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Boron Speciation in Soils Irrigated with Fresh and Effluent Municipal Waters

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Boron (B) excess/toxicity is an important disorder that can limit plant growth on soils of arid and semiarid environments. Although of considerable agronomic and environmental importance, our understanding of B biogeochemical behavior and fate is rather fragmented and limited (Gupta et al., 1985; Yermiyahu et al., 2001). Irrigation water is one of the main sources of high B levels resulting in toxicity in the field. Various fractionation/speciation techniques have been developed for soil B to distinguish its forms (Jin et al., 1987; Tsadilas et al., 1994; Hou et al., 1996) utilizing methods originally developed for selective extraction of different soil fractions. Surprisingly, only a few works have considered the necessity to include B-organic matter-bound forms in their schemes: synthetic soils were tested for B-organic fractions by Hou et al. (1996), and Yermiyahu et al. (2001) studied the effect of composted organic matter on B uptake by plants.

The objectives of the presented work were: (1) approach to detailed B speciation within principal humus and inorganic soil components, and (2) to evaluate B behaviour/potential mobility of soils irrigated with fresh and effluent waters.

Objects and Methods

The objects were two grumosol profiles in the western Galilee, Israel. Profile *AC* of highly consolidated soil material is filled with carbonate pellet debris and has high water pH of 8.24–8.34. Deep cracks are developed during the dry season due to high contents of the swelling clay minerals. The soils had been irrigated for four years: one profile - p. 1 with fresh waters, another one - p. 2, situated 15 m off, with effluent municipal water from the City of Akko (Acre). Samples were collected within the profile depths. Air-dried and sieved (1 mm) sample aliquots have been processed by a series of chemical extractions with subsequent B determination of the extract by the ICP-AES method. The extraction scheme (Table 1) is based mostly on the adopted soil chemistry procedures and also some specific works on the subject (Mehra and Jackson, 1960; Schwertmann, 1964; Duchaufour and Jacquin, 1975; Zonn, 1982; Plotnikova and Ponomareva, 1980; Orlov and Grishina, 1981; Schnitzer, 1982; Swift, 1996). Some basic soil parameters and components to verify the extraction scheme were also determined, namely: pH and conductivity of soil-water suspension and contents of Fe, Mn, Ca, Mg, and carbonates. We did not use the method of hot-water B extraction, which dominated for many years in soil testing for plant-available B, as many researchers marked some problems of material significance associated with this method, such as precision, problematic comparability of the basic soil parameters determined routinely, etc. (Miller and Vaughan, 1999; Shiffler et al., 2005).

Plastic labware was used throughout. The labware contacting samples and extracts were precleaned by filling them with or soaking them in 3% HNO_3 solution for 48 hours. The detection limit for B, calculated as three times the standard deviation of the procedural blank, was 0.02 ppm.

Results and Discussion

The total B contents in the soils studied were rather high—32.5–34.7 ppm for p.1 (fresh water) and 38.0–43.0

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Table 1 Soil boron extraction scheme

Step	Procedure	Fraction (extract)
1.	H_2O, 4 h, continuous agitation	Water soluble B compounds
2.	0.1 *M* HCl	De-calcination, B in carbonates
3.	0.1 *M* NaOH, separation with 1 *M* HCl	Humus acids, fraction I: black humic, hymatomelanic, and fulvic acids bound to exchangeable Ca
	3.1. acid-soluble portion	Fulvic acids (I)
	3.2. acid-insoluble portion	Humic acids (I)
	3.3. extracting with ethanol from freshly isolated humic acids, 8 h	Hymatomelanic acids (I)
4.	0.02 *M* NaOH, overnight at 60 °C, separation with 1 *M* HCl	Humus acids, fraction III: brown humic, hymatomelanic, and fulvic acids bound to clay minerals and non-refractory sesquioxides
	4.1. acid-soluble portion	Fulvic acids (III)
	4.2. acid-insoluble portion	Humic acids (III)
	4.3. Extracting with ethanol	Hymatomelanic acids (III)
5.	0.1 *M* NH_2OH-HCl	Easily-reducible Mn formations
6.	0.2 *M* $(NH_4)_2C_2O_4$ + 0.2 *M* $H_2C_2O_4$ pH3	Moderately reducible phases – amorphous Fe-hydrous oxides
7.	0.2 *M* Na-citrate + 0.05 *M* citric acid + $Na_2S_2O_4$, 30 min at 40 °C	Non-silicate (free, non-crystalline) Fe
8.	HCl:HF (1:1), shaken 12 h (x2)	Aluminosilicates
9.	0.2 *M* NaOH (x3)	Humin
10.	Difference of total and sum of extracted B fractions	Residual B

