

Effect of Dissolved Organic Carbon in Recycled Wastewaters on Boron Adsorption by Soils

Sabine Goldberg and Donald L. Suarez

ABSTRACT:

In areas of water scarcity, recycled municipal wastewaters are being used as water resources for nonpotable applications, especially for irrigation. Such wastewaters often contain elevated levels of dissolved organic carbon (DOC) and solution boron (B). Boron adsorption was investigated on eight arid-zone soils from California and one from Arizona as a function of equilibrium B concentration (0–100 mg L⁻¹) and solution pH (4–10). The B equilibrating solutions were prepared using either recycled wastewaters or synthetic wastewaters containing DOC up to 10 mg L⁻¹. The synthetic wastewaters were synthesized to have the same chemical composition as the recycled wastewaters but contained no DOC. Boron adsorption on the soils increased with increasing solution pH, reaching an adsorption peak near pH 9, and then decreased with further increases in solution pH. The pH-dependent amounts of B adsorption were not statistically significantly different at the 95% level of confidence for both types of waters. For all soils, B adsorption as a function of solution B concentration conformed to the Langmuir adsorption isotherm equation. Boron adsorption maxima, obtained using the Langmuir isotherm, were not statistically significantly different at the 95% confidence level for both types of waters. The constant capacitance surface complexation model was able to predict B adsorption as a function of solution pH using the soil chemical properties: aluminum oxide, inorganic carbon, organic carbon contents, and surface area. The magnitude of B adsorption as a function of solution pH and equilibrium solution B concentration was unaffected by the presence of DOC in the recycled wastewaters. This result indicates that these treated recycled wastewaters, because of their low DOC contents, will not affect B adsorption behavior of soils when used for irrigation of crops and landscape vegetation.

Key Words: Constant capacitance model, DOC, sewage effluent

(*Soil Sci* 2017;182: 94–100)

Arid and semiarid regions of the world are faced with critical shortages of freshwater supplies. Current agricultural production on irrigated lands can be sustained only if available freshwater sources are supplemented with new water supplies, either recycled wastewaters or brackish groundwaters. Treated municipal sewage effluent, usually referred to as treated wastewater or recycled wastewater, has been used successfully as a water resource for nonpotable applications in geographic areas experiencing water scarcity. For example, in Israel more than 50% of the total water used for irrigation of crops is recycled wastewater, and 86% of treated sewage is used for irrigation (Israel Water Authority, 2015). In California, the production of recycled water is governed by the US Environmental Protection Agency Guidelines for Water Reuse (US EPA, 2004) and by the State of California Department of Health Services Title 22 of the California Code of Regulations (State of California, 2000). Recycled water is defined by these entities (EPA and CA Department of Health Services) as reclaimed wastewater that has undergone primary, secondary, and tertiary treatment and disinfection, allowing it to be used for landscape irrigation and other nonpotable uses. In the United States, such reclaimed wastewater is distributed in an alternate network of “purple” pipes that are kept completely separate from the potable water conveyance system.

Boron is an essential micronutrient trace element required for plant growth that can become phytotoxic at higher concentrations.

USDA-ARS, US Salinity Laboratory, Riverside, California.

Address for correspondence: Dr Sabine Goldberg, USDA-ARS, US Salinity Laboratory, 450 W Big Springs Rd, Riverside, CA 92507. E-mail: Sabine.Goldberg@ars.usda.gov

Financial Disclosures/Conflicts of Interest: None reported.

Received September 20, 2016.

Accepted for publication April 18, 2017.

Supplemental digital contents are available for this article. Direct URL citations appear in the printed text and are provided in the HTML and PDF versions of this article on the journal's Web site (www.soilsci.com).

Copyright © 2017 Wolters Kluwer Health, Inc. All rights reserved.

ISSN: 0038-075X

DOI: 10.1097/SS.000000000000199

Boron concentrations in treated wastewater are usually elevated over those in freshwater, primarily because of the presence of laundry detergents (Zekri and Koo, 1994; Maurer et al., 1995; Reboll et al., 2000; Yermiyahu et al., 2011). For this reason, B is an element of potential concern when applying wastewater for irrigation. Long-term irrigation of golf course fairways in Colorado with recycled wastewaters resulted in statistically significant increases in soil solution B concentration over irrigation with surface water (Qian and Mecham, 2005). Statistically significant increases in soil solution B concentrations down to a depth of 1.5 m were also observed following 7+ years of irrigation of grapefruit trees in Israel with treated wastewater as compared with freshwater (Lado et al., 2012). In this study, greater movement of B into the soil profile was observed in the noncalcareous sandy soil than in the calcareous clayey soil. The authors attributed this result to the greater content of B adsorbing constituents: clay minerals, sesquioxides, organic matter, and calcite present in the calcareous clayey soil (Lado et al., 2012). However, the elevated pH of the calcareous soil (relative to the noncalcareous soil) would also have resulted in increased B adsorption. Eventually, of course, all soils will continue to increase in B content upon irrigation with elevated B irrigation water until they achieve a quasi-steady state (Goldberg and Suarez, 2006). Thus, B soil solution concentrations attained after long-term irrigation with wastewater could become toxic to B sensitive crops and impair their growth. Recycled wastewaters in other countries, for example, Israel, contain much more elevated concentrations of dissolved organic carbon (DOC) and B than California recycled wastewaters (Keren and Communar, 2009; Lado et al., 2012).

