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

3
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30

31 **Abstract**

32

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

39 We present B contents in agricultural soil samples (0-10 cm) collected in 33 European countries
40 (5.6 million km²) during the GEMAS (GEOchemical Mapping of Agricultural and grazing land
41 Soil) continental-scale project. The B content, determined by ICP-MS following hot aqua regia
42 extraction, varies in European agricultural soil from 0.5 to 49 mg/kg (median 2.42 mg/kg, n=
43 2108), which is somewhat similar to total B estimates for the Upper Continental Crust (17-47
44 mg/kg). Its spatial distribution in agricultural soil shows a patchy pattern with low values in
45 regions with granitic bedrock and high contents in soil formed over limestone and in volcanic
46 areas.

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

51

52 **Keywords:** topsoil, geochemical mapping, parent materials, continental scale

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55 **1. Introduction**

56

57 Boron is an essential nutrient for plants with variable concentrations required for
58 optimum growth (Kabata-Pendias and Pendias, 2001; Brown et al., 2002; Kabata-Pendias and
59 Mukherjee, 2007). In human health, there is only a narrow margin between boron deficiency
60 and excess uptake leading to toxicity (Keren and Bingham, 1985; Kot, 2009). Boron deficiency
61 in terrestrial plants has been reported in many countries and solutions are currently being

62 actively sought (Shorrocks, 1997; Shireen et al., 2018; Brdar-Jokanović, 2020). This deficiency
63 is the second most widespread micronutrient deficiency after zinc. It occurs when B leaches out
64 of soil, particularly in humid regions, and in areas with sandy soil having a low organic matter
65 content. Regions in north European countries and the Balkans are considered as endangered by
66 B deficiency (Shorrocks, 1997). In contrast to B deficiency, soil B toxicity is less abundant and
67 predominantly occurs in arid and semi-arid areas. Generally, soil with <0.5 mg/kg hot-water-
68 extractable B is considered deficient (Yau et al., 1994; Alloway, 1995, 2008). According to Sun
69 et al. (2019), 0.5-2.0 mg B/kg is the optimal soil B range, whereas lower (<0.5 mg B/kg) and
70 higher (>3 mg B/kg) indicate deficiency and toxicity, respectively. Prolonged periods of
71 drought and low soil temperature contribute to weak B uptake by plants, which results in B
72 deficiency both in warm and cold climates. Soil with high B retention capacity is usually
73 alkaline (high pH), and rich in clay, iron and aluminium oxides (Goldberg, 1997; Chen et al.,
74 2009;).

75 Boron in soil originates from the weathering of B-containing minerals from underlying
76 rocks. The most common B-bearing minerals are hydrated borates, such as borax
77 ($\text{Na}_2(\text{B}_4\text{O}_5(\text{OH})_4) \cdot 8\text{H}_2\text{O}$), kernite ($\text{Na}_2(\text{B}_4\text{O}_6(\text{OH})_2) \cdot 3\text{H}_2\text{O}$) and colemanite
78 ($\text{Ca}(\text{B}_3\text{O}_4(\text{OH})_3) \cdot \text{H}_2\text{O}$), which occur in evaporite deposits in closed basins in dry climates and
79 are the major economical resource for boron (Boyle, 1974). These minerals are soluble and can
80 be easily weathered. In Europe, however, B deposits are very rare and occur in Serbia
81 (colemanite; Piskanja Boron, Jarandol Basin), and as by-products in Italy (geothermal brines;
82 Bagnore, Larderello, Monte Gabbro, Piancastagnaio in Tuscany), and Germany (Stassfurt and
83 Hamburg Salt Dome; Permian salt deposits) as evidenced by Cassard et al. (2012, 2015) and
84 Demetriades and Reimann (2014). Another group of primary minerals containing B are
85 tourmaline group minerals, which are complex borosilicate minerals resistant to weathering
86 where the borate anion is a compound with Al, Fe, Mg, Na, Li and K, and are classified as

87 gemstones occurring in a variety of colours. Other forms of B minerals such as borophosphates,
88 borocarbonates and boroarsenates are rare. Among common rock-forming minerals, the highest
89 B contents are observed in micas and serpentine. Clay minerals can have a high B content, e.g.,
90 illite, glauconite and montmorillonite. Iron oxides such as haematite and goethite may have
91 high B concentrations, up to 300 mg/kg. Certain alkaline rocks (e.g., kimberlite, syenite) and
92 volcanic rock varieties (rhyolite) can concentrate boron. Tourmaline occurs commonly in
93 highly fractionated magmatic rocks and their fluid-altered products such as greisen. In
94 metamorphic rocks, the highest B contents occur in mica and graphite schist (Wedepohl, 1978).

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

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

108 Boron is an essential microelement for higher plants; it governs the productivity of both
109 agriculture and forestry and its deficiency is widespread. Boron has a close affinity with
110 calcium. Boron plays a significant role in plant cell division and shoot and root growth.
111 Moreover, boron improves plant reproduction (e.g., pollination, flowering, seed production...).

112 Another important role of boron is for the transport of sugars within the plant that are essential
113 for photosynthesis. The visible B deficiency symptoms are the deformation of roots, buds,
114 flowers, young leaves and fruits. In rare cases of B toxicity, the symptoms may vary from
115 necrosis of plant organs to death of the whole plant. In animals, B helps to regulate the calcium
116 release into the blood and enables the conversion of vitamin D into active form. The tendency
117 of B accumulation in animal and vegetable tissues may present a potential health risk to those
118 consuming food and water with high B content (Brown and Shelp, 1997; Pereira et al., 2021).

119 Compared to its natural origin, B is also released to a lesser extent, from human activities
120 by the use of borate-containing fertilisers and herbicides, the burning of plant-based products
121 such as wood, coal, or oil, and the release of waste from borate mining and processing (Woods,
122 1994). Boron also reaches the environment due to the use of borates and perborates in the home
123 and industry, through leaching from treated wood or paper, and from sewage and sewage sludge
124 disposal (Woods, 1994; EPA – OGWDW, 2008). Boron is also used in metallurgy for nuclear
125 shields and in electronics, as well as for the production of aviation and rocket propellants (Streit,
126 1994).

127 Boron behaviour in soil has been the subject of many studies as well as debates for
128 decades (Berger and Truog, 1945; Singh, 1964; Okazaki and Chao, 1968; Elrashidi and
129 O'Connor, 1982; Bussetti et al., 1995; Goldberg, 1997, Kabata-Pendias and Mukherjee, 2007;
130 Padbhushan and Kumar, 2017; Pereira et al., 2021). Boron has also been studied in water either
131 in groundwater (Casanova et al., 2005; Gonfiantini and Pennisi, 2006; Giménez and Morell,
132 2008) or in surface water, often using B isotopes (Chetelat et al., 2009; Guinoiseau et al., 2018).
133 Here we present the spatial distribution and geochemical behaviour of B in agricultural soil at
134 the European scale using the GEMAS data sets. The Geochemical Mapping of Agricultural and
135 grazing land Soil project (GEMAS) focused on the mapping of the background element
136 variation in soil at the European scale. Soil samples were collected by the Geochemistry Expert

137 Group of EuroGeoSurveys, over an area of 5.6 million km² in 33 European countries (Reimann
138 et al., 2012a; 2014a, b) and the project was carried out in cooperation with the European
139 Association of Metals (Eurometaux).

140 Reimann et al. (2016) discussed the use of low sampling densities (1 site/100 to 1 site/18
141 000 km²) for providing sufficient information for decision-making, rather than the costly and
142 time-consuming very high-density sampling (100s to 1000s of samples/km²) employed for
143 geochemical exploration or environmental monitoring. Their argument was based on the results
144 of previous studies using low sampling density geochemical mapping at regional to continental
145 scales (Garrett and Nichol, 1967; Armour-Brown and Nichol, 1970; Garrett et al., 2008; Smith
146 and Reimann, 2008; Cicchella et al., 2013; Birke et al., 2015). The aim of this paper is to
147 investigate the spatial distribution of hot aqua regia extractable B in European agricultural soil
148 with a specific focus on topsoil (Ap horizon) derived or developed on various parent materials,
149 using the GEMAS database (Reimann et al., 2014a, b).

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

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

159 **2. Materials and methods**

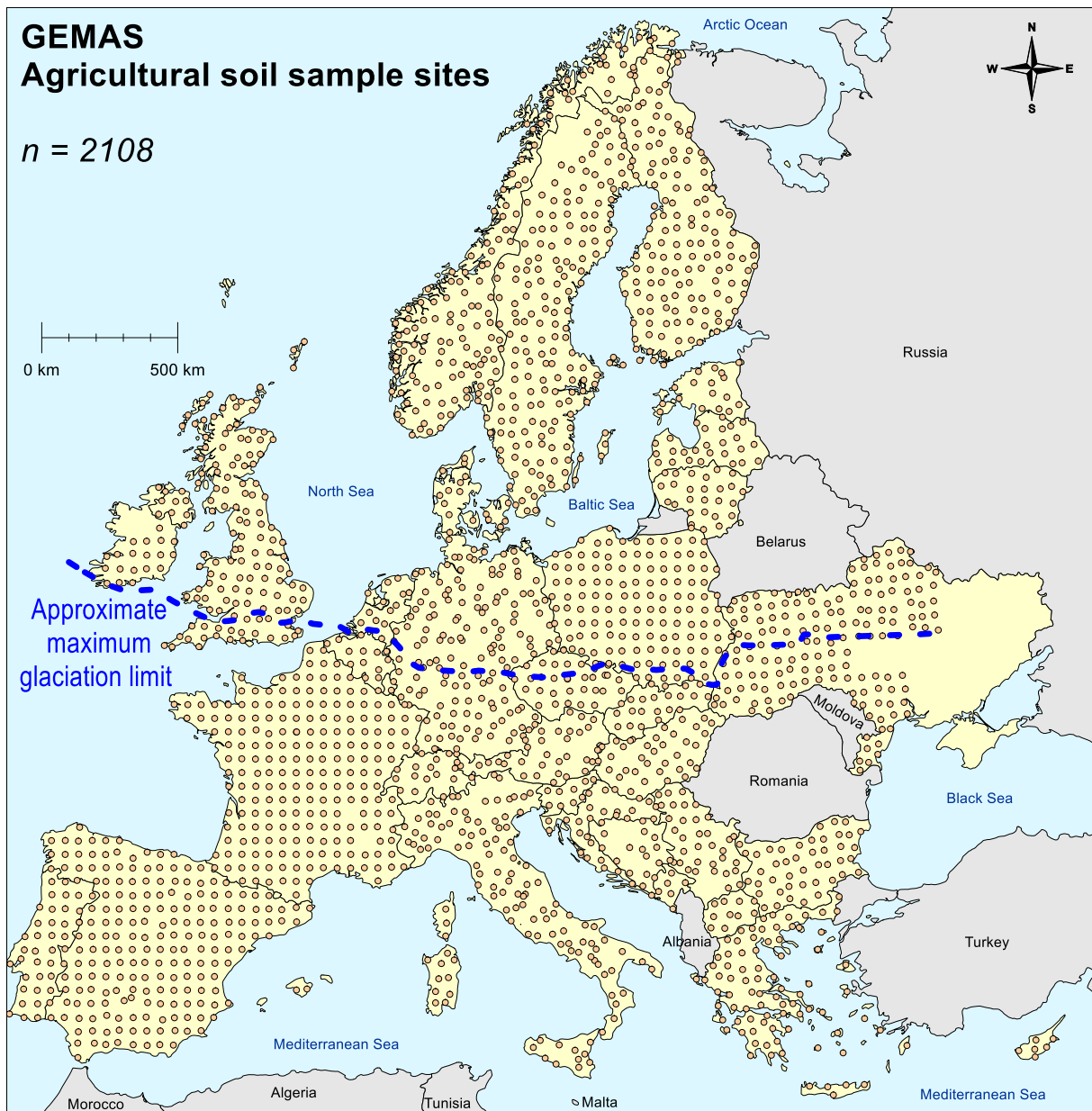
160 The GEMAS project (Reimann et al., 2014a, b) was conducted by the EuroGeoSurveys
161 Geochemistry Expert Group in partnership with the European Association of Metals

162 (Eurometaux). This project took advantage of the achievements of the first geochemical
163 mapping survey at the European continental-scale, i.e., the Geochemical Atlas of Europe of the
164 Forum of European Geological Surveys (FOREGS), the forerunner of EuroGeoSurveys
165 (Salminen et al., 1998; 2005; De Vos, Tarvainen et al., 2006). Figure 1 shows the distribution
166 of GEMAS project agricultural soil samples in 33 European countries, covering about 5.6
167 million km² (Reimann et al., 2012a; 2014a, b) for mapping the geochemical background
168 variation of major and trace elements. To achieve this objective, the soil sampling avoided
169 known contaminated sites, the immediate vicinity of industry or power plants, villages, towns,
170 cities, railway lines or major roads. The two types of soil samples have been collected at an
171 average density of 1 site per 2500 km² (Fig. 1). Grazing land soil (Gr; 0-10 cm depth; N=2024
172 samples) has been defined as land under permanent grass cover, and agricultural soil (Ap; 0-20
173 cm depth; N=2108 samples) refers to the ploughing layer of an agricultural arable field. At each
174 sample site, a composite sample (ca 3.5 kg) was generated from five sub-samples collected
175 from the corners and centre of a 10×10 m square.

176 Sample preparation (air-drying; sieving to <2 mm using a nylon screen; homogenisation
177 and splitting to 10 sub-samples) was carried out at the State Geological Institute of Dionyz Stur
178 (Slovakia). Boron was determined following a hot aqua regia (AR) extraction by inductively
179 coupled plasma-mass spectrometry (ICP-MS) at Bureau Veritas Mineral Laboratories in
180 Vancouver, Canada (Reimann et al., 2012a; Birke et al., 2014). The applied analytical
181 extraction protocol to the soil samples, prior to their analysis, was a 15 g aliquot of the unmilled
182 <2 mm fraction, leached in 90 ml of aqua regia for one hour at 95°C, and then made up to a
183 final volume of 300 ml with 5% HCl. The analytical and external quality control protocol is
184 described by Reimann et al. (2009; 2011; 2012c), Birke et al. (2014) and Demetriades et al.
185 (2014); in each batch of 20 samples, one replicate of the field duplicate and one project standard
186 were inserted.

