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Phytoremediation with Plants for Soils Polluted by Boron at Akdagmadeni Pb-Zn Mining District and Surroundings, Yozgat, Turkey

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ABSTRACT

The amount of elements in plants is important for biogeochemical explorations. In this study 28 plant species and soil samples were collected from boron deposit area in Akdağmadeni. Boron is determined in plants and soil samples. Additionally, statistical relations were established between the boron values of plant and soil samples.
Metal pollution has become one of the most serious environmental problems. Phytoremediation utilizes plants uptake contaminants and can potentially be used to remediate metal-contaminated sites.
The present study investigates boron uptake from soil by different organs of *Astragalus pycnocephalus Fischer* and *Verbascum euphraticum L.* The concentration of this metal was measured in the roots, shoots, leaves, and the soil. Assay results show that the highest accumulation of boron was found in the roots. In addition, the determination of an enrichement coefficient and a translocation factor showed that both plant types were suitable for phytoremediation of boron.

Keywords:*Biogeochemical, Heavy metals, Soil, Phytoremediation.*

1. INTRODUCTION

Boron (B) does not form naturally and has complex chemistry. Elemental B is found in solid phase at room temperature. While in contact with strong oxidants, B turns into an inert metalloid [1]. Despite it presents less amounts in nature, B commonly exists in lithosphere and hydrosphere. B amount in rocks is determined as 5-10 mg/kg [2] and in oceans it is around 4.5 mg/l [3].

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Event hough B is essential for plant growth in low concentrations, excessive concentrations in soils are very toxic to plants. Visual symptoms of B toxicity include leaf burn, i.e., chlorotic or necrotic patches often at the margins and tips of older leave sand reduced root and shoot elongation [4].

B is one of the essential micro-nutrition elements for plants. It is observed that B is one of the eight essential micronutrients, known as trace elements, required for the normal growth of most plants. It is the only non-metal among the plant nutrients [5].

Some studies asserts that, B take a part in lots of metabolic activities such as sugar transportation, cell wall synthesis, lignization, carbohydrate and RNA metabolism, respiration, phenol metabolism and membranes [6].

Main nutritional problem limiting the crop production is lack of usefulness of nutrients in the soil. In the plants growing at arid and semi-arid regions, B toxicity harms crop production [5, 7].

Some plants which were used for removing unwanted heavy metals from soil are called phytoremediation. Likewise to the change in amount of accumulated heavy metals, effect of the element on the substances synthesized by plant depends to species and mobility of the element. Phytoremediation is a new alternative technology for environmentally destructive physical and chemical remediation [4, 8] methods of pollutants in soil. The most important advantages of the method are effectiveness, easiness and cheapness and recently the most preferred method [9, 10]. Moreover, phytoremediation provides minimal environmental troubles since it does not change the soil matrix. Therefore, soil can be used for agricultural activities directly after from successful phytoremediation [11].

As current technologies for B removal are neutralize, considerable attention is being given to the use of B containe plants for B phytoremediation. Different types of phytoremediation strategies for B-polluted soils, have been studied: phytoextraction, phytorestoration, evapotranspiration and constructed wetlands.

Phytoextraction consists of planting containe plants that can take up a contaminant it to their upper parts. The contaminant is then removed by harvesting the plant shoots. To phytoextract a metal (or metalloid), plants must be able to develop in highly polluted soil sand accumulate the element in their aerial tissue. For phytoextraction, hyperaccumulator plants are preferred [4]. Two ratios are used to define a plant as a hyperaccumulator: the Enrcihment Coefficient (EC) and the Translocation Factor (TF). EC is the ratio of element concentration in the plant shoots or leaves or roots to its total concentration in the soil [12]. TF is the ratio of the element concentration in the plant shoots or roots to its concentration in the plant roots. If EC> 1 and TF > 1, the species may be classified as a hyperaccumulator [13, 14, 15].

The term hyperaccumulator was firstly used for plants containing nickel (1000 µg g-1) [16]. Lately, due to As content of fern, this term has been using more frequently [17]. However, B accumulator of plants is barely known in recent.

The purpose of this work was to determine the potential of *Astragalus pycnocephalus Fischer (A. pycnocephalus)* and *Verbascum euphraticum L. (V. euphraticum)* for B phytoremediation purposes.