Organic matter is considered to be an important sink for B adsorption in soils since highly significant correlations were found between soil carbon content and adsorbed B (Harada and Tamai, 1968; Elrashidi and O'Connor, 1982). Results from external applications of organic matter on B adsorption by soils are contradictory depending on whether the organic matter is in solid or dissolved form. Applications of solid organic forms, such as composted organic matter (Yermiyahu et al., 1995) and farmyard manure (Sharma et al., 2006), were found to enhance soil B adsorption. Treated wastewaters contain elevated concentrations of dissolved organic matter (Reboll et al., 2000; Lado et al., 2012). Soil B adsorption was suppressed with increasing application of dissolved organic

matter from sewage effluent in the range of DOC of 40 and 95 mg L⁻¹ (Communar and Keren, 2008).

Boron adsorption on soils is highly dependent on solution pH, and the complexation of B with dissolved organic matter from sewage effluent has been found to be pH dependent (Keren and Communar, 2009). However, the interactive effect of solution pH and DOC on B adsorption remains to be investigated. Dissolved organic matter is positively charged at low pH, as are the inorganic soil constituents: layer silicates and sesquioxides. Boron adsorption would be favored up to the point of zero charge of these materials. It has been observed experimentally that B adsorption on organic and inorganic constituents decreases above pH 9 to 10. The objectives of the current study were (1) to characterize B adsorption on soils as a function of solution pH and solution B concentration from wastewaters containing DOC at concentration levels found in California treated recycled wastewaters, (2) to compare these results to B adsorption occurring from synthetic wastewaters without DOC, and (3) to apply the constant capacitance model to describe the B adsorption data and to compare values of the resulting surface complexation constants.

MATERIALS AND METHODS

Surface horizons of eight arid-zone soil series from California and one from Arizona were collected as follows: Altamont and Yolo in 2000; Tranquillity in 2001; Arlington, Buren, Hanford, and Ramona in 2009; and Casa Grande and Carsitas in 2012. Soil classifications are provided in Table 1. The soils were air dried, sieved, thoroughly homogenized, and stored in 5-gallon plastic buckets. The less than 2-mm fraction was used for soil characterization and B adsorption experiments.

Soil physical and chemical characterization results are presented in Table 1. Soil pH was determined at a soil:solution ratio of 1:5 in 0.1 M NaCl solution. Percent clay contents were obtained from particle size distributions using the basic hydrometer method (Gee and Bauder, 1986). Surface areas were determined from a monolayer adsorption of ethylene glycol monoethyl ether (Cihacek and Bremner, 1979). Carbon contents were measured using a coulometer. Inorganic carbon (IOC) was determined directly using acidification and heating to 70°C, whereas organic carbon (OC) was obtained indirectly as the difference between total carbon measured using furnace combustion at 950°C and IOC. Free Fe and Al oxides were extracted using the citrate/citric acid buffer and hydrosulfite method of Coffin (1963). Subsequently, extract concentrations of Fe and Al

were determined by inductively coupled plasma optical emission spectrometry (ICP-OES).

Treated wastewaters were obtained from seven wastewater treatment facilities in Southern California. These recycled waters are delivered for landscape and golf course irrigation and other nonpotable uses by means of the “purple” pipes conveyance system. The chemical compositions of these wastewaters are provided in Table 2. For comparison purposes, two waters were synthesized in the laboratory to have similar chemical compositions as the Encina and Gafner recycled wastewaters. These synthetic wastewaters contained no added DOC. Their chemical analyses are provided at the bottom of Table 2. Analytical methods were as follows: ICP-OES for Na, Ca, Mg, K, and S concentrations; coulometric-amperometric titration for Cl (Cotlove et al., 1958); spectrophotometric (220 nm) determination for nitrate (American Public Health Association, 2012); and total alkalinity with samples titrated with standardized 10.0 mM HCl to the H₂CO₃-HCO₃⁻ inflection point. The Encina and Gafner wastewaters were chosen for simulation because they are the two wastewaters that contain the highest DOC contents. As can be seen in Table 2, the chemical compositions of the synthetic wastewaters are similar to their respective recycled wastewaters, except for the DOC contents of the synthetic waters, which are two orders of magnitude lower than those of the recycled waters.

Adsorption experiments were carried out in batch systems to determine B adsorption isotherms (amount of B adsorbed as a function of solution equilibrium solution B concentration) and B adsorption envelopes (amount of B adsorbed as a function of pH at fixed total initial B concentration). For the B adsorption isotherms, 20 g of air-dried soil was added to 50-mL centrifuge tubes and equilibrated with 20 mL of solution on a reciprocating shaker for 20 h. The equilibrating solutions contained 0, 2, 5, 10, 15, 25, 50, or 100 mg B L⁻¹ (from boric acid) and were prepared using recycled wastewater (Encina or Gafner) or synthetic wastewater (simulated Encina or Gafner). The reaction temperature was 23.5°C ± 0.2°C. After equilibration, the samples were centrifuged. The supernatants were analyzed for pH, filtered through 0.45-μm membrane filters, and analyzed for B concentration using ICP-OES. The amount of B adsorption was determined as the difference between the initial equilibrating solution B concentration and the final equilibrium B concentration. Experiments were carried out in duplicate.

