HEAVY METAL CONCENTRATIONS IN SOILS AND IRRIGATION WATERS IN THESSALY REGION, CENTRAL GREECE

I. K. Mitsios\textsuperscript{1*}, E. E. Golia\textsuperscript{1} and C. D. Tsadilas\textsuperscript{2}

\textsuperscript{1} University of Thessaly, Department of Agriculture, Crop Production and Rural Environment Laboratory of Soil Science
Fytokou Str., N.Ionia, 38 446 Magnissias Greece
\textsuperscript{2} Institute of Soil Classification and Mapping
Theophrastou Str., Larissa, 413 35 Greece
* Corresponding author: email: imits@uth.gr

ABSTRACT

The purpose of this work was to provide information on heavy metals concentration in soils and in irrigation water in Thessaly, Central Greece, where tobacco (Nicotiana tabacum) is cultivated. Tobacco tends to accumulate high levels of heavy metals, especially Cadmium. During the years 1998, 1999 and 2000, 795 surface soil samples (0-30 cm depth) and 200 water samples were collected from Karditsa, Larissa and Trikala areas. Soil samples were analyzed for pH, organic matter, electrical conductivity and clay content. Total (extraction with Aqua Regia) and available (DTPA extractable) heavy metal (Zn, Cu, Mn, Cd and Pb) concentrations were determined by FAAS and GF-AAS technique. The same technique was also used for the determination of the dissolved heavy metals in acidified (HNO\textsubscript{3}) water samples (pH<2).

The values of soil pH ranged between 4.3 and 8.4, organic matter content between 0.2 and 2.6%, electrical conductivity between 108 and 1100 µS cm\textsuperscript{-1} and clay content between 12 and 39%. Total concentration of extractable Zn, Cu, Mn, Cd and Pb (Aqua Regia method) ranged between 12 and 57, 5 - 61, 156 - 2231, 0.03 - 0.93 and 3 – 47 mg kg\textsuperscript{-1} dry soil, respectively and were all below European Community recommended limits. The concentration of heavy metals (DTPA method) in relation to total concentration (Aqua Regia method) was as follows: Cd: 17.8%, Pb: 6.7%, Cu: 3.8%, Mn: 1.9% and Zn: 1.6%. Significant negative correlation was found between soil pH and DTPA extractable Zn (0.48**) and Mn (0.78**). Total soil metals were significantly correlated with organic matter content Zn
(0.33**), Cu (0.48**), Pb (0.39**); soil clay Zn (0.32**) and Cu (0.35**). In irrigation water dissolved heavy metals in most cases, were not detectable.

INTRODUCTION

It is well known that micronutrients such as Iron (Fe), Manganese (Mn), Copper (Cu) and Zinc (Zn) are essential metals for plant growth and yield. However, plants may accumulate heavy metals existing in soils, such as Cadmium (Cd), Nickel (Ni), Chromium (Cr) and Lead (Pb) which are not essential for plant growth, but may cause serious problems to the environment [1]. The concentration of heavy metals in soil solution plays a critical role in controlling the availability of ions to plants [2]. The solubility and therefore the bioavailability of heavy-metal ions vary widely because many factors influence their concentration in soil solution. The most important factors affecting metal availability, are soil pH [3, 4], clay content [5] and organic matter content [6].

Heavy metal concentrations in soil are typically quantified and regulated on the basis of total metal content, regardless of their solubility. However, soils containing large amount of colloidal organic and mineral material, can sorb and immobilize these metals to a greater extent than soils with a low content of these reactive materials [7]. Available forms of heavy metals are determined using several extracting solutions such as, DTPA [8], AB-DTPA (Ammonium Bicarbonate DTPA) [9] and NH$_4$NO$_3$ [10, 11].

The objective of this work was:

I) to determine heavy metals (Zn, Cu, Mn, Cd and Pb) concentrations in soils and in irrigation water in Thessaly area, the most important agricultural area in Greece,

II) to determine the most important soil factors (chemical and physical) which influence heavy metals concentrations in soils, and

III) to investigate the relationship between available concentrations of heavy metals (DTPA method) and total concentrations (Aqua Regia method).

MATERIALS AND METHODS

A three years survey (1998 to 2000) was conducted in Thessaly region in order to determine heavy metals content in soil samples as well as in irrigation water samples. During the year 1998, 354 soil samples were collected, while 245 and 196 soil samples, from the same areas, were collected during the years 1999 and 2000 respectively.
Soil composite samples consisting of six sub samples, were collected from the upper layer (0-30cm depth) of each field. Soil samples were collected from 795 sites with two independent replicates for each sample. The samples were air-dried, sieved through a 2-mm sieve and analyzed for soil pH (1:1) [12], electrical conductivity (1:1), clay content (%) and organic matter (Walkley-Black method) [13]. Available metals were determined using diethylene-triamine-pentacetic acid (DTPA) buffered at pH 7.3 [8]. Air-dried soil (30g) was shaking up with 60mL of DTPA solution for 2h. Extracts were collected by filtration through Whatman® No.42 filter paper and analyzed for Zn, Cu, Mn, Cd and Pb concentrations.

