



## On boron turnover in plant–litter–soil system



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### ABSTRACT

Boron (B) is an indispensable constituent of plant lignin structures inherited by soil humus compounds. However, little is known about plant litter as a factor of B turnover in the plant–soil system. Also, the sources of soil available B and the mechanism of its release and mobility are poorly understood. In a series of experiments, we considered (1) leachates from decomposing plant litter and leaves and (2) soil–water mobile phase ('soil solution') as the carriers and sources of potentially available B compounds. The obtained data showed that plant litter is the main source of available and water–mobile compounds of B to the soils; this is 1 to 3 orders of magnitude higher than the B income with rain and aerosol precipitation, and even more than the income from rock weathering. We can assume that the B turnover occurs in a semi-closed system 'plant–litter–soil' ('plant–litter–soil organic matter–soil water mobile compounds–available B'). Mobile colloids of particular size of  $0.20 < d < 0.45 \mu\text{m}$  were found to be the main carrier of the soil available B. The character of B release from the colloids indicated at least two forms of B bonding: (1) easy-exchangeable, which is pH-dependent, and (2) firmly-bound B–organic complexes.

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### 1. Introduction

Boron (B) is an essential element for the healthy growth and functioning of higher plants (e.g. Blevins and Lukaszewski, 1998). Unlike most other micronutrients, plant roots require a continuous external supply of trace amounts of B, otherwise loss of membrane function occurs within minutes (Blaser–Grill et al., 1989). The concentration must be low enough not to have any adverse effect on plants. Apparently, the content of available B in the soil water–mobile phase ('soil solution') must be controlled by an effective buffer system (Asad et al., 1997). However, the turnover of B in plant–soil systems and the mechanism of replenishment of soil available B are poorly understood. The income with atmospheric precipitation and from rock weathering is often mentioned. However, concentration of B in precipitation, according to contemporary data, is rather low (e.g. Kot, 2009, 2015), while weathering seems to be too slow a process (Park and Schlesinger, 2002). Until recently, only a few works have considered soil organic matter as a factor

of the B turnover (e.g. Kot, 2009; Kot et al., 2012). For example, most studies on B in soil and the soil–plant system were focused on inorganic B interactions, and, as a rule, the experimentation involved high and very high doses of boric acid applied to clays and Fe/Al oxy-hydroxides. Little is known about the role of plant litter as a source of B in spite of the fact that plant B is a binding constituent of plant cell walls and membranes lignin (95–98% of the bulk plant B according to Matoh et al., 1992), whereby it enters soil humification processes. Kot et al. (2012) found a substantial part or even most of the soil B to be bound firmly (not exchangeably) to resistant fractions of humus, such as humin and humates, as well as to fulvates, confirming that these compounds are inherited from plant lignin. One could expect the plant litter and soil organic matter/humus to be a major source of available B.

Thereby, the important questions on B turnover in the plant–soil system arise, namely: (1) what the main source(s) of (available) B to soil is, (2) the role of plant litter, and (3) the role of soil humus (humic) substances.

The presented work consists of two parts, which include: (1) evaluation of B balance in the system 'soil–plant' based on both experimental data on B leaching from plant litter and leaves obtained in the presented work and the published data on atmospheric precipitation and rock weathering, and (2) experiments on the release of available B from the soil water–mobile phase ('soil solution').

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## 2. Material and methods

The objects were: (1) a collection of eastern Mediterranean soils, namely: Grumosol (FAO: Chromic Vertisol), Terra rossa (Cambisols), Loess (Calcic fluvisols), Sandy (Arenosols), Peaty-clay (Histosols), and Red sandy-loam (Hamra; FAO: Luvisols). The soils under study were irrigated in different modes: with fresh water, reclaimed waste-water and brackish water, with one plot of non-irrigated Grumosol. Some general parameters of the soils can be found in Table 1; (2) leaves and litter of three species of tree plants of different concentration of B (Table 2), and representing contrast ecosystem niches, namely: oak (*Quercus robur*), carob (*Ceratonia siliqua*), and willow (*Salix babylonica*).

The plant leaves and litter from under the same trees were put into plastic flowerpots – in accordance with the surface square from which they were collected. The freshly-picked leaves may reflect the initial stages of plant litter decomposition. Rain events were imitated by spraying of distilled water on the litter and leaves in a ratio of 1:1 of water to plant material, by weight, to maintain the plant material as wet and enable the decomposition process. In due time, the pots were sprayed with the usual portion of water, and 3 h later, an additional portion of water was sprayed on to enable washing through the decomposing material; the percolated leachates were collected in the under-pot saucer and filtered through the Whatman membrane filters with a pore size of 0.45  $\mu\text{m}$ .

Soil water extracts were obtained by sporadic gentle handle shaking of the soil with added distilled water in a ratio of 1:1, by weight, for 30 min and were then separated onto colloidal dimensions with membrane filters with pore sizes of 0.20, 0.45 and 1.20  $\mu\text{m}$ .

Boron in the leachates and extracts was concentrated on B-specific ion-exchange compounds grafted with N-methyl-glucamine (NMG) functional groups, namely (1) Amberlite IRA 743 resin (Sigma-Aldrich, Steiheim, Switzerland) and (2) NMG-fibre, for large volume extracts (Ikeda et al., 2011), supplied from Department of Applied Chemistry and Biotechnology, Chiba University, Japan. The unique efficiency and specificity of the N-methyl-glucamine functional group toward B was exploited. The NMG-functional group forms very stable complexes with  $\text{B}(\text{OH})_3$ ,  $\text{B}(\text{OH})_4^-$  (Lyman and Preuss, 1957) and probably with other B compounds. The mechanism of complexation of boric acid and borate with N-methyl-glucamine group is still a matter of discussion (e.g. Yoshimura et al., 1998; Lou and Foutch, 2015).