187 The practical detection limit was estimated from the uncensored results of project
188 replicate samples by calculating regression line coefficients with the ‘reduced major axis line’
189 procedure (Demetriades, 2011; Demetriades et al., 2022) and the value for B is 0.76 mg/kg,
190 with an analytical precision at $\pm 14\%$ at the 95% confidence interval (Reimann et al., 2009). The
191 unbalanced analysis of variance (ANOVA) has given the following results for the geochemical
192 (natural), sampling (site) and analytical variance: 87%, 0.0%, 13%, respectively (Reimann et
193 al., 2009; Demetriades et al., 2014). The generated geochemical data set is compositional as
194 element contents are reported in wt. % or mg/kg sum up to a constant and are thus not free to
195 vary (Reimann et al., 2012d). Compositional data plot in the Aitchison simplex (Aitchison,
196 1986; Buccianti et al., 2006; Pawlowsky-Glahn and Buccianti, 2011) and only order statistics
197 should be used in the statistical processing of geochemical data. The colour surface maps were
198 produced by kriging, based on a careful variogram analysis (Filzmoser et al., 2014). Kriging
199 was used to interpolate values from the irregularly distributed sampling sites into unsampled
200 space to generate a regular grid. Class boundaries for the colour surface maps are based on
201 percentiles (5, 25, 50, 75, 90 and 95).

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203
204 *Figure 1. Sample locations (dots) of the ploughed agricultural soil (Ap-samples; $n=2108$ –*
205 *without the 110 East Ukraine samples) and the approximate maximum extension of glaciation.*
206 *Map projection: Lambert Azimuthal Equal Area (ETRS_1989_LAEA), with central meridian at*
207 *10° . Plotted with Golden Software's Surfer version 28 and modified from Négre et al., 2021).*
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209 **3. Results**

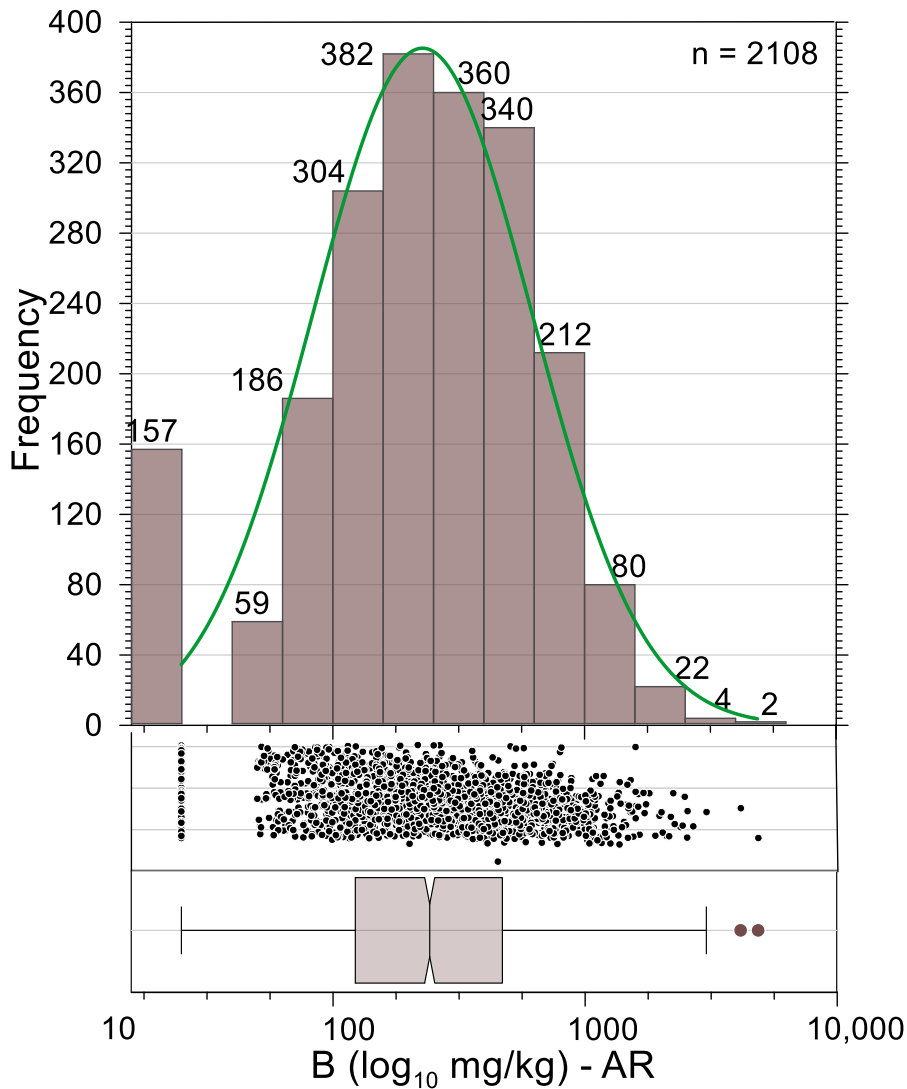
210 **3.1. Boron contents in agricultural soil**

211 The range of aqua regia extractable B contents in GEMAS Ap soil samples is from <0.5 to 49
212 mg/kg, with 7% of the values being below the detection limit (0.8 mg/kg) and a median value
213 of 2.4 mg/kg. In Gr soil samples, the range is similar, from <0.5 to 41 mg/kg, with 7% of the

214 values being below the detection limit and a median value of 2.6 mg/kg. The Ap soil median
215 value of 2.4 mg/kg is several times lower than the value estimated for the Upper Continental
216 Crust (UCC); the value itself varies depending on different studies, e.g., from 17 to 47 mg/kg
217 as given by Rudnick and Gao (2005) and Hu and Gao (2008), respectively, indicating poor
218 extractability of B in acid-leach methods. Compared to the estimated total B average in UCC,
219 the AR extractable values reported here are exceptionally low with a ratio GEMAS Ap
220 soil/UCC between 0.142 and 0.051. This very low ratio range is observed because most of the
221 B in nature is bound in AR-insoluble minerals, like tourmaline (silicate mineral group
222 containing 2.8 to 3.6% B; Slack and Trumbull, 2011; Wimmer et al., 2015), and some micas.
223 Soluble evaporitic B minerals are rare in Europe. Tourmaline as the main B-bearing phase
224 occurs in granitic and metamorphic rocks (schist and marble), and as resistant to weathering
225 heavy minerals can be found in sedimentary rocks such as sandstone, siltstone, mudstone and
226 conglomerate. Additionally, from the analytical point of view, B can also be partly volatilised
227 and lost during hot aqua regia acid extraction (Reimann et al., 2009).

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

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Figure 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 log₁₀. Plotted with Golden Software's Grapher version 24.

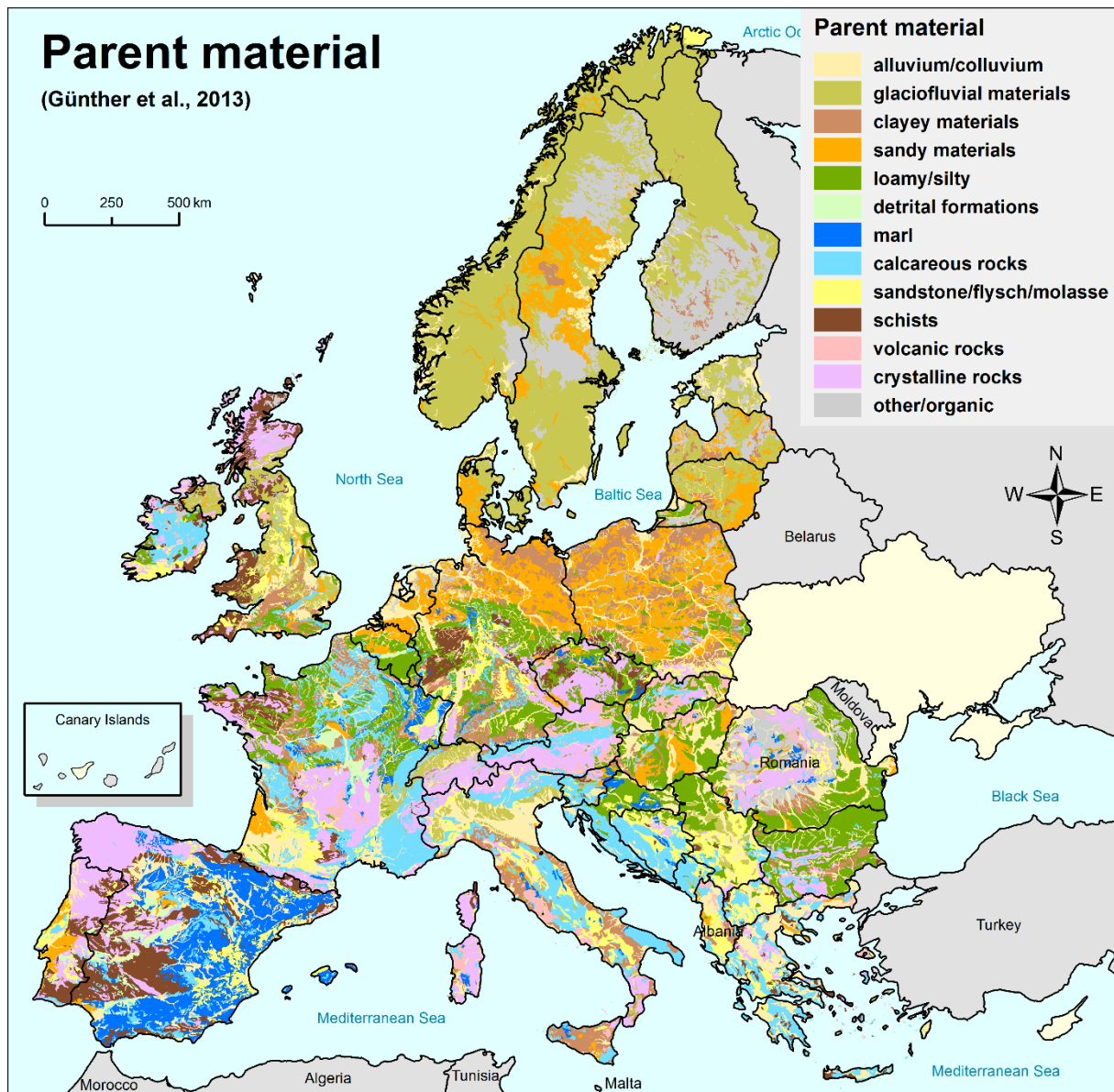
3.2. Comparison of B boxplots for the AR extraction with assigned bedrock categories

246 The geochemical mapping of chemical elements determined on the GEMAS soil samples
 247 often evidenced a link between the element spatial distribution and the lithology of the
 248 underlying bedrock (Scheib et al., 2012; Ladenberger et al., 2013; Négrel et al., 2015; 2018a;
 249 2019). In all geochemical maps, a geological separation is obvious between northern Europe,
 250 marked by the predominance of old crystalline (>1 billion years) and metamorphic rocks, and
 251 the rest of Europe with younger magmatic rocks (<1 billion years to recent) and large

252 sedimentary basins. However, when generalising European bedrock geology, there are two
253 major problems to be recognised: (i) too many small units are often defined on geological maps
254 impeding a reasonable subgrouping of samples that are large enough for meaningful statistical
255 comparison, and (ii) a geological map shows age relations whereas lithology is more
256 appropriate for geochemical applications.

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

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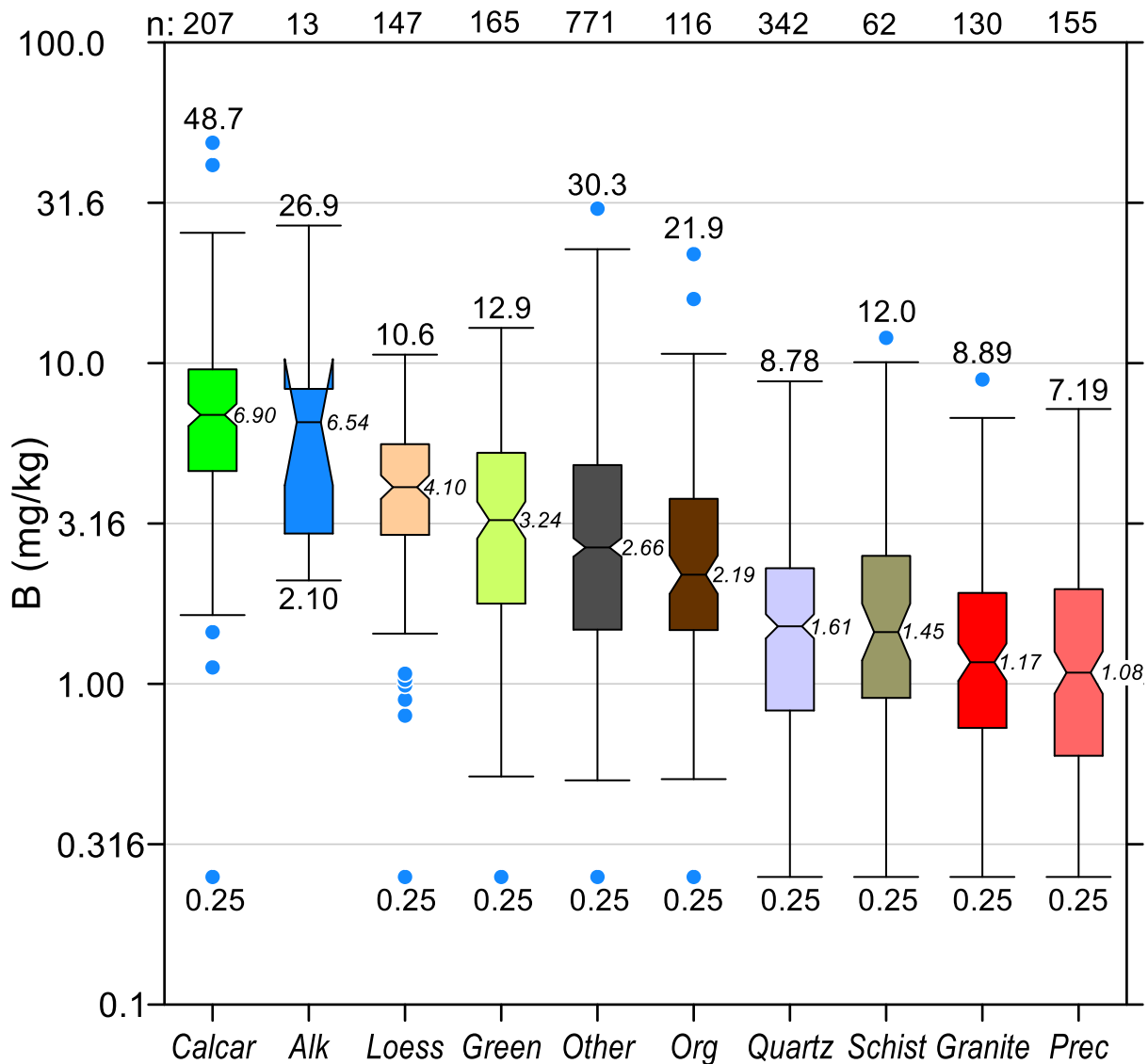
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Figure 3. Map of parent materials in Europe showing the distribution of various lithologies across the continent, modified from Günther et al. (2013) and adapted from Negrel et al. (2015). Plotted with Esri's ArcGIS version 10.6.1.