The soil samples were analyzed and the plant species identification confirmed by chemistry analyses. B accumulation in the shoots, leaves and roots of the plants and B concentrations in the soil were determined. Finally, to establish whether the species acted as an accumulator in the study site, the TF and EC were calculated. Furthermore, plant species are defined by phytoremediation method.

2. MATERIAL AND METHOD

2.1. The Study Area

In this study, the plant and soil samples were collected from an area of the metamorphic and granitic rocks in the Akdagmadeni mining district where 120 km East of Yozgat province Central Anatolia (Figure 1)

Figure 1. Location map of the study area.

Magmatic rocks in the area have granitic and syenitic characteristics. According to modal and mineralogical analyses, granitic rocks have monzogranitic composition. Granitic rocks in the study area are cropping out with E-W strike. Besides, it is cropping out in a very limited

area. Upper Cretaceous-Paleocene aged granites are cross cutting metamorphic rocks [18, 19] (Figure 2).

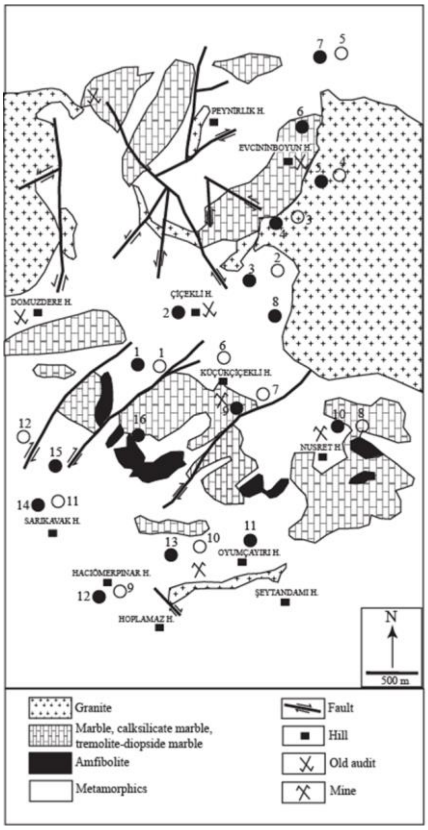

Figure 2. Topographical map of surroundings of Akdagmadeni Pb-Zn deposit and soil-plant sample locations [Modified from 19] (●: *A. pycnocephalus Fischer,* o: *V. euphraticum L.*).

Primary sulphide and oxide minerals found in the Akdagmadeni Pb-Zn mine are sphalerite, galenite, pyrite, chalcopyrite, pyrotin, bornite, molybdenite, sulfosalts, magnetite, hematite, ilmenite and rutile. Secondary minerals found in the mine are limonite, sericite, martite, chalcosine and covellite. Besides, graphite is commonly present in wall rock and ore bodies. Garnet, clinopyroxene, epidote, tremolite, calcite, quartz, chlorite and lesser amount of vezuvian, vollastonite, actinolite, clinozoisite, titanite, fluorite and ilvaite are present as gangue minerals. In addition, fluorite and barite veinlets are present in marble and syenite [19].

The plant samples, together with their roots and soils were taken from twenty-eight sites (sixteen *A. pycnocephalus* and two teen *V. euphraticum*) of the study area. Among the plant species that grow in this area, *A. pycnocephalus* and *V. euphraticum* were examined for B content in this study. These plants were chosen because they are native and dominant species in the study area (Figure3).

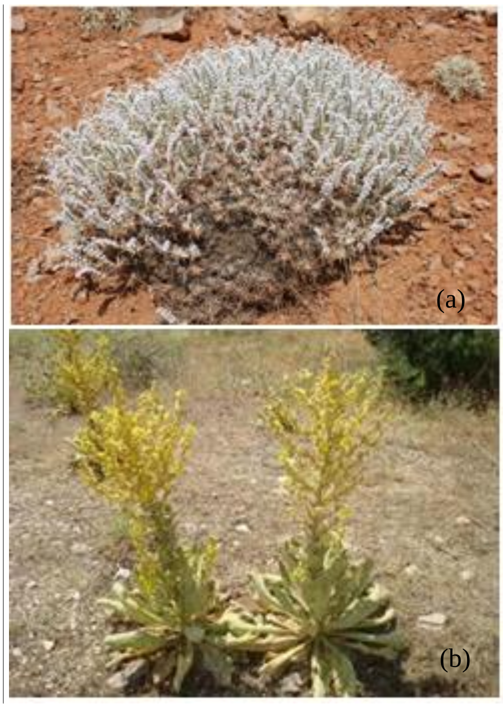

Figure 3. The photographs of the plant species; (a) *A. pycnocephalus,* (b) *V. euphraticum.*

