Distinguishing Boron Desorption from Mineral Dissolution in Arid-Zone Soils

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Boron release from six arid-zone soil samples from the San Joaquin Valley of California was investigated as a function of reaction time, solution pH, and suspension density. A multiple batch extraction experiment was performed for 362 d to distinguish B desorption from B released from mineral dissolution. Amounts of B released decreased rapidly and reached a low constant value after about 6 mo of reaction time. Slopes of the B release curves for the last eight extractions approached zero (constant release rate), indicating that this B release was from mineral dissolution. We also did a shorter term experiment that contained added Mg and silicate in solution. These experiments were conducted to evaluate the contribution of B release from dissolution of B-containing Mg silicate minerals. We determined that most of the B released from the soils can be attributed to release from sorption sites rather than resulting from dissolution of B-containing Mg silicates. Various B soil tests were evaluated for their ability to measure native extractable adsorbed B. The diethylenetriaminepentaacetic acid (DTPA)–sorbitol extract was the best measure of available adsorbed B but still only extracted 48% of the amount of B released in the long-term experiment. The greatest amount of B was extracted at the lowest suspension density for DTPA–sorbitol (92%) and phosphate buffer pH 6.6 (95%). These extractants are recommended for quantifying native extractable adsorbed B, which must be considered in application of chemical speciation transport models to describe B movement in soils. Incorporation of our results will allow improved predictions of soil solution B concentrations under diverse agricultural and environmental conditions.

Boron is an essential micronutrient element for plants; however, the range between deficient and toxic concentrations is smaller for B than for any other plant nutrient element. Boron deficiency often occurs in coarse-textured soils in humid regions and can be triggered by liming of acid soils due to increased adsorption at higher pH (Reisenauer et al., 1973). Boron toxicity results from high levels of B in soils, additions of B via irrigation waters, and lack of adequate drainage (Nable et al., 1997).

Compared with other phytonutrient elements, the soil chemistry of B is simple. Boric acid is a very weak, monobasic Lewis acid that accepts a hydroxyl ion to form the borate anion, $B(OH)_4^-$. Boron does not undergo volatilization or oxidation–reduction reactions in soils. Boron-containing minerals can be either minerals derived from igneous or metamorphic rocks, precipitates from evaporating brines, or altered or in situ formed clay minerals. Primary minerals containing B, like tourmaline, dissolve very slowly, while hydrated B minerals, like borax and ulexite, that form under extreme evaporative conditions and are very soluble, dissolve rapidly. These B solid phases do not control the concentration of B in most soil solutions (Goldberg, 1993). Boron may also be released into soil solution from B in tetrahedral sites of clay minerals (Jasmund and Lindner, 1973; Su and Suarez, 2004) or amorphous aluminosilicate phases.

Adsorption reactions are generally dominant in controlling the soil solution B concentration. Plants respond only to the B activity in soil solution; B retained on soil surfaces and in soil solids is not perceived as toxic by plants (meaning that it is not di-

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Table 1. Characteristics of the soils used in this study.

Soil sample	Total B	Surface area	Inorganic C	Organic C	Free Fe	Free Al	Electrical conductivity	pH
	mg kg^{-1}	m^2 g^{-1}			%		dS m^{-1}	
Lillis 5/2002	153	168	0.24	0.77	1.11	0.0927	3.6	7.8
Lillis 8/2002		125	0.016	0.81	0.963	0.0026		
Lillis 3/2004		132	0.045	0.84	0.955	0.0024		
Lillis 7/2004		133	0.052	0.91	0.924	0.0823		
Traver	222	73.4	0.0029	0.36	0.611	0.103	40.9	8.0
Twisselman	349	85.5	0.0014	0.47	0.508	0.0651	80.4	7.4

rectly available to plants) until it is released to the soil solution (Keren et al., 1985). While B adsorption reactions by soils and soil minerals have been investigated very extensively, a much smaller set of studies has focused on B desorption reactions (see Goldberg, 1993, and references therein). The assumption is often made that B adsorption–desorption reactions occur virtually instantaneously and reversibly, justifying the use of B adsorption data to describe B desorption behavior. However, information on the reversibility of B adsorption is contradictory. For some soils, the B desorption isotherm closely mirrors the adsorption isotherm (Hatcher and Bower, 1958; Elrashidi and O'Connor, 1982). For other soils, B desorption exhibits hysteresis, meaning that the desorption isotherm does not correspond to the adsorption isotherm (Elrashidi and O'Connor, 1982).

