Environ Geochem Health (2023) 45:9469–9475
https://doi.org/10.1007/s10653-022-01448-w

ORIGINAL PAPER

The dynamics of boron when amending agricultural soil of the Mediterranean basin with biosolids: trials in leaching columns

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Received: 19 March 2022 / Accepted: 28 November 2022 / Published online: 14 December 2022

Abstract There is mainly a lack of boron (B) in soils with low amounts of organic matter and in acidic and sandy soils. This is especially true in irrigated land or humid regions, where leaching can occur. The results from studying the amount of available B will reveal the status of B in the soil of a specific plot of land. The experimentation was performed as a controlled study using leaching columns. A container was placed at the end of the columns to collect the infiltrated water. Three treatments were performed by applying different amounts of biosolids (T_{40}: 40,000 kg ha^{-1}, T_{80}: 80,000 kg ha^{-1}, T_{120}: 120,000 kg ha^{-1}), as well as a blank test or control treatment (T_0). We conclude that the mobility of B in soil was generally low despite the addition of organic matter and humidity to the soil. This is an indication that there is no clear risk of aquifers being contaminated with B or plants being impacted by toxicity due to this micronutrient.

Keywords Boron · Leachate · Agricultural soil · Ceramic cluster · Mediterranean basin

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Introduction

There is mainly a lack of boron (B) in soils with low amounts of organic matter and in acidic and sandy soils in humid regions or irrigated crops. Organic matter is the reservoir for most of the B available in soils (Jordán et al., 2022). B shortcomings are often connected to droughts, when root activity decreases in the topsoil (Abdala et al., 2015). Balanced soil fertility provides the plants with increased vigour and their roots with increased growth. The result is an optimal absorption of B and other nutrients. Soil reactions, which can impact the availability of B for plants, vary greatly. Most of the B available in the soil is in its organic matter (Jordán et al., 2022). Organic matter forms a complex with B to extract it from the soil solution when there are high levels of B after fertilising the soil with it. The organic matter in the soil breaks down to resupply the soil solution and maintain suitable amounts of B when levels drop due to crop absorption or leaching (Almendro et al., 2001). Soils with low amounts of organic matter have a lower capability of supplying B and generally require more frequent fertilisations with B, with lower doses of application. Organic matter in the soil must break down to release B; therefore, conditions such as cool and humid or hot and dry climates, which decrease the breakdown of organic matter, will lower the amount of B available in the soils (Abdala et al., 2015). Meanwhile, sandy soils with good drainage are more likely to have a lack of B during heavy rains due to their high leaching potential (Abdala et al., 2015). These soils may need more frequent fertilisations with B. However, if the subsoil texture is fine (higher clay content) under horizons with a sandy surface, they may need less frequent applications of B (Jordán et al., 2022). In general, the total amount of B is higher in clay soils, but its availability for plants can be low in these soils due to the resistance that keeps B in clay surfaces (Galán et al., 2008).

The availability of B for plants decreases as the pH of the soil increases, especially at a pH level greater than 7. However, strongly acidic soils (pH < 5) also tend to have a low amount of B available due to the sorption of B in iron and aluminium oxide surfaces of mineral soils. Some crops with high requirements of B need a pH greater than 6.5 for optimal growth. However, there are often temporary deficits of B, especially when soils have an alkaline pH level (Navarro-Pedreño et al., 2003; Jordán et al., 2021). Microorganisms break down the organic matter of the soil, which means the B available for plants is released from organic compounds. Conditions that favour improved microbial activity are adequately aerated humid and warm soils. On the other hand, soil conditions that hinder optimal microbial activity are drought, humid and cold soils (Abdala et al., 2015), and insufficient tillage (sub-par aeration). In droughts, the topsoil dries out. Thus, plant roots cannot feed on the surface layer of the soil, which is where most of the available B is produced. A dry climate also limits the availability of B because it restricts the flow of water that carries the B available in the solution. Crops are more susceptible of having a lack of B during droughts in soils with low amounts of available B.