For the B adsorption envelopes, 5 g of air-dried soil were added to 50-mL centrifuge tubes and equilibrated with 25 mL of solution containing 5 mg B L⁻¹ (from boric acid) on a reciprocating shaker. The equilibrating solutions were prepared using the same recycled wastewater (Encina or Gafner) or synthetic wastewater (simulated

TABLE 1. Classifications and Physical and Chemical Characterization of Soils

| Soil Series | Clay | pH | SA | IOC | OC | Fe | Al |
|--|------|-----|--------------------------------|---------|------|-------|--------|
| | % | | m ² g ⁻¹ | % | | | |
| Altamont (fine, smectitic, thermic Aridic Haploxerert) | 23 | 6.6 | 103 | 0.0010 | 0.96 | 0.77 | 0.058 |
| Arlington (coarse-loamy, mixed thermic Haplic Durixeralf) | 5.8 | 7.5 | 13.8 | 0.0085 | 0.52 | 0.333 | 0.0222 |
| Buren (fine-loamy, mixed, superactive, thermic Haplic Durixeralf) | 5.0 | 7.1 | 10.0 | 0.0007 | 0.19 | 0.259 | 0.0156 |
| Casa Grande (fine-loamy, mixed, superactive, hyperthermic Typic Natrargid) | 21.6 | 7.6 | 87.4 | 0.19 | 0.37 | 0.355 | 0.0331 |
| Carsitas (mixed, hyperthermic Typic Torripsamment) | 3.8 | 7.7 | 14.6 | 0.25 | 0.45 | 0.208 | 0.0107 |
| Hanford (coarse-loamy, mixed, nonacid, thermic Typic Xerorthent) | 9.6 | 6.8 | 17.5 | 0.0053 | 0.72 | 0.489 | 0.0314 |
| Ramona (fine-loamy, mixed, thermic Mollic Haploxeralf) | 2.1 | 7.6 | 7.03 | 0.0048 | 0.14 | 0.225 | 0.0155 |
| Tranquillity (fine, smectitic, thermic Sodic Haploxerert) | 48.9 | 7.8 | 168 | 0.045 | 0.76 | 1.13 | 0.0837 |
| Yolo (fine-silty, mixed, nonacid, thermic Mollic Xerofluvent) | 23.3 | 7.0 | 97.9 | <0.0007 | 1.0 | 0.982 | 0.0834 |

SA, surface area.

TABLE 2. Chemical Compositions of the Recycled Wastewaters

| Water | pH | Na ⁺ | Ca ²⁺ | Mg ²⁺ | K ⁺ | Cl ⁻ | NO ₃ ⁻ | SO ₄ ²⁻ | HCO ₃ ⁻ | B | DOC | EC | SAR |
|-----------------------------|-----|-----------------------------------|------------------|------------------|----------------|-----------------|------------------------------|-------------------------------|-------------------------------|-------|--------------------|--|------|
| | | mmol _c L ⁻¹ | | | | | | | - mg L ⁻¹ - | | dS m ⁻¹ | (mmol L ⁻¹) ^{1/2} | |
| Inland Empire RP-1 | 7.8 | 4.40 | 1.94 | 0.78 | 0.369 | 2.66 | 0.38 | 1.05 | 2.93 | 0.228 | 3.83 | 0.80 | 4.09 |
| Inland Empire RP-5 | 8.3 | 4.34 | 2.42 | 0.91 | 0.366 | 1.96 | 0.41 | 0.99 | 2.92 | 0.315 | 4.18 | 0.86 | 3.65 |
| Inland Empire CCWRF | 7.4 | 4.75 | 2.21 | 0.92 | 0.441 | 4.95 | 0.07 | 1.19 | 2.84 | 0.260 | 3.70 | 0.89 | 4.15 |
| Orange County Green Acres | 7.6 | 8.87 | 4.03 | 1.97 | 0.494 | 7.71 | 0.21 | 4.09 | 3.46 | 0.372 | 5.63 | 1.55 | 5.41 |
| Vallecitos Water District | 7.2 | 6.81 | 3.91 | 2.36 | 0.440 | 6.32 | 0.66 | 4.55 | 4.31 | 0.287 | 7.44 | 1.54 | 4.09 |
| Gafner Treatment Plant | 8.3 | 8.77 | 4.01 | 2.56 | 0.531 | 8.39 | 0.09 | 4.29 | 5.38 | 0.317 | 9.00 | 1.83 | 5.13 |
| Encina Wastewater Authority | 6.6 | 8.17 | 3.81 | 2.42 | 0.508 | 6.41 | 1.39 | 3.98 | 1.30 | 0.335 | 10.1 | 1.56 | 4.92 |
| Synthetic Encina Wastewater | 8.1 | 8.42 | 3.94 | 2.02 | 0.520 | 8.26 | 1.50 | 3.64 | 1.50 | 0.487 | <0.5 | 1.53 | 5.18 |
| Synthetic Gafner Wastewater | 7.3 | 8.41 | 2.62 | 2.05 | 0.548 | 8.51 | 0.10 | 3.65 | 1.05 | <0.1 | <0.5 | 1.16 | 5.86 |

EC, electrical conductivity; SAR, sodium adsorption ratio.

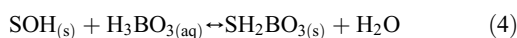
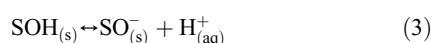
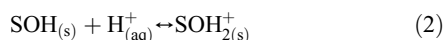
Encina or Gafner), as had been used in the B adsorption isotherm experiments. The equilibrating solutions were adjusted to the desired pH values with 0.5 mL containing varying proportions of 1 M NaCl or 1 M HCl and 1 M NaOH. The reaction temperature was 24.1°C ± 0.6°C. The reaction time, centrifugation and filtration conditions, and pH and B concentration analyses were identical to those used for the B adsorption isotherm experiment described previously. Experiments were carried out in duplicate.

The Langmuir adsorption isotherm equation:

$$B_{\text{ads}} = \frac{KB_{\text{eq}}M}{1 + KB_{\text{eq}}} \quad (1)$$

where B_{ads} is the B adsorption (mg kg⁻¹), B_{eq} is the equilibrium B concentration (mg L⁻¹), M is the maximum B adsorption (mg kg⁻¹), and K is a parameter (L mg⁻¹), was fit to the experimental B adsorption isotherm data using the nonlinear least-squares optimization program, ISOTHERM (Kinniburgh, 1985). Direct fitting of adsorption data using the nonlinear Langmuir equation avoids the problems of biased parameters and changes in error distributions generated by the various linear transformations. Of course, as with all adsorption isotherm equations, application of the Langmuir equation to describe adsorption data should be considered as a curve-fitting exercise (Sposito, 1982).

