Effect of Soil Copper and Foliar Copper Applications on Micronutrient Contents of Tomato Plants

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In this study, effects of both soil copper applications (SCuA) and foliar copper application (FCuAF) on micronutrient contents (copper, iron, manganese and zinc) of tomato plants were investigated. For this purpose, Cu was applied as a factorial combination of rate (0 [S1], 1000 [S2] and 2000 mg kg^{-1} [S3], soil) and frequencies (no application[F1], biweekly [F2] and weekly [F3], foliar). Two separate experiments were conducted to observe effects of different Cu containing chemicals. Two fungicides, Gunner and Tenn-Cop 5E (containing Cu oxychloride and copper salts of fatty and rosin acids, respectively), were used for foliar copper applications. $CuSO₄·5H₂O$ was used to provide to soil. Both in the experiment-I (Gunner, Cu oxychloride) and in the experiment II (Tenn-Cop 5E, copper salts of fatty and rosin acids), Cu and Mn contents of plant samples increased with increasing of SCuA and FCuAF. Fe contents of leaf and fruit samples were affected by SCuA and decreased with increasing of SCuA. Root Fe content generally decreased with increasing of both SCuA and FCuAF. Leaf, fruit and root Zn contents were affected by both SCuA and FCuAF and Zn contents of plant samples decreased with increasing SCuA and FCuAF. As a result, both SCuA and FCuAF, especially aiming to control plant diseases, showed different effects on Cu, Fe, Mn and Zn contents of tomato plants. It was determined that, by taking into account the amount and frequency of applications, the Cu doses applied either to soil or leaf were too high. Thus, it would be useful to conduct more in detailed studies to determine Cu toxicity limits on tomato plants at different soil pH levels by gradually decreasing Cu doses.

Key Words: Cu application, Micronutrients (Cu, Fe, Mn and Zn), Tomato, Greenhouse.

INTRODUCTION

Copper, lead, manganese, zinc, iron, *etc.* were chosen as representative trace metal ions whose levels in the environment represent a reliable index of environment pollution¹. According to Bowen², trace metals such

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as Cu, Co, Cr (IV), Al, B, As (III), Be, Cd, Mo, Ni, Se (IV) and Ti, even in low concentrations, can be harmful to plants and humans. Among trace metals, copper is taken up by plants as Cu^{2+} and possibly as low molecule organic complexes and also partly as inorganic complexes. Although Cu is an essential metal for various metabolic processes, it is only required in trace amounts and becomes toxic at high concentrations³. Copper is present in unpolluted soils in the range of 2 to 40 mg kg^{-1} . Polluted soils, however, contain up to $100 \text{ mg} \text{ kg}^{-1}$ copper⁴. For most crop species, the critical toxicity level of copper in leaves is considered to be above 20-30 mg kg-1 dry weight⁵.

Application of manure obtained from pigs fed with commercial cattle feed increases copper content of soil results in Fe, Zn and Mo deficiencies in plants⁶. Arduini *et al.*⁷ reported that the Mn and Zn contents of roots decreased in all species (*Pinus pinea* L., *Pinus pinaster* Ait. and *Fraxinus angustifolia* Vahl) with increasing Cu supply. Hale *et al.*⁸ observed that increasing level of copper applications to tomato plants decreased plant growth rate. Especially, root development was much affected. The same workers also reported that plant organs (stem, leaf and root) showed different reactions to copper. Lidon and Henriques⁹ observed that increasing copper concentrations resulted in an increase in copper level in root and shots. They also reported that Zn uptake decreased with increasing copper concentrations, while N, P, K, Na, Ca, Mg, B, Mo and Al uptake and translocation did not seem to be correlated with Cu treatments.

Sonmez¹⁰ reported that the leaf, stem and biomass decreased with increasing Cu supply to soil in tomato plants and that the N, Mn and Cu contents of plant tissues increased with increasing Cu supply to soil, whereas the P, K, Ca and Fe contents of plants tissues decreased. The same worker also observed that the Mg content of stem decreased with increasing Cu supply to soil while leaf and root Mg contents were not affected and that the Zn contents of leaf and root decreased with increasing Cu supply to soil but not in the stem.

