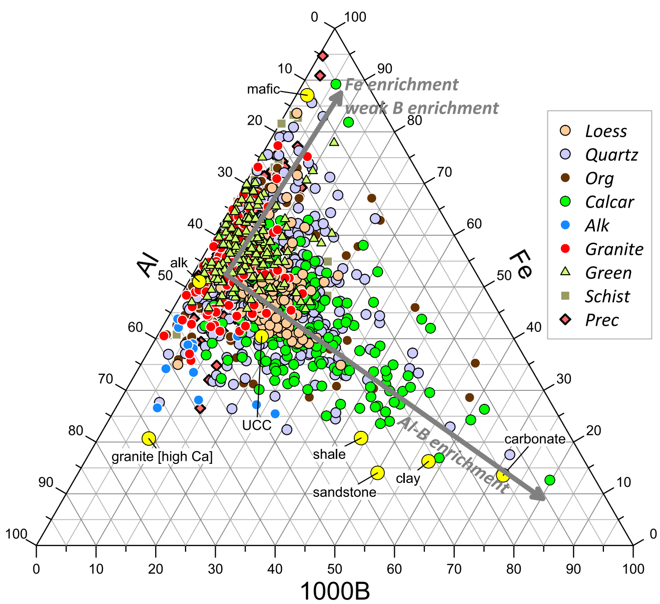

Fig. 8. B–Fe–Al (in molecular proportions) distribution in GEMAS soil samples, for AR extraction in the lithological parent material subgroups plotted together with bedrock compositions (yellow circles) according to Parker (1967). Arrows denote compositional weathering trends or enrichment/loss. Data are classified according to the lithological parent material subgroups 'Loess', 'Quartz' (soil developed on coarse-grained sandy deposits), 'Org' (organic soil), 'Calcar' (carbonate rocks), 'Alk' (alkaline rocks), 'Granite', 'Green' (greenstone or ultramafic rocks), 'Schist', 'Prec' (Precambrian gneiss), from Reimann et al. (2012a, 2012b). Plotted with Golden Software's Grapher version 24. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Eynde et al. (2020a) demonstrated that the adsorption at low pH (<5) is dominated by ferrihydrite nanoparticles (e.g., natural metal (hydr)oxide fraction), with a B adsorption density like that of goethite. Under this condition, B adsorption by organic matter is low and even if the soil is rich in organic matter, ferrihydrite nanoparticles contribute to around half of the total B adsorption. At higher pH, B is controlled by the adsorption to organic matter. A portion of the Fe and Al oxides, as well as other possible adsorption sites, are generally coated or occluded by organic matter and become active only after the removal of the organic matter (Marzadori et al., 1991).

4.3.3. *The role of Fe—Mn oxides and hydroxides*

The correlation between B and Fe (Fig. 10a), with an R^2 of around 0.55, was earlier reported by Reimann et al. (2012a), and the correlation between B and Mn (Fig. 10b) has a similar R^2 correlation (0.56). This moderate correlation can be explained by the competition between the different secondary phases in the control of B contents and indicates a larger variety of Fe and Mn minerals present in soil than just oxides and hydroxides. In comparison, with the clear correlation of the CEC for the different types of clays and B retention in soil, it can be assumed that Fe, Al and Mn oxides and hydroxides play a subordinate role in controlling B behaviour (Spivack et al., 1987).

4.4. *Influence of soil organic matter on boron content*

The role of organic matter in B ad- or de-sorption processes in soil is still under debate. Marzadori et al. (1991) and Sarkar et al. (2014) demonstrated that the amount of B adsorbed was considerably greater after the organic matter had been removed from soil. They observed that higher amounts of Fe and Al are extractable after the destruction of organic matter leading to the hypothesis that part of the Fe and Al oxides are coated or occluded by organic matter and are made active after removal of the organic matter. In the Ap soil samples, there is no significant correlation between organic matter (TOC wt%) and B contents