Reclamation of high-B soils is reported to require about three times as much leaching water as reclamation of saline soils (Reeve et al., 1955; Bingham et al., 1972), indicating a stronger retention mechanism for B than for soluble salts. In actuality, reclamation depends on soil pH and the quantity and affinity of adsorption sites. Griffin and Burau (1974) examined the kinetics of B desorption from soil and observed that the desorption reaction was almost complete after 10 h, although it continued for up to 72 h. The term *regeneration* has been used to describe the observed increases in soluble B after reclamation in the laboratory (Rhoades et al., 1970; Peryea et al., 1985a,b) and in the field (Bingham et al., 1972). This regeneration was attributed to the weathering of B-containing minerals and to B release from decomposing organic matter (Rhoades et al., 1970). However, the results of Rhoades et al. (1970) and Peryea et al. (1985a,b) were based on column studies where solution in small pores or adjacent to soil particles may not have been fully equilibrated with the leachate analyzed. Thus it is not clear whether this was B release from mineral dissolution or from reequilibration of B in micro- and macropores. Su and Suarez (2004) did observe long-term B release from two natively high-B soils after extensive leaching and considered this release as likely from the silicate mineral palygorskite (Su and Suarez, 2004).

Prediction of solution B concentration using chemical speciation transport models such as UNSATCHEM (Suarez and Šimůnek, 1997) requires an accurate determination of the amount of native desorbable B present in soils. Extraction for short periods of time is believed to result mainly in B desorption rather than mineral dissolution, which is a much slower process (Su and Suarez, 2004). Adsorption reactions are considered to control the amount of water-soluble B available for plant uptake. This would indicate that B soil tests, because they are designed to measure plant-available B, could be used as measures of native extractable adsorbed B. Examples of such soil tests are: NH_4OAc (Gupta and Stewart, 1975), $CaCl_2$–mannitol (Cartwright et al., 1983), and DTPA–sorbitol (Miller et al., 2000). Bicarbonate extracts are routinely used to determine plant-available phosphate in soils (Olsen et al., 1954; Watanabe and Olsen, 1965). Phosphate extracts have been used as measures of adsorbed anions in arid-zone soils (Fujii et al., 1988; Martens and Suarez, 1997; Gao et al., 2004).

The objectives of this study were: (i) to determine long-term B release rates from arid-zone soils so as to separate solution B, desorbed B, and B from the dissolution of B-containing minerals, and (ii) to evaluate various extractants for their ability to measure native extractable adsorbed B in soils.

MATERIALS AND METHODS

Four surface soil samples (0–45 cm) were collected from Section 4–2 of the Broadview Water District on the west side of the San Joaquin Valley of California (36°49′56.56″ N, 120°33′7.80″ W). These soil samples are all classified as Lillis silty clay loam (a very-fine, smectitic, thermic Halic Haploxerert) but differed in their clay content. Two of the soil samples are presently being used in large soil columns to investigate B transport (Shouse et al., personal communication, 2008). Two additional soil samples (0–20 cm) had been collected from the west side of the San Joaquin Valley in Kern County and used in a prior B release study of Su and Suarez (2004). The Traver silt loam is classified as a coarse-loamy, mixed, superactive, thermic Natric Haploxeralf (Section 7, Township 32S, Range 26E). The Twisselman clay loam is classified as a fine, mixed, superactive, calcareous, thermic Typic Torriorthent (Section 21, Township 25S, Range 21E).

Soil chemical characteristics are listed in Table 1. Total B was determined using the Na_2CO_3 fusion described by Hossner (1996). Soluble B and pH were determined in a saturation extract as described by Rhoades (1982). Surface areas were measured using ethylene glycol monoethyl ether adsorption (Cihacek and Bremner, 1979). Free Fe and Al oxides were extracted with a sodium citrate–citric acid buffer and sodium hydrosulphite (Coffin, 1963) and determined by inductively coupled plasma optical emission spectrometry (ICP–OES). Carbon contents were measured using C coulometry. Inorganic C contents were quantified using an acidification module and heating, total C was measured by combustion at 950°C, and organic C was determined by difference. Mineral identification in the soils was made using x-ray diffraction after Mg saturation of the whole soil and the <20-µm fraction before and after reaction in the experiment.