2.2. Preparation of Samples

2.2.1. Soil Samples

The soil samples were also collected at a depth of 20–25 cm and surrounding the roots of the plant. After transportation to lab, large stones and plant debris were removed from the soil samples, air dried at room temperature, and sieved through a 2-mm nylon sieve.

Soils typically undergo two stages of preparation consisting of drying and screening. At BVML (Bureau Veritas Minerals LaBatories) we dry these materials at 60°C to minimize loss of volatile elements (eg. Mercury). However, for some analyses drying at < 40°C may be required for specific weak leaches. Soils is screened to -180 microns (-80 mesh ASTM). Analysis consists typically of two stages comprising extraction of the desired elements into a solution and element determination by instrumental analysis of the solution. Extraction can be partial to measure only the interesting portions (eg. sulphides) of the elements or the extraction can be total to measure the total abundance of the elements from all minerals in the sample. BVML offers two principle means of determination; Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma-Mass spectrophotometry (ICP-MS). ICP-OES measures the light-waves and light intensities to determine what elements are present in the solution and the quantities of each. ICP-MS measures the element concentrations by counting the atoms for each element present in the

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solution. Generally, ICP-MS can determine concentrations that are 1 to 2 orders of magnitude lower compared to ICP-OES [20].

Typically the ICP-MS or ICP-OES are selected for soil surveys to provide the broadest array of elements coupled with lowest detection limits (B:1 mg/kg) to ensure maximum exploration power at ACME Analytical Labs, Vancouver, Canada [20].

2.2.2. Plant Samples

The plant samples were randomly collected from the sites determined in accordance with a pattern representing the whole characteristics of the Akdagmadeni mining area. After collection, the plants were separated into shoots and roots. Plant shoots were rinsed thoroughly in deionized water while roots were properly washed with tap water and finally with deionized water to remove all visible soil particles. The washed plant samples were air-dried at room temperature.

ICP-MS has become a popular technique in the multi element analysis since the first commercial instrument became available in 1980s. Semi quantitative analysis by ICP-MS has proven to be a powerful tool for fast screening, in addition, it does not require the element of interest to be present in the calibration standard, making it especially useful for the analysis of unknown samples [21].

Higher temperatures are required for ashing up or flameless burning of the plant samples and previous studies suggested temperatures varying from 475 ^{0}C up to 600 ^{0}C [22]. The dried plant samples (approximately 2.0–3.0 g) were ashed by heating at 250 ^{0}C, and then the temperature was gradually increased to 500 ^{0}C for two hours [23]. Analyzed using ICP-OES and ICP-MS techniques at ACME Analytical Labs, Vancouver, Canada [20].

The ashed samples were digested for an hour at 95 ^{0}C by using the mixture of HCl - HNO_3- H_2O (6 ml of the mixture of 1:1:1 was used per 1.0 g of the ashed sample). Then the ashed samples were analysed by Aqua Regia digestion after extraction by using microwave digestion system [21]. Precision value were calculated according to repeated analysis values. The ashed samples analysed by ICP-MS for ultralow detection limits which is as follow; B: 1 mg/kg.