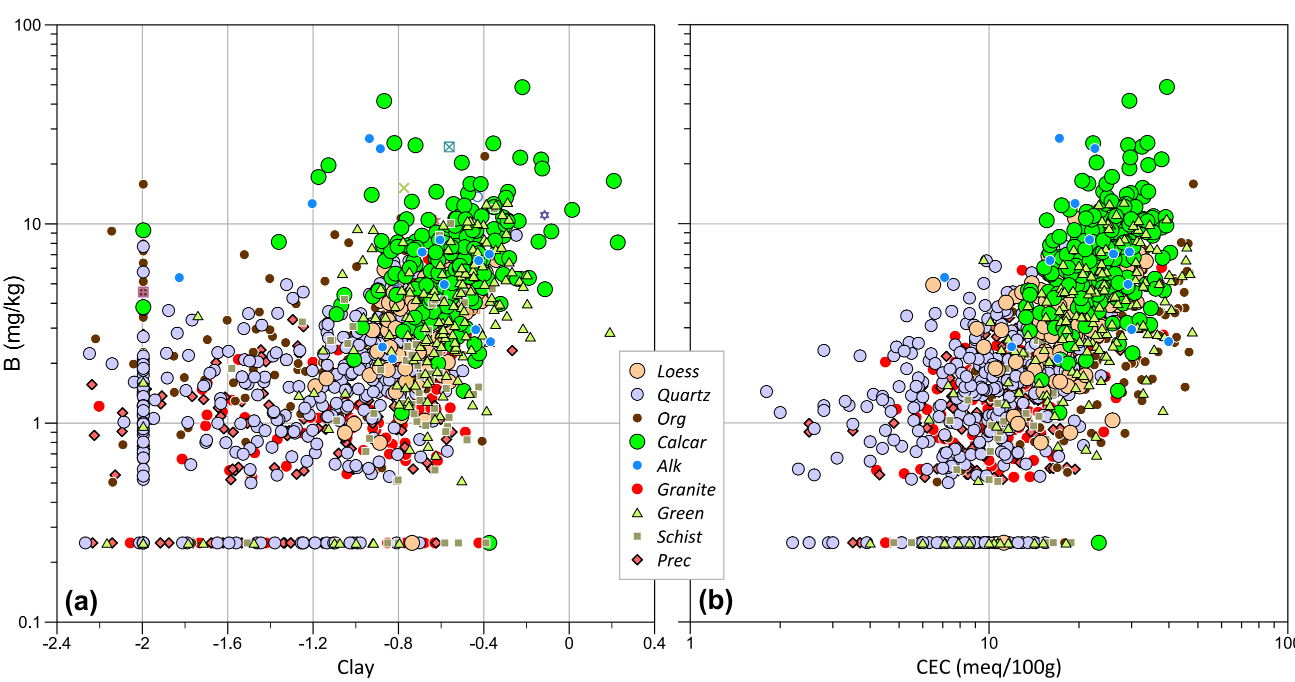

Fig. 9. (a) Plot of clay (%) and B (mg/kg) content in European Ap soil samples. (b) Plot of cation exchange capacity (CEC, meq/100 g eq. milliequivalent of hydrogen (H^+) per 100 g of dry soil) and B (mg/kg) content in European Ap soil samples. Data are classified according to the lithological parent material subgroups 'Loess', 'Quartz' (soil developed on coarse-grained sandy deposits), 'Org' (organic soil), 'Calcar' (carbonate rocks), 'Alk' (alkaline rocks), 'Granite', 'Green' (greenstone or ultramafic rocks), 'Schist', 'Prec' (Precambrian gneiss), from Reimann et al. (2012a, 2012b). Y-axis linear log_{10} scale for (a); X and Y-axis linear log_{10} scale for (b). (a) and (b) Plotted with Golden Software's Grapher version 24. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