A multiple batch extraction technique similar to that used by Su and Suarez (2004) was used to determine B release rates. Duplicate soil samples were reacted at 1:10 solid/solution ratios by shaking in 0.1 mol L^{-1} NaCl solution for the first three extractions and in 0.01 mol L^{-1} NaCl solution for subsequent extractions. The reaction times were 12 h for the first 20 extractions; subsequent extractions were done on a monthly basis. The initial 20 extractions for the Traver and Twisselman soils were discarded because subsamples had been analyzed in the study of Su and Suarez (2004). The experiment was continued for 362 d. Twenty grams of air-dry soil were placed into 250-mL polypropylene centrifuge bottles and equilibrated with 200 mL of NaCl solution. The suspensions were shaken intermittently on a reciprocating shaker. After each reaction time, the suspensions were centrifuged. The supernatants were decanted and replaced with fresh extracting solution. The decantates were passed through 0.45-μm filters and analyzed for B concentration using ICP–OES. Cumulative B release was corrected for solution carryover at each extraction step and soil loss during the course of the experiment.

A second multiple batch extraction experiment was conducted in the presence of elevated solution concentrations of Mg and Si to suppress the dissolution of any Mg silicate minerals that might be present because it has been suggested that these minerals contain B (Page, 1968). By suppressing mineral dissolution and the release of B from these silicates, we can attribute the B release to B desorption alone. This experimental procedure was as described above with the following modifications from the 362-d experiment: (i) one set of extraction solutions contained 20 mmol Mg L^{-1} and 0.534 mmol Si L^{-1} in addition to the NaCl; (ii) a second set of extraction solutions contained only NaCl as in the previous experiment and was run as a control treatment; and (iii) five extractions were performed over 3 d, with reaction times of 12 h each.

A diverse set of extractants was used to measure B release. These soil extractions were performed in triplicate. We extracted the soil samples with 1.0 mol L^{-1} NH_4OAc (pH 7.2) and 0.01 mol L^{-1} $CaCl_2$–0.05 mol L^{-1} mannitol (pH 7.8). These extractions had been used to diagnose a wide range of B concentrations, from potentially deficient to potentially toxic, in Australian soils (Cartwright et al., 1983). The $CaCl_2$–mannitol procedure had also been recommended to measure leachable soil B by Rhoades et al. (1970). An extracting solution consisting of 0.005 mol L^{-1} DTPA, 0.01 mol L^{-1} $CaCl_2$, 0.1 mol L^{-1} triethanolamine adjusted to pH 7.3, and 0.2 mol L^{-1} sorbitol was also evaluated. This DTPA–sorbitol method has been recommended by the North American Proficiency Testing Program for estimating the potential soil bioavailability of B and the trace metal nutrients Zn, Cu, Mn, and Fe (Miller et al., 2000). The suspension density for the above extractions was 10 g soil/20 mL solution. The reaction times were as specified in their procedures: 1 h for NH_4OAc and $CaCl_2$–mannitol and 2 h for DTPA–sorbitol.

Soil samples were reacted with 0.1 mol L^{-1} Na_2CO_3 (pH 11) both for 2 h at a suspension density of 10 g soil/20 mL solution and for 20 h at a suspension density of 5 g soil/25 mL solution. Boron release into a 0.1 mol L^{-1} NaCl solution (pH 4.1) was also quantified by shaking for 20 h at a suspension density of 5 g soil/25 mL solution, as had been done previously in the study of Goldberg et al. (2005). A series of phosphate extractants and phosphate buffers was used to cover the pH range 2.6 to 12.3. The reaction time was 20 h at a suspension density of 5 g soil/25 mL 0.1 mol L^{-1} phosphate solution. Specifically, the solutions were: 0.05 mol L^{-1} H_3PO_4 + 0.05 mol L^{-1} KH_2PO_4 (pH 2.6), 0.1 mol L^{-1} KH_2PO_4 (pH 4.4), 0.05 mol L^{-1} KH_2PO_4 + 0.05 mol L^{-1} K_2HPO_4 (pH 6.7), 0.1 mol L^{-1} K_2HPO_4 (pH 8.6), and 0.1 mol L^{-1} K_3PO_4 (pH 12.3).

The effect of suspension density was investigated using both the DTPA–sorbitol and the 0.05 mol L^{-1} KH_2PO_4 + 0.05 mol L^{-1} K_2HPO_4 phosphate extracts. Extractions were performed at suspension densities of 200, 71.4, 34.5, and 17 g L^{-1}. For the DTPA–sorbitol extract, suspension densities of 500 and 6.7 g L^{-1} were also investigated.