276 Soil developed on or derived from carbonate ('Calcar') and alkaline ('Alk') parent
277 materials shows the highest B median values. While the silicate-derived soil (e.g., 'Prec',
278 'Granite', 'Schist' and 'Quartz' parent materials subgroups) has the lowest median value
279 confirming that initial B content in soil depends on parent material and the degree of weathering
280 (Biggar and Fireman, 1960; Padbhushan and Kumar, 2015). This can be compared with the
281 mean values for total B content for the main lithological end-members defined by Parker

282 (1967). Mafic and alkaline rocks display the lowest B mean content, 5 and 9 mg/kg,
 283 respectively, followed by granite with a mean value of 9 mg/kg, carbonate rocks and sandstone
 284 have intermediate mean values of 20 and 35 mg/kg, respectively, and the highest B mean
 285 contents are in shale (100 mg/kg) and clay (230 mg/kg).

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Figure 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, b). Y-axis linear log₁₀ scale. Plotted with Golden Software's Grapher version 24.

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

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309 **4. Discussion**

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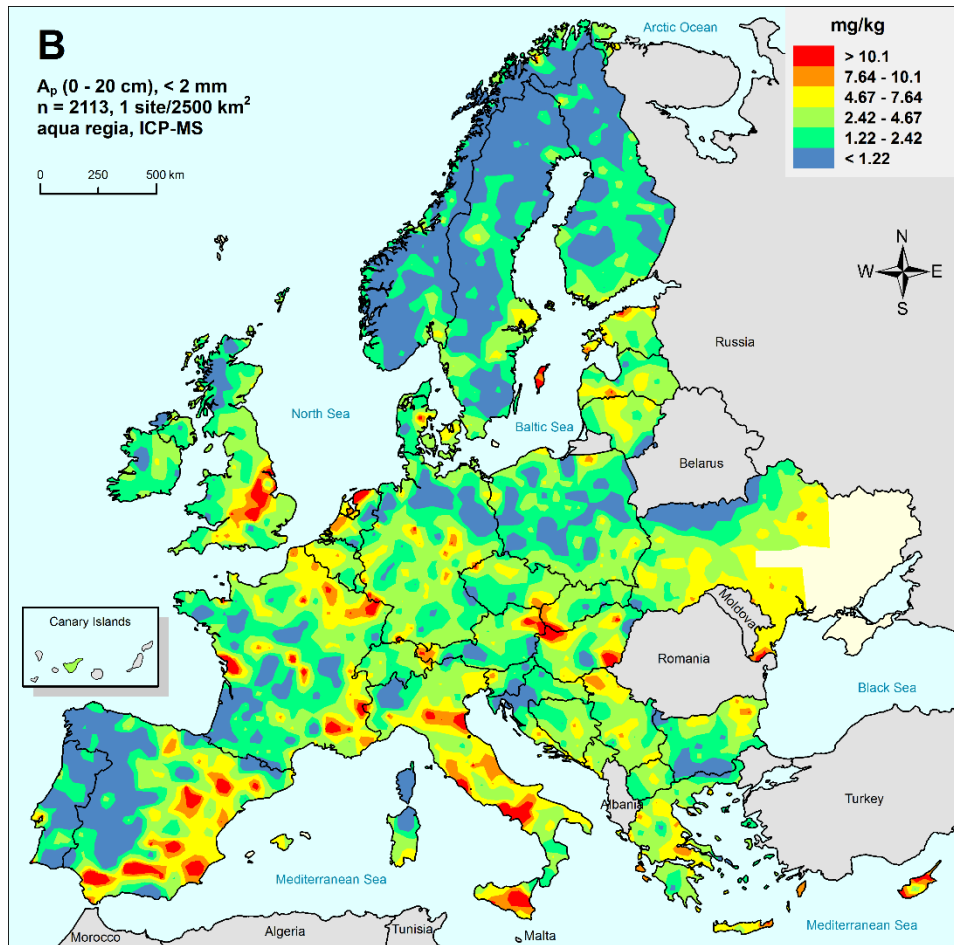
311 **4.1. Spatial distribution of boron in European soil**

312

313 The geochemical map of AR extractable B of agricultural soil samples (Fig. 5) shows
314 unexpected patterns with patchy anomalies and a large variation at the regional scale. High B
315 contents are observed over most of the known limestone-chalk (carbonate) areas, not only in
316 the south (eastern and southern Spain, Italy with Sicily, Provence-Alpes-Cote-d'Azur in France,
317 Cyprus and Hellenic islands), but also in northern Europe, e.g., in southern and central England,
318 on the islands of Gotland and Öland in Sweden and along the coast of Estonia. Agricultural soil
319 samples with high B concentrations in north-eastern and central Germany, north-eastern France,
320 as well as in central Europe (Slovakia, Hungary) can be explained by the presence of limestone
321 lithologies. Jurassic limestone seems to be particularly enriched in boron. The classical
322 principal component analysis (PCA) of the Ap samples (Table 4; Birke et al., 2017) revealed

323 one principal component (PC) with high positive loads for soil pH, associated with B and Ca
324 (PC 5: pH_{CaCl_2} -B-Ca). Elevated and anomalous positive PC scores of PC 5 confirm the
325 distribution of anomalous AR extractable B in soil originating from carbonate parent materials.
326 Some of the B anomalies are clearly related to areas with young and recent volcanic activity
327 (e.g., in Italy). Shale (especially black shale) and marine clayey sediments are another source
328 of elevated B contents in soil; for example, in central Sweden (postglacial marine clay, black
329 shale), Estonia (black shale), and England (mudstone, clay). Apart from the specific bedrock
330 and alkaline soil pH, in southern Europe and the Mediterranean region, high B concentrations
331 in soil prevail due to warm climate and low precipitation rates.

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



344

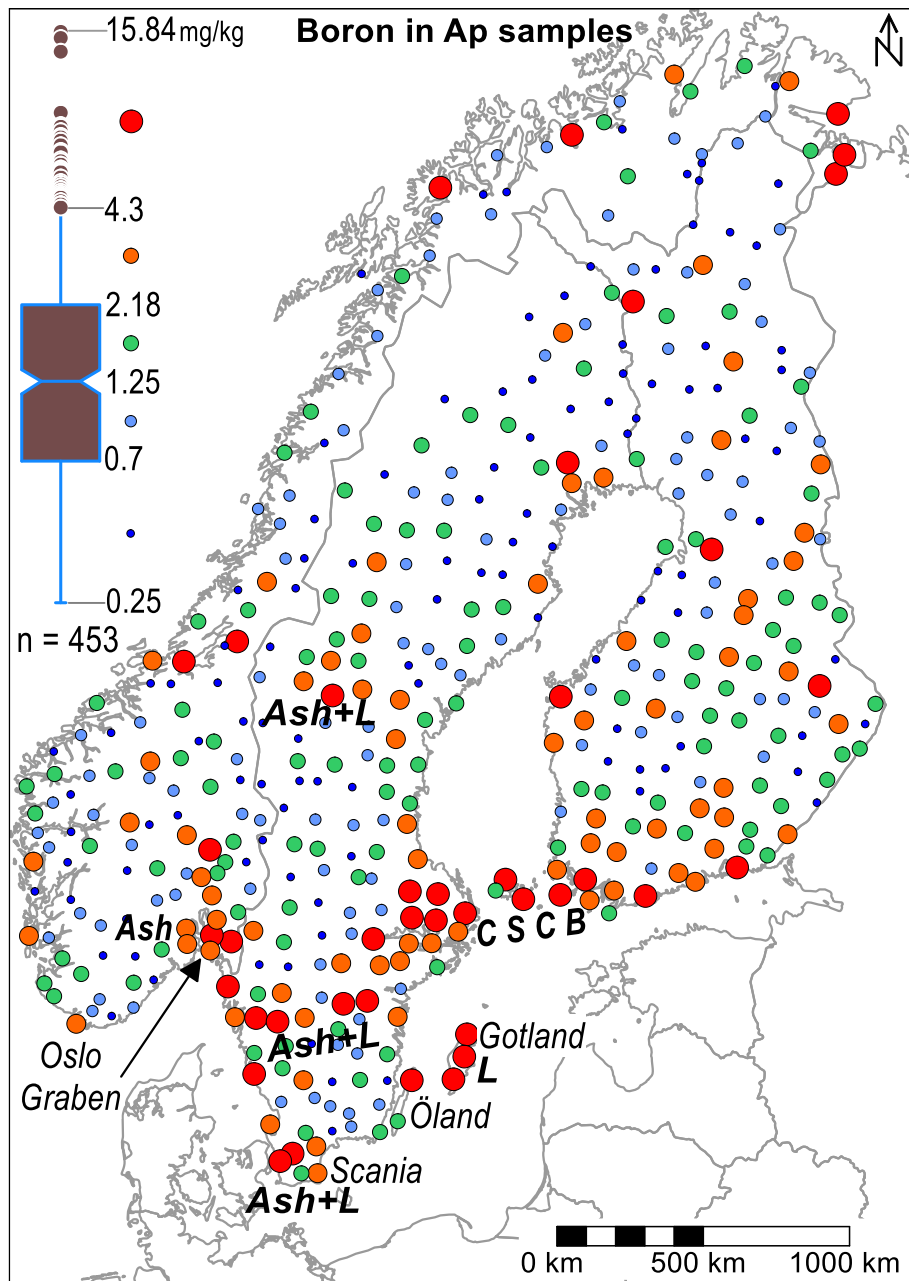
345 *Figure 5. Soil geochemical map of hot aqua regia extractable B contents for ploughed*
 346 *agricultural soil (A_p , n=2113). Map plotting kriging parameters: cell size = 5 000 m, search*
 347 *radius = 1 000 000 m. Plotted with Esri's ArcGIS version 10.3.*

348

349 The geochemical map of AR extractable B (Fig. 5) reflects its natural sources, and its
 350 spatial distribution seems to be governed mainly by weathering type and degree, Quaternary
 351 history and the underlying parent materials. The role of mineralisation is considered minor
 352 because, according to the ProMine Mineral Database of the ore deposits in Europe (Cassard et
 353 al., 2012, 2015; Demetriades and Reimann, 2014; map not shown), primary (tourmaline) and
 354 secondary (sedimentary and evaporite deposits) B mineral deposits in Europe are rare and rather
 355 small. The low B content in soil of Northern Europe is possibly due to low soil pH and the
 356 resulting leaching can be discussed as a subset in Fennoscandian countries (Fig. 6). With the
 357 local class divisions, the B anomalies are better defined and can be easily explained by: (i) the

358 presence of post-glacial clay in central Sweden and southern Finland (so-called Central
359 Scandinavian Clay Belt; Ladenberger et al., 2013); (ii) the Palaeozoic limestone which occurs
360 on Gotland, Öland and Scania, and (iii) the Palaeozoic alum shale occurring in southern
361 Sweden, and in central Sweden by the Caledonian mountain front south-west of Östersund
362 (Jämtland) as well as in the Oslo Graben.

363 The PCA results of the clr-transformed data (e.g. CoDA approach) also provided one PC
364 that includes B (PC7: B-K-[-Mo, -U], Table 5, Birke et al., 2017) related to lithology (parent
365 material). The PC 7 score anomalies can be mainly explained by geogenic sources (e.g., sandy
366 sediments of the last glaciation in northern Germany and Poland; glaciofluvial material in the
367 Baltics; carbonate lithologies in the United Kingdom, north-eastern France and eastern
368 Hungary; the Central Scandinavian Clay Belt, see Fig. 5). Thus, B originating predominantly
369 from geological formations and the observed spatial variation in agricultural soil depends on
370 the lithology complemented by the AR extraction capacity, and the subsequent control by the
371 prevailing secondary phases or processes (e.g., adsorption on clay particles and Fe-Al oxides,
372 organic matter accumulation and low pH), as well as climate.