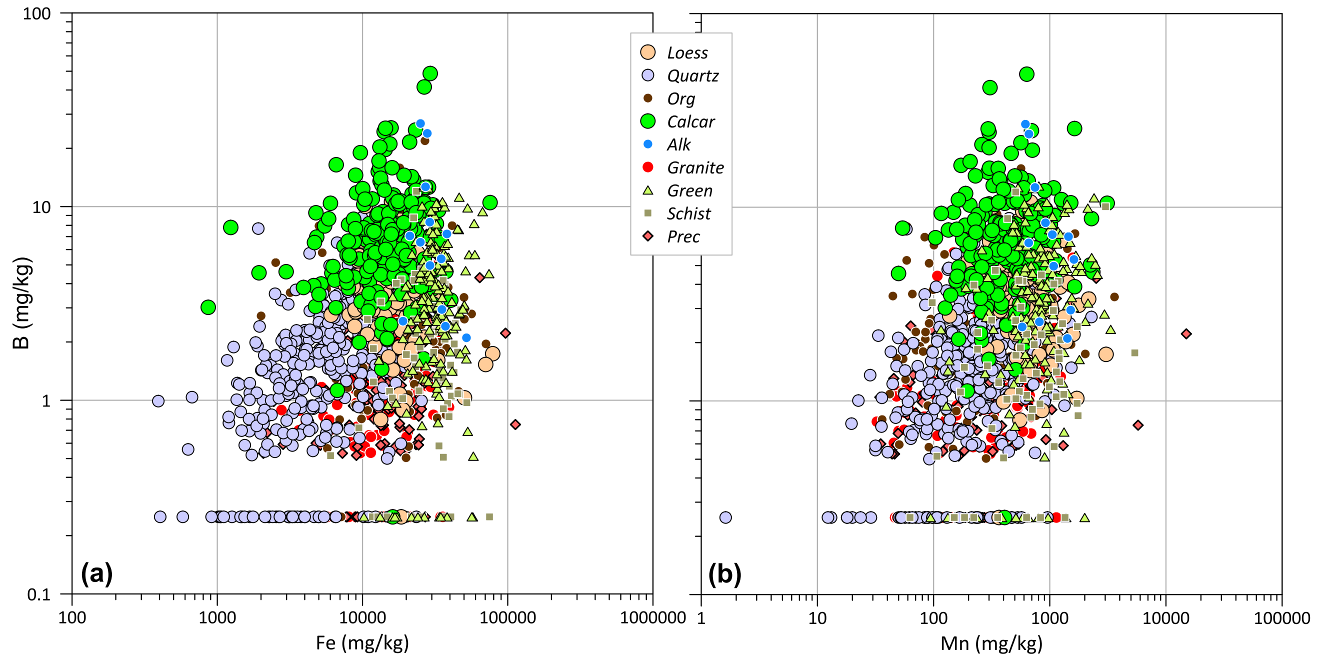

Fig. 10. (a) Plot of Fe (mg/kg) and B (mg/kg) contents, (b) Mn (mg/kg) and B (mg/kg) contents in European Ap soil samples. Data are classified according to the lithological parent material subgroups ‘Loess’, ‘Quartz’ (soil developed on coarse-grained sandy deposits), ‘Org’ (organic soil), ‘Calcar’ (carbonate rocks), ‘Alk’ (alkaline rocks), ‘Granite’, ‘Green’ (greenstone or ultramafic rocks), ‘Schist’, ‘Prec’ (Precambrian gneiss) from Reimann et al. (2012a, 2012b). X and Y-axis linear $\log_{10}$ scale. Plotted with Golden Software’s Grapher version 24. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