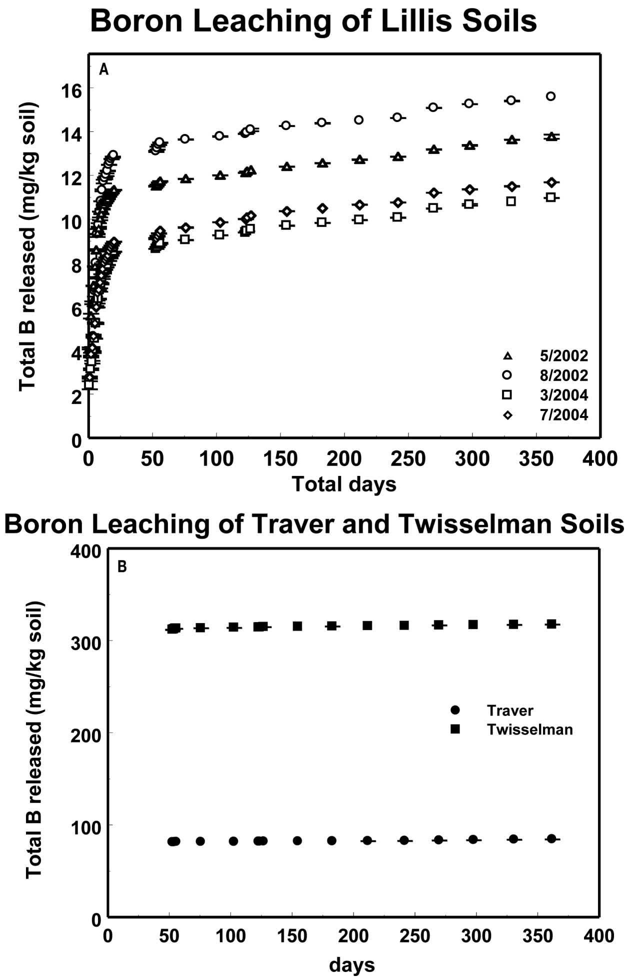

Fig. 1. Cumulative B released from (a) four Lillis soil samples and (b) the Traver and Twisselman soils as a function of sequential extraction with 0.1 mol L^{-1} NaCl solution for the first three extractions and 0.01 mol L^{-1} NaCl for subsequent extractions. The initial 20 extractions of the Traver and Twisselman soils were discarded because subsamples had been analyzed in the study of Su and Suarez (2004). Error bars represent one standard deviation from the mean of two replicates.

RESULTS AND DISCUSSION

The cumulative amounts of B released from the soil samples are depicted in Fig. 1a for the Lillis soils. It is evident that most of the B was released in the first 20 leachings, followed by a region of linear (constant) increase in total B with subsequent leachings. Figure 1b shows the B release from the Traver and Twisselman soils. The data from the first 20 leachings were obtained from Su and Suarez (2004) because subsamples of soils collected by these authors were used in our study. Again, there was a large release of B in the first 20 leachings, followed by a region of linear increase. The B increase after the first 20 leachings is on the order of only 2 to 8% of the total B released. These soils differed widely in their total B release, with Twisselman releasing 23 times as much B as the Lillis soils. The amounts of B extracted decreased rapidly and reached a constant low value after about 6 mo of total reaction time. Slopes

Table 2. Soluble B extracted from selected soil samples.

B source	Lillis 5/2002	Traver	Twisselman
	mg B kg^{-1} soil		
Total B released	13.8 ± 0.09	84.4 ± 0.04	317 ± 0.03
Solution B	0.94	8.55	62.0
B from long-term mineral dissolution	2.73	5.96	6.25
B release suppressed by Mg and Si	0.74	18.2	21.7
B desorbed	9.39	51.7	227.
B desorbed, % of released B	68.0	61.2	71.6

of the B release curves as a function of time for the last eight extractions were not statistically significantly different from zero at the 95% confidence level for five of the six soil samples. The only exception was the Traver soil, where the 95% confidence interval for the slope was $0.00091 < m < 0.005$. We consider that the B solubilized in the final eight extractions represents the constant release rate of B from slowly soluble mineral phases at pH 6.5 to 7.5.

By extrapolating the amount of long-term constant dissolution to the earlier extractions, we can calculate the contribution of this B pool to the total B released. The amounts of B released from this fraction, long-term mineral dissolution, are indicated in Table 2. We calculated that only a small part of the total B originated from this B weathering source.

The amount of B present in a saturation extract of the soil is reported in Table 2. Subtraction of this quantity, in addition to the subtraction of the B released from long-term weathering, from the total quantity released to the solution allowed us to calculate the apparent adsorbed B. This calculation assumed that the mineral phase did not contain an additional source of highly soluble B. This assumption appears reasonable because B-containing minerals in soils are either minerals of very high solubility with rapid dissolution kinetics that would dissolve at the first addition of water, such as colemanite or other borate minerals related to evaporites, or minerals having relatively slow dissolution kinetics, such as the silicate minerals. Highly soluble borate minerals are found in evaporite deposits and would long since have been dissolved out of our study soils by winter rainfall events. If present, these salts would be released in the saturation extract reported as soluble B in Table 2.