Cu-containing fertilizers, fungicides and bactericides has been used extensively in the greenhouses in the Antalya, Turkey in recent decades with the use of such materials tending to increase year by year. Kaplan¹¹ found that the percentage of soils containing DTPA-extractable Cu greater than the critical toxicity level (20 mg kg^{-1}) was 8.1 in Antalya, Turkey and that the Cu content of tomato leaf samples ranged between 2.4 and 1490 mg kg⁻¹ (mean 166.5 mg kg⁻¹) and the concentration in leaf samples was very high due to the intensive use of foliar applied copper-containing chemicals.

Applications of Cu containing fertilizer, pesticides and fungicides to leaf or soil have increased gradually over the years in Mediterranean region and Cu accumulation has reached dangerous levels. Therefore, the

effect of both soil Cu applications (SCuA) and foliar Cu application frequencies (FCuAF) on micronutrient contents of tomato plants are investigated.

EXPERIMENTAL

Pot experiments were conducted in a computer-controlled greenhouse located in Antalya, Turkey. Pots were filled with a Xerorthent soil (Entisol) with the following chemical and physical properties: clay textured (530.4) g kg⁻¹ clay, 367.2 g kg⁻¹ silt and 102.4 g kg⁻¹ sand); pH 6.5 (1:2.5 soil:water ratio); 26.0 g kg-1 organic matter; total carbonates equivalent to 44.0 g kg⁻¹; total N 0.18 %; extractable P 110.80 mg kg⁻¹; extractable K 241.8 mg kg-1; extractable Ca 2750.0 mg kg-1; extractable Mg 541.2 mg kg-1; DTPAextractable Fe 92.35 mg kg⁻¹; DTPA- extractable \overline{Z} n 14.80 mg kg⁻¹, DTPAextractable Mn 295.80 mg kg^{-1} and DTPA-extractable Cu 15.30 mg kg^{-1} . The details of the experiments were reported by Sonmez *et al.*¹².

Two separate experiments were carried out, each using different cupric fungicide: Cu oxychloride or copper salts of fatty and rosin acids. The former contains 25 % Cu oxychloride and is sold as a powder. The latter is a liquid fungicide containing 58 % copper salts of fatty and rosin acids, equivalent to 51.4 mg/L metallic Cu. Copper was applied to soil as $CuSO₄·5H₂O$ with 24.5 % copper. $CuSO₄·5H₂O$ is blue, bright crystal and soluble in water. Tomato [*Lycopersicon esculentum* (L.) mill cv. F144] was selected for this study as a test plant. The seedlings of tomato were obtained from the West Mediterranean Agricultural Research Institute, Antalya, Turkey.

Experimental design: 20 kg of air-dried soil are passed through a 4 mm mesh sieve and mixed with 5 kg of a 75 % turf $+ 25$ % perlite mixture and distributed in 25 L pots, fertilized with mono ammonium phosphate and potassium sulphate (36 kg N ha⁻¹, 80 kg P ha⁻¹ and 112 kg K ha⁻¹). Copper was applied to soil at three different rates [0 (S1), 1000 (S2) and 2000 mg kg-1 (S3)] as CuSO4.5H2O. One seedling of tomato (*Lycopersicon esculentum* (L.) Mill cv. F144) was planted per pot. Fungicides were applied at three different frequencies [control, no application (F1), biweekly $(F2)$ and weekly $(F3)$]. The treatments were set up based on Kaplan¹¹. Trials were set up in a completely randomized factorial design with 9 treatments; 3 levels of Cu application to soil and 3 frequencies of fungicide application to leaves, in all possible combinations.

Processes during and at the end of the experiment period

Pots were incubated for 2 weeks without plants after addition of copper sulphate to soil and before planting. Copper application to leaves started at 4 weeks after planting. The seedlings were allowed to grow for a period of 8 months. All pots were fertilized with the drip irrigation system once a week with mono ammonium phosphate, potassium nitrate, ammo-

nium nitrate and magnesium sulfate. Total amounts of nutrients provided to each pot were: 195 kg N ha⁻¹, 62 kg P ha⁻¹, 177 kg K ha⁻¹ and 16 kg Mg ha⁻¹. Pots also received 3.0 kg Fe ha⁻¹, 3.0 kg Mn ha⁻¹, 1.13 kg Zn ha⁻¹, 0.38 kg B ha⁻¹ and 0.08 kg Mo ha⁻¹. Fertilizers were applied based on local recommendation.