Balanced soil fertility generally leads to plants absorbing B in an improved way. The increased plant vigour and improved root growth rate enable an increased absorption of B and other nutrients. Therefore, we must examine the results of soil analyses carefully and apply the recommended doses of nutrients that are present in low or insufficient amounts. B is more readily available for plant roots when the topsoil has been tilled. Soil tillage mixes it up and improves aeration and drainage. These are optimal conditions for organic matter to break down, which releases the available B. As crop production systems move towards less or no soil tillage, organic matter will build up on the topsoil or near it, and it may not break down quickly (Jordán et al., 2021). Thus, the availability of B will increasingly depend on the levels of humidity of the surface, and the administration of fertilisers could become more important.

Spain is one of the main producers of ceramic tiles and frits in the world. Over 93% of the industries that comprise these sectors are located within a radius of 50 km s (Fig. 1) in the province of Castellón (Sorli et al., 2004). The ceramic area is comprised by the towns of Nules, Villarreal, Castellón, Onda, Alcora, Ribesalbes, Sant Joan de Moró and Villafamés (Sorli et al., 2004). Over 200 companies that produce ceramic tiles have moved to this area, as well as more than 25 that manufacture ceramic glazes, frits and colours (Galindo et al., 2013). The main atmospheric emission of this industry is NOx, especially in companies that produce frits and glazes, as they work at higher temperatures. They also emit CO, CO_2, suspended particles and condensates, which include borates linked to the condensation of borate vapours emitted when melting ceramic frits (Aucejo et al., 1997; Sorli et al., 2004; Galindo et al., 2013). According to Aucejo et al. (1997), the limit value of soluble B in soils is 1.3 mg/kg. Sorli et al. (2004) detected high levels of leachable B in soils in the ceramic district of Castellón, both in alluvial coastal soils and in calcareous pre-coastal soils. Natural calcareous soils of Castellón province are poor in organic matter (Jordán et al., 2022). One of the most used materials for the organic amendment of soils is biosolids (Jordán et al., 2021).

In light of these premises, and considering the situation of agricultural soils in the ceramic cluster, the following study objectives emerged: (a) to characterise the leaching behaviour of B present in the soils and the biosolids used as an organic amendment of agricultural soils with high total levels of total B; (b) to determine the level of mobility of B through the profile; and (c) to analyse the quality of the leached waters, looking at the presence of B in the topsoil.

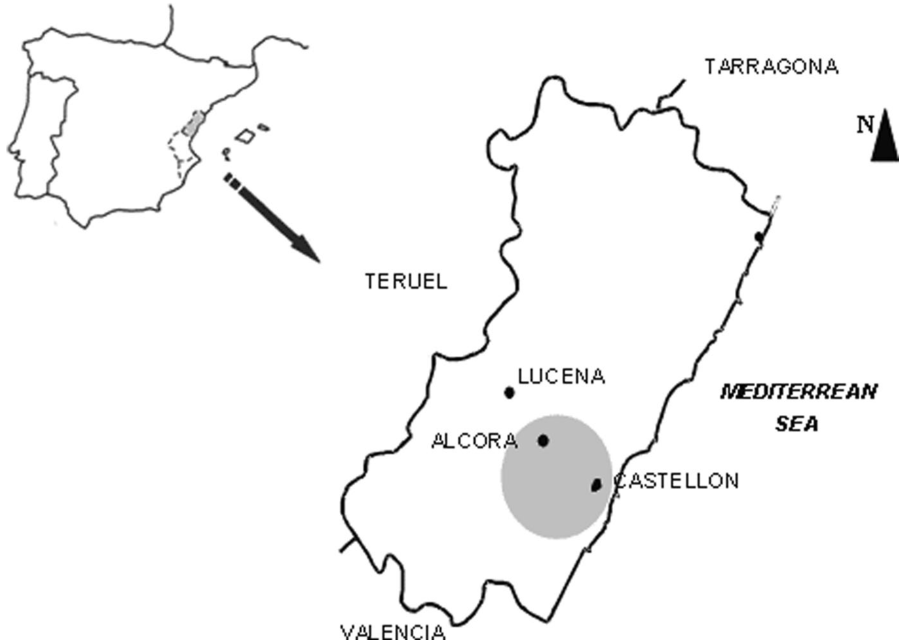

Fig. 1 Location of the area studied (Scale 1:2,000,000)