The results in Table 2 indicate that the natively high extractable B soils, Traver and Twisselman, also had higher long-term release of B than the other soils examined. This long-term release is considered to have come from a relatively insoluble mineral phase. Twisselman and Traver released 6.0 and 6.3 mg B kg^{-1} yr^{-1}, respectively from the mineral phase, while the Lillis soil samples released only 2.7 to 3.5 mg B kg^{-1} yr^{-1}. These are maximum rates related to our leaching experiments, with repeated removal of the reaction products. Under field conditions, the rates would be much lower due to buildup of Mg and Si reaction products, as discussed below.

Palygorskite, a magnesium aluminum phyllosilicate clay mineral, was identified earlier as the likely B-containing mineral in the Traver and Twisselman soils (Su and Suarez, 2004). We conducted additional x-ray diffraction studies on these soils using the methodology proposed by Gionis et al. (2007). We observed an x-ray peak at 1.04 nm, which is regarded as the major diagnostic peak for palygorskite (Gionis et al., 2007), for both the Traver and Twisselman soils, as observed earlier by Su and Suarez (2004). This palygorskite peak was prominent in the whole soil and likely absent in the patterns for the clay fraction, where only a small 1.0-nm peak, assigned to illite, was present. These results suggest that the palygorskite may occur as a coating on other larger particles. This is not entirely surprising because palygorskite has been reported to occur as fibrous networks adhering, for example, onto dolomite surfaces (Akbulut and Kadir, 2003). In contrast to the other soils, the Lillis soil had no peak at 1.04 nm in either the clay fraction or the whole soil. However, the Gionis et al. (2007) procedure for palygorskite identification contains additional steps. Upon heating to 350°C, the reference palygorskite did not collapse to 0.93 nm as stated by Gionis et al. (2007), nor did the soil samples (a slight collapse to 1.03 nm). Further heating to 550°C caused destruction of the peaks from the palygorskite reference mineral (Ward's Natural Science, San Luis Obispo, CA), as indicated by Gionis et al. (2007). However, this heating step did not alter the 1.03-nm peak in the soils. These results suggest that additional evaluation of the Gionis et al. (2007) method is required and that the identification of palygorskite in our soils is ambiguous.

Soils having lower amounts of native extractable B would be expected to have lesser amounts of B-containing minerals that release B. Although the percentage of mineral B was low for the Traver and Twisselman soils, this is due to the very high solution and adsorbed B concentrations. The B released from a relatively insoluble mineral phase for the Traver and Twisselman soils was approximately twice that for the Lillis soil (see Table 2).

Boron release from dissolution of Mg silicates is expected to be greatly suppressed in the presence of elevated concentrations of Mg and Si. Neaman and Singer (2000) observed Si and Mg release from specimen palygorskites essentially in proportion to their occurrence in the solid phase and calculated that the dissolution rate was, as expected, greatly suppressed in the presence of Mg and Si reaction products. These authors extrapolated the Si concentration vs. dissolution rate to a zero net dissolution rate at 82 mg L^{-1} Si (2.93 mmol L^{-1}) and 10 mmol L^{-1} Mg. The thermodynamic stability and solubility of palygorskite is not listed in available thermodynamic databases. However, the stability diagram developed by Singer and Norrish (1974) based on dissolution studies indicates that our Mg and Si solution activities exceeded those required for palygorskite saturation at our solution pH values (>7). We thus conclude that there was sufficient Mg and Si present in solution to avoid palygorskite dissolution if the mineral were present.

The B release in the presence of 20 mmol L^{-1} Mg and 0.534 mmol L^{-1} Si is shown in Fig. 2a for the Lillis soils and Fig. 2b