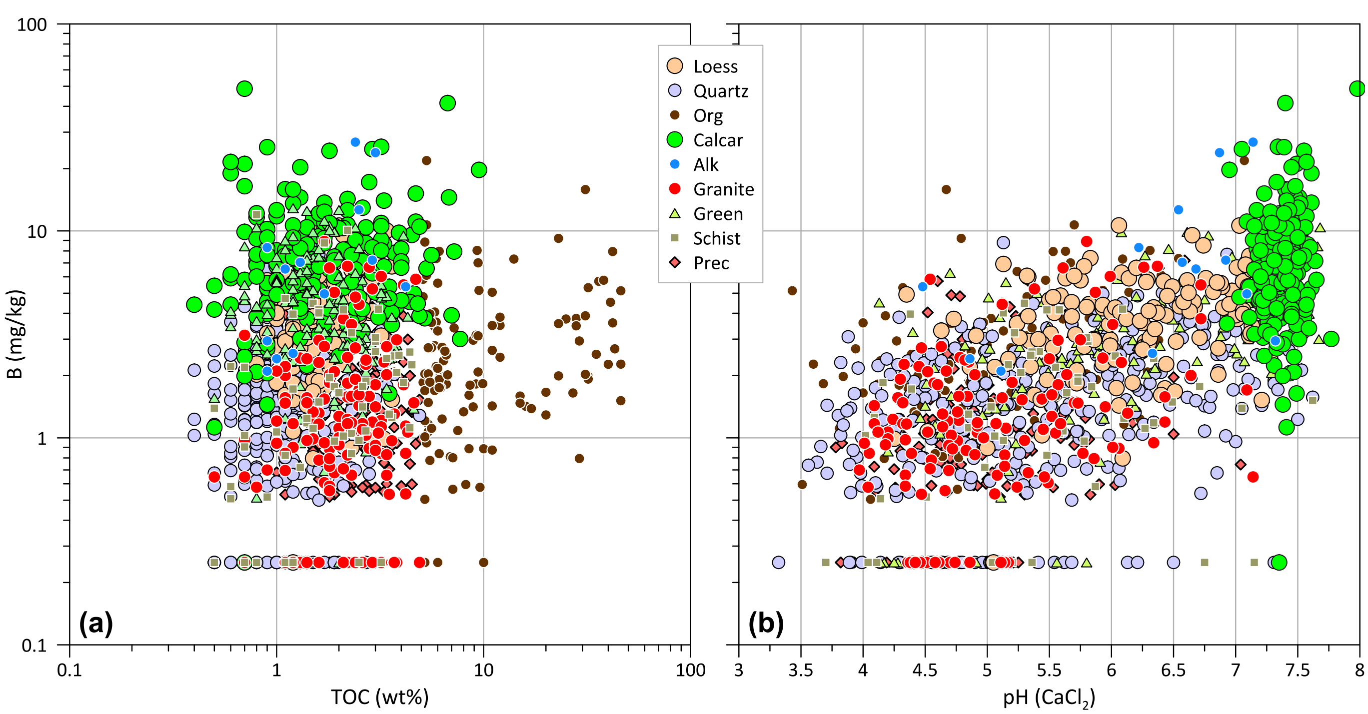

Fig. 11. (a) Plot of Total Organic Carbon (TOC wt%) and B (mg/kg) contents in European Ap soil samples. (b) Plot for Ap samples of B contents vs. pH for $CaCl_2$ extraction in European Ap soil samples. Data are classified according to the lithological parent material subgroups ‘Loess’, ‘Quartz’ (soil developed on coarse-grained sandy deposits), ‘Org’ (organic soil), ‘Calcar’ (carbonate rocks), ‘Alk’ (alkaline rocks), ‘Granite’, ‘Green’ (greenstone or ultramafic rocks), ‘Schist’, ‘Prec’ (Precambrian gneiss) from Reimann et al. (2012a, 2012b). X and Y-axis linear $\log_{10}$ scale for (a) and Y-axis linear $\log_{10}$ scale for (b). Plotted with Golden Software’s Grapher version 24. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

