Journal of Environmental Science and Engineering, 5 (2011) 1596-1603

Can Industrial By-products Be Used as Tools in Sustainable Agriculture?

B. Tóth, L. Lévai and Sz. Veres

Department of Agricultural Botany and Crop Physiology, Institute of Plant Sciences, Centre for Agricultural and Applied Economic Sciences, University of Debrecen, Debrecen 4032, Hungary

Received: April 20, 2011 / Accepted: June 1, 2011 / Published: December 20, 2011.

Abstract: The goal of our study is to present results about the effects of selected industrial wastes—sewage sludge, lime sludge, compost—on the physiological parameters of plants. Maize seedlings (*Zea mays L cvs. Norma SC*) were used in soil plant (rhizobox) and nutrient solution plant system. The filtrates of the examined materials were used in the nutrient solution and the raw materials in the soil. Dry matter accumulation of shoots and roots, relative chlorophyll contents and the contents of some elements were measured in the plants grown on the nutrient solution. The examined materials contain some useful elements for plants e.g. Cu, Fe, K, and Mg and plenty of toxic metals e.g. Al, Cr. Root growth in the rhizoboxes was monitored, as well as that of roots in the experiment using soil. This type of growth was more intensive with the use of lime sludge than with of sewage sludge. On the other hand, the results were better at the sewage sludge than the lime sludge on the nutrient solution.

Key words: Chlorophyll, industrial wastes, plants growth, root.

1. Introduction

Phytoremediation involving the use of plants together with the application of amendments for remediation of a polluted soil is a more natural approach to remediation when compared to some current remediation practices [1-3]. Cunningham and Berti [4] showed that vascular plants remove pollutants from the environment. Plants can absorb metals from soils and sediments through their root/rhizome systems, as a common phenomenon of phytoremediation. Phytoremediation is an effective, low cost, preferred clean up option for moderately contaminated areas [5]. The heavy metal uptake potential largely varies with plant species, metal availability in the system and other environmental conditions. Hyperaccumulator plants, such as *Braccica napus* (Cr, Cu, Hg, Pb), *Medicago sativa* (Cr) and *Helianthus annus* (Cr, Pb, Zn) [6] are capable of concentrating trace elements in their harvestable biomasses, thereby offering a sustainable treatment option for metal-contaminated soils [7].

There is increasing interest in the agricultural application of sludge obtained from wastewater treatment plants, due to the possibility to recycle valuable components: N, P and other plant nutrients [8, 9]. Prior to depositing sewage sludge onto farmlands, it is important to first identity its metal contents, as there is a risk of toxic element accumulating in the soil [10]. Municipal sewage sludge generally contained higher concentrations of heavy metals such as Cu, Pb or Cd than that found in soils [11]. It has been established that low concentration of elements such as Cu, Mo, Ni, Zn, Mn and Fe are essential for plant growth [12]. Above certain levels, these elements become toxic to plants [13].

There are several strategies available to limit heavy metal uptake by plants [14]. $CaCO_3$ application increased the pH of soil amended with sludge, which reduced metal uptake by rice, wheat and cabbage [15].

Corresponding author: B. Tóth, pre-doctor, main research fields: physiological examination of industrial by-products. E-mail: btoth@agr.unideb.hu.

Liming is being applied as a management tool to immobilize heavy metals in soils, biosolids and mine tailings, thereby reducing their availability for plant uptake and leaching into ground water.