2.3. Enrichment Coefficient (EC) and Translocation Factors (TF)

The EC was considered to determine the quantity of heavy metals absorbed by the plant from soil. This is an index of the plant to accumulate a particular metal with respect to its concentration in the soil and is calculated using the formula [24, 25, 26]:

Enrcihment Coefficient (EC) = (Metal amount in plant / Metal amount in soil)

To evaluate the potential of plant species for phytoremediation, the TF was considered. This ratio is an indication of the ability of the plant to translocate metals from the roots to the aerial parts of the plant [12, 26, 27]. It is represented by the ratio:

Translocation Factor (TF) = (Metal amount in the leaf or shoot of the plant / metal amount in the root of plant)

Translocation factor and enrichment coefficient can be used in evaluation of heavy metal accumulation in plants. Translocation factor greater than 1 indicates that metals are transported from root to leaves whereas; enrichment coefficient value greater than 1 indicates that plant can be identified as hyperaccumulator [14, 15, 28]. Some researchers assert that some plants are hyperaccumulator despite that the enrichment coefficients of those are less than 1 [28].

According to the studies conducted lately, translocation factor and enrichment coefficient of plants must be greater than 1 in order to classify that plant as hyperaccumulator [14, 15].

All the enrichment coefficients of *A. pycnocephalus* and *V. euphraticum* samples taken from study area are greater than 1. However, translocation factors of *A. pycnocephalus* and *V. euphraticum* are less than 1 at all locations except A9 and V5 (Table 1 and 2).

Table 1. B content in root, shoot, soil and leaf of *A. pycnocephalus* (A1-A16) in the study area (mg/kg).

Plant	Soil	Root	Shoot	Leaf
A1	5	220	77	100
A2	4	287	235	99
A3	2	186	139	153
A4	11	398	188	139
A5	6	378	173	169
A6	11	386	252	68
A7	7	98	65	43
A8	6	234	80	62
A9	7	127	39	130
A10	12	523	106	192
A11	5	234	203	150
A12	5	195	169	49
A13	2	407	152	202
A14	12	212	73	56
A15	6	352	154	182
A16	16	370	194	197
Min	2	98	39	43
Max	16	523	252	202
Mean	7.3	287.9	143.6	124.4
S. D.	3.9	117.5	64.2	56.6

Table 2. B content in root, shoot, soil and leaf of *V. euphraticum* (V1-V12) in the study area (mg/kg).

Plant	Soil	Root	Shoot	Leaf
V1	3	335	241	114
V2	3	473	195	112
V3	7	306	136	107
V4	4	436	152	162
V5	5	115	151	75
V6	5	475		94
V7	4	286	217	140
V8	4	162		66
V9	5	357	262	146
V10	7	518	209	304
V11	2		210	226
V12	12		171	350
Min	2	115	136	66
Max	12	518	262	350
Mean	5.08	346.3	194.4	158
S. D.	2.6	134.6	41.3	90.1

3. Results and Discussion

3.1. Boron Concentrations in Soils

B holds in soil depends upon many factors, such as, B concentration of the soil, texture, cations exchange capacity, organic matter, exchangeable ion composition and the type of clay and mineral coating on clay.

B content of soil samples taken from where *A. pycnocephalus* and *V. euphraticum* grow on listed in Table 1 and 2. B concentration of soil depends on the plant species. Maximum and minimum B concentration of soil on which *A. pycnocephalus* and *V. euphraticum* plants grown are 2-16 mg/kg and 2-12 mg/kg respectively. In figure 3, it can be seen that soil values are lower than values of plant tissues.

In the study conducted at Kavala Prefecture area located at North of the Greece, B amount in soil were determined between 8.3-26.6 mg/kg [29]. In the soil sample taken from Rajasthan area of India, B amount is 0.01 ppm [5].

Depending on the parent material and disintegration degree of parent material, total B content of soil changes from 20 mg/kg to 200 mg/kg. In addition, B content of sandy soils is 5-20 mg/kg and clay and humic soils contain 30 to 80 mg/kg B [11].

3.2. Boron Concentrations in Plants

Metal concentration of plants changes with species of plants. Plants carry metals they obtained from soil either to water by its roots or to other tissues [30].

Total B amount of soils changes between 2-200 ppm and plants can benefit from less than 5% of this amount [31].

Total 28 plant samples were taken from Akdagmadeni Pb-Zn mine and its surroundings. B concentrations in roots of *A. pycnocephalus* and *V. euphraticum* are lowest at locations A7 (98 mg/kg) and V5 (115 mg/kg) and highest at locations A10 (523 mg/kg) and V10 (518 mg/kg). B concentrations in shoot and leaves of *V. euphraticum* are higher than that of *A. pycnocephalus* (Table 1 and 2). At almost every location, B concentrations in the roots of both plants are higher than the concentrations in shoot and leaves. However, in root and leaves at location A9; in shoot at location V5 have higher B values (Figure 4).