Materials and methods

We conducted the study in a greenhouse, continuously monitoring environmental parameters such as the temperature and humidity using a hygro-thermometer placed inside the central chamber. The experimentation was performed as a controlled study using leaching columns that met OECD (2004) standards (Fig. 2). To do so, we cut a PVC pipe with 10.5 cm of inner diameter into 20 cm-long pieces and created 80 cm-high columns with them. Each column had four differentiated sections measuring 20 cm each: 0–20 cm, 20–40 cm, 40–60 cm and 60–80 cm. These sections allowed us to conduct a differentiated study of the mobility of B through soil horizons (which do not correspond to genetic horizons due to soil formation processes) for each depth interval (Navarro-Pedreño et al., 2003). A container was placed at the end of the columns to collect the infiltrated water. Several authors (Almendro et al., 2001; Nuñez et al., 2002; Lewis & Sjöstrom, 2010; and Jordán et al., 2017) have conducted and validated similar trials.

Three treatments were performed by applying different amounts of biosolids (T_{40}: 40.000 kg ha^{-1}, T_{80}: 80,000 kg ha^{-1}, T_{120}: 120,000 kgha^{-1}), as well as a blank test or control treatment (T_0). The biosolid was applied to the surface and mixed it with the soil to simulate tilling, making a homogenous mixture of the biosolid with the first 20 cm of soil. The soil used to carry out this experience was agricultural soil from an area located just north of the town of Castellón.

The goal was to plant fodder and horticultural crops in this soil, using sewage sludge as fertiliser. The activity of the machinery in charge of adapting the terrain structurally altered the soil. As such, there was no clear differentiation of horizons. The main properties of the soil chosen for this experience are shown in Table 1.

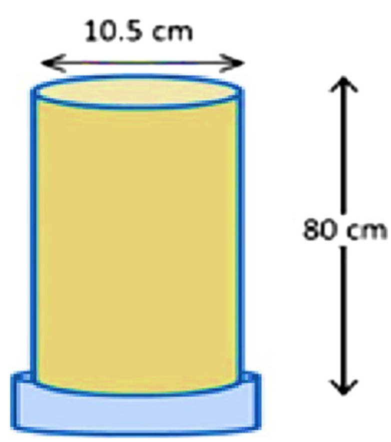

Fig. 2 Columns used in the experiment

Table 1 Characteristics of the soil used in the study

Parameter		Value	Parameter		Value
Texture			*Mineralogy*		
Sand 20 < ∅ < 2000 µm	%	26	Soil	Quartz	Calcite
Silt 2 < ∅ < 20 µm	%	35	Clay fraction	Quartz	Illite
Clay ∅ < 2 µm	%	39	Total elements		
pH		8.02	Al	g/kg	20.1
EC	µS/cm	77.7	B	mg/kg	39.1
Oxidisable C	g/kg	1.8	Ca	g/kg	226.2
Org. M. $_{oxid}$	g/kg	2.9	Cd	µg/kg	228
N Kjeldahl	g/kg	0.6	Cr	mg/kg	20.9
P	mg/kg	16.70	Fe	g/kg	12.8
Extracted ammonium acetate			K	g/kg	4.2
Ca	g/kg	5.342	Li	mg/kg	9.1
K	g/kg	0.149	Mg	g/kg	4.9
Mg	g/kg	0.256	Mn	mg/kg	170.2
Na	g/kg	0.069	Mo	mg/kg	1.9
Extracted DTPA			Na	g/kg	0.490
Cu	mg/kg	0.33	Ni	mg/kg	19.2
Mn	mg/kg	0.98	Sr	mg/kg	39.83
Zn	mg/kg	0.22	Zn	mg/kg	33.5

The soil had a basic pH and would therefore have an alkaline reaction. This entails that there could be issues with the availability of most nutrients, and that we could have to make acidic amendments to decrease the pH, facilitate the mobility of the elements and improve the soil's structure. The amount of equivalent calcium carbonate was high, as traditionally occurs with soils of the Spanish Mediterranean coast. The amount of organic matter was very low compared to the normal amount expected for farmland soil, which should be between 30 and 50 g/kg. Regarding the amount of assimilable nutrients (extracted with ammonium acetate and with DTPA), all elements were present in low or very low levels, except for Ca. There was a high presence of total B in the soil (> 39 $mgkg^{-1}$).