373

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

378

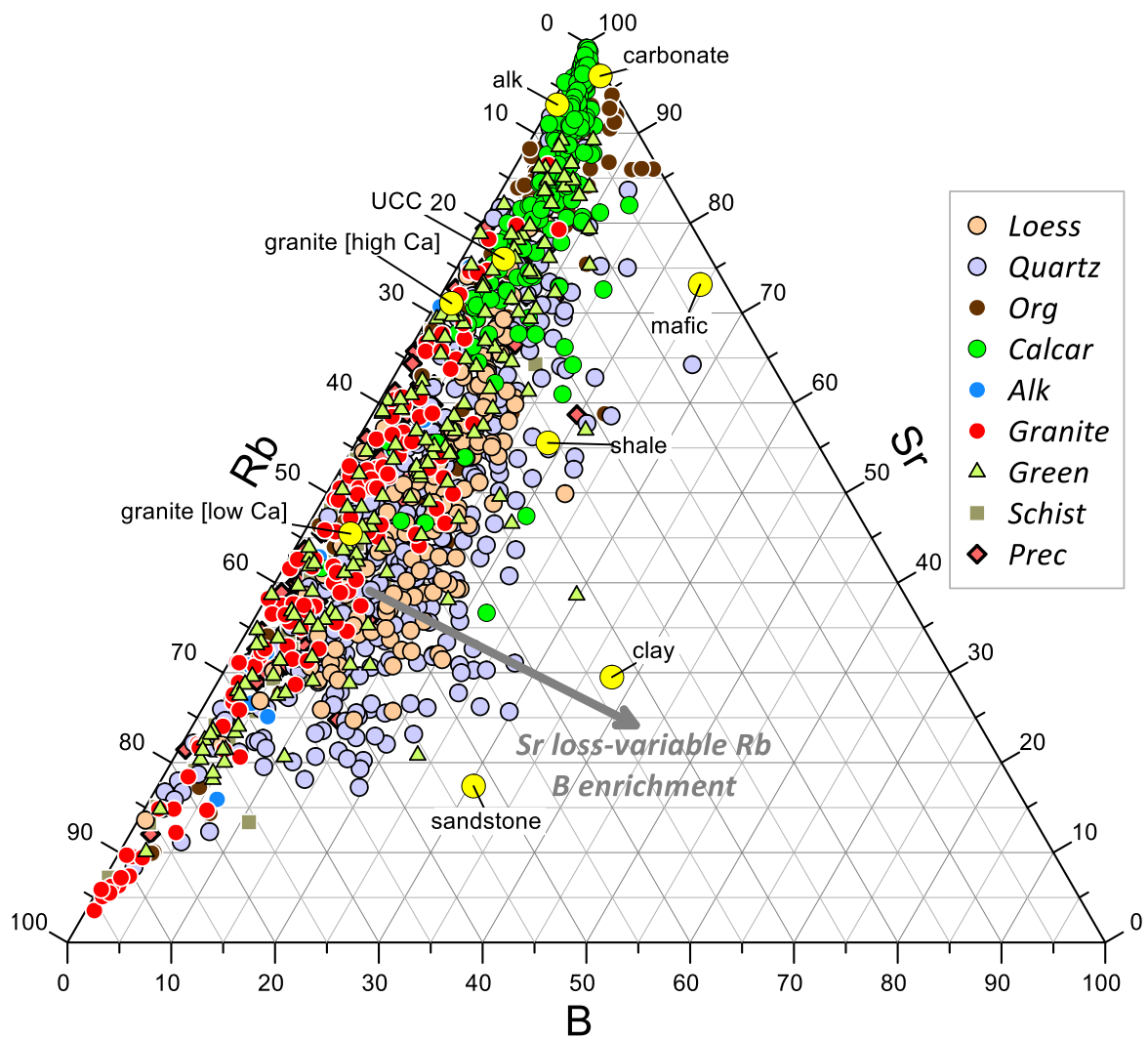
379 **4.2. Role of weathering on boron behaviour**

380 In addition to B, rubidium (Rb) and strontium (Sr) can be used as tracers for weathering
 381 (Négre et al., 2018c). Mobile Sr is indicative of the weathering of both silicate and carbonate
 382 rocks, and relatively immobile Rb is a direct tracer of silicate weathering as it is essentially

383 absent in carbonates (Rb = 3 mg/kg; Parker, 1967) compared to Sr (610 mg/kg; Parker, 1967).
384 While Sr shows a strong affinity for Ca and in carbonate minerals, Rb, as a large +1-charged
385 cation, substitutes for K in common aluminosilicate minerals such as micas and feldspar. The
386 chemical weathering of the most commonly Sr-bearing phases from the silicate host rock, (e.g.,
387 the primary phases apatite, plagioclase, K-feldspar, biotite and muscovite) or their alteration
388 products (epidote and clay minerals) control the Sr mass balance in a crystalline environment
389 (Brantley et al., 1998; Négrel et al., 2018c). Further, Rb mobility in the environment is generally
390 extremely low because after being released during weathering, it is strongly adsorbed by the
391 clay fraction of soil, more than potassium (Goldschmidt, 1954; Wampler et al., 2012).
392 Complementary to B, Rb-Sr can be used to evaluate the input from parent materials and
393 chemical weathering trends in a ternary plot in molecular proportions in the GEMAS Ap
394 samples using the AR results (Négrel et al., 2015, 2021).

395 Figure 7 illustrates the Sr, Rb and B contents for the lithological parent material
396 subgroups except the unclassified bedrock ('*Other*'). The GEMAS Ap data are plotted together
397 with the mean value of the main lithological endmembers taken from Parker (1967), e.g.,
398 plutonic and metamorphic rocks, and shale, carbonate rocks and sand-sandstone, and the upper
399 continental crust (UCC) average from Rudnick and Gao (2003). In Figure 7, the main spread
400 of data along the Rb axis (Négrel et al., 2018b) reflects the variation in Rb content between the
401 sedimentary (carbonate) and mafic (ultramafic rocks) endmember parent materials (low Rb
402 content) to granite (intermediate Rb content), both with high Sr and low B contents. The
403 closeness of a soil sample approaching the 100% apex along the Sr axis and 0% along the Rb
404 axis is an indication of similarity to the carbonate lithological endmember. The evolution along
405 the Rb axis overpassing the granite lithological endmember is a measure of the geochemical
406 maturity of soil with respect to the weathering of underlying parent materials, e.g., silicates
407 endmember weathering and enrichment in Rb-bearing minerals resistant to weathering (K-

408 feldspars, for example) as stated by Négrel et al. (2018b). The arrowhead line denotes
 409 compositional trends of weathering of the different rock types and increased weathering causes
 410 Sr loss and B enrichment, as well as variable Rb enrichment. The B enrichment is more marked
 411 in soil developed on coarse-grained sandy deposits, loess and granite, in relation to the presence
 412 of secondary phases as described hereafter.
 413



414
 415 *Figure 7. Distribution of hot aqua regia extractable B–Sr–Rb contents (in molecular*
 416 *proportions) in the GEMAS Ap soil samples classified according to the lithological parent*
 417 *material subgroups plotted together with bedrock compositions (yellow circles) according to*
 418 *Parker (1967). The grey arrow denotes compositional weathering trends or enrichment/loss.*
 419 *Data are classified according to the lithological parent material subgroups ‘Loess’, ‘Quartz’*
 420 *(soil developed on coarse-grained sandy deposits), ‘Org’ (organic soil), ‘Calcar’ (carbonate*
 421 *rocks), ‘Alk’ (alkaline rocks), ‘Granite’, ‘Green’ (greenstone or ultramafic rocks), ‘Schist’,*

422 *'Prec' (Precambrian gneiss) from Reimann et al. (2012a, b). Plotted with Golden Software's*
423 *Grapher version 24.*

424

425 **4.2. Influence of secondary phases**

426

427 *4.2.1. General considerations for B behaviour in secondary phases*

428

429 Boron adsorption in soil is mainly controlled by the presence of Al and clay minerals,
430 as well as Fe-Al-Mn oxides and hydroxides (Sims and Bingham, 1967, 1968a, b; Goldberg,
431 1997). Adsorption reactions (Goldberg, 1997; Van Eynde et al., 2020b) were described by
432 empirical or phenomenological models (Langmuir or Freundlich equations, Keren equation),
433 chemical surface complexation models (e.g., constant capacitance, triple-layer, surface charge
434 variable surface potential). Boron is an essential micronutrient for plants, but the uptake is only
435 related to B activity in soil aqueous solution and, thus, B adsorbed by soil particles is not
436 perceived as toxic by plants. The control of B by secondary phases is important in terms of
437 weathering and its circulation in the ecosystems. Boron adsorption on various Al and Fe oxide
438 minerals, both crystalline and amorphous phases, has been previously evidenced (Fleming,
439 1980; Goldberg and Glaubig, 1985; Tamuli et al., 2017 and references therein; Kumari et al.,
440 2017; Van Eynde et al., 2020a and references therein). Adsorption increases between pH 5.5
441 and 8.5, exhibiting a peak in the pH range of 8 to 10 and then decreases at pH >10 (Wear and
442 Patterson, 1962; Goldberg and Glaubig, 1986). The magnitude of B adsorption is greater for
443 amorphous materials and decreases with increasing crystallinity of the solid.

444

445

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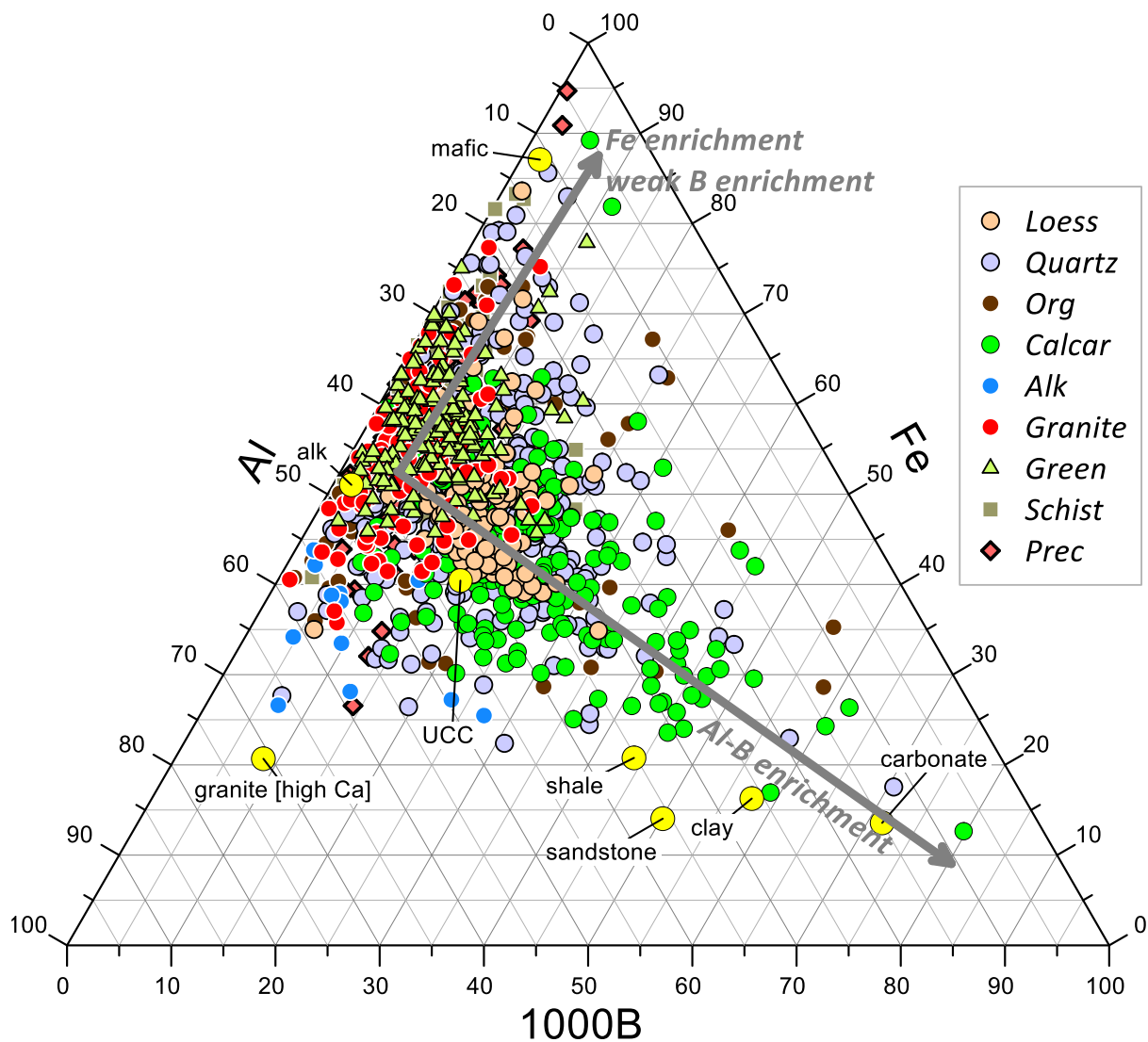
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449

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

450 secondary phases (Ataman, 1967). In Figure 8, representing the AR results for B–Fe–Al, the
 451 main spread of data along the arrowhead line denotes compositional trends of increased control
 452 of B by clay minerals (as denoted by the lithological endmember clay) and Al oxides, mainly
 453 marked in soil developed on or derived from (i) carbonate rocks ('Calcar'), (ii) coarse-grained
 454 sandy deposits ('Quartz') and (iii) organic soil ('Org'). The role of Fe oxides is marked by a
 455 lower B enrichment than that observed for Al.



456
 457 *Figure 8. B–Fe–Al (in molecular proportions) distribution in GEMAS soil samples, for AR*
 458 *extraction in the lithological parent material subgroups plotted together with bedrock*
 459 *compositions (yellow circles) according to Parker (1967). Arrows denote compositional*
 460 *weathering trends or enrichment/loss. Data are classified according to the lithological parent*
 461 *material subgroups 'Loess', 'Quartz' (soil developed on coarse-grained sandy deposits), 'Org'*
 462 *(organic soil), 'Calcar' (carbonate rocks), 'Alk' (alkaline rocks), 'Granite', 'Green'*

463 (greenstone or ultramafic rocks), 'Schist', 'Prec' (Precambrian gneiss), from Reimann et al.
464 (2012a, b). Plotted with Golden Software's Grapher version 24.

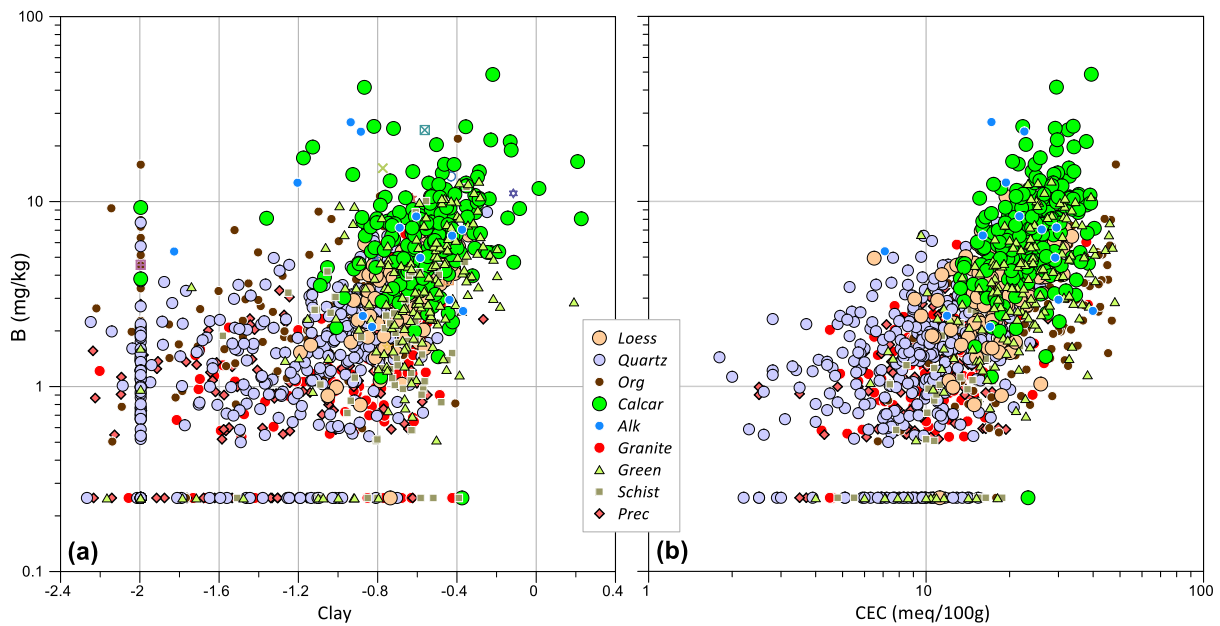
465

466 4.2.2. The clay content and role of the cation exchange capacity (CEC)

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

475 The B and clay contents are compared in Figure 9a. The classical representation of clay
476 (%) vs. B (mg/kg) contents shows the existence of heteroscedasticity in the data. To overcome
477 this, the B contents are plotted on a logarithmic scale and the clay contents are expressed as a
478 binary logit function, i.e., a logistic transformation according to $\log[P/(100-P)]$, where P is the
479 clay content (Négre et al., 2023). No clear trend is observed in Figure 9a for all soil samples.
480 However, a more visible set of trends occurs for soil developed on loess, carbonate rocks
481 ('Calcar') and greenstone ('Green') as these parent materials are sources of clay overburden
482 resulting from the weathering processes, especially in a warm and humid climate. The
483 correlation between B and Al, with an R^2 of around 0.61, was earlier reported by Reimann et
484 al. (2012a) and is not shown here. This correlation, although moderate, can be explained by the
485 fact that kaolinite, the most aluminous mineral, hardly fixes large amounts of B compared to
486 other minerals such as illite or chlorite (Hingston, 1964).