2. Methods and Data

2.1 Nutrient Solution Experiment—Growth of Plants

Maize (*Zea mays L cvs. Norma SC*) seedlings were used in the experiments. After surface sterilization, seeds were then soaked in 10 mM $CaSO_4$ for 4 hours and then germinated on moistened filter paper at 25 ^oC. The seedlings were transferred to a continuously aerated nutrient solution of the following composition: 2.0 mM $Ca(NO_3)_2$, 0.7 mM K_2SO_4, 0.5 mM $MgSO_4$, 0.1 mM KH_2PO_4, 0.1 mM KCl, 1 µM H_3BO_3, 1 µM $MnSO_4$, 10 µM $ZnSO_4$, 0.25 µM $CuSO_4$, 0.01 µM $(NH_4)_6Mo_7O_{24}$. Iron was added to the nutrient solution as Fe(III)-EDTA at a concentration of 10 µM. For different treatments, 91, 100 and 66 $mL{\cdot}dm^{-3}$ of compost, lime sludge and sewage sludge were added to the nutrient solutions, respectively. The filtrates were made from 17 g examined materials and 170 mL distilled water. The prepared solutions were shaken for 2 hours and then vacuum filtrated. The seedlings, 12 for each basic treatment, were grown under controlled environmental conditions (light/dark regime 10/14 h at 24/20 ^oC, relative humidity of 65-70% and a photosynthetic photon flux of 300 $\mu mol\ m^{-2}{\cdot}s^{-1}$) in growth chamber. The volume of experiment pots were 1.7 L, with one pot containing 5 plants. The pH of the control nutrient solution was 4.4.

The sewage sludge and compost originated from poppy shell-based alkaloid production (ALKALOIDA Chemicals Co. Ltd.). The sewage sludge was mixed into various kinds of shavings, as bulking agents, and used as a covering material for waste rock piles. The lime sludge comes from metallurgical waste transformer plant (Ore, Mineral and Waste Recycling Works of The Borsod Limited Share Company).

2.2 The Element Contents of the Examined Materials

The element contents of materials were determined using an OPTIMA 3300 DV ICP-OA Spectrophotometer. 10 mL HNO_3 (65v/v%) were added to each gram of the samples for overnight incubation. Then, the samples were pre-digested for 30 min at 60 °C. Finally, 3 mL H_2O_2 (30 m/m%) were added for a 90 min boiling at 120 °C. The solution was filled up to 50 mL, homogenised and filtered through MN 640 W filter paper.

2.3 Relative Chlorophyll Contents

The relative chlorophyll contents were investigated using a Chlorophyll Meter, SPAD-502 (Minolta). The relative chlorophyll contents of the 2nd and 3rd leaves of the maize were measured. The number of repetitions was 60.

2.4 Dry Matter Accumulation

The dry matter of shoots and roots were measured with the use of thermal gravimetric analysis, after drying at 85 ºC for 48 h.

2.5 Rhizobox Experiment

Calcareous chernozem soil was collected from a depth 0-30 cm. 245 g of soil were placed into the each rhizobox and 5g of the investigated materials (compost, sewage sludge, lime sludge). The control contained 250 g soil. The soil was moistened to 50% of field capacity, i.e. 19 mL of distilled water were used per rhizobox. Each rhizobox contained 3 plants. The number of repetitions was three per treatment.

The applied soil characteristic parameters were the pH_{KCl} 5.71, pH_{H2O} 6.58. The content of $CaCO_3$ was 0.202%, the humus content was 3.54%. The contents of the main elements of the soil were the following: 332 $mg{\cdot}kg^{-1}$ from Na, 176 $mg{\cdot}kg^{-1}$ from Mg, 6.04 $mg{\cdot}kg^{-1}$ from S, 5.79 $mg{\cdot}kg^{-1}$ from Cu, 7.9 $mg{\cdot}kg^{-1}$ from Zn and 262 $mg{\cdot}kg^{-1}$ from Mn.

3. Results and Discussion

To know the soluble portion of applied by-products, the contents of elements were determined in water filtrates of raw material (Table 1). These materials contain many useful elements for plants (e.g. iron, potassium, zinc or magnesium) and some harmful ones also (e.g. aluminum, chrome). Metal toxicity is usually connected with low soil pH in cultivated plants. Acidity increases the availability of aluminium, manganese, and iron, which are abundant in mineral soils. The pH of lime sludge is very alkaline (10.77), the pH of sewage sludge is 8.83, while this value is 8.79 for the compost material. The largest concentration of Al, Fe and Mn were measured in the lime sludge. The quantity of aluminium was approx 46.5 times higher in the lime sludge than in the sewage sludge. The amount of iron was 4.5 times higher in the lime sludge than in the compost. This value was about 4 times higher in the case of manganese.

The content of chromium was the highest in the lime sludge. The average content of chromium in the soil is 50-1,000 mg·kg^{-1} [16]. Thus, the quantity of Cr in the examined materials is outside this range.