Leaf samples were collected after 1 week with fungicide applications to leaves were completed. At the end of the 8 month experiment period, plants were harvested. At harvest, plants were washed by distilled water and separated into leaf, stem and root and dried in a forced-air oven at 65ºC to constant weight. The leaf, stem and root samples were ground separately in a stainless mill to pass through a 20 mesh screen and kept in clean polyethylene bags for analysis.

Chemical and statistical analysis

The soil used in the experiments was chemically analyzed after they had been air-dried and passed through a 2 mm sieve. Total carbonates were determined according to the calcimeter method of Nelson¹³. Soil texture was determined by hydrometer method¹⁴ and organic matter by the Walkley-Black¹⁵. Extractable P content was extracted¹³ by NaHCO₃ and determined by a molybdate colorimetric method¹⁶, extractable K, Ca and Mg were extracted with CH₃COONH₄ and determined by atomic absorption spectrophotometry (AAS)¹⁷. Soil Cu, Fe, Mn and Zn were extracted with diethylene tetraamine pentaacetic acid (DTPA)¹⁸ and then determined in the obtained extract by AAS.

Dried plant samples (leaf, stem and root) of 0.5 g each were digested with 10 mL $HNO₃/HClO₄ (4:1)$ acid mixture on a hot plate. The samples were then heated until a clear solution was obtained. The same procedure was repeated several times. The samples were filtered and diluted to 100 mL using distilled water. Concentrations of Cu, Fe, Mn and Zn in the digestates were determined by using AAS^{19} .

Statistical analysis was carried out using the MSTAT-C software. Means were compared by analysis of variance (Anova) and the LSD test at $p \leq$ 0.05. A factorial analysis was used to determine interaction effects of Cu application to soil and leaves on micronutrient contents of tomato plants.

RESULTS AND DISCUSSION

Experiment I (Gunner, Cu oxychloride)

Leaf Cu content was only significantly affected by FCuAF, increasing of FCuAF caused an increase in leaf Cu content and highest Cu level was obtained with treatment F3 (Table-1). SCuA and FCuAF independently affected Cu content of fruit samples and there was no significant interactive effect between these applications. Fruit Cu content increased with increasing of both SCuA and FCuAF and the highest Cu contents were

obtained with treatment F3, application S2 and S3 (Table-1). Root Cu content was significantly affected by SCuA, FCuAF and interactive effects between these applications. In all foliar treatments (F1, F2 and F3), increasing of SCuA resulted in an higher Cu content in root samples. The highest Cu contents were obtained with application S3 (Table-1). However, increasing of FCuAF did not resulted in significant differences in root Cu content in application S1. In application S2 and S3, root copper contents increased with increasing of FCuAF and the lowest copper contents were obtained with treatment F1 (Table-1). In general, increasing of SCuA and FCuAF caused an increase in Cu contents of plant samples. Quarilli *et al.*²⁰ reported that Cu accumulation increased with increasing Cu concentration in 17-day-old tomato seedlings grown in nutrient solutions containing Cu at 0, 5 or 50 μ M. Sonmez¹⁰ and Rhoads *et al.*²¹ pointed out that tissue Cu content increased (particularly in the roots) with increasing Cu rate. Ivanova²² found that the prolonged use of copper-based agrochemicals resulted in high copper accumulations which depend on length and dosage of fungicide application. Similarly, Tagliavini *et al.*²³ observed that root Cu concentration increased linearly with soil Cu content. The present results are in agreement with literatures.