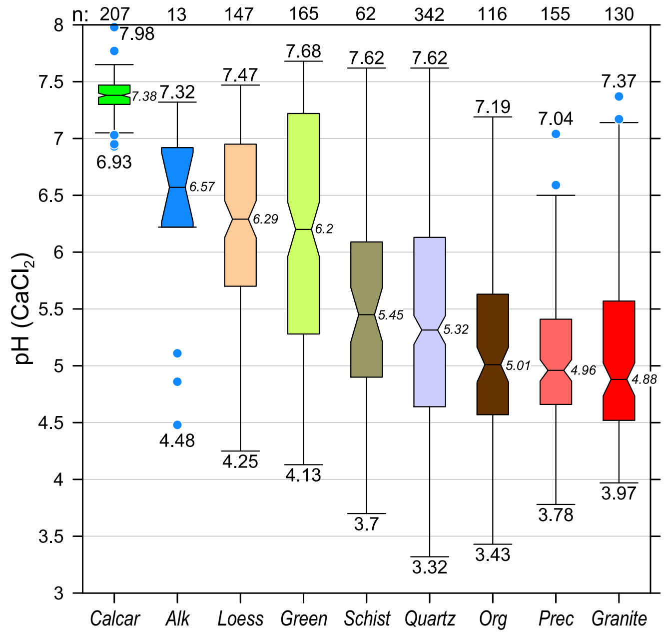

Fig. 12. Boxplot comparison of pH in Ap soil samples according to the parent material. Modified from Fabian et al. (2014). Data are classified according to the lithological parent material subgroups 'Calcar' (carbonate rocks), 'Alk' (alkaline rocks), 'Loess', 'Green' (greenstone or ultramafic rocks), 'Schist', 'Quartz' (soil developed on coarse-grained sandy deposits), 'Org' (organic soil), 'Prec' (Precambrian gneiss) and 'Granite' (Reimann et al., 2012a, 2012b). The parent material subgroup 'Other' is excluded. Plotted with Golden Software's Grapher version 24. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

($R^2 < 0.4$), as illustrated in Fig. 11a, indicating that no direct role can be ascribed to organic matter in the control of B contents in Ap soil.

4.5. Influence of soil pH on boron content

The median pH value using a 0.01 M $CaCl_2$ solution for the Ap agricultural soil samples is 5.77, and its statistical distribution is bimodal with a strongly acidic and slightly alkaline soil at around pH 5 and 7.5, respectively (Reimann et al., 2011, 2014a, 2014b). The pH spatial distribution patterns evidenced by Fabian et al. (2014) reflect the dual role of lithology and climate at the continental scale of Europe. The pH median value of Ap soil samples in northern Europe is about one unit more acidic than those in southern Europe, i.e., median pH of 5.2 and 6.3, respectively. This distinct pH difference indicates that there are around one hundred times more protons available in northern than southern European soil, a feature that can help control B contents in soil. Fig. 12 shows the variation of soil pH in parent material subgroups, and Fig. 13 the relationship among B contents, parent material subgroups and pH. Low pH values occur in soil developed over or derived from silicate parent materials ('*Granite*', '*Schist*', Precambrian gneiss, '*Prec*'), and high pH values, as expected, in soil developed on or derived from carbonate bedrock ('*Calcar*'), however, with an exceptionally low range of pH variation. The other feature is the low median pH value observed in areas where the Ap soil samples are organic matter-rich ('*Org*'; Fig. 12). Therefore, the acid-base properties of soil in Europe are mainly derived from a combination of climate and geology. Spreading of fertilisers onto agricultural soil can influence its pH, but this anthropogenic impact is difficult to detect because of the dominance of the natural factors evoked before (bedrock and climate) in determining the pH of agricultural soil at the continental scale.

The correlation between B and pH, with a coefficient of determination (R^2) of around 0.56 (Fig. 11b) does not exhibit any particular feature. Neither the role of the varying B adsorption capacities according to pH (increase from pH 5.5 to 8.5, exhibit a peak in the pH range 8.5 to 10, and decrease from pH 10 to 11.5; Wear and Patterson, 1962;