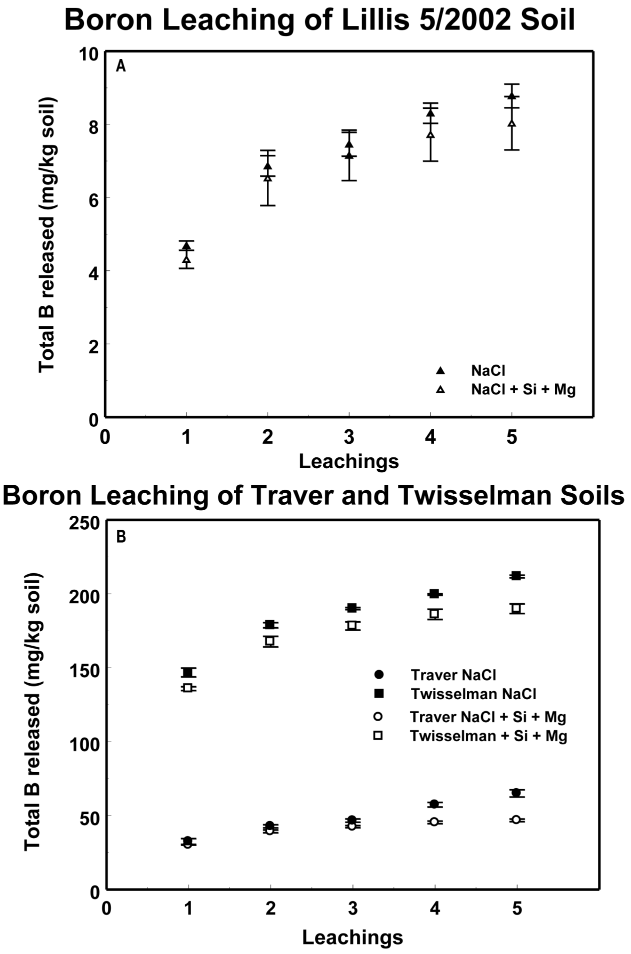

Fig. 2. Cumulative B released from (a) the Lillis 5/2002 soil sample and (b) the Traver and Twisselman soils as a function of sequential extraction with 0.1 mol L^{-1} NaCl solution for the first three extractions and 0.01 mol L^{-1} NaCl for subsequent extractions in NaCl only (solid symbols) and in the presence of 0.534 mmol Si L^{-1} and 20 mmol Mg L^{-1} and NaCl (open symbols). Error bars represent one standard deviation from the mean of two replicates.

for the Traver and Twisselman soils. These quantities of released B in the presence of the high Mg and Si solution concentrations were found to range from 72 to 92% of the amount of B release attributed to adsorption in the related experiment without suppression of dissolution, which is also shown in Fig. 2. The difference in release into these two solutions is either dissolution from some relatively soluble B-containing mineral or differences related to different chemical conditions for B desorption or to kinetics.

Boron release from the Lillis soils was not statistically significantly different into NaCl solutions than into NaCl + Si + Mg solutions (see Fig. 2a) but the Si + Mg solutions did release less B, despite having no identifiable B-containing mineral. In contrast, the Traver and Twisselman soils, with x-ray peaks possibly suggesting palygorskite, did have statistically significant suppression of B release in the presence of high solution concentrations of Mg and Si. If we calculate the difference in B release from the two reactions, we have another intermediate pool of B that may be attributed to the dissolution of a mineral phase or to the kinetics of B desorption.

The minimum amount of B attributed to adsorbed B is obtained by assuming that all of this intermediate B pool is from a soluble B-containing mineral, and subtracting this amount and the saturation extract solution B, as well as B from long-term mineral weathering, as shown in Table 2. The minimum values of B attributed to desorption are thus 61% of the total for Traver and 72% for Twisselman. The adsorbed B is the bulk of the B released to solution from these soils, with lesser quantities attributed to soluble B, as well as to B from mineral dissolution. Thus B release from these soils can be considered to be mostly a desorption process. The mineral dissolution component is, at maximum, 25% of the total B released for Lillis, 29% for Traver, and only 8.8% for Twisselman.

Various extractants were evaluated for their ability to measure native extractable adsorbed B. Table 3 lists the amount of B released by each extracting solution. Experimental conditions including suspension density and reaction time were described above. The short reaction times for the extractions should favor B desorption over mineral silicate dissolution reactions. As can be seen from Table 3, the largest amounts of B extracted occurred at the more extreme pH values. These extract data agree with the adsorption behavior of B as a function of solution pH, which is parabolic and exhibits an adsorption maximum around pH 9. The much reduced B adsorption at low and high pH is in agreement with the greater amount of desorption or extraction at these pH values. Silicate dissolution is substantial at very low and very high pH values and could lead to additional B release.