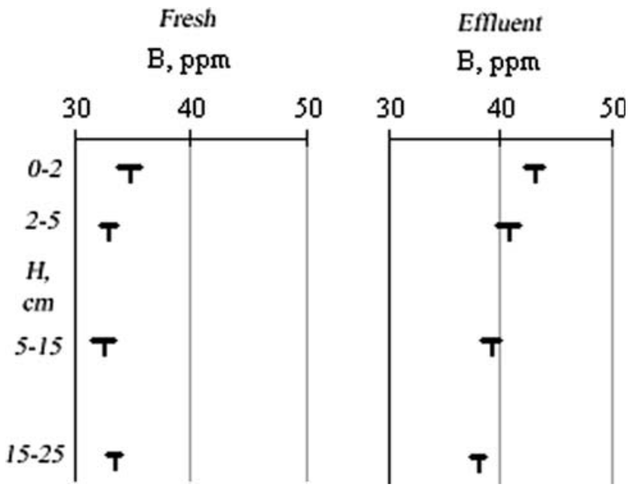


Fig. 1 Contents of boron of grumosol profiles irrigated four years with fresh and effluent municipal water

ppm for p. 2 (effluent water) (Fig. 1). Typical soil B concentrations reported are 2 to 100 ppm, whereas most of the earth's soils contain <10 ppm (Kabata-Pendias and Pendias, 1995). B contents in the effluent-irrigated profile were 17–25% as higher compared to the ''fresh'' one.

To all appearances, the ''soft'' extraction with distilled water reflects the contents of the most labile components of the soils. Water B concentrations were from 0.15 ppm in the upper 0–2 cm to analytical zero (<0.02 ppm) in the lower 15–25 cm for p.1, while it was significantly higher for the p.2—from 0.52 to 0.19 ppm, that is, disproportionately higher than the increase of the total B contents (Fig. 2). According to some authors, B contents in interstitial water in the range of 0.5 to 5.0 ppm may have a deleterious effect on plant growth (Gupta et al., 1985).

The 0.1 *M* HCl soluble fraction contains the elements co-precipitated with carbonates that are a loosely bound phase and liable to change with environmental conditions. Renan and Gupta (1991) found that extraction with 0.05 *M* HCl worked well for predicting B bioavailability to crop plants in acid soils. In our case, in spite of the high contents of carbonates, including carbonate detritus—10.3–11.5%, B contents of 0.1 *M* HCl extract was only 0.14–0.19 ppm and 0.21–0.33 ppm, i.e., some 0.4–0.6% and 0.6–0.8% of total B contents, correspondingly (Fig. 2).

The B pool within the extractable humus fractions turned out to be one of the three major B pools of all extractable fractions (Fig. 3). Moreover, B contents within humus acids of p. 2 ''effluent'' were 1.8–2.5 times higher compared to p. 1 ''fresh''. More condensed and chemically and microbially resistant components of extractable humus acids were the most effective B concentrator: for the p. 1 ''fresh'' they were humic acids (I) as well as hymatomelanic acids (I) (Fig. 4). B has been detected in all the humus fractions separated for the p. 2 ''effluent,'' first of all,

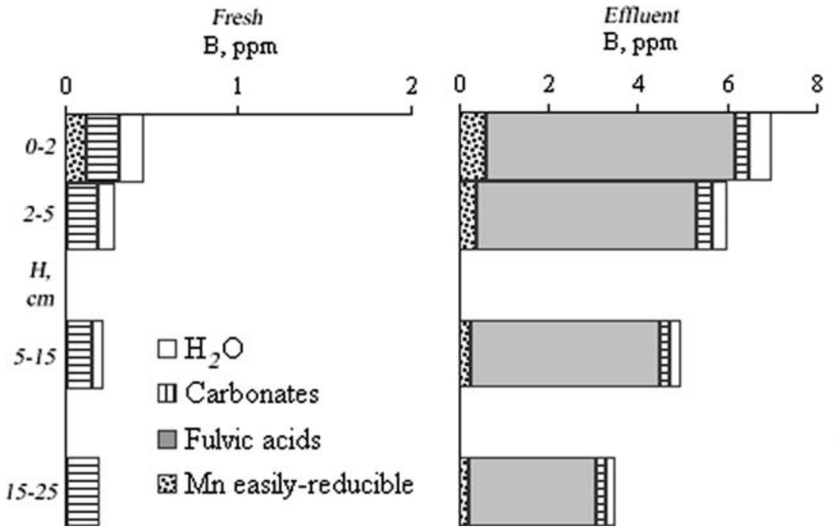


Fig. 2 Contents of boron of mobile/(potentially) bioavailable fractions of the soil