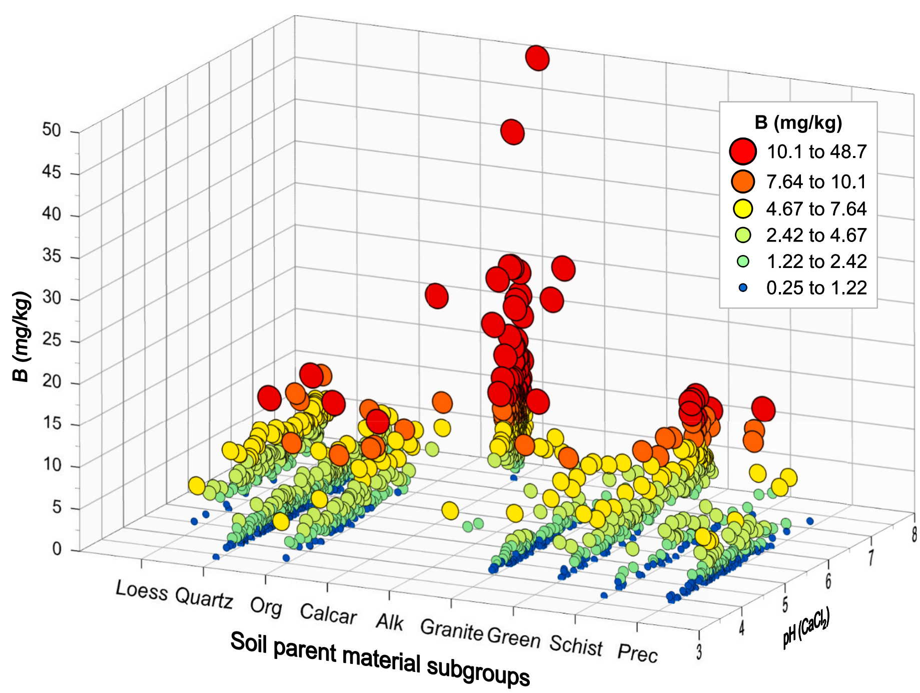

Fig. 13. 3D XYZ plot of Ap soil Parent Material groups vs. B and pH ($CaCl_2$). Boron data are classified according to the lithological parent material subgroups 'Loess', 'Quartz' (soil developed on coarse-grained sandy deposits), 'Org' (organic soil), 'Calcar' (carbonate rocks), 'Alk' (alkaline rocks), 'Granite', 'Green' (greenstone or ultramafic rocks), 'Schist', 'Prec' (Precambrian gneiss) from Reimann et al. (2012a, 2012b). Plotted with Golden Software's Grapher version 24. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Goldberg and Glaubig, 1986), nor the lime impact often regularly used to increase soil pH, which should increase B fixation in soil (Couch and Grim, 1968) appear to affect B absorption in soil. Several studies indicate a smaller influence of the soil pH compared to the dominant role of the soil CEC in controlling B sorption in soil (Raza et al., 2002; Matula, 2009). In addition, the contents of clay minerals and Al oxides rather than those of Fe oxides and Mn hydroxides are the soil properties that affect B adsorption in soil (Goldberg, 1997; Steiner and Lana, 2013; Van Eynde et al., 2020a, 2020b) rather than soil pH.

5. Conclusions

The GEMAS agricultural Ap soil geochemical database of Europe allows the chemical variation in soil composition at the continental scale to be studied. Several factors are scrutinised including lithology, secondary phases, anthropogenic impact, geochemical processes (ad- and ab-sorption), pH, and climate.

The soil B chemical signature was investigated using the hot aqua regia (AR) extraction results. The B median value in soil, around 2.42 mg/kg, is lower than the value observed in the Upper Continental Crust because most of B in nature is bound in AR-insoluble minerals, like tourmaline. The hot aqua regia leach dissolves some of the soil's primary and secondary phases, and releases weakly bound B from the soil particles, hence indicating transport, either addition or removal.

The parent material categories highlight B sources in soil, with the highest stock in areas with alkaline and carbonate bedrocks, whereas low B concentrations in soil have been identified in regions with silicate bedrock and sandy postglacial sediments.

In European soil, the spatial distribution of B on geochemical maps seems to be controlled mainly by the nature of the lithological formations and their spatial distribution, complemented by the B solubility in AR extraction. The formation of oxides, hydroxides and clays are key processes controlling B fixation. Boron fixation by Fe, Al, and Ca secondary phases and sorption on clay minerals can be correlated with the cation exchange capacity of soil (CEC). Even if the role of organic matter in the soil B cycle is a matter of debate, no direct role can be ascribed to organic matter (expressed as total organic carbon, TOC) in the control of the B contents in Ap soil. The soil pH, although increases B mobility and its leaching out from soil, does not appear to be a critical parameter for B retention in soil.

The spatial distribution of B contents in agricultural soil helps to identify the regions that may need additional B supplementation with fertilisers. Proper B supply in arable soil, apart from improving plant growth and reproduction, can also help to prevent the adverse effects of Al toxicity in soil with a low pH.

CRediT authorship contribution statement

Philippe Négrel: Writing – original draft, Supervision, Investigation, Conceptualization. **Anna Ladenberger:** Writing – original draft, Methodology, Conceptualization. **Alecos Demetriades:** Writing – review & editing, Project administration, Funding acquisition. **Clemens Reimann:** Writing – review & editing, Resources, Project administration, Methodology. **Manfred Birke:** Writing – review & editing, Resources, Project administration, Methodology. **Martiya Sadeghi:** Writing – review & editing, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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