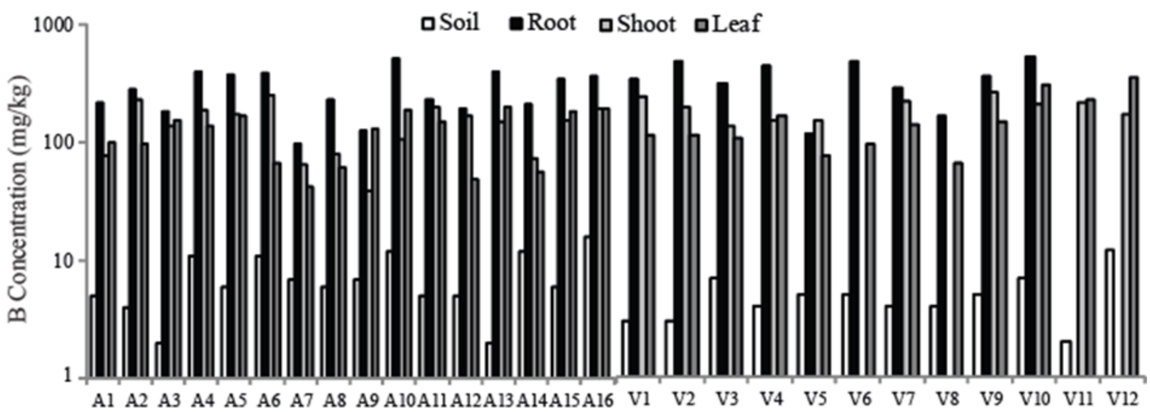

Figure 4. Distrubition of B in root, leaf, shoot and soil of A. pycnocephalus and V. euphraticum according to distance (mg/kg).

3.3. Enrichment Coefficient (EC) and Translocation Factor (TF)

Enrichment coefficient is important for determining phytoremediation degree of plant species [32].

There are 4 standards for considering a plant as hyperaccumulator. One of these standards is EC. Plants carry metals from soil to its tissues and store them in proper tissue [15, 33].

EC of all samples taken from *A. pycnocephalus* and *V. euphraticum* are greater than 1. However, in *A. pycnocephalus,* highest (203 mg/kg) and lowest (5 mg/kg) enrichment coefficient values are present, enrichment coefficient of *V. euphraticum* are between these values (Table 1 and 2) (Figure 5).

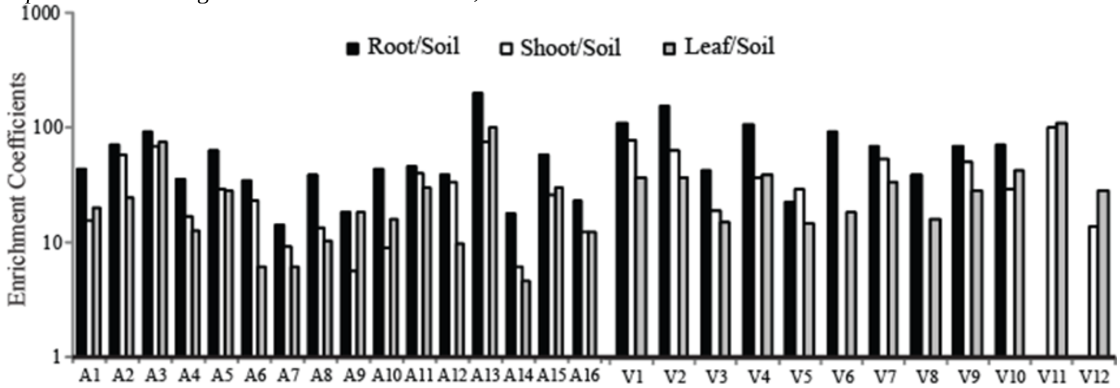

Figure 5. Enrichment coefficient for root, shoot and leaf of *A. pycnocephalus* and *V. euphraticum*.