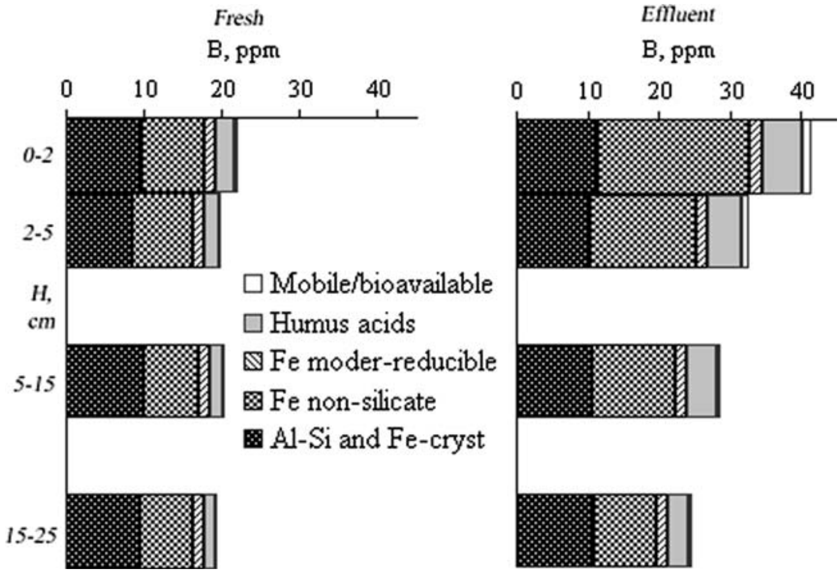


Fig. 3 Contents of boron of principal components of the soil

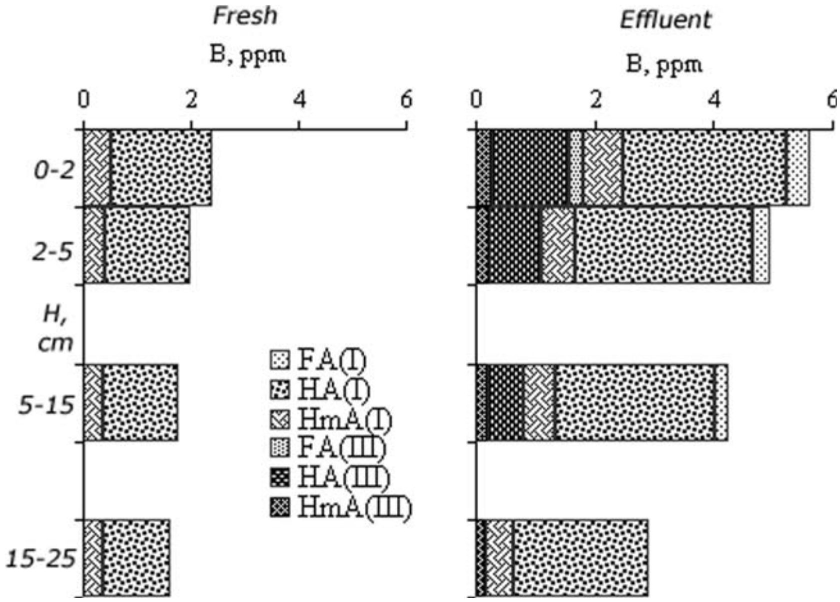
humic acids (I) and (III), as well as hymatomelanic acids (I) and (III). At that, a noticeable quantity of B was bound to fulvic acids (Fig. 4) that are mobile in soil solutions and natural waters. Thus, the humus of grumosol studied is an effective B concentrator. Moreover, a major B pool, including excess B unloaded with effluent waters, was bound to the most condensed and resistant soil organic components—humic acids and hymatomelanic acids of fraction I, related to exchangeable Ca, as well as to humic acids and hymatomelanic acids of fraction III ‘‘bound exchangeably to sesquioxides and aluminosilicates’’ (Ponomareva and Plotnikova, 1980). Contamination with excess B resulted in the existence of significant mobile organically bound B pool within fulvic acids.