We presumed that NMG-functional groups can compete with B polyol compounds, which are ubiquitous in biological systems and the inherited soil organic matter, for the complexing of B compounds. To check this assumption, an experiment on extraction of B with Amberlite IRA 743 from B-mannitol complexes/mixture was performed. During the experiment, the solutions of 0.05 M mannitol and 0.0015 M B-B(OH)<sub>3</sub> in distilled water, i.e. in the ratio of 33:1 approximately, were prepared and

**Table 2**

Concentration of B and K in plant leaves and litter, mg kg<sup>-1</sup>, d.w.

	Oak ( <i>Quercus robur</i> )	Carob ( <i>Ceratonia siliqua</i> )	Willow ( <i>Salix babylonica</i> )
	Leaves/litter	Leaves/litter	Leaves/litter
B	45.9/71.1	51.5/113	167/80.0
K	4800/7320	5370/11,540	16,900/8200

adjusted to pH values of 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, and 8.5 with solutions of 0.1 M NaOH and 0.1 M HCl. All variants were made in triplicate.

As Makkee et al. (1985) showed, at a mannitol concentration of at least 0.5 M and at a B-B(OH)<sub>3</sub> concentration of 0.1 M, i.e. the mannitol to B ratio of 5:1, the free boric acid concentration was essentially zero at pH values greater than ~8 and the bis-mannitol ester and the mono-mannitol ester were present at a ratio of 9:1. According to Geffen et al. (2006) complexation of B(OH)<sub>3</sub> with mannitol as a function of the pH showed that at pH ~7.7 and higher and for a mannitol to B-B(OH)<sub>3</sub> ratio of 5:1 and at pH 8.8 for a mannitol to B-B(OH)<sub>3</sub> ratio of 2:1, complexation goes to completion. That is, at the mannitol and B(OH)<sub>3</sub> concentrations and ratio set in the present experiment, boric acid must have been complexed completely at pH ~8 and higher.

The results of the experiment are shown in Fig. 1.

One can see that at pH ~8.0–8.5, where B(OH)<sub>3</sub> was expected to be as 100% bound with mannitol, from 47.7 to 52.3% of B was effectively taken away by B-specific NMG-functional groups of Amberlite IRA 743. Most probably, the same effect took place during application of Amberlite IRA 743 and NMG-fibre to the samples of soil-water extract and leachates from plant litter and leaves. From this, in all probability, the application of the NMG-grafted compounds affected not only boric acid and borates in the extracts and the leachates, but also the B-polyol complexed compounds.

The results of the experiment showed that NMG-groups can compete effectively with polyol compounds for the bonding of B. Thus it can be concluded that extraction with the compounds grafted with NMG-functional groups can affect not only dissolved boric acid and borates, but also B naturally complexed compounds.

As Irschik et al. (1995) found, the naturally occurring biological compounds of B isolated from microorganisms (boromycin, aplasmomycin and tantrolon B) as well as the sorbitol and rhamnogalacturan-II complexes from plants (Kobayashi et al., 1996) are involved in the complexation of the polyols type. Given the ubiquity of -OH groups in biological molecules, more examples will no doubt be found (Power and Woods, 1997). In addition, it is quite probable that other types of B complexation may be observed, particularly with nitrogen (e.g. as with serine; Woods, 1996).

**Table 1**

General parameters of the soils investigated.

Soil	Treatment	B total, mg kg <sup>-1</sup>	pH	C <sub>org</sub> , %	EC (1:3), ds m <sup>-1</sup>	N total, mg kg <sup>-1</sup>	Al <sub>2</sub> O <sub>3</sub> , %	CaO, %
Grumosol (Akko)	Fresh water	78.2	7.4	1.65	0.2	9.1	7.29	7.48
	RWW	84.2	7.3	1.49	0.4	13.2	12.0	1.67
	Non-irrigated	84.2	7.8	0.90	0.2	8.2	13.2	3.30
Grumosol (Hula valley)	Fresh water + manure	89.0	7.9	2.96	0.4	15.5	13.9	4.87
	Fresh water + mineral fertilisers	86.3	8.0	1.50	0.4	18.9	13.3	7.63
Terra rossa	Fresh water	86.8	7.5	3.59	0.3	20.2	11.3	5.67
	RWW + manure	85.2	7.6	11.1	0.6	38.5	10.9	7.18
Hamra (sandy loam)	Fresh water	58.1	7.5	1.10	0.3	7.7	1.59	1.27
	RWW	60.1	7.3	0.65	0.5	43.2	3.14	0.43
Peaty-clay (Hula valley)	Fresh water + mineral fertilisers	88.3	7.5	6.78	2.6	18.1	12.2	8.43
	Sandy	62.1	7.7	0.15	0.9	16.4	1.66	1.36
Loess	Fresh water	67.8	7.5	0.61	0.7	32.4	1.47	1.47
	Organic farming	58.4	6.8	0.61	0.4	91.3	1.59	0.99
	RWW	81.1	7.7	0.93	0.4	15.5	6.65	5.40
	RWW	81.3	7.9	0.89	0.6	17.7	7.25	4.89
	Brackish water	79.8	7.8	0.97	0.7	34.2	5.78	5.43

RWW – reclaimed waste water.

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