The quantity of sodium was very high in all the examined materials. This value was more than 900 mg·kg^{-1} in the lime sludge. This amount was two times higher than that in the compost and four times higher than that found in the sewage sludge. The contents of elements were also measured in the raw materials because these were used for the rizobox experiment (Table 2).

The contents of elements were higher in the raw materials than in the filtrates. The highest concentration of Cr, Cu, Fe and Na were measured in the lime sludge. The highest quantities of Al, K, Mg, P, Sr and Zn were measured in the sewage sludge.

Plants can uptake these elements which may cause different effects on their growth and development. Therefore, we examined the amounts of selected up-taken elements in the roots and shoots of maize (Table 3).

Larger concentrations of aluminium were measured in the roots than in the shoots. We suppose that the Al was accumulated in the roots and the root-to-shoot transfer is retarded. The Al concentrations were highest in the roots of treated plants and as a consequence, the observed growth of the shoots and roots was greater than that of the control. The concentrations of Al were about 23 times higher in the maize treated by compost than in the control. The investigated materials have effect on pH.

When compost was added to the nutrient solution pH increased with 0.65, this pH value for the sewage sludge was 0.85, in comparison to the control. The pH was increased by 2.23 with the lime sludge. The toxic effects of aluminium are primarily root-related [17]. The root system becomes stubby as a result of

Table 1 Contents of some elements in the water filtrates of the examined wastes (compost, lime sludge, sewage sludge) (mg·kg^{-1}).

Examined materials	Examined elements (mg·kg^{-1})										
	Al	Cr	Cu	Fe	K	Mg	Mn	Na	P	Sr	Zn
Compost	31.40	0.46	0.48	53.50	419.00	728.00	2.79	452.00	62.50	6.09	1.80
Lime sludge	219.00	1.34	0.61	241.00	108.00	153.00	4.91	924.00	1.84	0.67	2.88
Sewage sludge	4.71	0.57	0.11	64.40	167.00	190.00	1.15	218.00	6.20	1.50	0.69

Table 2 Contents of some elements in the raw materials of the examined wastes (compost, lime sludge, sewage sludge) (mg·kg^{-1}).

Examined materials	Examined elements (mg·kg^{-1})										
	Al	Cr	Cu	Fe	K	Mg	Mn	Na	P	Sr	Zn
Compost	7,227	25.50	53.00	9,883	1,485	3,693	337	1,475	10,063	102.00	251.00
Lime sludge	3,440	169.00	185.00	118,500	1,010	5,055	1,983	5,419	162	157.00	106.00
Sewage sludge	17,349	41.30	109.00	21,098	2,878	5,548	496	2,163	21,289	195.00	473.00

Table 3 The concentration of examined elements (Al, Cr, Cu, Fe, Na, Sr, Zn) in the roots and shoots of maize (mg·kg^{-1}) affected by compost, sewage sludge, lime sludge.

Examined materials	Examined elements in the roots of maize (mg·kg^{-1})										
	Al	Cr	Cu	Fe	K	Mg	Mn	Na	P	Sr	Zn
Control	62.43	2.91	24.43	264	63,865	5,224	260	1,407	10,313	8.91	159
Compost	1,486	6.00	33.63	1,051	61,347	5,544	803	1,221	12,678	10.70	143
Sewage sludge	242.66	1.67	23.96	357	65,470	5,760	274	1,018	8,885	6.70	126
Lime sludge	717	19.56	30.26	602	61,838	4,991	343	1,121	8,490	6.92	108
	Examined elements in the shoots of maize (mg·kg^{-1})										
Control	23.07	0.72	16.06	71.86	76,739	2,302	73.30	217	2,524	6.26	89.10
Compost	20.83	0.39	16.16	73.80	65,551	2,265	92.20	254	12,292	7.25	63.73
Sewage sludge	13.29	0.73	16.96	63.60	84,928	2,444	82.33	259	11,429	6.70	69.96
Lime sludge	10.57	0.65	15.43	57.43	78,496	2,115	73.46	234	10,249	5.04	59.53

inhibition of elongation of the main axis and lateral roots [18]. The severity of inhibition of root growth is a suitable indicator of genotypic differences in aluminium toxicity [19]. The contents of chromium were also higher in the roots than in the shoots. These values were below the control in the shoots when compost and lime sludge were added to the nutrient solution. The amount of copper was higher, approximately twice that found in the roots than in the shoots, when the compost and the lime sludge were examined. This value increased by 1.5 at the control and the sewage sludge. For most crop species, the critical toxicity level of copper in the leaves is above 20-30 µg·g^{-1} dry weight [20]. There are, however, marked differences in copper tolerance between plant species (e.g. bean is much more tolerant than corn); these differences are directly related to the copper content of the shoots [21].