The experimental B adsorption isotherm and B adsorption envelope data were also described using the constant capacitance surface complexation model. A detailed description of this model is provided in Goldberg (1992). In the current model application, the following protonation, dissociation, and B surface complexation reactions are considered:



where $\text{SOH}_{(s)}$ represents reactive surface functional groups present in soils, such as hydroxyls on oxide minerals, aluminols on the edges of clay minerals, and carboxyl and phenol groups on organic matter. Following the convention of the constant capacitance model, anion

surface complex formation reactions are written starting with the completely protonated acids and neutral surface functional groups. Despite this convention, the aqueous speciation reaction for B ($\text{p}K_a = 9.2$; Owen, 1934) is included. Boron adsorption reactions form both trigonal (Eq. 4) and tetrahedral (Eq. 5) surface species, in agreement with experimental spectroscopic observations (Su and Suarez, 1995) on oxide minerals.

Equilibrium constant expressions for the surface complexation reactions, Eqs. (2) to (5), are as follows:

$$K_+(\text{int}) = \frac{[\text{SOH}_2^+]}{[\text{SOH}][\text{H}^+]} \exp(F\psi/RT) \quad (6)$$

$$K_-(\text{int}) = \frac{[\text{SO}^-][\text{H}^+]}{[\text{SOH}]} \exp(-F\psi/RT) \quad (7)$$

$$K_B(\text{int}) = \frac{[\text{SH}_2\text{BO}_3]}{[\text{SOH}][\text{H}_3\text{BO}_3]} \quad (8)$$

$$K_{B-}(\text{int}) = \frac{[\text{SH}_3\text{BO}_4^-]}{[\text{SOH}][\text{H}_3\text{BO}_3]} \exp(-F\psi/RT) \quad (9)$$

where square brackets represent concentrations (mol L⁻¹), F is the Faraday constant (C mol⁻¹), ψ is the surface potential (V), R is the molar gas constant (J mol⁻¹ K⁻¹), T is the absolute temperature (K), and $e^{-F\psi/RT}$ is an electrostatic potential term that can be considered as a solid-phase activity coefficient correcting for charge present on the surface complex. The mass balance equation for the surface functional group is:

$$\text{SOH}_T = [\text{SOH}] + [\text{SOH}_2^+] + [\text{SO}^-] + [\text{SH}_2\text{BO}_3] + [\text{SH}_3\text{BO}_4^-] \quad (10)$$

and the surface charge balance equation is:

$$\sigma = [\text{SOH}_2^+] - [\text{SO}^-] - [\text{SH}_3\text{BO}_4^-] \quad (11)$$

where σ is the surface charge (mol_c L⁻¹).

The computer program FITEQL 4.0 (Herbelin and Westall, 1999), which contains the constant capacitance model, was used to fit the B surface complexation constants to the experimental B adsorption isotherm and B adsorption envelope data using nonlinear

| TABLE 3. Langmuir Adsorption Isotherm Parameter Values and Their SD | | | | | | |
|---|-------------------------|--------------------------|----------------|-------------------------|--------------------------|----------------|
| Soil | Synthetic Wastewater | | | Reclaimed Wastewater | | |
| | K (L mg ⁻¹) | M (mg kg ⁻¹) | R ² | K (L mg ⁻¹) | M (mg kg ⁻¹) | R ² |
| Altamont | 0.054 ± 0.01 | 7.9 ± 0.7 | 0.966* | 0.026 ± 0.009 | 12.2 ± 2.6 | 0.936* |
| Arlington | 0.055 ± 0.03 | 3.6 ± 1 | 0.767* | 0.06 ± 0.04 | 3.7 ± 0.8 | 0.809* |
| Buren | 0.0059 ± 0.003 | 14.1 ± 5.6 | 0.851* | 0.013 ± 0.004 | 6.5 ± 1.1 | 0.906* |
| Carsitas | 0.0078 ± 0.005 | 10.7 ± 6.0 | 0.948* | 0.013 ± 0.008 | 8.1 ± 3.5 | 0.928* |
| Casa Grande | 0.015 ± 0.002 | 38.1 ± 2.4 | 0.995* | 0.016 ± 0.001 | 39.0 ± 1.8 | 0.997* |
| Hanford | 0.016 ± 0.003 | 16.7 ± 2.0 | 0.974* | 0.018 ± 0.001 | 17.5 ± 1.1 | 0.991* |
| Ramona | 0.015 ± 0.001 | 6.7 ± 4 | 0.631* | 0.045 ± 0.002 | 4.0 ± 0.7 | 0.922* |
| Tranquillity | 0.0032 ± 0.002 | 141 ± 58 | 0.988* | 0.0015 ± 0.02 | 295 ± 260 | 0.988* |
| Yolo | 0.016 ± 0.002 | 21.3 ± 1.8 | 0.996* | 0.030 ± 0.005 | 15.7 ± 1.5 | 0.986* |

*Represents significance at the 95% level of confidence. Encina wastewater was used for the Altamont, Arlington, Buren, Hanford, Ramona, and, Tranquillity soils. Gafner wastewater was used for the Carsitas, Casa Grande, and Yolo soils.