Regarding the biosolid applied in this study, we used sewage sludge from a wastewater treatment plant located in the l'Alcalatén district (Castellón), at the heart of the ceramic cluster. The composition of this biosolid is shown in Table 2.

Table 2 Biosolid composition (dry matter)

Parameter	Unit	Value	Parameter	Unit	Value
Humidity	%	83	Oxidisable C	%	20.2
Org M. 500 °C	%	61.2	Org. Oxid. M	%	34.1
Al	g/kg	12.23	Mg	g/kg	5.69
As	mg/kg	1.0	Mn	mg/kg	153
Ba	mg/kg	539	N	g/kg	42.15
Ca	g/kg	58.02	Na	g/kg	9.75
Cd	mg/kg	39.1	Ni	mg/kg	292
Cr	mg/kg	29	P	mg/kg	2375
Cu	mg/kg	415	Pb	mg/kg	89
Fe	g/kg	42.35	B	mg/kg	4
Hg	µg/kg	1.6	Ti	mg/kg	20
K	g/kg	1.47	Zn	mg/kg	2163

To establish the highest possible level of similarity between real conditions and the experiment, the soil in the columns was supplied an amount of water every seven days that equated to 75 mm of rain a week which is similar to the total amount of irrigation water provided when growing vegetables. The water was supplied through a device that simulated short bouts of rain or a flood irrigation system whereby the water covered the surface and then seeped into the soil. We took samples of soil from the columns three times during the study, leaving two months in between each sampling. Leached water was collected during each round of sampling as well as the soil from the columns.

Before analysing the total amount of the elements, we conducted a wet mineralisation of the sample with HNO_3 y H_2O_2 using electrothermal radiation (microwaves). The method used to measure the total B is based on the quantitative reaction that occurs between azometin-H and B, at a pH of 5.1 and in the presence of nitriloacetic acid (Bingham, 1982). This combination produces a coloured compound whose structure is not well known, but whose amount is proportional to the concentration of the element in the sample. Its absorbance is then measured at 410 nm (Keren & Bingham, 1985; Lachica, 1976). To establish the amount of B soluble in water that was in the soil, we performed an extraction with deionised water. The amount of B was established using the azometin-H method at a pH value of 5.1, the same as for the total amount. This technique was also used to establish the presence of B in leachates.

ANOVA test was used to assess the statistical significance of the results, analysing both the effect of the treatments and the depth for the analysed parameters (*, **, *** indicate significance at levels of $p = 0.05$, 0.01 and 0.001 respectively; ns: not significant in tables). The confidence interval (C.I.) is also shown at $p = 0.05$ to justify the difference among treatments.

Results and discussion

The contents of B are only lightly affected by the treatments (Table 3). In general, the concentration of this element in the biosolid does not seem to significantly increase the amount that is present in the soil, and there are only slight variations among treatments and throughout the soil profile.

For soluble B, there are no significant variations with the treatment or depth (Table 4). It is worth noting the high values of the first sample compared to the following ones, as well as the tendency to build up towards the end of the column in the last sampling. Therefore, there is a slow displacement of this micronutrient over time towards the lower horizon. Several authors (Aucejo et al., 1997; Sorli et al., 2004; Galindo et al., 2013) observed the following as regards the evolution of soluble and total B: the total contents of B follow the same patterns as soluble B. However, other authors observed more pronounced differences in calcareous soil (Goldberg & Forster, 1991), indicating greater storage capacity in these soils, which are rich in $CaCO_3$. This is due to the availability of B for plants decreasing as the pH of the soil increases, especially at a pH level close to 8, among other factors.