Iron contents of leaf and fruit samples were affected by SCuA and the highest Fe contents were observed with application S1 (Table-1). Iron contents of leaf and fruit samples were decreased by increasing level of SCuA. On the other hand, increasing of FCuAF did not have an effect on Fe contents of leaf and fruit samples. Root Fe content was significantly affected by SCuA, FCuAF and interactive effects between these applications. In treatment F1, F2 and F3, increasing of SCuA resulted in an lower Fe content in root samples. The highest Fe contents were obtained with application S1. Increasing of FCuAF resulted in a decrease in root Fe content in application S1 and lowest Fe content was obtained with treatment F3. In application S2 and S3; increasing of FCuAF did not result in significant differences in root Fe content (Table-1). The decrease in Fe content of root samples may relate with the decrease in root growth as a result of high level Cu application. Heavy metals, in particular Cu, are known to be displace Fe from chelate complexes forming corresponding heavy metal chelates. This may be important in limiting Fe uptake and utilization, either by reducing Fe chelate translocation to roots or within the plant itself by the effect of the heavy metal on centres of physioloical activity for Fe^{24} . Lidon and Henriques²⁵ reported that shoot and root Fe concentrations decreased at copper toxicity in rice. Shoot Fe concentration decreased at > 0.05 mg Cu L⁻¹, while in the root Fe concentration decreased above this level of Cu. Similarly, Alva and Chen³ found that increase in concentrations of external Cu decreased the uptake Fe and Zn by the citrus

seedlings. Sonmez¹⁰ reported that the Fe content of plant tissues decreased with increasing Cu supply to soil in tomato plants. Ouzounidou²⁶ reported that high Cu contents in plant tissues negatively influenced uptake and translocation of Fe in roots and above-ground parts.

Mn contents of leaf was significantly affected by SCuA, FCuAF and interactive effects between these applications. In all foliar treatments (F1, F2 and F3), increasing of SCuA resulted in an higher Mn content in leaf samples. The highest Mn contents were obtained with application S3 (Table-1). However; increasing of FCuAF did not resulted in significant differences in Mn contents of leaf in application S1 and S2. In application of S3, Mn contents of leaf increased with increasing of FCuAF and lowest Mn content was obtained with treatment F1 (Table-1). While Mn contents of fruit was affected by SCuA and the lowest Mn content was obtained with application S1, increasing of FCuAF did not affect on fruit Mn content (Table-1). Mn contents of root was significantly affected by SCuA, FCuAF and interactive effects between these applications. In all foliar treatments (F1, F2 and F3), increasing of SCuA resulted in an higher Mn content in root samples. The highest Mn contents were obtained with application S3 (Table-1). However, the increase of FCuAF did not resulted in significant differences in root Mn content in application S1. In application of S2 and S3, root Mn content increased with increasing of FCuAF and highest Mn contents were obtained with treatment F3 (Table-1). In general, increasing of SCuA and FCuAF caused an increase in Mn contents of plant samples. In present study with the translocation of copper and other micronutrients in tomato plants, Pich and Scholz 27 observed that high Cu supply increased the concentration of Mn in all of the plant organs. Similarly, Sonmez¹⁰ reported that the Mn contents of plant tissues increased with increasing Cu supply to soil in tomato plants. Data obtained in this experiment support finding reported by Pich and Scholz²⁷ and Sonmez¹⁰.

SCuA and FCuAF independently affected Zn contents of leaf, fruit and root samples and there was no significant interactive effect between these applications. The Zn contents of leaf, fruit and root decreased with increasing level of both SCuA and FCuAF. The highest Zn contents were obtained with application S1 and treatment F1 (Table-1). Because of the antagonism effect between Zn and $Cu^{24,28}$, Zn contents of plants decreased with increasing level of Cu applications. Morishita *et al.*²⁹ determined that levels of Cu, Mn and Zn in the roots of rice and tomato increased with increasing rates of Cu, Mn and Zn, respectively, but in tomato they reached a maximum and then fell. Lidon and Henriques⁹ reported that Zn uptake decreased with increasing Cu concentrations. Sonmez¹⁰ found that the Zn contents of leaf and root decreased with increasing Cu supply to soil in tomato plants but not in the stem.

Copper application to soil (SCuA) affected total yield, fruit number, dry root weight and plant height ($p < 0.01$). The results of growth and yield of the experiment were previously reported by Sonmez *et al.*¹² . The highest total yield, fruit number, plant height and dry root weight were obtained when no copper was applied to soil (S1), performance traits decreased from S1 to S3. The increasing of FCuAF affected dry root weight and plant height after the 5th week and resulted in a decrease in dry root weight and plant height. The smallest dry root weight and plant heights were observed¹² in treatment F3.