The concentration of iron was about the control level in the shoots of treated plants. Larger concentration was measured in roots.

The amount of iron was approx 4.5 times higher in the roots of maize treated with the compost and twice as high in the lime sludge treatment. Iron toxicity is a serious problem in crop production on waterlogged soils; it is the second most severe yield-limiting factor in wetland rice [22].

The critical toxicity contents are above 500 mg·Fe·kg^{-1} leaf dry weight, but this is very much dependant on other factors, such as the contents of other mineral nutrients [23]. Iron toxicity may also play a role under dry land conditions and is probably an early event of drought-induced damage in photosynthetic tissue caused by iron-catalyzed formation of oxygen free radicals in the chloroplast [24].

The content of sodium in shoots was the highest in the control, compared to the otherwise treated plants. The concentration of Na increased in the roots when plants were treated with the compost, sewage sludge and lime sludge. The application of the sewage sludge increased the amount of Na by approximately 42 mg·kg^{-1}, the compost by 37 mg·kg^{-1} and the lime sludge by 17 mg·kg^{-1}.

According to Johnston et al. [25], the supply of 100 µM Na^+ enhanced growth and alleviated the visual symptoms and sodium may be classified as a mineral nutrient for at least some of the C_4 species in the families [26]. However, the conclusion of Brownell [26] that sodium is essential for higher plant species in which the C_4 pathway is operative is not justified. In all these studies, C_4 species, such as maize, have not been included, i.e. species which are typically natrophobic and have similar growth rates in the absence and presence of sodium supply [27]. According to present knowledge sodium is essential for many, but not all C_4 species, and it is not essential for C_3.

The content of zinc was approximately two times higher in the roots than in the shoots in all cases. The largest concentration Zn was measured in the control than in the treated plants. The amount of zinc decreased in the shoots by approximately 25 mg·kg^{-1} when plants were treated with compost, by 20 mg·kg^{-1} when treated with the sewage sludge treatment and approximately with 30 mg·kg^{-1} when the lime sludge was added to the nutrient solution.

The critical toxicity levels in the leaves of crop plants are from as low as 100 μg·Zn·g^{-1} dry weight [28] to more than 300 μg·Zn·g^{-1} dry weight, the latter values being more typical. Increasing soil pH by liming is the most effective procedure for decreasing both zinc content and zinc toxicity in plants [29].

The heavy metal toxicity may decrease growth, so the dry matter accumulation of shoots and roots of maize were measured during the experiments (Table 4).

In nearly all the cases, the dry matter accumulation values were found around the control value, except for the compost, for which the dry matter accumulation of roots and shoots were below the control level. The dry matter accumulation of the roots decreased by 15.6 mg and the dry matter accumulation of the shoots by 8.6 mg when the compost was added to the nutrient solution. There were no significant differences in comparison to the control. The dry matter contents of roots increased by 2.5 mg when the lime sludge was added to the nutrient solution and by 20 mg when the sewage sludge was. The dry matter accumulation of shoots increased by 43 mg in the lime sludge treatment and by 93 mg in the sewage sludge.

The dry matter production nutrient supply curve has three clearly defined regions. In the first, the growth rate increases with increasing nutrient supply. In the second, the growth rate reaches a maximum and remains unaffected by nutrient supply. In the third, the growth rate falls with increasing nutrient supply.

Low chlorophyll contents affect photosynthetic activities. The decreasing dry matter accumulation can be explained by the lower level of the chlorophyll contents (Table 5).