The three B soil tests released, on average, 8.5% for NH_4OAc, 32% for $CaCl_2$–mannitol, and 48% for DTPA–sorbitol of the total amount of B released minus B from long-term mineral dissolution in the long-term experiment (indicated at the bottom of Table 3 for reference). Of the three extractants, DTPA–sorbitol should be considered as the best measure of plant-available B and natively adsorbed soil B. Indeed, the DTPA–sorbitol method also gave the highest correlation with plant B content for container-grown melons (*Cucumis melo* L.) compared with NH_4OAc and 1:1 water/soil extracts (Goldberg et al., 2003); however, none of the extractants were effective in quantifying adsorbed B. This is not entirely surprising because B adsorption on soils is mostly ion specific, meaning that there is limited competition for adsorption sites. Thus, unlike cation exchange, B is mostly not displaced by other ions or chemicals. The extracting solution thus needs to be dilute because there is an equilibrium between the solution and the adsorbed phase. Boron forms strong diol complexes with sugar alcohols such as mannitol and sorbitol, thus reducing the free B in solution and enhancing further extraction of B from the adsorbed phase.

We consider that all of the B released in the above experiments, except for the long-term weathering pool, is available for plant uptake. The various phosphate extracts released 34 to 61% of the amount of B desorbed in the long-term experiment. Not surprisingly, the larger amounts of B were extracted at the low (2.6 and 4.4) and high (12.3) pH values. At these pH values B adsorption is reduced, thus enhancing the transfer of B from the adsorbed to the solution phase. The NaCl solution extracted about one-third of the B desorbed in the long-term experiment, while the Na_2CO_3 extracts released 21 to 38%. For Na_2CO_3, the amount of desorbed

Table 3. Boron released by various soil tests and extracting solutions.

Extractant	Lillis 5/2002	Lillis 8/2002	Lillis 3/2004	Lillis 7/2004
	mg B kg^{-1} soil			
NH_4OAc, pH 7.2	1.22 ± 0.02	0.744 ± 0.001	0.620 ± 0.01	0.815 ± 0.001
$CaCl_2$–mannitol, pH 7.8	4.82 ± 0.12	2.82 ± 0.02	2.50 ± 0.02	3.00 ± 0.05
DTPA–sorbitol, pH 7.3	6.52 ± 0.03	4.25 ± 0.05	3.71 ± 0.03	4.46 ± 0.07
Na_2CO_3, 500 g L^{-1}, pH 11.1	2.95 ± 0.04	1.91 ± 0.04	1.61 ± 0.03	2.00 ± 0.05
Na_2CO_3, 200 g L^{-1}, pH 11.1	5.46 ± 0.11	3.45 ± 0.07	2.94 ± 0.06	3.46 ± 0.08
0.1 mol L^{-1} NaCl, pH 4.1	4.64	2.93	2.62	2.99
0.05 mol L^{-1} H_3PO_4 + 0.05 mol L^{-1} KH_2PO_4, pH 2.6	8.36 ± 0.01	5.75 ± 0.09	4.42 ± 0.08	5.71 ± 0.06
0.1 mol L^{-1} KH_2PO_4, pH 4.4	7.47 ± 0.17	5.01 ± 0.11	4.52 ± 0.05	5.12 ± 0.04
0.05 mol L^{-1} KH_2PO_4 + 0.05 mol L^{-1} K_2HPO_4, pH 6.8	6.82 ± 0.17	4.20 ± 0.16	3.75 ± 0.01	4.38 ± 0.06
0.1 mol L^{-1} K_2HPO_4, pH 8.6	4.84 ± 0.31	2.81 ± 0.02	2.65 ± 0.03	3.24 ± 0.08
0.1 mol L^{-1} K_3PO_4, pH 12.3	7.30 ± 0.03	4.61 ± 0.15	3.95 ± 0.04	4.72 ± 0.10
Native B released—long-term mineral dissolution B	11.0	12.1	8.23	8.80

B was a function of suspension density, with the greater amount of B desorption occurring at the lower suspension density.

The suspension density effect was investigated in greater detail for a phosphate buffer and the DTPA–sorbitol extract. Decreasing suspension density should increase extraction efficiency as increasing the solution relative to the solid shifts the mass of B in solution relative to that on the adsorbed phase, assuming an equilibrium between solution B and adsorbed B concentrations. As can be seen from Fig. 3, B desorption varied with suspension density from 6.7 to 500 g L^{-1}. The greatest amount of desorption was observed at the lowest suspension density: 6.7 g L^{-1} for DTPA–sorbitol and 17 g L^{-1} for the phosphate buffer at pH 6.6. The amounts desorbed, 10.1 mg B kg^{-1} soil (92%) for DTPA–sorbitol and 10.4 mg B kg^{-1} soil (95%) for the phosphate buffer, are in excellent agreement with the amount of native B desorbed plus solution B in the long-term leaching experiment: 11.0 mg B kg^{-1} soil. The good correspondence between phosphate buffer and DTPA–sorbitol extract B obtained during short reaction times (20 h for phosphate and 2 h for DTPA–sorbitol) and the B obtained from a 1-yr leaching experiment (corrected for the very slow constant dissolution from a likely silicate phase) strongly suggests that the extracted B originated from one or more adsorbed phases.