least-squares optimization. Constant capacitance input parameter values were fixed at capacitance = 1.06 F m⁻², protonation constant, log K_a = 7.35, and dissociation constant, log K₋ = -8.95 (Goldberg and Glaubig, 1986). The total number of reactive functional groups is obtained from the surface site density, N_s = 2.31 sites nm⁻² (recommended for natural particles by Davis and Kent, 1990), using the expression following:

$$SOH_T = \frac{S_A C_s 10^{18}}{N_A} N_s \quad (12)$$

where S_A is the surface area (m² g⁻¹), C_s is the soil concentration (g L⁻¹), and N_A is Avogadro number. The ability of the constant capacitance model to describe B adsorption using surface complexation constants predicted from soil chemical parameters using the following equations (Goldberg et al., 2000)

$$\begin{aligned} \text{Log}K_{B-} = & -4.83 - 0.375\text{ln}(\text{SA}) + 0.167\text{ln}(\text{OC}) \\ & + 0.111\text{ln}(\text{IOC}) + 0.466\text{ln}(\text{A1}) \end{aligned} \quad (13)$$

$$\text{Log}K_{+} = 5.73 - 0.102\text{ln}(\text{OC}) - 0.198\text{ln}(\text{IOC}) - 0.622\text{ln}(\text{A1}) \quad (14)$$

$$\begin{aligned} \text{Log}K_{-} = & -10.44 + 0.302\text{ln}(\text{OC}) + 0.0584\text{ln}(\text{IOC}) \\ & + 0.302\text{ln}(\text{A1}) \end{aligned} \quad (15)$$

was also evaluated. The chemical properties were those provided in Table 1. Their analyses are described in paragraph 2, above.

RESULTS AND DISCUSSION

Analysis of the recycled wastewaters (Table 2) shows a range of DOC values from 3.8 to 10 mg L⁻¹. These values are much lower than the values cited for treated wastewater in Israel, which range from 40 to 138 mg L⁻¹ (Keren and Communar, 2009; Lado et al., 2012). Boron concentrations of the California wastewaters were relatively uniform, ranging from 0.23 to 0.37 mg L⁻¹. These concentrations are elevated relative to freshwater concentrations, but are in an acceptable range for most crops (Maas, 1986). Boron adsorption isotherms were determined on our nine soils using equilibrating solutions made with recycled wastewaters or synthetic wastewaters synthesized to contain the same concentrations of chemical constituents as the respective recycled wastewaters. Nonlinear least-squares optimization (Kinniburgh, 1985) was used to fit the Langmuir isotherm equation to the experimental adsorption

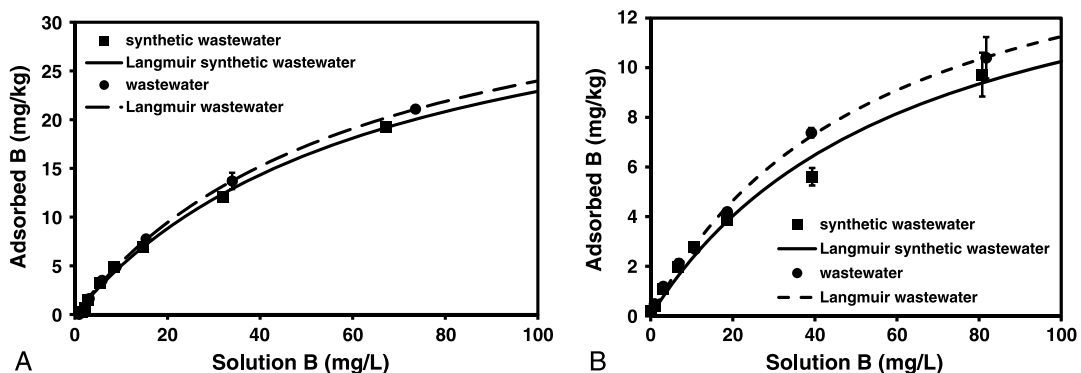


FIGURE 1. Boron adsorption as a function of solution B concentration from synthetic and recycled wastewaters by (A) Casa Grande soil, (B) Hanford soil. Experimental data are represented by squares for synthetic wastewater and circles for recycled wastewater. Langmuir adsorption isotherm fits are represented by a solid line for synthetic wastewater and a dashed line for recycled wastewater. Error bars represent SD of two replicates. The x-axis error bars are contained within the symbols.

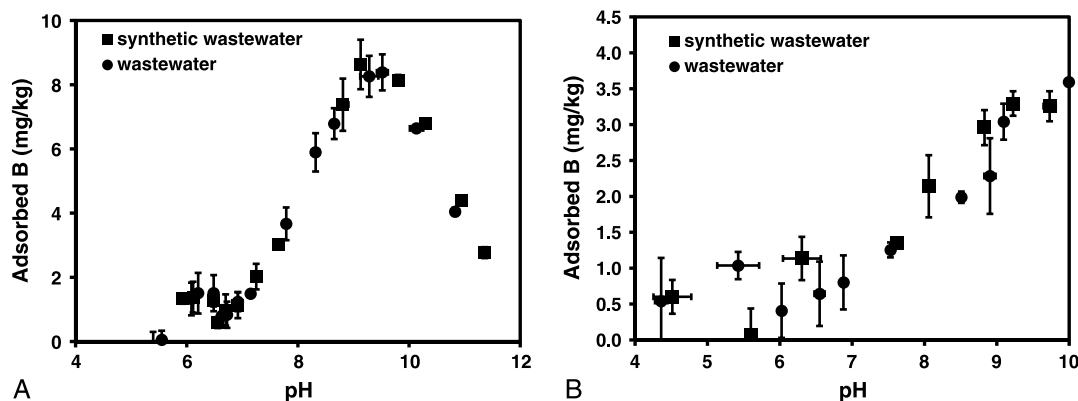


FIGURE 2. Boron adsorption as a function of solution pH from synthetic and recycled wastewaters by (A) Casa Grande soil, (B) Ramona soil. Experimental data are represented by squares for synthetic wastewater and circles for recycled wastewater. Error bars represent SD of two replicates. The x-axis error bars are contained within the symbols.