487



488

489 *Figure 9. (a) Plot of clay (%) and B (mg/kg) content in European Ap soil samples. (b) Plot of*
 490 *cation exchange capacity (CEC, meq/100g eq. milliequivalent of hydrogen (H⁺) per 100 g of*
 491 *dry soil) and B (mg/kg) content in European Ap soil samples. Data are classified according to*
 492 *the lithological parent material subgroups 'Loess', 'Quartz' (soil developed on coarse-grained*
 493 *sandy deposits), 'Org' (organic soil), 'Calcar' (carbonate rocks), 'Alk' (alkaline rocks),*
 494 *'Granite', 'Green' (greenstone or ultramafic rocks), 'Schist', 'Prec' (Precambrian gneiss),*
 495 *from Reimann et al. (2012a, b). Y-axis linear log₁₀ scale for (a); X and Y-axis linear log₁₀ scale*
 496 *for (b). (a) and (b) Plotted with Golden Software's Grapher version 24.*

497

498 The cation exchange capacity (CEC) defines the relative ability of soil to store nutrients,
 499 particularly the cations through the maximum quantity of total cations that a soil is capable of
 500 holding at a given pH value. The CEC of a soil sample depends on its clay and humus contents,
 501 e.g., the higher the clay and/or humus content, the higher the CEC is. The clay type in the soil
 502 may also have a role in the CEC values. The median for CEC in Ap soil is 16.4 meq/100 g.
 503 Weathering intensity and climate may also impact the CEC value, as given by the clear
 504 difference in the Ap soil samples between northern (low CEC-median for the Ap samples 12
 505 meq/100 g) and southern Europe (higher CEC-median for the Ap samples 19 meq/100 g); the
 506 values being higher in southern European soil samples. As for clays, the content break occurs
 507 at the southern limit of the last glaciation (Fig. 1), separating the young soil in northern Europe
 508 from the much older and more weathered soil in southern Europe. High CEC values are either

509 due to soil rich in organic matter or clay. This can be further emphasised by comparing the B
510 content with the CEC values for Ap soil in Figure 9b, where the B – CEC relationship differs
511 according to the lithological parent material subgroups. Low CEC values are often observed in
512 soil developed on silicate bedrocks (*'Granite'*, Precambrian gneisses *'Prec'*) and soil developed
513 on coarse-grained sandy deposits (*'Quartz'*), both with low clay and humus (e.g., organic
514 matter) contents. Conversely, the highest B – CEC values are observed for carbonate-derived
515 soil (*'Calcar'*), organic soil (*'Org'*), and *'Loess'*, reflecting the high amount in clay and/or
516 organic matter. The scatter of the B – CEC data in Figure 9a mimics that of the B content vs.
517 the clay content reflecting well the role of clay in the CEC.

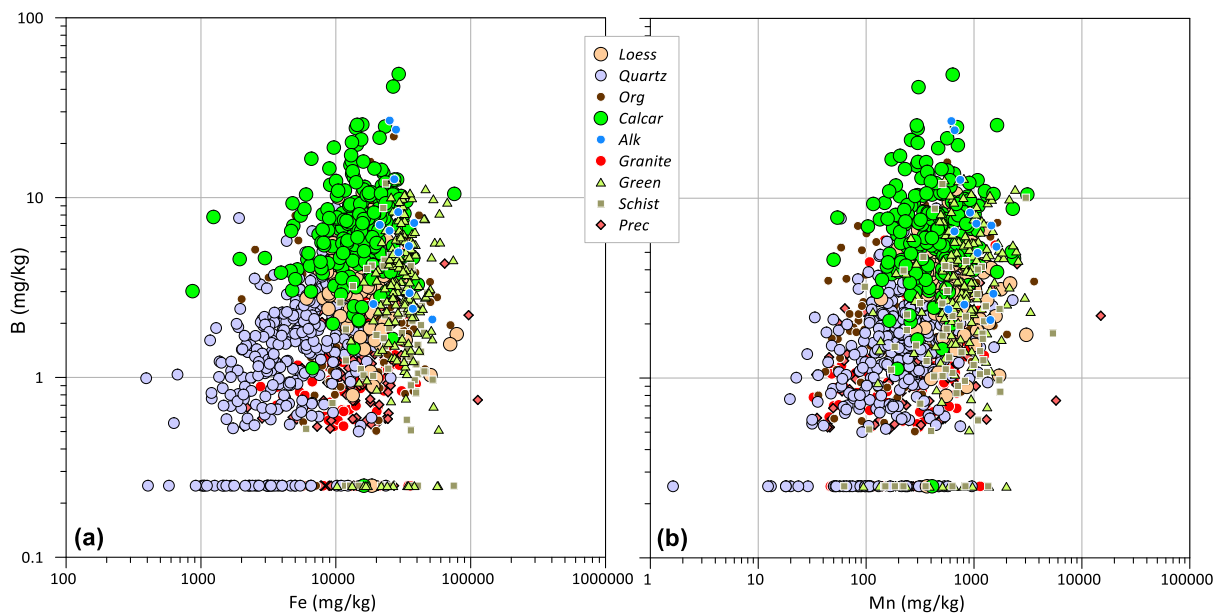
518 Parfitt et al. (1995) reported a high CEC for smectite and the lowest for kaolinite.
519 Goldberg et al. (1993b) showed that B adsorption on kaolinite increased within a range of pH
520 from 3 to 6, with a peak between pH 6 and 8.5, and decreased from pH 8.5 to 11. For B
521 adsorption on montmorillonite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

527 Similar to kaolinite, B adsorption on the common Fe oxides increases from pH 3 to 6,
528 with a peak between pH 6 and 8.5, and then decreases from pH 8.5 to 11 (Goldberg et al.,
529 1993b), and the modelling suggests an inner-sphere adsorption mechanism for goethite.
530 Recently, Van Eynde et al. (2020a) demonstrated that the adsorption at low pH (<5) is
531 dominated by ferrihydrite nanoparticles (e.g., natural metal (hydr)oxide fraction), with a B
532 adsorption density like that of goethite. Under this condition, B adsorption by organic matter is
533 low and even if the soil is rich in organic matter, ferrihydrite nanoparticles contribute to around

534 half of the total B adsorption. At higher pH, B is controlled by the adsorption to organic matter.
 535 A portion of the Fe and Al oxides, as well as other possible adsorption sites, are generally coated
 536 or occluded by organic matter and become active only after the removal of the organic matter
 537 (Marzadori et al., 1991).

538 *4.2.3. The role of Fe-Mn oxides and hydroxides*

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



547
 548 *Figure 10. (a) Plot of Fe (mg/kg) and B (mg/kg) contents, (b) Mn (mg/kg) and B (mg/kg)*
 549 *contents in European Ap soil samples. Data are classified according to the lithological parent*
 550 *material subgroups 'Loess', 'Quartz' (soil developed on coarse-grained sandy deposits), 'Org'*
 551 *(organic soil), 'Calcar' (carbonate rocks), 'Alk' (alkaline rocks), 'Granite', 'Green'*
 552 *(greenstone or ultramafic rocks), 'Schist', 'Prec' (Precambrian gneiss) from Reimann et al.*

553 (2012a, b). X and Y-axis linear \log_{10} scale. Plotted with Golden Software's Grapher version
554 24.

555

556 4.3. Influence of soil organic matter on boron content

557

558 The role of organic matter in B ad- or de-sorption processes in soil is still under debate.

559 Marzadori et al. (1991) and Sarkar et al. (2014) demonstrated that the amount of B adsorbed

560 was considerably greater after the organic matter had been removed from soil. They observed

561 that higher amounts of Fe and Al are extractable after the destruction of organic matter leading

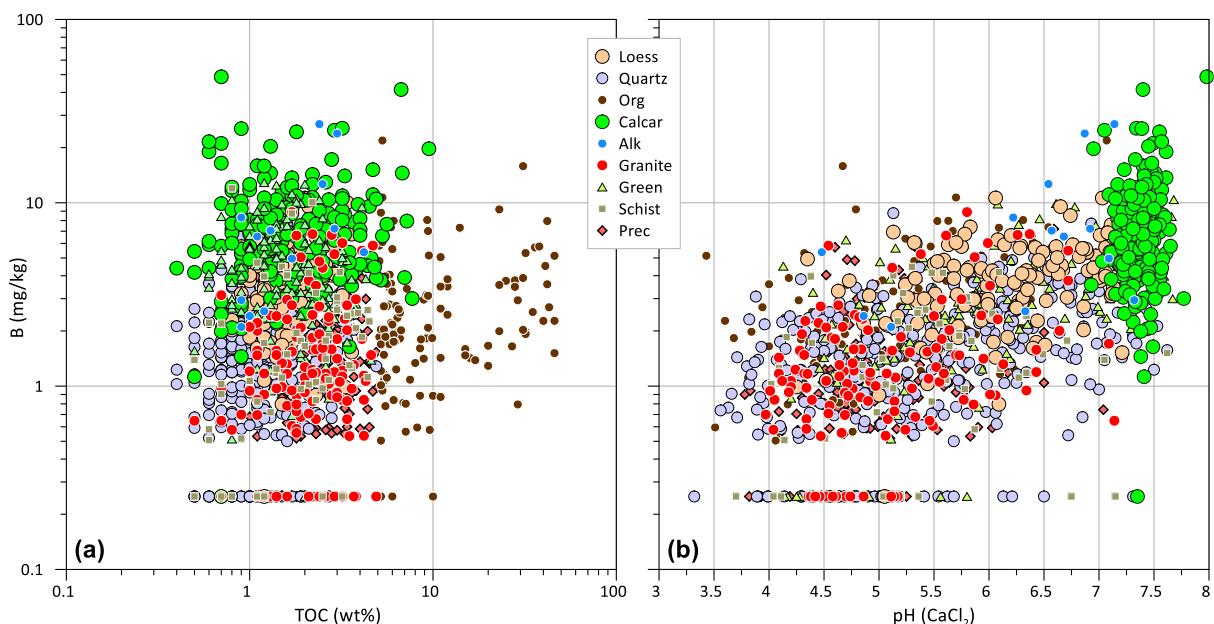
562 to the hypothesis that part of the Fe and Al oxides are coated or occluded by organic matter and

563 are made active after removal of the organic matter. In the Ap soil samples, there is no

564 significant correlation between organic matter (TOC wt. %) and B contents ($R^2 < 0.4$), as

565 illustrated in Figure 11a, indicating that no direct role can be ascribed to organic matter in the

566 control of B contents in Ap soil.



567

568 Figure 11. (a) Plot of Total Organic Carbon (TOC wt. %) and B (mg/kg) contents in European

569 Ap soil samples. (b) Plot for Ap samples of B contents vs. pH for CaCl_2 extraction in European

570 Ap soil samples. Data are classified according to the lithological parent material subgroups

571 'Loess', 'Quartz' (soil developed on coarse-grained sandy deposits), 'Org' (organic soil),

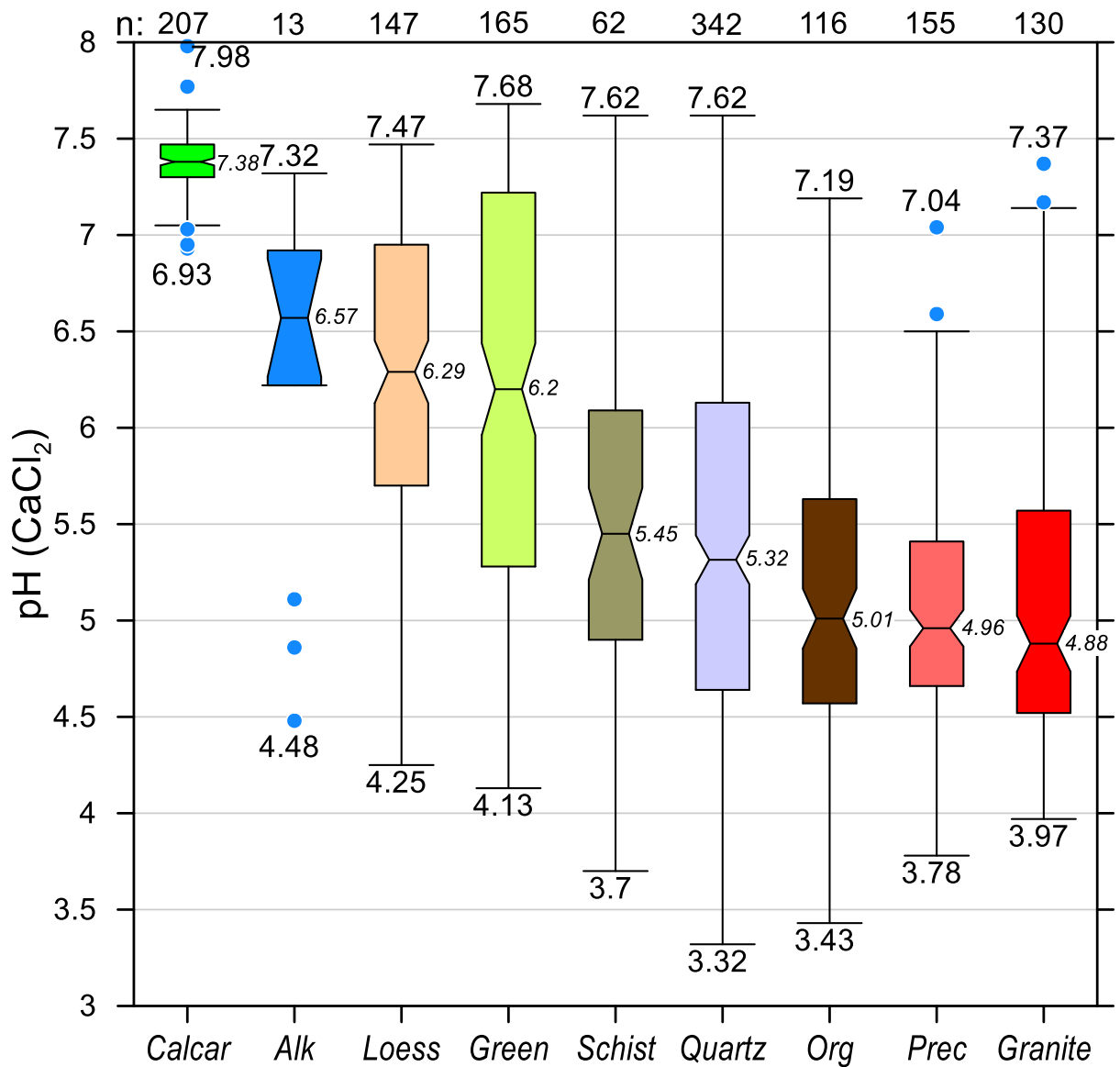
572 'Calcar' (carbonate rocks), 'Alk' (alkaline rocks), 'Granite', 'Green' (greenstone or ultramafic

573 rocks), 'Schist', 'Prec' (Precambrian gneiss) from Reimann et al. (2012a, b). X and Y-axis
574 linear log₁₀ scale for (a) and Y-axis linear log₁₀ scale for (b). Plotted with Golden Software's
575 Grapher version 24.