The compost, sewage sludge and lime sludge contain some iron (content of iron in the compost: 9,883 mg·kg^{-1}; the content of iron in the sewage sludge is 21,098 mg·kg^{-1}; and this value is 118,500 mg·kg^{-1} in the lime sludge).

Table 4 Effects of different matters (compost, lime sludge, sewage sludge) on the dry matter accumulation of shoots and roots of maize seedlings (mg·plant^{-1}).

Examined materials	Dry matter of shoots and roots (mg·plant^{-1})	
	Roots	Shoots
Control	101.5 ± 0.05	318.2 ± 0.11
Compost	85.9 ± 0.02	309.6 ± 0.13
Lime sludge	104.0 ± 0.01	361.8 ± 0.02
Sewage sludge	121.6 ± 0.04	411.2 ± 0.10

Table 5 Relative chlorophyll contents of the 2nd and 3rd leaves of corn in the measurements taken on the 6th, 9th and 11th days (Spad Units). Significant difference in comparison to the control: *$p < 0.05$; **$p < 0.01$.

Examined materials	2nd leaves of maize		
	6th day	9th day	11th day
Control	38.14 ± 4.95	48.20 ± 2.85	49.31 ± 5.12
Compost	41.26 ± 5.82	43.07 ± 4.68*	47.37 ± 3.60
Lime sludge	38.10 ± 4.78	44.05 ± 2.08	47.40 ± 2.86
Sewage sludge	34.07 ± 7.75	47.27 ± 4.08	47.92 ± 4.10
	3rd leaves of maize		
Control	30.06 ± 6.06	43.43 ± 2.49	45.87 ± 1.98
Compost	32.11 ± 6.85	38.85 ± 3.50**	44.83 ± 3.27
Lime sludge	33.69 ± 3.64	42.88 ± 3.39	47.71 ± 1.62
Sewage sludge	32.13 ± 5.19	41.77 ± 4.60	46.75 ± 4.30

Table 6 Effects of examined materials (compost, sewage sludge, lime sludge) on the daily and nightly growth of roots of maize (mm).

Examined materials	Growth of roots (mm)	
	Daily	Nightly
Control	18.266 ± 7.28	21.931 ± 8.64
Compost	21.142 ± 6.39	23.777 ± 5.97
Lime sludge	19.714 ± 7.55	21.928 ± 7.12
Sewage sludge	18.531 ± 7.04	22.218 ± 7.31

The relative chlorophyll content increased in the 2nd leaves of maize when compost was applied on the 6th day. The relative chlorophyll contents decreased in the sewage sludge on the 6th day. These values decreased in the 2nd leaves of the treated plants on the 9th and 11th days. The relative chlorophyll contents decreased significantly in the 2nd and 3rd leaves on the 9th day. The chlorophyll contents of 3rd leaves were lower than those in the 2nd leaves. The relative chlorophyll contents of the 3rd leaves decreased by 9 Spad Units in the compost treatment on the 6th day. These values were 4.5 Spad Units in the lime sludge and approximately 2 Spad Units in the sewage sludge. The decease was not so considerable on the 9th and 11th days.

The major function of magnesium in green leaves is its role as the central atom of the chlorophyll molecule. The proportion of the total magnesium bound to chlorophyll depends very much on the magnesium supply [30]. Depending on the magnesium nutritional status, between 6% and 25% of the total magnesium is bound to chlorophyll. In most instances, growth is depressed and visual symptoms of magnesium deficiency occur when the proportion of magnesium in the chlorophyll exceeds 20-25%. Photosynthesis is strongly inhibited even by 5 mM magnesium in the external solution [31].

After the examination of the nutrient solution the plant-soil system was also examined. The growth and length of roots were measured (Table 6).

Root growth was more intensive at night than in the daytime. There were no significant differences in comparison to the control. Root length increased by approximately 3 mm in the compost in the daytime periods and approximately 2 mm in the nighttime periods. The growth of roots was around that of the control in the lime sludge treatment in the nighttime period and increased 1.5 mm in the daytime period in comparison with the control. This value was around that of the control in the sewage sludge in the daytime period and somewhat increased in the nighttime period.