Total concentration of heavy metals was determined using Aqua Regia (HCl-HNO₃, 3:1) extraction method [14]. 3g of soil sample had been digested for 2h at 180°C. Cadmium and Lead were determined by atomic absorption spectrophotometry (AAS) using the Graphite Furnace technique. Furthermore, Zn, Cu and Mn were determined by flame AAS. Deuterium background corrections were used in the analysis of Cd and Pb [15,16].

Certified Reference Material (C R M) (No 141R, calcareous loam soil) by B C R (Community Bureau of Reference) was also analyzed for the verification of the accuracy of trace element determination in soils.

Dissolved metals in irrigation water samples were determined soon after sampling. A 200 mL sample of irrigation water was filtered through a 0.45µm membrane filter. The filtrate was acidified with 0.6 mL of 1:1 HNO₃ [17]. The concentration of heavy metals was measured using Graphite Furnace AAS technique.

A t-test was used to determine if there was significant difference among the concentration of heavy metals during the period of the investigation. The t-tests used, were: comparisons of two independent sets of data and the paired comparisons, at the 99% and 95% levels of probability.

RESULTS AND DISCUSSION

Table 1 shows heavy metals concentration in irrigation water samples averaged over the years 1998 to 2000.

The values of pH in irrigation water samples ranged between 6.9 and 7.5, while electrical conductivity had a minimum value of 198 µS cm⁻¹ and a maximum value of 1110 µS cm⁻¹.

The concentration of heavy metals in irrigation water samples was, in most cases, not detectable. Maximum values of heavy metal concentration in all cases were lower than those imposed by the EC.
Table 2 shows the minimum, maximum, mean and coefficients of variation of chemical and physical properties of soil samples, collected during the years 1998, 1999 and 2000. Soil pH values ranged between 4.3 and 8.4, while electrical conductivity ranged between 108 and 1100 µS cm\(^{-1}\). The mean value of organic matter content (%) was 1.2 during the years 1998 and 2000. The percentage of soil clay content ranged between 11.5 and 39.

Table 3 shows the concentration of available heavy metals (DTPA method) in soil samples during the years 1998, 1999 and 2000. Using a t-test it was found that there was no statistical difference among the three years. The concentration of available heavy metals ranged as follows: Zn (0.03-5.5), Cu (0.10-7.0), Mn (0.60-128) mg kg\(^{-1}\) dry soil, Cd (0.1-137) and Pb (23-2865) µg kg\(^{-1}\) dry soil. The coefficient of variation, in all cases was higher than 50%, indicating a high degree of variability in the concentration of available heavy metals in soil samples.

Table 4 shows the total concentrations of heavy metals (Aqua Regia method) during the same period. Total concentrations of heavy metals ranged as follows: Zn (12-57), Cu (5-61), Mn (156-2231) mg kg\(^{-1}\) dry soil, Cd (30-930) and Pb (2963-47300) µg kg\(^{-1}\) dry soil.

To assess the relative availability of heavy metals as a fraction of the total the ratio of the available concentration (DTPA) to the total concentration (\(\frac{C_{\text{DTPA}}}{C_{\text{Aqua Regia}}} \times 100\)) was calculated for each metal. The percentages obtained for each year were: Zn: 2.2, Cu: 4.6, Mn: 1.9, Cd: 20.2, Pb: 5.2 in 1998, Zn: 1.5, Cu: 3.4, Mn: 2.2, Cd: 20.0, Pb: 7.1 in 1999 and Zn: 1.0, Cu: 3.4, Mn: 1.7, Cd: 13.2, Pb: 7.4 in 2000. The highest percentage was found for Cadmium (13.2-20.2), while for the other metals it ranged from about 1 to less than 10%. Therefore, the element of primary concern as a soil pollutant, Cadmium, had the highest general availability as measured by DTPA extractability. That result agrees with other investigations [19].

In Table 5 the maximum permitted values of heavy metal concentration in soils that have been evaluated by the European Community are shown. In all cases soil samples from the area studied had lower values of heavy metal concentrations than those permitted from the European Community regulation.

Soil samples were classified according to MAFF classification [21] based on the concentration of available heavy metals. Table 6 shows the classification of available Zn, Cu and Mn in five soil classes.

Table 7 shows the distribution of soil samples among soil pH classes according to the MAFF, 1988 classification.
Only a small number of soil samples had a pH value lower than 5 during the three years period. No soil sample with a pH value higher than 8.5 was found.