Experiment II (Tenn-Cop 5E, copper salts of fatty and rosin acids)

Copper contents of leaf was only significantly affected by FCuAF. Increasing of FCuAF caused an increase in leaf Cu content. The highest Cu content was obtained with treatment F3 (Table-2). SCuA and FCuAF independently affected Cu content of fruit samples and there was no significant interactive effect between these applications. Copper contents of fruit increased with increasing of both SCuA and FCuAF and the highest Cu contents were obtained with treatment F3 and application S2 and S3 (Table-2). Root Cu content was significantly affected by SCuA, FCuAF and interactive effects between these applications. In all foliar treatments (F1, F2 and F3), increasing of SCuA resulted in a higher Cu content in root samples. The highest Cu contents were obtained with application S3 (Table-2). However, the increasing of FCuAF did not resulted in significant differences in root Cu content in application S1. In application of S2 and S3, copper contents of root increased with increasing of FCuAF and the highest Cu contents was obtained with treatment F3 (Table-2). Increasing of both SCuA and FCuAF caused in an increase in Cu contents of plant samples. Liu *et al.*³⁰ reported that the Cu content in roots of *Z. mays* increased with increasing solution concentration of Cu^{2+} . Lin *et al.*³¹ observed that the copper content in roots, hypocotyls, cotyledons and leaves increased with increasing Cu concentration. Similarly, Sonmez¹⁰ and Alva *et al.*³² observed that the Cu concentration in leaves and roots increased substantially with an increase in the Cu rate. The present results are consistent with literatures.

Iron contents of leaf and fruit samples was affected by SCuA and FCuAF and the lowest Fe contents were observed with application S3 and treatment F3 (Table-2). Iron content of leaf samples was decreased by increasing level of both SCuA and FCuAF. Iron contents of root was significantly affected by SCuA, FCuAF and interactive effects between these applications. In all foliar treatments (F1, F2 and F3), increasing of SCuA resulted in an lower Fe content in root samples. The highest Fe contents were obtained with application of S1 (Table-2). However; the increasing of FCuAF did not change Fe content of root samples in application of S1.

TABLE-1 EFFECTS OF SOIL COPPER APPLICATIONS (SCuA) AND FOLIAR Cu APPLICATION FREQUENCIES (FCuAF) ON MICRONUTRIENTS CONTENTS OF LEAF, FRUIT AND ROOT SAMPLES IN THE EXPERIMENT I (GUNNER, Cu OXYCHLORIDE)

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¹Means in the same column followed by the same letter are not significantly different at 5 % probability level by LSD test.

²Means in the same row followed by the capital and bold same letter are not significantly different at 5 % probability level by LSD test.

Table-2 EFFECTS OF SOIL COPPER APPLICATIONS (SCuA) AND FOLIAR Cu APPLICATION FREQUENCIES (FCuAF) ON
MICRONUTRIENTS CONTENTS OF LEAF, FRUIT AND ROOT SAMPLES IN THE EXPERIMENT II (TENN-COP 5E, COPPER SALTS
OF FATTY AND ROSIN ACIDS)

¹Means in the same column followed by the same letter are not significantly different at 5 % probability level by LSD test.

²Means in the same row followed by the capital and bold same letter are not significantly different at 5 $%$ probability level by LSD test.

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In application of S2 and S3, Fe contents of root decreased with increasing of FCuAF and lowest Fe content was obtained with treatment of F2 and F3 (Table-2). Similar to the experiment I, the decrease in Fe content of root samples may relate with the decrease in root growth as a result of high level Cu application. The iron contents of plants decreased with increasing level of Cu applications. A similar response was reported in citrus seedlings, rice, miniature rose plant, tomato and cowpea by Alva and Chen³, Lidon and Henriques²⁵, Zheng *et al.*³³, Sonmez¹⁰ and Kopittke and Menzies³⁴.