576

577 **4.4. Influence of soil pH on boron content**

578 The median pH value using a 0.01 M CaCl₂ solution for the Ap agricultural soil samples
579 is 5.77, and its statistical distribution is bimodal with a strongly acidic and slightly alkaline soil
580 at around pH 5 and 7.5, respectively (Reimann et al., 2011; 2014a, b). The pH spatial
581 distribution patterns evidenced by Fabian et al. (2014) reflect the dual role of lithology and
582 climate at the continental scale of Europe. The pH median value of Ap soil samples in northern
583 Europe is about one unit more acidic than those in southern Europe, i.e., median pH of 5.2 and
584 6.3, respectively. This distinct pH difference indicates that there are around one hundred times
585 more protons available in northern than southern European soil, a feature that can help control
586 B contents in soil. Figure 12 shows the variation of soil pH in parent material subgroups, and
587 Figure 13 the relationship among B contents, parent material subgroups and pH. Low pH values
588 occur in soil developed over or derived from silicate parent materials ('Granite', 'Schist',
589 Precambrian gneiss, 'Prec'), and high pH values, as expected, in soil developed on or derived
590 from carbonate bedrock ('Calcar'), however, with an exceptionally low range of pH variation.
591 The other feature is the low median pH value observed in areas where the Ap soil samples are
592 organic matter-rich ('Org'; Fig. 12). Therefore, the acid-base properties of soil in Europe are
593 mainly derived from a combination of climate and geology. Spreading of fertilisers onto
594 agricultural soil can influence its pH, but this anthropogenic impact is difficult to detect because
595 of the dominance of the natural factors evoked before (bedrock and climate) in determining the
596 pH of agricultural soil at the continental scale.

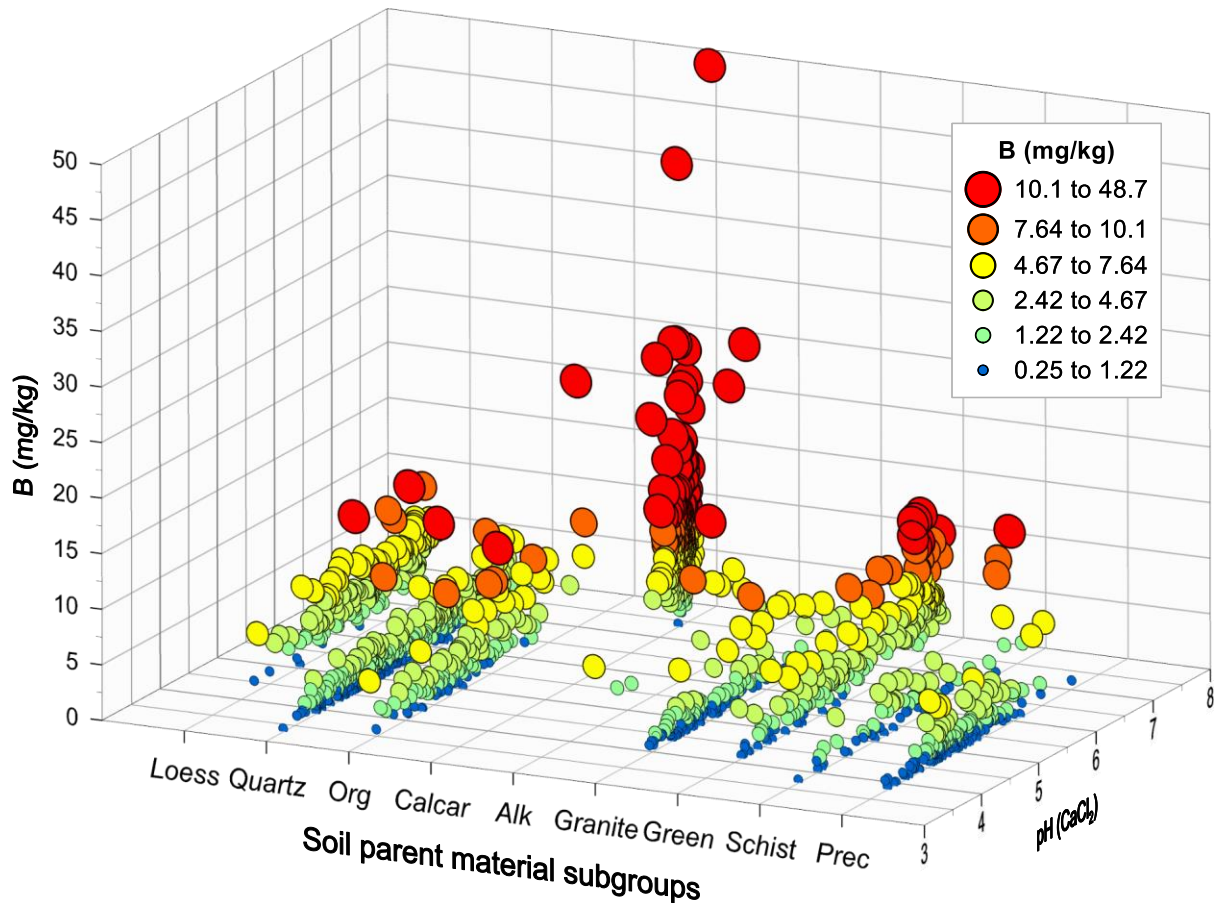


597

598

599

600 *Figure 12. Boxplot comparison of pH in Ap soil samples according to the parent material.*
 601 *Modified from Fabian et al. (2014). Data are classified according to the lithological parent*
 602 *material subgroups 'Calcar' (carbonate rocks), 'Alk' (alkaline rocks), 'Loess', 'Green'*
 603 *(greenstone or ultramafic rocks), 'Schist', 'Quartz' (soil developed on coarse-grained sandy*
 604 *deposits), 'Org' (organic soil), 'Prec' (Precambrian gneiss) and 'Granite' (Reimann et al.,*
 605 *2012a, b). The parent material subgroup 'Other' is excluded. Plotted with Golden Software's*
 606 *Grapher version 24.*



607

608 *Figure 13. 3D XYZ plot of Ap soil Parent Material groups vs. B and pH (CaCl₂). Boron data*
 609 *are classified according to the lithological parent material subgroups 'Loess', 'Quartz' (soil*
 610 *developed on coarse-grained sandy deposits), 'Org' (organic soil), 'Calcar' (carbonate rocks),*
 611 *'Alk' (alkaline rocks), 'Granite', 'Green' (greenstone or ultramafic rocks), 'Schist', 'Prec'*
 612 *(Precambrian gneiss) from Reimann et al. (2012a, b). Plotted with Golden Software's Grapher*
 613 *version 24.*
 614

615 The correlation between B and pH, with a coefficient of determination (R^2) of around
 616 0.56 (Fig. 11b) does not exhibit any particular feature. Neither the role of the varying B
 617 adsorption capacities according to pH (increase from pH 5.5 to 8.5, exhibit a peak in the pH
 618 range 8.5 to 10, and decrease from pH 10 to 11.5; Wear and Patterson, 1962; Goldberg and
 619 Glaubig, 1986), nor the lime impact often regularly used to increase soil pH, which should
 620 increase B fixation in soil (Couch and Grim, 1968) appear to affect B absorption in soil. Several
 621 studies indicate a smaller influence of the soil pH compared to the dominant role of the soil
 622 CEC in controlling B sorption in soil (Raza et al., 2002; Matula, 2009). In addition, the contents

623 of clay minerals and Al oxides rather than those of Fe oxides and Mn hydroxides are the soil
624 properties that affect B adsorption in soil (Goldberg, 1997; Steiner and Lana, 2013, Van Eynde
625 et al., 2020a, b) rather than soil pH.

626

627 **4. Conclusions**

628

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

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

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

642 In European soil, the spatial distribution of B on geochemical maps seems to be
643 controlled mainly by the nature of the lithological formations and their spatial distribution,
644 complemented by the B solubility in AR extraction. The formation of oxides, hydroxides and
645 clays are key processes controlling B fixation. Boron fixation by Fe, Al, and Ca secondary
646 phases and sorption on clay minerals can be correlated with the cation exchange capacity of
647 soil (CEC). Even if the role of organic matter in the soil B cycle is a matter of debate, no direct

648 role can be ascribed to organic matter (expressed as total organic carbon, TOC) in the control
649 of the B contents in Ap soil. The soil pH, although increases B mobility and its leaching out
650 from soil, does not appear to be a critical parameter for B retention in soil.

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

655

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675 **References**

- 676 Adcock, D., McNeill, A.M., McDonald, G.K., Armstrong, R.D., 2007. Subsoil constraints to crop
677 production on neutral and alkaline soils in south-eastern Australia: a review of current knowledge
678 and management strategies. *Aust. J. Exp. Agr.* 47, 1245–1261.
- 679 Aitchison, J., 1986. *The statistical analysis of compositional data*. Chapman & Hall, London, 416 pp.

680 Alloway, B.J., 1995. *Heavy Metals in Soils*. Blackie Academic & Professional, Chapman and Hall,
681 London, UK, 368 pp.

682 Alloway, B.J., 2008. *Micronutrient Deficiencies in Global Crop Production*, Springer, Dordrecht, 354
683 pp.

684 Amiotte Suchet, P., Probst, J.-L., Ludwig, W., 2003. Worldwide distribution of continental rock
685 lithology: implications for the atmospheric/soil CO₂ uptake by continental weathering and alkalinity
686 river transport to the oceans. *Global Biogeochem. Cycles*, 17, 1038–1051.

687 Armour-Brown, A. & Nichol, I., 1970. Regional geochemical reconnaissance and the location of
688 metallogenic provinces. *Economic Geology*, 65(3), 312–330.

689 Ataman, G., 1967. La géochimie du bore et du gallium dans les minéraux argileux. *Chem. Geol.*, 2,
690 297–309.

691 Barber, S.A., 1995. *Soil Nutrient Bioavailability: A Mechanistic Approach*. John Wiley and Sons, New
692 York, USA, 432 pp.

693 Berger, K.C., Truog, E., 1945. Boron availability in relation to soil, reaction and organic matter content.
694 *Soil Sci. Soc. Am. Proc.*, 10, 113–116.

695 Biggar, J.W., Fireman, M., 1960. Boron adsorption and release by soils. *Soil Sci. Soc. Am. J.*, 24, 115–
696 120.

697 Birke, M., Reimann, C., Fabian, K., 2014. Analytical Methods Used in the GEMAS Project. Chapter 5
698 In: C. Reimann, M. Birke, A. Demetriades, P. Filzmoser, P. O'Connor (Editors), *Chemistry of*
699 *Europe's agricultural soils – Part A: Methodology and interpretation of the GEMAS data set*.
700 *Geologisches Jahrbuch (Reihe B102)*, Schweizerbarth, Hannover, 41–46.

701 Birke, M., Rauch, U., Stummeyer, J., 2015. How robust are geochemical patterns? A comparison of low
702 and high sample density geochemical mapping in Germany. *J. Geochem. Expl.*, 154, 105–128.

703 Birke, M., Reimann, C., Rauch, U., Ladenberger, A., Demetriades, A., Jähne-Klingberg, F., Oorts, K.,
704 Gosar, M., Dinelli, E., Halamic, J., The GEMAS Project Team, 2017. GEMAS: Cadmium
705 distribution and its sources in agricultural and grazing land soil of Europe - original data versus clr-
706 transformed data. *J. Geochem. Expl.*, 173, 13–30.

707 Boyle, R.W., 1974. Elemental associations in mineral deposits and indicator elements of interest in
708 geochemical prospecting. Energy, Mines and Resources Canada, Geological Survey Paper 74-45,
709 40 pp. <https://doi.org/10.4095/102553>.

710 Brantley, S.L., Chesley, J.T., Stillings, L.L., 1998. Isotopic ratios and release rates of strontium
711 measured from weathering feldspars. *Geochem. Cosmochim. Acta* 62, 1493–1500.

712 Brdar-Jokanović, M., 2020. Boron toxicity and deficiency in agricultural plants. *Int. J. Molecular Sci.*,
713 21(4), 1424.

714 Brown, P.H., Shelp, B.J., 1997. Boron mobility in plants. *Plant and Soil*, 193, 85–101.

715 Brown, P.H., Bellaloui, N., Wimmer, M.A., Bassil, E.S., Ruiz, J., Hu, H., Pfeffer, H., Dannel, F.,
716 Romheld, V., 2002. Boron in plant biology. *Plant Biol.*, 4, 205–223.