Another standard for hyperaccumulator plants is TF. Values of TF greater than 1 are important for selection of plants for phytoremediation [26, 34]. TF greater than 1 indicates that elements are transported from roots to shoots and roots to leaves whereas; values lower than 1 suggests that element mobility is low and it cannot be transported to shoot and leaves [27].

TF of *A. pycnocephalus* at location A9 is higher than 1 (1.02 mg/kg) and of *V. euphraticum* at location V5 is higher than 1. TF of both plant species at all other locations are less than 1 (Table 1 and 2) (Figure 6).

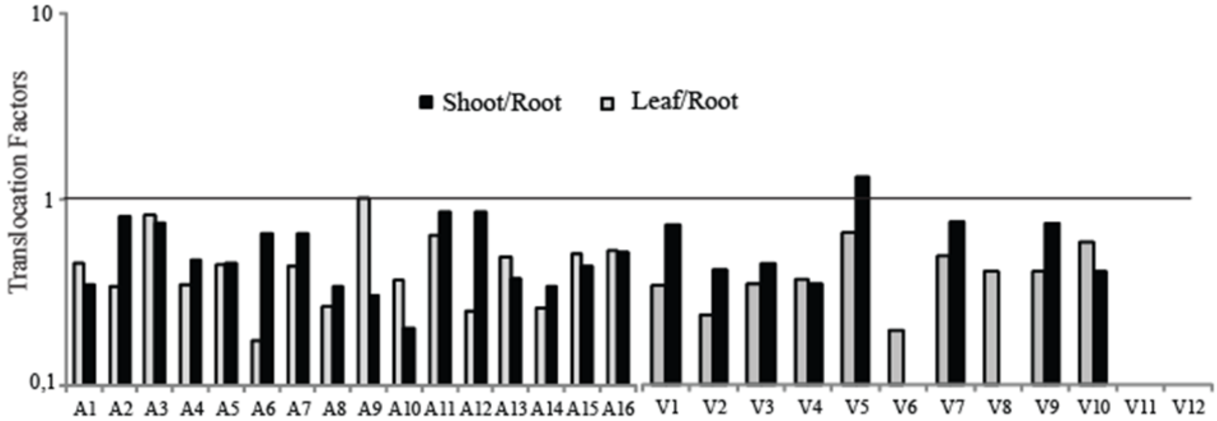

Figure 6. Translocation factors for root, shoot and leaf of *A. pycnocephalu*s and *V. euphraticum*.

Mellemet al. [35] suggested that accumulation potential of plants towards heavy metal depends on the availability of the metals in the soil/ growth media as well as on the plant genotype. But in the this study, the EC and TF were less in the hypoaccumulator (A9 and V5 samples outside, *A. pycnocephalus* and *V. euphraticum*). This may be due to the hyperaccumulator accumulating more metals and leave hypoaccumulator free from metal toxicity. If the EC and TF values are above one, the plant is suitable for phytoremediation [24,26] in the present investigation both EC and TF values are above one, in the hyperaccumulator (*A. pycnocephalus* and *V. euphraticum,* A9 and V5 samples), it is suggested that they are best suited for phytoextraction of B toxicity. Based on the result obtained on EC and TF, it is suggested that *A. pycnocephalus* and *V. euphraticum*, is best suited for remediating B contamination.

5. CONCLUSIONS

In the present study, the elemental contents of the plants (*A. pycnocephalus* and *V. euphraticum*) and soil taken from Akdağmadeni Pb-Zn deposit areas are chemically analyzed. The B concentrations in the soil were compared with the B concentrations of the natural plant. It was observed that there was a relation between the B concentration of only the leaves, shoots and roots of *A. pycnocephalus* and *V. euphraticum* plant sand the B concentration of the soil.

B concentrations in root, shoot and leaf of *A. pycnocephalus* and *V. euphraticum* are higher than the B concentration of soil. By this study, according to values of element concentrations, EC and TF, both two plants are hyperaccumulator plants for B and these plant species are determined as phytoremediation. This means that the phytoremediation plant can take B from the soil.

This species was reflected B in soil and their used phytoremediation for B. The phytoremediation could be successfully used for hyperaccumulator plants in order to take heavy metals away from soil without damaging the environment and it is important for recognition of plant species.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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