Calcium plays a key role in protecting root growth against low pH stress. The calcium requirement for root growth is not fixed but is rather a function of both pH and the concentration of other cations, including aluminum. On average, a molar ratio of calcium to total cations of 0.15 is needed in the soil solution for maximum root growth. The lime sludge contains 278,400 $mg \cdot kg^{-1}$ calcium, the sewage sludge 123,988 $mg \cdot kg^{-1}$. The growth of roots increased significantly in the daytime when the lime sludge was used and at night when the compost was applied.

4. Conclusions

The investigated materials contain lots of elements. The larger concentration of Al, Cr, Cu, Fe, Mn, Na and Zn were measured in the lime sludge than in compost or sewage sludge. Highest concentration of K, Mg and P were measured in the compost.

The plants take up these elements which may cause different effects on their growth and development. The amount of up-taken elements also was measured. Of the examined elements, larger concentration was measured in the roots than in the shoots. This is advantageous for crop production because we especially use the shoots of crop plants. The dry matter production, which is the main aim of crop production, depends on nutrient supply. The investigated materials also contain many useful elements for plants, which are essential for growth. Dry matter accumulation of roots increased by 2.5 mg when the lime sludge was added and 20 mg when the sewage sludge was added to the nutrient solution. The dry matter accumulation of shoots increased by 43 mg in the lime sludge and 93 mg in the sewage sludge. These results suggest the potential application of lime sludge and especially sewage sludge as nutrient supplementary materials in crop production.

Further examinations are needed to examine the potential and combined application in fields.

References

[1] P. Burgos, A. Pérez de Mora, E. Madajon, F. Cabrera, Assisted natural remediation of trace element polluted soils, Sustainable Organic Waste Management for Environmental Protection and Food Safety 2 (2005) 65-68.

[2] D.J. Walker, R. Clemente, A. Roig, M.P. Bernal, The effects of soil amendments on heavy metal bioavailability in two contaminated Mediterranean soils, Environmental Pollution 122 (2003) 303-312.

[3] D.J. Walker, R. Clemente, M.P. Bernal, Contrasting effects of manure and compost on soil pH, heavy metal availability and growth of *Chenopodium album* L. in a soil contaminated by pyritic mine waste, Chemosphere 57 (2004) 215-224.

[4] S.D. Cunningham, W.R. Berti, Remediation of contaminated soils with green plants: An overview, In Vitro Cell Dev. Biol. 29 (1993) 207-212.

[5] S.J. Weis, P. Weis, Metal uptake, transport and release by wetland plants: Implications for phytoremediation and restoration, Environment International 30 (2004) 685-700.

[6] S. McCutcheon, Schnoor, Phytoremediation, John Wiley & Sons, New Jersey, 2003, p. 19.

[7] R. Tappero, E. Peltier, M. Grafe, Hyperaccumulator Alyssum murale relies on a different metal storage mechanism for cobalt than for nickel, New Phytology 175 (2007) 641-654.

[8] J.L. Smith, Cycling of nitrogen through microbial activity, in: J.L. Hatfield, B.A. Stewart (Eds.), Advances in Soil Sciences, Lewis Publishers, Boca Raton, 1994, pp. 91-120.

[9] J.W.C. Wong, K.M. Lal, D.S. Su, M. Fang, Availability of heavy metals for *Brassica chinensis* grown in an acidic loamy soil amended with domestic and industrial sewage sludge, Water Air Soil Pollut. 128 (2001) 339-353.

[10] M. Angelidis, R.J. Gibbs, Chemistry of metals in anaerobically treated sludges, Water Research 23 (1989) 29-33.

[11] R.L. Chaney, Health risk associated with toxic metal in municipal sludge, in: G. Bitton, B.L. Damron, G.T. Edds (Eds.), Ann Arbor Science, Ann Arbor, MI, USA, 1980, pp. 59-83.

[12] R.D. Reeves, A.M.J. Baker, Metal-accumulating plants, in: I. Raskin, D. Ensley (Eds.), Phytoremediation of Toxic Metals Using to Clean Up the Environment, John Wiley and Sons, New York, 2000, pp. 193-230.

[13] M.J. Blaylock, J.W. Huang, Phytoremediation of toxic metals, in: I. Raskin, D. Ensley (Eds.), Phytoremediation of Toxic Metals: Using Plants to Clean up Environment, John Wiley and Sons, New York, 2000, pp. 53-70.