717 Bucciatti, A., Pawlowsky-Glahn, V., Mateu-Figueras, G. (Editors), 2006. Compositional data analysis
718 in the geosciences: from theory to practice. Geological Society, London, 224 pp.

719 Bussetti, S.G. de, Ferreiro, E.A., Helmy, A.K., 1995. Sorption of boron by hydrous Al-oxide. *Clays Clay*
720 *Miner.*, 43, 58–62.

721 Caritat, P. de, Reimann, C., NGSa Project Team, GEMAS Project Team, 2012. Comparing results from
722 two continental geochemical surveys to world soil composition and deriving Predicted Empirical
723 Global Soil (PEGS2) reference values. *Earth Planet. Sci. Lett.* 319-320, 269–276.

724 Casanova, J., Négrel, Ph., Blomqvist, R., 2005. Boron isotope fractionation in groundwaters as an
725 indicator of past permafrost conditions in the fractured crystalline bedrock of the fennoscandian
726 shield. *Wat. Res.* 39(2-3), 362–370.

727 Cassard, D., Bertrand, G., Maldan, F., Gaàl, G., Kaija, J., Aatos, S., Angel, J.M., Arvanitidis, N., Ballas,
728 D., Billa, M., Christidis, C., Dimitrova, D., Eilu, P., Filipe, A., Gazea, E., Inverno, C., Kauniskangas,
729 E., Maki, T., Matos, J., Meliani, M., Michael, C., Mladenova, V., Navas, J., Niedbal, M., Perantonis,
730 G., Pyra, J., Santana, H., Serafimovski, T., Serrano, J.J., Strengell, J., Tasev, G., Tornos, F., Tudor,
731 G., 2012. ProMine pan-European mineral deposit database: a new dataset for assessing primary
732 mineral resources in Europe. Workshop on: Mineral Resources Potential Maps: A Tool for
733 Discovering Future Deposits. 12th–14th March 2012, Nancy, France, Proceedings, pp. 9–13.

734 Cassard, D., Bertrand, G., Billa, M., Serrano, J.J., Tourlière, B., Angel, J.M., Gaál, G., 2015. ProMine
735 mineral databases: New tools to assess primary and secondary mineral resources in Europe. Chapter
736 2 In: Weihed, P. (Editor), 3D, 4D and Predictive Modelling of Major Mineral Belts in Europe.
737 Mineral Resource Reviews. Springer International Publishing, 9–58; https://doi.org/10.1007/978-3-319-17428-0_2.

739 Chen, W.T., Ho, S.B., Lee, D.Y., 2009. Effect of pH on boron adsorption-desorption hysteresis of soils.
740 *Soil science*, 174(6), 330-338.

741 Chetelat, B., Liu, C.Q., Gaillardet, J., Wang, Q.L., Zhao, Z.Q., Liang, C.S., Xiao, Y.K., 2009. Boron
742 isotopes geochemistry of the Changjiang basin rivers. *Geochim. Cosmochim. Acta* 73(20),
743 6084–6097.

744 Cicchella, D., Lima, A., Birke, M., Demetriades, A., Wang, X., De Vivo, B., 2013. Mapping
745 geochemical patterns at regional to continental scales using composite samples to reduce the
746 analytical costs. *J. Geochem. Expl.*, 124, 79–91.

747 Couch, E.L., Grim, R.E., 1968. Boron fixation by illites. *Clays Clay Miner.*, 16, 249–256.

748 Demetriades, A., 2011. Understanding the Quality of Chemical Data from the Urban Environment –
749 Part 2: Measurement Uncertainty in the Decision-making Process. Chapter 6 In: C.C. Johnson, A.
750 Demetriades, J. Locutura, R.T. Ottesen (Editors), Mapping the Chemical Environment of Urban
751 Areas. John Wiley & Sons Ltd., Chichester, U.K., 77–98.
752 <https://doi.org/10.1002/9780470670071.ch6>.

753 Demetriades, A., Reimann, C., 2014. Mineral deposits in Europe. Chapter 3 In: C. Reimann, M. Birke,
754 A. Demetriades, P. Filzmoser & P. O'Connor (Editors), Chemistry of Europe's Agricultural Soils –
755 Part B: General Background Information and Further Analysis of the GEMAS Data Set. Geologisches Jahrbuch (Reihe B103), Schweizerbarth, Hannover, 71–78.

757 Demetriades, A., Reimann, C., Filzmoser, P., 2014. Evaluation of GEMAS Project Quality Control
758 Results. Chapter 6 In: C. Reimann, M. Birke, A. Demetriades, P. Filzmoser, P. O'Connor (Editors),
759 Chemistry of Europe's Agricultural Soils – Part A: Methodology and Interpretation of the GEMAS
760 Data Set. Geologisches Jahrbuch (Reihe B102), Schweizerbarth, Hannover, 47–60.

761 Demetriades, A., Johnson, C.C. Argyraki, A., 2022. Quality Control Procedures. Chapter 7 In:
762 Demetriades, A., Johnson, C.C., Smith, D.B., Ladenberger, A., Adánez Sanjuan, P., Argyraki, A.,
763 Stouraiti, C., Caritat, P. de, Knights, K.V., Prieto Rincón, G. & Simubali, G.N. (Editors),
764 International Union of Geological Sciences Manual of Standard Methods for Establishing the Global
765 Geochemical Reference Network. IUGS Commission on Global Geochemical Baselines, Athens,
766 Hellenic Republic, Special Publication, 2, 387–428. <https://doi.org/10.5281/zenodo.7307696>.

767 De Vos, W., Tarvainen, T., Salminen, R., Reeder, S., De Vivo, B., Demetriades, A., Pirc, S., Batista,
768 M.J., Marsina, K., Ottesen, R.T., O'Connor, P., Bidovec, M., Lima, A., Siewers, U., Smith, B.,
769 Taylor, H., Shaw, R., Salpeteur, I., Gregorauskiene, V., Halamić, J., Slaninka, I., Lax, K., Gravesen,
770 P., Birke, M., Breward, N., Ander, E.L., Jordan, G., Duris, M., Klein, P., Locutura, J., Bel-lan, A.,
771 Pasieczna, A., Lis, J., Mazreku, A., Gilucis, A., Heitzmann, P., Klaver, G., Petersell, V., 2006.
772 Geochemical Atlas of Europe. Part 2 - Interpretation of Geochemical Maps, Additional Tables,
773 Figures, Maps, and Related Publications. Geological Survey of Finland, Espoo, 618 pp.;
774 <http://weppi.gtk.fi/publ/foregsatlas/>.

775 Elrashidi, M.A., O'Connor, G.A., 1982. Boron sorption and desorption in soils. Soil Sci. Soc. Am. J.,
776 46, 27–31.

777 EPA – OGWDW, 2008. Boron. In: Regulatory Determinations Support Document for Selected
778 Contaminants from the Second Drinking Water Contaminant Candidate List (CCL 2). EPA Report
779 815-R-08-012, 27 pp.

780 Fabian, C., Reimann, C., Fabian, K., Birke, M., Baritz, R., Haslinger, E., The GEMAS Project Team,
781 2014, GEMAS: Spatial distribution of the pH of European agricultural and grazing land soil. Appl.
782 Geochem., 48, 207–216.

783 Filzmoser, P., Reimann, C., Birke, M., 2014. Univariate Data Analysis and Mapping. Chapter 8 In: C.
784 Reimann, M. Birke, A. Demetriades, P. Filzmoser, P. O'Connor (Editors), Chemistry of Europe's
785 Agricultural Soils – Part A: Methodology and Interpretation of the GEMAS Data Set. Geologisches
786 Jahrbuch (Reihe B102), Schweizerbarth, Hannover, 67–81.

787 Fleming, G.A., 1980. Essential micronutrients. I: Boron and molybdenum. In: B.E. Davies (Ed.),
788 Applied Soil Trace Elements. John Wiley and Sons, New York, 155–197.

789 Garrett, R.G., I. Nichol, I., 1967. Regional geochemical reconnaissance in eastern Sierra Leone.
790 Transactions Institution Mining and Metallurgy (Section B: Applied earth science), 76, B97–B112.

791 Garrett, R.G., Reimann, C., Smith, D.B., Xie, X., 2008. From geochemical prospecting to international
792 geochemical mapping: a historical overview. *Geochem.: Expl. Env. Anal.*, 8, 205–217.

793 Giménez, F.E., Morell, E.I., 2008. Contributions of boron isotopes to understanding the
794 hydrogeochemistry of the coastal detritic aquifer of Castellón Plain, Spain. *Hydrogeol. J.*, 16,
795 547–557.

796 Goldberg, S., 1997. Reactions of boron with soils. *Plant and Soil*, 193, 35–48.

797 Goldberg, S., Forster, H.S., Heick, E.L., 1993a. Temperature effects on boron adsorption by reference
798 minerals and soils. *Soil Sci.*, 156, 316–321.

799 Goldberg, S., Forster, H.S., Heick E.L., 1993b. Boron adsorption mechanisms on oxides, clay minerals,
800 and soils inferred from ionic strength effects. *Soil Sci. Soc. Am. J.*, 57, 704–708.

801 Goldberg, S., Glaubig, R.A., 1985. Boron adsorption on aluminum and iron oxide minerals. *Soil Sci.*
802 *Soc. Am. J.*, 49, 1374–1379.

803 Goldberg, S., Glaubig, R.A., 1986. Boron adsorption on California soils. *Soil Sci. Soc. Am. J.*, 50,
804 1173–1176.

805 Goldschmidt, V.M., 1954. *Geochemistry*, Oxford University, London, 730 pp.

806 Gonfiantini, R., Pennisi, M., 2006. The behaviour of boron isotopes in natural waters and in water–rock
807 interactions. *J. Geochem. Expl.*, 88(1-3), 114–117.

808 Guinoiseau, D., Louvat, P., Paris, G., Chen, J.B., Chetelat, B., Rocher, V., Guerin, S., Gaillardet, J.,
809 2018. Are boron isotopes a reliable tracer of anthropogenic inputs to rivers over time? *Sci. Tot. Env.*,
810 626, 1057–1068.

811 Günther, A., Van Den Eeckhaut, M., Reichenbach, P., Hervás, J., Malet, J.-P., Foster, C., Guzzetti, F.,
812 2013. New developments in harmonized landslide susceptibility mapping over Europe in the
813 framework of the European soil thematic strategy. *Proceedings second world landslide forum*, 3-7
814 October 2011, Rome. In: *Conference Proceedings: C. Margottini, P. Canuti, K. Sassa (eds),*
815 *Landslide Science and Practice, Part I, vol. 1. Springer-Verlag, Heidelberg, pp. 297–301.*
816 https://doi.org/10.1007/978-3-642-31325-7_39.

817 Hingston, F.J., 1964. Reactions between boron and clays. *Soil Res.*, 2(1), 83–95.

818 Hu, Z., Gao, S., 2008. Upper crustal abundances of trace elements: A revision and update. *Chem. Geol.*,
819 253, 205–221.

820 Jones, J.B. Jr., 2008. Plant mineral nutrition. In: *Agronomic Handbook. Management of crops, soils and*
821 *their fertility. CRC Press, Boca Raton, Florida, USA, 325 pp.*

822 Kabata Pendias, A. and Pendias, H., 2001. *Trace elements in soils and plants. CRC Press, Inc., Boca*
823 *Raton, Florida, 413 pp.*

824 Kabata-Pendias, A., Mukherjee, A.B., 2007. *Trace Elements from Soil to Human. Springer Verlag,*
825 *Berlin, Heidelberg, 550 pp.*

826 Keren, R., Bingham, F.T., 1985. Boron in water, soils, and plants. *Adv. Soil Sci.*, 1, 229–276.

827 Kot, F.S., 2009. Boron sources, speciation and its potential impact on health. *Rev. Env. Sci.*
828 *Bio/Technol.*, 8, 3–28.

829 Kumari, K., Singh, A., Nazir, G., Kumar, P., Shukla, A.K., 2017. Adsorption and desorption of boron
830 in cultivated soils of Himachal Pradesh, *International Journal of Chemical Studies*, 5 (6), 1712–1716.

831 Ladenberger, A., Andersson, M., Reimann, C., Tarvainen, T., Filzmoser, P., Uhlbäck, J., Morris, G.,
832 Sadeghi, M. 2013. Geochemical mapping of agricultural soils and grazing land (GEMAS) in Norway,
833 Finland and Sweden – regional report. Geological Survey of Sweden, SGU-rapport 2012:17, 160
834 pp.; <http://resource.sgu.se/produkter/sgurapp/s1217-rapport.pdf>;
835 https://www.researchgate.net/publication/260872161_Geochemical_mapping_of_agricultural_soils_and_grazing_land_GEMAS_in_Norway_Finland_and_Sweden_-_regional_report.

836

837 Marzadori, C., Antisari, L. V., Ciavatta, C., Sequi, P., 1991. Soil organic matter influence on adsorption
838 and desorption of boron. *Soil Sci. Soc. Amer. J.*, 55(6), 1582–1585.

839 Matula, J., 2009. Boron sorption in soils and its extractability by soil tests (Mehlich 3, ammonium
840 acetate and water extraction). *Plant, Soil Env.*, 55(1), 42–49.

841 Négrel, Ph., Sadeghi, M., Ladenberger, A., Reimann, C., Birke, M., The GEMAS Project Team, 2015.
842 Geochemical fingerprinting and sources discrimination in soils and sediments at continental scale.
843 *Chem. Geol.*, 396, 1–15.

844 Négrel, Ph., De Vivo, B., Reimann, C., Ladenberger, A., Cicchella, D., Albanese, S., Birke, M., De Vos,
845 W., Dinelli, E., Lima, A., O' Connor, P.J., Salpeteur, I., Tarvainen, T., The GEMAS Project Team,
846 2018a. U-Th signatures of agricultural soil at the European continental scale (GEMAS): Distribution,
847 weathering patterns and processes controlling their contents. *Sci. Tot. Env.*, 622–623, 1277–1293.

848 Négrel, Ph., Ladenberger, A., Reimann, C., Birke, M., Sadeghi, M., The GEMAS Project Team., 2018b.
849 Distribution of Rb, Ga and Cs in agricultural land soils at European continental scale (GEMAS):
850 Implications for weathering conditions and provenance. *Chem. Geol.*, 479, 188–203.