Some B quantity has been released from the p. 2 ‘‘effluent’’ and the uppermost 0–2 cm of p. 1 ‘‘fresh’’ with a hydroxylamine-hydrochloride solution that is believed to dissolute some easily reducible amorphous Mn and Fe formations—0.57–0.16 ppm (1.3–0.4% of total B) and 0.12 ppm (0.35%), correspondingly (Fig. 2). These formations are thermodynamically unstable under the anoxic circumstances and are attacked by benthic organisms (Li et al., 2001).

Another reagent fairly selective for dissolving moderately reducible amorphous Fe minerals is the oxalic acid/ammonium oxalate buffer (Schwertmann, 1964). The latter reagent was used in some sequential extraction schemes for leaching the moderately reducible fraction, being more effective over hydroxylamine hydrochloride (Zonn, 1982). In our case, this fraction contained 1.48–1.39 ppm B of ‘‘fresh’’ and 1.73–1.47 ppm B of ‘‘effluent’’ soil (Fig. 3).

The Na-citrate/Na-dithionite buffer is adequate for dissolving non-crystalline Fe oxides (free Fe, non-silicate Fe) (Mehra and Jackson, 1960; Zonn, 1982). This extract along

Fig. 4 Contents of boron of humus fractions of the soil: FA, fulvic acids; HA, humic acids; HmA, hymatomelanic acids



with the next step (aluminosilicates and crystalline Fe minerals) released the most sizeable pool of Fe during the study. The extraction yielded a considerable B quantity—7.95–6.75 ppm of ''fresh'' and 21.38–9.00 ppm of ''effluent'' soil, i.e., 23.5–20.2% and 49.7–23.7% of total B contents, correspondingly (Fig. 3). Moreover, whereas distribution of this B fraction is rather monotonous of the ''fresh'' profile, this is highly enriched in the upper 0–5 cm of the ''effluent'' one, indicating strong excess-B dependence on Fe unloaded with the effluent water.

Sequential dissolving with HCl + HF affected clay minerals and Fe crystalline minerals (Zonn, 1982). This step gave a large portion of B that is about equal to the preceding fraction for both the ''fresh'' and the ''effluent'' profiles (Fig. 3). This may indicate this fraction to be a conservative ''historical'' B pool, not involved in the active soil B transformations.

Surprisingly, no B has been detected in humin fraction. This fraction may also represent humus of aluminosilicates' intra-layers and minerals' mesopores. In our case, the humin extract obtained was of an intensive dark-brown colour that is typical of concentrated soil humus compounds. Recent investigations have shown that humin moieties exhibit sorption capacities several times greater than those of humic acids (Bucheli and Gustafsson, 2000). Nevertheless, in our case humin fraction turned to be sterile of B contents. Presumably, the rather harsh previous extraction step with HCl + HF could de-mineralise humin residue. A softer procedure for dissolving aluminosilicates should be tested instead.

A portion of B within residual pool, evaluated as a difference between total B contents and the sum of the extracted B fractions, is presented in Figure 5. One can conclude that four-year irrigation with effluent municipal waters has converted a major part of the most inert and resistant B compounds into extractable forms.

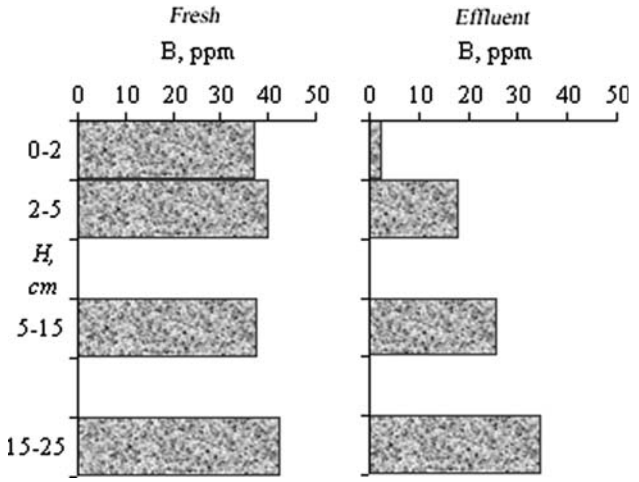


Fig. 5 Contents of boron in residual soil fraction

Thus, B contents in the effluent-irrigated soil were noticeably higher compared to the ''fresh'' one after four years of irrigation. Contents of B within mobile/(potentially) bioavailable fractions (water-soluble, fulvic acids, and amorphous Mn) increased dramatically in the ''effluent'' soil. However, the major B pool has been found within refractory organic—humic and hymatomelanic acids and inorganic components—amorphous and crystalline Fe minerals, aluminosilicates, and unidentified residue moieties.

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