Table 3 Total B content (mg/kg m.s.) in each horizon and treatment

Sampling		Treatment								ANOVA
		T_0		T_{40}		T_{80}		T_{120}		
Day	Depth	Mean	C.I.	Mean	C.I.	Mean	C.I.	Mean	C.I.	F
60	20	69	12	45	5	53	10	59	11	*
	40	55	7	47	9	52	8	52	6	ns
	60	52	7	42	9	49	11	51	10	ns
	80	51	2	48	11	48	13	55	18	ns
F		ns		ns		ns		ns		
120	20	60	10	47	4	59	9	55	2	**
	40	57	20	53	15	48	12	47	2	ns
	60	51	11	52	6	59	16	49	5	ns
	80	55	18	56	21	50	6	49	8	ns
F		ns		ns		ns		**		
180	20	47	2	40	21	52	4	54	1	ns
	40	46	6	42	7	44	9	48	2	ns
	60	47	4	47	5	50	13	45	3	ns
	80	43	8	45	5	48	12	38	19	*
F		ns		ns		ns		*		

Table 4 Soluble B content (μg/kg m.s.) in each horizon and treatment

Sampling		Treatment								ANOVA
		T_0		T_{40}		T_{80}		T_{120}		
Day	Depth	Mean	C.I.	Mean	C.I.	Mean	C.I.	Mean	C.I.	F
60	20	527	546	491	230	323	224	400	275	ns
	40	510	215	415	110	484	114	250	170	**
	60	528	290	501	521	321	405	348	165	ns
	80	520	339	412	220	461	279	272	99	ns
F		ns		ns		ns		ns		
120	20	243	499	218	387	212	245	375	535	ns
	40	276	294	329	367	175	157	198	269	ns
	60	329	510	250	440	276	569	330	525	ns
	80	241	259	299	429	226	395	252	163	ns
F		ns		ns		ns		ns		
180	20	342	903	323	340	185	356	305	658	ns
	40	219	401	223	225	210	254	59	37	ns
	60	205	247	175	148	227	281	136	99	ns
	80	170	92	131	115	87	57	49	59	*
F		ns		ns		ns		ns		

The analytical results of the presence of B in leachates indicate that there is a tendency, albeit not statistically significant, to increase with treatment and decrease over time (Table 5). No conclusive connections can be established regarding the mobility of B present in the soil. In no case did we detect values of B higher than the regulatory limits for drinking water, which is an indication that there is no clear risk of aquifer contamination with B.

Conclusions

After assessing and discussing the results in the previous section, we conclude that despite the soil having high amounts of B, its mobility in the soil is generally low, despite the addition of organic matter from the biosolid used and the humidity (watering). This is an indication that there is no clear risk of aquifer contamination with B. This is undoubtedly a starting point to perform a mathematical study to model and assess the evolution and mobility of this element in calcareous and alluvial soils. The recommended doses of B must be applied if the levels of available B are low, especially in crops with high requirements of this element, such as alfalfa. The presence of B in soils must be determined before adding biosolids. The authors recommend expanding this study to other zones of agriculture coexisting with industries in countries of the Mediterranean region of Europe.

Table 5 B content (μg/L) in leachates

Treatment	Sampling					
	60 days		120 days		180 days	
	Mean	C.I.	Mean	C.I.	Mean	C.I.
T_0	166	35	179	25	119	53
T_{40}	185	63	162	33	149	78
T_{80}	175	58	195	28	158	37
T_{120}	180	55	159	50	179	12
F-ANOVA	ns		ns		ns	

Authors' contributions MMJ and JN-P contributed to conceptualization and methodology; MMJ and JB contributed to investigation; MBA-C and EG-S contributed to validation; FP and MMJ contributed to formal analysis and data curation; MMJ contributed to writing—original draft preparation; MMJ contributed to writing—review and editing; JB contributed to supervision.

Funding No funding application.

Availability of data and material Data available on request from the authors.

Code availability No application.

Declarations

Conflict of interest The authors declare no conflict of interest.

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