data. The quality of the fit of the Langmuir isotherm is indicated by R^2 and was significant at the 95% level of confidence for all soils. For all nine soils, the resulting soil B adsorption maxima, M , for the two types of waters, synthetic wastewater versus recycled wastewater, were not statistically significantly different at the 95% level of confidence (Table 3). This result indicates that the magnitude of soil B adsorption as a function of solution B concentration is unaffected by DOC concentrations up to 10 mg L^{-1} in the recycled wastewaters. Figure 1 presents experimental B adsorption data and Langmuir isotherm fits for the Casa Grande (Fig. 1A) and Hanford (Fig. 1B) soils. For both soils, the amount of B adsorption (mg/kg) at each solution B concentration (mg/L) is not statistically significantly different at the 95% confidence level between the two types of waters (with the exception of the 40 mg B/L solution concentration for the Hanford soil).

Boron adsorption as a function of solution pH was determined on the nine soils using equilibrating solutions containing 5 mg B L^{-1} made from either the recycled wastewater or the respective synthetic wastewater. Figure 2 presents experimental B adsorption envelope data for the Casa Grande (Fig. 2A) and Ramona (Fig. 2B) soils. For both soils, there was no statistically significant difference at the 95% level of confidence between the amounts of soil B adsorption for the two types of waters when considering the SD of

data points closely adjacent in pH value. This result indicates that the magnitude of soil B adsorption as a function of solution pH is not statistically affected by the DOC concentrations in the recycled wastewaters. We note that the error bars are larger for the determination of B envelopes as compared with the B isotherms (compare Figs. 1 and 2). For complete B adsorption data, see supplemental figures (Supplemental Digital Content 1, <http://links.lww.com/SS/A51>).

Our results can be compared with those of previous studies where the effect of DOM on soil B adsorption was investigated. Communar and Keren (2008) measured B adsorption by extracted and resuspended DOM at 50 mg/kg DOC at 15.5 mg B L^{-1} in solution and pH 7.7 for DOM material generated by activated sludge treatment (DOM-1). Another DOM material obtained from an aeration treatment process on sewage (DOM-2) had a B adsorption of 33 mg/kg DOC at 4.9 mg B L^{-1} in solution. However, upon treating a loamy sand soil with DOM-1 at a concentration of 67 mg C L^{-1} and DOM-2 at a concentration 144 mg C L^{-1} and a sandy loam soil with DOM-1 at a concentration of 105 mg C L^{-1} and DOM-2 at a concentration 172 mg C L^{-1} , Communar and Keren (2008) stated that the B adsorption capacity of the two soils was not affected by the presence of DOM as compared with untreated soil samples, which had a concentration of 20 mg C L^{-1} for the loamy sand and 45 mg C L^{-1} for the

TABLE 4. Boron Surface Complexation Constants for the Constant Capacitance Model

| Soil | Adsorption Isotherm Data | | Adsorption Envelope Data | |
|------------------|--------------------------|------------------|--------------------------|------------------|
| | Synthetic Water | Wastewater | Synthetic Water | Wastewater |
| | $\log K_{B-}$ | $\log K_{B-}$ | $\log K_{B-}$ | $\log K_{B-}$ |
| Altamont | -8.01 | -7.89 | -7.04 | -7.31 |
| Arlington | -7.62 | -7.61 | -6.74 | -6.81 |
| Buren | -7.49 | -7.60 | -6.33 | -6.43 |
| Carsitas | -7.98 | -7.76 | -6.71 | -6.76 |
| Casa Grande | -7.82 | -7.80 | -7.49 | -7.48 |
| Hanford | -7.32 | -7.24 | -6.83 | -6.60 |
| Ramona | -7.58 | -7.37 | -6.57 | -6.70 |
| Tranquillity | -8.19 | -8.16 | -7.54 | -7.74 |
| Yolo | -7.96 | -7.88 | -7.36 | -7.29 |
| Average \pm SD | -7.77 ± 0.29 | -7.70 ± 0.28 | -6.96 ± 0.43 | -7.01 ± 0.45 |

sandy loam. They found B adsorption maxima of 19.0 mg L⁻¹ for untreated and 20.1 mg L⁻¹ for DOM-1-treated and 18.7 mg L⁻¹ for DOM-2-treated loamy sand. Furthermore, they found B adsorption maxima of 30.3 mg L⁻¹ for untreated and 29.4 mg L⁻¹ for DOM-1-treated and 29.7 mg L⁻¹ for DOM-2-treated sandy loam. Although the authors did not provide statistical comparisons, they considered these soil B adsorption maxima to be similar (see Table 6 of their study). Therefore, our results that the magnitude of soil B adsorption as a function of solution B concentration and solution pH was unaffected by the presence of DOC at 10 mg L⁻¹ are consistent with those of Communar and Keren (2008).