851 Négrel, Ph., Pauwels, H., Chabaux, F., 2018c. Characterizing multiple water-rock interactions in the
852 critical zone through Sr-isotope tracing of surface and groundwater. *Appl. Geochem.*, 93, 102–112.

853 Négrel, Ph., Ladenberger, A., Reimann, C., Birke, M., Demetriades, A., Sadeghi, M., The GEMAS
854 Project Team., 2019. GEMAS: Geochemical background and mineral potential of emerging tech-
855 critical elements in Europe revealed from low-sampling density geochemical mapping. *Appl.*
856 *Geochem.*, 111, 104425.

857 Négrel, Ph., Ladenberger, A., Reimann, C., Birke, M., Demetriades, A., Sadeghi, M., The GEMAS
858 Project Team, 2021. GEMAS: Geochemical distribution of Mg in agricultural soil of Europe. *J.*
859 *Geochem. Expl.*, 221, 106706.

860 Négrel, Ph., Ladenberger, A., Reimann, C., Demetriades, A., Birke, M., Sadeghi, M. & The GEMAS
861 Project Team, 2023. GEMAS: Chemical weathering of silicate parent materials revealed by

862 agricultural soil of Europe. *Chemical Geology*, 639, 121732 (14 pp.);
863 <https://doi.org/10.1016/j.chemgeo.2023.121732>.

864 Okazaki, E., Chao, T.T., 1968. Boron adsorption and desorption by some Hawaiian soils. *Soil Sci.*, 105,
865 255–259.

866 Padbhushan, R., Kumar, D., 2015. Soil boron fractions and response of green gram in calcareous soils.
867 *J. Plant. Nutr.*, 38, 1143–1157.

868 Padbhushan, R., Kumar, D., 2017. Fractions of soil boron: A review. *The Journal of Agricultural*
869 *Science*, 155(7), 1023–1032.

870 Parfitt, R.L., Giltrap, D.J., Whitton, J.S., 1995. Contribution of organic matter and clay minerals to the
871 cation exchange capacity of soils. *Comm. Soil Sci. Plant Anal.*, 26(9-10), 1343–1355.

872 Parker, R.L., 1967. Composition of the Earth's crust. Chapter D. In: Fleischer, M. (Ed.), (Techn. Editor),
873 *Data of Geochemistry*. U.S. Geological Survey Professional Paper, 440-D (17 pp).

874 Pawlowsky-Glahn, V., Buccianti, A., 2011. *Compositional data analysis: theory and applications*.
875 Wiley, Chichester, 378 pp.

876 Pereira, G.L., Siqueira, J.A., Batista-Silva, W., Cardoso, F.B., Nunes-Nesi, A., Araújo, W.L., 2021.
877 Boron: More Than an Essential Element for Land Plants? *Frontiers Plant Sci.*, 11, 2234.

878 Raza, M., Mermut, A.R., Schoenau, J.J., Malhi, S.S., 2002. Boron fractionation in some Saskatchewan
879 soils. *Canadian J. Soil Sci.*, 82(2), 173–179.

880 Reimann, C., Demetriades, A., Eggen, O.A., Filzmoser, P., The EuroGeoSurveys Geochemistry Expert
881 Group, 2009. The EuroGeoSurveys geochemical mapping of agricultural and grazing land soils
882 project (GEMAS) – Evaluation of quality control results of aqua regia extraction analysis. Geological
883 Survey of Norway, Trondheim, NGU report 2009.049, 94 pp.
884 http://www.ngu.no/upload/Publikasjoner/Rapporter/2009/2009_049.pdf.

885 Reimann, C., Demetriades, A., Eggen, O.A., Filzmoser, P., EuroGeoSurveys Geochemistry Working
886 Group, 2011. The EuroGeoSurveys geochemical mapping of agricultural and grazing land soils
887 project (GEMAS) – Evaluation of quality control results of total C and S, total organic carbon (TOC),
888 cation exchange capacity (CEC), XRF, pH, and particle size distribution (PSD) analysis. NGU
889 Report 2011.043. Geological Survey of Norway, Trondheim, 92 pp.;
890 http://www.ngu.no/upload/Publikasjoner/Rapporter/2011/2011_043.pdf.

891 Reimann, C., Caritat, P. de, GEMAS Project Team, NGS Project Team, 2012a. New soil composition
892 data for Europe and Australia: Demonstrating comparability, identifying continental-scale processes
893 and learning lessons for global geochemical mapping. *Sci. Tot. Env.*, 416, 239–252.

894 Reimann, C., Flem, B., Fabian, K., Birke, M., Ladenberger, A., Négrel, Ph., Demetriades, A.,
895 Hoogewerff, J., The GEMAS Project Team, 2012b. Lead and lead isotopes in agricultural soils of
896 Europe - the continental perspective. *Appl. Geochem.*, 27, 532–542.

897 Reimann, C., Demetriades, A., Birke, M., Eggen, O. A., Filzmoser, P., Kriete, C., EuroGeoSurveys
898 Geochemistry Expert Group, 2012c. The EuroGeoSurveys Geochemical Mapping of Agricultural

899 and grazing land Soils project (GEMAS) – Evaluation of quality control results of particle size
900 estimation by MIR prediction, Pb-isotope and MMI[®] extraction analyses and results of the GEMAS
901 ring test for the standards Ap and Gr. Geological Survey of Norway, Trondheim, NGU report
902 2012.051, 136 pp. http://www.ngu.no/upload/Publikasjoner/Rapporter/2012/2012_051.pdf.

903 Reimann, C., Filzmoser, P., Fabian, K., Hron, K., Birke, M., Demetriades, A., Dinelli, E., Ladenberger,
904 A., The GEMAS Project Team, 2012d. The concept of compositional data analysis in practice - Total
905 major element contents in agricultural and grazing land soils of Europe. *Sci. Tot. Env.*, 426, 196–
906 210.

907 Reimann, C., Birke, M., Demetriades, A., Filzmoser, P., O'Connor, P. (Editors), 2014a. Chemistry of
908 Europe's Agricultural Soils – Part A: Methodology and Interpretation of the GEMAS Data Set.
909 *Geologisches Jahrbuch (Reihe B)*, Schweizerbarth, Stuttgart, 528 pp.

910 Reimann, C., Birke, M., Demetriades, A., Filzmoser, P., O'Connor, P. (Editors), 2014b. Chemistry of
911 Europe's Agricultural Soils – Part B: General Background Information and Further Analysis of the
912 GEMAS Data Set. *Geologisches Jahrbuch (Reihe B)*, Schweizerbarth, Stuttgart, 352 pp.

913 Reimann, C., Ladenberger, A., Birke, M., Caritat, P. de, 2016. Low density geochemical mapping and
914 mineral exploration: application of the mineral system concept. *Geochem. Expl. Env. Anal.*, 16,
915 48–61.

916 Rudnick, R.L., Gao, S., 2003. The composition of the continental crust. In: Holland, H.D., Turekian,
917 K.K. (Eds.), *Treatise on Geochemistry*, vol. 3. The Crust. Elsevier-Pergamon, Oxford, pp. 1–64.
918 <https://doi.org/10.1016/b0-08-043751-6/03016-4>.

919 Salminen, R., Tarvainen, T., Demetriades, A., Duris, M., Fordyce, F.M., Gregorauskiene, V., Kahelin,
920 H., Kivisilla, J., Klaver, G., Klein, P., Larson, J.O., Lis, J., Locutura, J., Marsina, K., Mjartanova, H.,
921 Mouvet, C., O'Connor, P., Odor, L., Ottonello, G., Paukola, T., Plant, J.A., Reimann, C., Schermann,
922 O., Siewers, U., Steenfelt, A., Van Der Sluys, J., Williams, L., 1998. FOREGS Geochemical
923 Mapping Field Manual. Geological Survey of Finland, Espoo, Guide 47, 36 pp.;
924 http://tupa.gtk.fi/julkaisu/opas/op_047.pdf.

925 Salminen, R., Batista, M.J., Bidovec, M., Demetriades, A., De Vivo, B., De Vos, W., Đuriš, M., Gilucis,
926 A., Gregorauskienė, V., Halamić, J., Heitzmann, P., Lima, A., Jordan, G., Klaver, G., Klein, P., Lis,
927 J.z., Locutura, J., Marsina, K., Mazreku, A., O'Connor, P., Olsson, S.Å., Ottesen, R.T., Petersell, V.,
928 Plant, J.A., Reeder, S., Salpeteur, I., Sandström, H., Siewers, U., Steenfelt, A., Tarvainen, T., 2005.
929 Geochemical atlas of Europe. Part 1 – Background information, methodology and maps. Geological
930 Survey of Finland, Espoo, 525 pp.; <http://weppi.gtk.fi/publ/foregsatlas/>.

931 Sarkar, D., De, D.K., Das, R., Mandal, B., 2014. Removal of organic matter and oxides of iron and
932 manganese from soil influences boron adsorption in soil. *Geoderma*, 214, 213–216.

933 Scheib, A.J., Flight, D.M.A., Birke, M., Tarvainen, T., Locutura, J., GEMAS Project Team, 2012. The
934 geochemistry of niobium and its distribution and relative mobility in agricultural soils of Europe.
935 *Geochem. Expl. Env. Anal.*, 12, 293–302.

936 Shafiq, M., Ranjha, A.M., Yaseen, M., Mehdi, S.M., Hannan, A., 2008. Comparison of Freundlich and
937 Langenmuir adsorption equations for boron adsorption on calcareous soils. *Journal of Agricultural*
938 *Research*, 46, 141–148.

939 Shireen, F., Nawaz, M. A., Chen, C., Zhang, Q., Zheng, Z., Sohail, H., Sun, J., Cao, H., Huang, Y., Bie,
940 Z., 2018. Boron: functions and approaches to enhance its availability in plants for sustainable
941 agriculture. *Intern. J. Molec. Sci.*, 19(7), 1856.

942 Shorrocks, V.M., 1997. The occurrence and correction of boron deficiency. *Plant and soil*, 193(1),
943 121–148.

944 Sims, J.R. Bingham, F.T., 1967. Retention of boron by layer silicates, sesquioxides, and soil materials,
945 I. Layer silicates. *Soil Sci. Soc. Am. Proc.*, 31, 728–732.

946 Sims, J.R. Bingham, F.T., 1968a. Retention of boron by layer silicates, sesquioxides, and soil materials.
947 II. Sesquioxides. *Soil Sci. Soc. Am. Proc.*, 32, 364–369.

948 Sims, J.R. Bingham, F.T., 1968b. Retention of boron by layer silicates, sesquioxides, and soil materials,
949 III. Iron- and aluminium-coated layer silicates and soil materials. *Soil. Sci. Soc. Am. Proc.*, 32, 369–
950 373.

951 Singh, S.S., 1964. Boron adsorption equilibrium in soils. *Soil Sci.*, 98, 383–387.

952 Slack, J.F., Trumbull, R.B., 2011. Tourmaline as a recorder of ore-forming processes. *Elements*, 7(5),
953 321–326.

954 Smith, D.B., Reimann, C., 2008. Low-density geochemical mapping and the robustness of geochemical
955 patterns. *Geochem. Expl. Env. Anal.*, 8, 219–227.

956 Spivack, A.J., Palmer, M.R., Edmond, J.M., 1987. The sedimentary cycle of the boron isotopes.
957 *Geochim. Cosmochim. Acta*, 51(7), 1939–1949.

958 Steiner, F., Lana, M.D.C., 2013. Effect of pH on boron adsorption in some soils of Paraná, Brazil.
959 *Chilean J. Agri. Res.*, 73(2), 181–186.

960 Streit, B., 1994. *Lexikon Ökotoxikologie* (in German), Zweite aktualisierte und verbesserte Auflage,
961 VCH Verlagsgesellschaft mbH, Weinheim, 899 pp.

962 Sun, A., Gou, D., Dong, Y., Xu, Q., Cao, G., 2019. Extraction and analysis of available boron isotopes
963 in soil using multicollector inductively coupled plasma mass spectrometry, *J. Agric. Food Chem.*,
964 67, 7183–7189.

965 Takkar, P.N., 1996. Micronutrient research and sustainable agricultural productivity in India, *Journal of*
966 *the Indian Society of Soil Science*, 44, 562–581.

967 Tamuli, B., Bhattacharyya, D., Borua, N.G., Basumatary, A., 2017. Adsorption-Desorption Behaviour
968 of Boron in Soils of Assam. *Asian J. Chem.*, 29, 1011–1017.

969 Van Eynde, E., Mendez, J.C., Hiemstra, T., Comans, R.N., 2020a. Boron adsorption to ferrihydrite with
970 implications for surface speciation in soils: Experiments and modeling. *ACS Earth and Space*
971 *Chemistry*, 4(8), 1269–1280.

972 Van Eynde, E., Weng, L., Comans, R.N., 2020b. Boron speciation and extractability in temperate and
973 tropical soils: A multi-surface modeling approach. *Appl. Geochem.*, 123, 104797.

974 Wampler, J.M., Krogstad E.J., Elliott W.C., Kahn B., Kaplan D.I., 2012. Long-term selective retention
975 of natural Cs and Rb by highly weathered coastal plain soils. *Environ. Sci. Technol.*, 46, 3837–3843.

976 Wimmer, M.A., Goldberg, S., Gupta, U.C., 2015. 8 Boron. *Handbook of plant nutrition*, 305.

977 Wear, J.I., Patterson R.M., 1962. Effect of Soil pH and Texture on the Availability of Water-Soluble
978 Boron in the Soil. *Soil Sci. Soc. Amer. J.*, 26, 344–346.

979 Wedepohl, K.K. 1978. *Handbook of Geochemistry*. Berlin, Heidelberg, New York: Springer-Verlag.
980 ISBN 3 540 09022 3.

981 Woods, W.G., 1994. An introduction to boron: history, sources, uses, and chemistry. *Env. Health*
982 *perspec.* 102 (suppl 7), 5–11.

983 Yau, S.K., Hamblin, I., Ryan, I., 1994. Phenotypic variation in boron toxicity tolerance in barley, durum
984 and bread wheat. *Radin*, 13, 20–25.

985 Zhang, X., Li, M.J., Zhan, L.Q., Wu, W., Liu, H.B., 2020. Boron availability in top-and sub-soils as
986 affected by topography and climate. *Nutrient Cycling in Agroecosystems*, 118(1), 91–101.

987 Zubovic, P., Sheffey, N.B., Stadnichenko, T., 1967. Distribution of minor elements in some coals in the
988 Western and Southwestern regions of the Interior Coal Province. *US Geol. Surv. Bull.*, 1117 (D),
989 1–33.