[14] S. Kuo, E.J. Jellum, A.S. Baker, Effects of soil type, mining and sludge application on zinc and cadmium availability to Swiss chard, Soil Science 139 (1985) 122-130.

[15] H.N. Chen, C.R. Zheng, C. Tu, Z.G. Shen, Chemical methods and phytoremediation of soil contaminated with heavy metals, Chemosphere 41 (2000) 229-234.

[16] A.M. Zayed, N. Terry, Chromium in the environment: Factors affecting biological remediation, Plant Soil 249 (2003) 139-156.

[17] G.J. Taylor, The physiology of aluminum phytotoxicity, in: H. Sigel, A. Sigel (Eds.), Metal Ions in Biological Systems, Marcel Dekker, New York, 1988, pp. 123-163.

[18] F. Klotz, W.J. Horst, Genotypic differences in aluminum tolerance o soybean (*Glycine max.* L.) as affected by ammonium and nitrate-nitrogen nutrition, J. Plant Physiol. 132 (1988) 702-707.

[19] C.D. Foy, A.L. Fleming, G.R. Burns, W.H. Armiger, Characterization of differential aluminium tolerance among varieties of wheat and barley, Soil Sci. Soc. Am. Proc. 31 (1967) 513-521.

[20] A.D. Robson, D.J. Reuter, Diagnosis of copper deficiency and toxicity, in: J.F. Loneragan, A.D. Robson, R.D. Graham (Eds.), Copper in Soils and Plants, Academic Press, London, 1981, pp. 287-312.

[21] G. Bachthaler, A. Stritesky, Wachstumsuntersuchungen an Kulturpflanzen auf einem mit Kupfer überversorgten Mineralboden, Bayer. Landwirtsch. Jahrb. 50 (1973) 73-81.

[22] G.J.D. Kirk, A.R. Ahmad, P.H. Nye, Coupled diffusion and oxidation of ferrous iron in soils. II. A model of the diffusion and reaction of O_2, Fe^{2+}, H^+ and HCO_3^- in soils and a sensitivity analysis of the model, J. Soil Sci. 41 (1990) 411-431.

[23] M. Yamauchi, Rice bronzing in Nigeria caused by nutrient imbalances and its control by potassium sulfate application, Plant Soil 117 (1989) 275-286.

[24] A.H. Price, G.A.F. Hendry, Iron-catalysed oxygen radical

formation and its possible contribution to drought damage in nine native grasses and three cereals, Plant Cell Environ. 14 (1991) 477-484.

[25] M. Johnston, C.P. Grof, P.F. Brownell, The effect of sodium nutrition on the pool sizes of intermediates of the C4 photosynthetic pathway, Aust. J. Plant Physiol. 15 (1988) 749-760.

[26] P.F. Brownell, Sodium as an essential micronutrient element for plants and its possible role in metabolism, Adv. Bot. Res. 7 (1979) 117-224.

[27] E.J. Hewitt, Essential and functional methods in plants, in: A. Robb, W.S. Pierpoint (Eds.), Metals and Micronutrients: Uptake and Utilization by Plants' 8D, Academic Press, New York, 1983, pp. 313-315.

[28] A. Ruano, Ch. Poshenrieder, J. Barcelo, Growth and biomass partitioning in zinc-toxic bush beans, J. Plant Nutr. 11 (1988) 577-588.

[29] M.C. White, A.M. Decker, R.L. Chaney, Differential cultivar tolerance in soybean to phytotoxic levels of soil Zn. I. Range of cultivar response, Argon. J. 741 (1979) 121-126.

[30] G. Michael, Über die Aufnahne und Verteilung des Magnesiums und dessen Rolle in der höheren grünen Pflanze, Z. Pflanzenernaehr, Dueng. Bodenkd. 25 (1941) 65-120.

[31] W. Wu, J. Peters, G.A. Berkowitz, Surface charge-mediated effects of Mg^{2+} on K^+ flux across the chloroplast envelope are associated with regulation of stromal pH and phototsynthesis, Plant Physiol. 97 (1991) 580-587.