The constant capacitance model was applied to the experimental soil B adsorption data. Separate computer optimizations were carried out for the adsorption isotherm and adsorption envelope data because the experimental soil concentrations were not the same. Final model convergence could not be obtained when attempting to simultaneously optimize constants for both the trigonal, Eq. (4), and tetrahedral, Eq. (5), B surface species. Intermediate model results obtained from FITQL iterations (FITEQL 4.0, Herbelin and Westall, 1999), completed before divergence occurred, showed the tetrahedral B species to be the dominant B surface complex, thus suggesting that convergence would occur using solely the tetrahedral B species. Therefore, the model was fit optimizing exclusively the tetrahedral B surface constant, log K_{B-}, Eq. (9). Table 4 provides values of log K_{B-} optimized for both the adsorption isotherm and adsorption envelope data obtained using both synthetic and recycled wastewaters. The averages of the log K_{B-} values for the synthetic versus recycled waters were very close in value and not statistically significantly different at the 95% level of confidence. In addition, the average log K_{B-} values for the B adsorption isotherm data were not statistically significantly different from the average log K_{B-} values for the B adsorption envelope data at the 95% confidence level. These modeling results are in agreement with the experimental finding that the magnitude of B adsorption was unaffected by the DOC concentrations present in the recycled wastewater.

The ability of the constant capacitance model to predict B adsorption as a function of solution pH is shown in Fig. 3 for the Tranquillity soil. As previously described in the study of Goldberg et al. (2000), the surface complexation constants were calculated by entering the soil chemical properties (Table 1): surface area, OC content, IOC content, and aluminum oxide content into the prediction equations, Eq. (13) to Eq. (15). These surface complexation constants were then used in the constant capacitance model to predict soil B

TABLE 5. Surface Complexation Constants Obtained Using the Prediction Equations of Goldberg et al. (2000)

| Soil | log K _{B-} | Log K _t | Log K _c |
|--------------|---------------------|--------------------|--------------------|
| Altamont | -8.67 | 8.87 | -11.72 |
| Arlington | -8.23 | 9.11 | -12.07 |
| Buren | -8.72 | 9.92 | -12.62 |
| Carsitas | -8.24 | 8.91 | -12.13 |
| Casa Grande | -8.45 | 8.28 | -11.87 |
| Hanford | -8.15 | 8.95 | -11.89 |
| Ramona | -8.43 | 9.58 | -12.62 |
| Tranquillity | -8.30 | 7.91 | -11.46 |
| Yolo | -8.52 | 8.71 | -11.62 |

adsorption as a function of solution pH. The FITEQL program was run in speciation mode, without optimizing any surface complexation constants. The model was able to predict B adsorption on the experimental data for both the synthetic and recycled wastewater in the pH range 8.5 to 11 (Fig. 3). The model overpredicted B adsorption in the pH range 7.5 to 8.5. Table 5 provides predicted surface complexation constant values obtained using the prediction equations, Eq. (13) to Eq. (15) from Goldberg et al. (2000), for all nine soils. The B surface complexation constants of Table 5 were obtained using Eq. (13), whereas the B surface complexation constants of Table 4 were optimized. The protonation-dissociation constants of Table 5 were obtained using Eq. (14) and Eq. (15), whereas these two constants were fixed in the optimization to obtain the B surface complexation constants of Table 4.

The results of this study indicate that the magnitude of soil B adsorption both as a function of equilibrium solution B concentration and solution pH was unaffected (not statistically significantly different) by the presence of DOC in recycled wastewaters at the concentrations found in Southern California. The findings in our study are explained by the fact that the recycled “purple pipe” wastewaters, having received tertiary treatment, contain low amounts of DOC, less than 10 mg L⁻¹. In contrast, the DOC contents of some secondary treated wastewaters used for irrigation in Israel range from 35 to 138 mg L⁻¹ (Keren and Communar, 2009; Lado et al., 2012). These Israeli wastewaters also contain highly elevated solution B concentrations (220–1,015 mg L⁻¹) confounding the evaluation of the effect of DOC on soil B adsorption. The results of the current study indicate that recycled “purple pipe” wastewaters, treated according to the US EPA Guidelines for Water Reuse (US EPA, 2004) and Title 22 of the California Code of Regulations (State of California, 2000) and used for landscape irrigation, did not affect soil solution B concentration and the B adsorption behavior of the soils because of their very low DOC contents.

ACKNOWLEDGMENTS

The authors thank Ms. P. Xiong and Mr. J. Casian for technical assistance.

REFERENCES

American Public Health Association. 2012. Standard Methods for the Examination of Water and Wastewater. Rice E. W., R. B. Baird, and A. D. Eaton (eds.). American Water Works Association, Washington, D.C., 1496 pp.
 Cihacek L. J., and J. M. Bremner. 1979. A simplified ethylene glycol monoethyl ether procedure for assessing soil surface area. Soil Sci. Soc. Am. J. 43:821–822.
 Coffin D. E. 1963. A method for the determination of free iron oxide in soils and clays. Can. J. Soil Sci. 43:7–17.

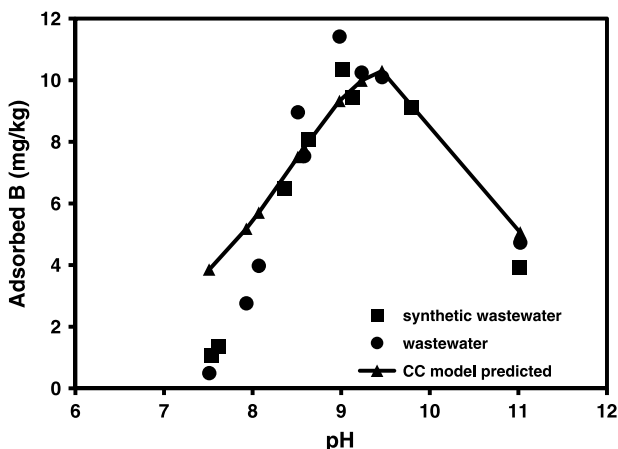


FIGURE 3. Boron adsorption as a function of solution pH from synthetic and recycled wastewaters by Tranquillity soil. Experimental data are represented by squares for synthetic wastewater and circles for recycled wastewater. The constant capacitance model prediction is represented by a solid line.