SCuA and FCuAF independently affected Mn contents of leaf samples and there was no significant interactive effect between these applications. Leaf Mn content increased with increasing level of SCuA and the highest Mn content was obtained with application S3. Similarly, the increasing of FCuAF caused an increase and the highest Mn content was obtained with treatment F3 (Table-2). Increasing of both SCuA and FCuAF caused an increase in leaf Mn content. Fruit Mn content was significantly affected by SCuA, FCuAF and interactive effects between these applications. In treatment of F1; increasing of SCuA did not change in fruit Mn content. In treatment of F2 and F3, increasing of SCuA resulted in an higher Mn content in fruit samples. The lowest Mn contents were obtained with application S1 (Table-2). However; increasing of FCuAF did not caused significant differences in fruit Mn content in application S1. In application of S2 and S3, fruit Mn content initially increased and later decreased with increasing of FCuAF and highest Mn content was obtained with treatment F2 (Table-2). Mn contents of root was only affected by SCuA. Mn contents of root increased with increasing level of SCuA and the highest Mn content was obtained with application of S3. On the other hand, FCuAF did not change in root Mn content. The present results are in confirmity with the results of Pich and Scholz²⁷ and Sonmez¹⁰.

SCuA and FCuAF independently affected Zn contents of leaf and fruit samples and there was no significant interactive effect between these applications. Zn contents of leaf and fruit decreased with increasing level of both SCuA and FCuAF and the lowest Zn content was obtained with application of S3. The increasing of FCuAF caused a decrease and highest Zn contents was obtained with treatment F1 (Table-2). Zn contents of root was significantly affected by SCuA, FCuAF and interactive effects between these applications. In treatment of F1 and F2, increasing of SCuA resulted in an lower Zn content in root samples. The highest Zn contents were obtained with application of S1. In treatment of F3, increasing of SCuA did not change in Zn contents of root (Table-2). Increasing of FCuAF resulted in a decrease in Zn contents of root in all soil applications (S1, S2 and S3) and highest Zn content was obtained with treatment of F1 (Table-2). Similar to experiment I, Zn contents of plant tissues decreased with

increasing level of Cu applications. Data obtained in the present study support findings reported by Morishita et al.²⁹, Lidon and Henriques⁹ and Sonmez 10 .

The results of growth and yield of the experiment were previously reported by Sonmez et al.¹². Total yield, fruit number, dry root weight and plant height were affected by the level of Cu application to soil ($p < 0.01$) and the greatest total yield, fruit number, plant height and dry root weight were obtained when copper was not applied. Also the Cu application to leaves resulted in a decrease in dry root and copper application to soil and leaves led to a sharper decrease in dry root weight than when copper was only applied to soil¹².

Conclusion

Both in the experiment-I in which fungicide Gunner (containing copper oxychloride) and in the experiment-II in which fungicide Tenn-Cop 5E (containing copper salts of fatty and rosin acids) were used as copper source, combined applications of Cu to soil and leaves could be more deleterious to plants than when Cu is applied only to soil or leaves¹². Cu contents were affected from FCuAF in leaf samples, from independently both SCuA and FCuAF in fruit samples and from both SCuA and FCuAF in root samples.Cu contents of plant samples increased with increasing of SCuA and FCuAF. Fe contents of leaf and fruit samples were affected from only SCuA in the experiment I and from both SCuA and FCuAF in the experiment II, Fe contents of these samples decreased with increasing level of both SCuA and FCuAF. Fe content of root samples was generally affected in negative way showing an decrease with increasing of both SCuA and FCuAF in experiment I and II. Mn contents of leaf, fruit and root were affected by both SCuA and FCuAF. Generally, Mn contents of all plant samples were increased with increasing of SCuA and FCuAF in both experiment I and experiment II. Zn contents of leaf, fruit and root were affected by both SCuA and FCuAF and Zn contents of plant samples decreased with increasing level of SCuA and FCuAF.

As a result, both SCuA and FCuAF, especially aiming to control plant diseases, showed different effects on Cu, Fe, Mn and Zn contents of tomato plants. It was determined that, by taking into account the amount and frequency of applications, the Cu doses applied either to soil or leaf were too high.