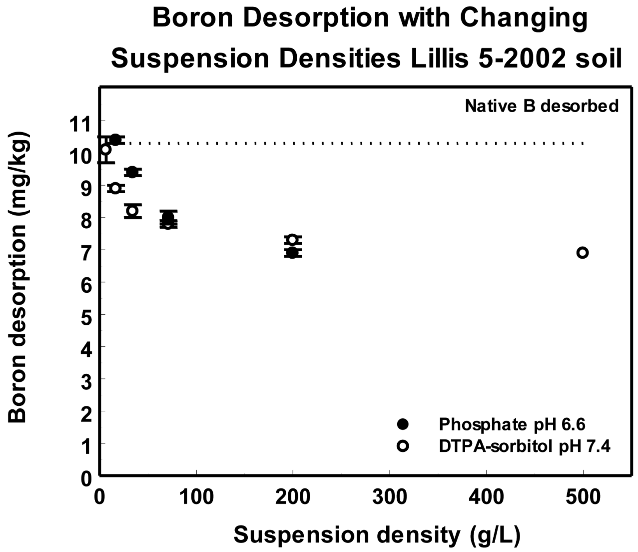

Fig. 3. Boron desorption as a function of suspension density for a phosphate buffer (0.05 mol L^{-1} KH_2PO_4 + 0.05 mol L^{-1} K_2HPO_4 pH 6.6) and diethylenetriaminepentaacetic acid (DTPA)–sorbitol extract. Native extractable B desorbed in the long-term leaching experiment is indicated with a dashed line. Error bars represent one standard deviation from the mean of three replicates.

Based on these desorption experiments with various extracting agents and suspension densities, we recommend that low suspension densities (7–17 g L^{-1}) should be used for quantifying native extractable adsorbed B in arid-zone soils. This is in contrast to the recommendations for B soil tests that use high suspension densities (200–500 g L^{-1}) to characterize plant-available soil B and which we observed to remove only a small fraction of the total adsorbed B. We expect that similar results would be obtained for any soil that contained a high quantity of adsorbed B, especially one with high B affinity or a large number of adsorption sites.

Based on these results, we conclude that current extraction methods underestimate adsorbed B, resulting in underestimation of B release from arid-zone soils containing native B. The new proposed extraction methods with low suspension densities (phosphate buffer and DTPA–sorbitol) quantify >90% of the adsorbed B. The release of B from mineral dissolution is a minor component of total B released to solution but nonetheless can be significant when B concentrations in soils are low. Although geologically significant, B release from the mineral phase can be neglected in most agronomic situations. Accurate prediction of long-term B concentration or B loading to the subsurface when a soil is extensively leached may require consideration of such B release.

Our data do not support the need to consider B "regeneration" (Rhoades et al., 1970; Peryea et al., 1985a,b) or the kinetics of B release (Griffin and Burau, 1974) beyond the 2- to 20-h extraction time. Our long-term B release did not decrease with time, in contrast to the earlier reported increases in B on leaving samples stagnant between leaching steps (Rhoades et al., 1970; Peryea et al., 1985a,b). Release from an intermediate moderately soluble B-containing mineral is unlikely. Earlier results (Rhoades et al., 1970) may be explained alternatively by incomplete extraction of adsorbed native B with $CaCl_2$–mannitol. As can be seen in Table 3, this solution, although better than NH_4OAc, extracts lesser proportions of native B than DTPA–sorbitol and phosphate extracts. Boron adsorption and desorption are highly pH-dependent reactions (Goldberg et al., 2005). Therefore, decreases in the solution pH during leaching experiments, as expected due to the production and retention of observed CO_2 in stored wet soils, as observed by Peryea et al. (1985b), would result in increases in the solution B concentration due to desorption and could explain their B release with time.

This investigation has shown that B desorption can be separated from mineral dissolution under conditions of a long-term reaction time. These results also indicate that current methods underestimate the quantity of adsorbed B in arid lands. For the purposes of describing B transport in soils under agricultural conditions, these results are important because native extractable adsorbed B must be considered in the application of chemical speciation transport models such as UNSATCHEM (Suarez and Šimůnek, 1997) if long-term simulations are made. Incorporation of native extractable adsorbed B will allow improved predictions of soil solution B concentrations under diverse agricultural and environmental conditions. We also conclude that a new extraction method is needed because the existing extraction methods do not adequately characterize the adsorbed B pool. An improved extraction method should consider low suspension densities.

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