- Communar G., and R. Keren. 2008. Boron adsorption by soils as affected by dissolved organic matter from treated sewage effluent. *Soil Sci. Soc. Am. J.* 72:492–499.
- Cotlove E., H. V. Trantham, and R. L. Bowman. 1958. An instrument and method for automatic, rapid, accurate, and sensitive titration of chloride in biologic samples. *J. Lab. Clin. Med.* 51:461–468.
- Davis J. A., and D. B. Kent. 1990. Surface complexation modeling in aqueous geochemistry. *Rev. Mineral.* 23:117–260.
- Elrashidi M. A., and G. A. O'Connor. 1982. Boron sorption and desorption in soils. *Soil Sci. Soc. Am. J.* 46:27–31.
- Gee G. W., and J. W. Bauder. 1986. Particle-size analysis. *In: Methods of Soil Analysis*. Part 1. 2nd ed. Klute A., et al. (eds.). Agron. Monogr. 9, ASA and SSSA, Madison, WI, pp. 383–411.
- Goldberg S. 1992. Use of surface complexation models in soil chemical systems. *Adv. Agron.* 7:233–329.
- Goldberg S., and R. A. Glaubig. 1986. Boron adsorption on California soils. *Soil Sci. Soc. Am. J.* 50:1173–1176.
- Goldberg S., S. M. Lesch, and D. L. Suarez. 2000. Predicting boron adsorption by soils using soil chemical parameters in the constant capacitance model. *Soil Sci. Soc. Am. J.* 64:1356–1363.
- Goldberg S., and D. L. Suarez. 2006. Prediction of anion adsorption and transport in soil systems using the constant capacitance model. *Surface complexation modeling*. *In: Interface Science and Technology Series*. Lützenkirchen J. (ed.). Elsevier, Amsterdam, pp. 491–517.
- Harada T., and M. Tamai. 1968. Some factors affecting behaviour of boron in soil. I. Some soil properties affecting boron adsorption of soil. *Soil Sci. Plant Nutr.* 14:215–224.
- Herbelin A. L., and J. C. Westall. 1999. FITEQL: A computer program for determination of chemical equilibrium constants from experimental data. Rep. 99–01, Version 4.0, Dep. of Chemistry, Oregon State Univ., Corvallis.
- Israel Water Authority. 2015. Welcoming Note: Towards World Water Form VII. Integrated Water Resources Management—The Israeli model. 7th World Water Forum 2015. <http://www.water.gov.il/Hebrew/Pages/Water-Authority-Info.asp> (accessed May 1, 2017).
- Keren R., and G. Communar. 2009. Boron sorption on wastewater dissolved organic matter: pH effect. *Soil Sci. Soc. Am. J.* 73:2021–2025.
- Kinniburgh D. G. 1985. ISOTHERM. A Computer Program for Analyzing Adsorption Data. Report WD/ST/85/02. British Geological Survey, Wallingford, United Kingdom.
- Lado M., A. Bar-Tal, A. Azenkot, S. Assouline, I. Ravina, Y. Emer, P. Fine, S. Dasberg, and M. Ben-Hur. 2012. Changes in chemical properties of semi-arid soils under long-term secondary treated wastewater irrigation. *Soil Sci. Soc. Am. J.* 76:1358–1369.
- Maas E. V. 1986. Salt tolerance of plants. *Appl. Agric. Res.* 1:12–26.
- Maurer M. A., F. S. Davies, and D. A. Graetz. 1995. Reclaimed wastewater irrigation and fertilization of mature 'Redblush' grapefruit trees on spodosols in Florida. *J. Am. Hort. Sci.* 120:394–402.
- Owen B. B. 1934. The dissociation constant of boric acid from 10 to 50°C. *J. Am. Chem. Soc.* 56:1695–1697.
- Qian Y. L., and B. Mecham. 2005. Long-term effects of recycled wastewater irrigation on soil chemical properties on golf course fairways. *Agron. J.* 97:717–721.
- Reboll V., M. Cerezo, A. Roig, V. Flors, L. Lapena, and P. Garcia-Agustin. 2000. Influence of wastewater vs groundwater on young *Citrus* trees. *J. Sci. Food Agric.* 80:1441–1446.
- Sharma K. R., P. C. Srivastava, P. Srivastava, and V. P. Singh. 2006. Effect of farmyard manure application on boron adsorption-desorption characteristics of some soils. *Chemosphere* 65:769–777.
- State of California. 2000. Code of Regulations, Title 22, Division 4, Chapter 3. Water Recycling Criteria. California Department of Public Health, Berkeley, CA.
- Sposito G. 1982. On the use of the Langmuir equation in interpretation of "adsorption" phenomena. II. The "two-surface" Langmuir equation. *Soil Sci. Soc. Am. J.* 46:1147–1152.
- Su C., and D. L. Suarez. 1995. Coordination of adsorbed boron: A FTIR spectroscopic study. *Environ. Sci. Technol.* 29:302–311.
- US EPA. 2004. Guidelines for Water Reuse. EPA 625/R-048/108, Environmental Protection Agency, Washington, DC.
- Yermiyahu U., R. Keren, and Y. Chen. 1995. Boron sorption by soil in the presence of composted organic matter. *Soil Sci. Soc. Am. J.* 59:405–409.
- Yermiyahu U., A. Ben-Gal, and R. Keren. 2011. Boron. *In: Use of treated wastewater in agriculture: Use and impacts on the soil environment and crops*. Levy G. J., P. Fine, and A. Bar-Tal (eds.). Blackwell Publishing, Oxford, UK, pp. 216–233.
- Zekri M., and R. C. J. Koo. 1994. Treated municipal wastewater for citrus irrigation. *J. Plant Nutr.* 17:693–708.