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REFERENCES

- 1. H.A. Scroeder, Trace Elements and Nutrition, Faber & Faber (1973).
- 2. H.J.M. Bowen, Environmental Chemistry of the Elements, Academic Press, London, p. 237 (1979).
- 3. A.K. Alva and Q. Chen, *Soil Sci.*, **159**, 59 (1995).
- 4. H. Ozbek, Z. Kaya, M. Gök and H. Kaptan, Soil Science, Çukurova University Agriculture Faculty Press No. 16, Adana, Turkey (1999).
- 5. A.D. Robson and D.J. Reuther, Diagnosis of Copper Deficiency and Toxicity, Academic Press, London and Orlondo, p. 287 (1981).
- 6. D. Saurbeck, Fonktionen, Gufle und Belastbarkeit des Bodens aus Agruktulturche Mischer Sicht, Kohlhammer, Stutgart (1984).
- 7. I. Arduini, D.L. Godbold, A. Onnis and A. Stefani, *Chemosphere*, **36**, 739 (1998).
- 8. J.C. Hale, D.P. Ormred, P.J. Laffey and O.B. Allen, *Environ. Pollut.*, **39**, 53 (1985).
- 9. F.C. Lidon and F.S. Henriques, *J. Plant Nutr.*, **16**, 1449 (1993).
- 10. S. Sonmez, *Asian J. Chem.*, **19**, 2151 (2007).
- 11. M. Kaplan, *J. Plant Nutr.*, **22**, 237 (1999).
- 12. S. Sonmez, M. Kaplan, N.K. Sonmez, H. Kaya and I. Uz, *Scientia Agricola*, **63**, 213 (2006).
- 13. R.E. Nelson, Carbonate and Gypsum, Madison, Wisconsin, p. 181 (1982).
- 14. P.R. Day, Particle Fractionation and Particle Size Analysis, Madison, Wisconsin: SSSA, p. 545 (1982).
- 15. D.W. Nelson and L.E. Sommers, Total Carbon, Organic Carbon and Organic Matter, Madison, Wisconsin, p. 539 (1982).
- 16. S.R. Olsen and L.E. Sommers, Phosphorus, Madison, Wisconsin, p. 403 (1990).
- 17. B. Kacar, Chemical Analyses of Plant and Soil III, Soil Analyses. Ankara University Agriculture Faculty, Press No. 3, Ankara, Turkey (1995).
- 18. W.L. Lindsay and W.A. Norvell, *Soil Sci. Soc. Am. Proc.*, **42**, 421 (1978).
- 19. B. Kacar, Chemical Analyses of Plant and Soil, Ankara University Agriculture Faculty. Press No. 453, Ankara, Turkey (1972).
- 20. O. Quariti, N. Boussama, M. Zarrouk, A. Cherif and M.H. Ghorbal, *Phytochemistry*, **45**, 1343 (1997).
- 21. F.M. Rhoads, R.D. Barnet and S.M. Olson, *Proc. Soil Crop Sci. Soc. Florida*, **51**, 18 (1992).
- 22. A.S. Ivanova, *Agrokhimiya*, **10**, 76 (1987).
- 23. M. Tagliavini, D. Bassi and B. Marangoni, *Sci. Hort.*, **54**, 13 (1993).
- 24. K. Mengel and E.A. Kirkby, Principles of Plant Nutrition, International Potash Institute Bern, Switzerland (1982).
- 25. F.C. Lidon and F.S. Henriques, *Soil Sci.*, **154**, 130 (1992).
- 26. G. Ouzounidou, *Environ. Exp. Bot.*, **34**, 165 (1994).
- 27. A. Pich and G. Scholz, *J. Exp. Bot.*, **47**, 41 (1996).
- 28. H. Marschner, Mineral Nutrition of Higher Plants, Academic Press, London (2003).
- 29. T. Morishita, A. Yamaguchi and Y. Ohta, *Soil Sci. Plant Nutr.*, **29**, 219 (1983).
- 30. D.H. Liu, W.S. Jiang and W.O. Hou, *J. Environ. Sci. (China)*, **13**, 228 (2001).
- 31. J.X. Lin, W.S. Jiang, D.H. Liu, *Biores. Technol.*, **86**, 151 (2003).
- 32. A.K. Alva, B. Huang, O. Prakash and S. Paramasivam, *J. Plant Nutr.*, **22**, 1687 (1999).
- 33. Y.B. Zheng, L.P. Wang and M.A. Dixon, *Hortscience*, **39**, 1116 (2004).
- 34. P.M. Kopittke and N.W. Menzies, *Plant Soil*, **279**, 287 (2006).