Figure 1 shows the frequency distribution of soil samples among five classes of available Zn, Cu and Mn during the years 1998 to 2000. The highest percentage of soil samples (85% of soil samples during the year 1998, 93% in 1999 and 93% in 2000) was classified in the first class where the concentration of available Zn was very low (< 1 mg kg\(^{-1}\) dry soil). Only a small number of soil samples (50 in 1998, 15 in 1999 and 14 in 2000) appeared to have Zn concentration between 1 to 3 mg kg\(^{-1}\) dry soil, which was characterized as a low concentration of available Zn, according to MAFF classification. Soil samples with a concentration of available Zn higher than 8mg kg\(^{-1}\) dry soil were not found.

The concentration of available Cu in most soil samples (351, in 1998; 245, in 1999; 192, in 2000) ranged between 0.3 and 3 mg kg\(^{-1}\) dry soil. In the first year of this investigation no soil sample had a concentration of available Cu higher than 3 mg kg\(^{-1}\) dry soil, while during the years 1999 and 2000, five and two soil samples respectively, had very high concentrations of available Cu (> 3 mg kg\(^{-1}\) dry soil).

The concentration of available Mn was lower than 50mg kg\(^{-1}\) dry soil in a large number of soil samples: 333, in 1998, 230, in 1999 and 192, in 2000. However, 21 soils in the year 1998, 15 in the year 1999 and 4 soils in the year 2000 had a high concentration of available Mn (>50 mg kg\(^{-1}\) dry soil).

Table 8 shows the mean values of available heavy metals concentration among soil pH classes. It was found that when the pH value of the soils was above 5 the mean values of available Zn during 1999 and 2000 were approximately the same. When soil pH ranged between 5.8 and 6.5, the mean value of available Cu concentration was approximately the same during the three year period while the mean value of available Mn concentration decreased when soil pH values increased. In 1998 and 1999 the mean concentration of available Cd and available Pb were almost the same.

Mean total values of heavy metals concentration in relation to soil pH indices are shown in Table 9. Total concentration of Zn and Cu did not vary among soil pH classes.

Figure 2 illustrates the relationship between mean available heavy metals concentration and soil pH while Fig. 3 shows the relationship between mean total heavy metals concentrations and soil pH averaged over the three year period.

There was a linear negative regression between mean concentration of available Mn and soil pH. The values of soil pH did not affect the total concentration of heavy metals,
however the total mean concentration of Mn in soils with pH between 7.5 and 8.5 was 41.1% lower than the total Mn concentration in soil samples with pH between 5.0 and 5.8.

The ratio of available concentration to total concentration of heavy metals ($C_{\text{DTPA}}/C_{\text{Aqua Regia}}\times100$), averaged over the three years, was for Mn and Cd higher in soils with a pH between 4.0 and 5.0. However, as pH increased, the Mn and Cd ratio decreased. Those results show that soil acidity affects the levels of micronutrients available to plants [22, 23].

Correlation analysis was used to establish relationships between available and total concentrations of heavy metals and soil physicochemical parameters.

Table 10 shows the correlation coefficients in soils from Thessaly area over three years (1998 to 2000) period time.

Significant negative correlation was found between soil pH and DTPA extractable Zn (0.48**) and Mn (0.78**). Total Mn concentration was negatively correlated to soil pH, whereas the correlation between total Cd concentration and soil pH was positive. Total concentrations of heavy metals were significantly correlated with organic matter content Zn (0.33**), Cu (0.48**), Pb (0.39**) and soil clay [Zn (0.32**) and Cu (0.35**)]. Total concentration of all metals studied correlated significantly with their available concentrations, with Mn exhibiting the highest correlation coefficient ($r=0.61**$). Available and total concentrations of Zn and Cu were significantly correlated with soil clay content. Available Mn concentration had a significant negative correlation with electrical conductivity of soil samples. There was an interaction among concentration of metals studied; high total Zn concentrations correlated with high total concentrations of Cu, Mn, Cd and Pb.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to European Community for financial support of the Project 96/T/35 entitled: “Monitoring and minimizing heavy metals content in tobacco”.

CONCLUSIONS

Dissolved heavy metals in irrigation water samples in most cases were not detectable. The highest percentage of soil samples had very low (< 1 mg kg$^{-1}$ dry soil) available (DTPA method) Zn concentrations. Available Cu and Mn concentrations had values lower than 3 and 50 mg kg$^{-1}$ dry soil respectively.
All soil samples had lower values of total heavy metals concentrations (Aqua Regia method) than those permitted by the European Community regulation.

The concentration of heavy metals (DTPA method) in relation to total concentration was as follows: Cd: 17.8%, Pb: 6.7%, Cu: 3.8%, Mn: 1.9% and Zn: 1.6%. Cadmium appeared to be the most available heavy metal as the ratio of available Cd concentration to total concentration was higher than the others metals.

A significant negative correlation was found between soil pH and extractable Zn and Mn (DTPA method). Total concentrations of heavy metals (Zn, Cu and Pb) were significantly correlated with organic matter content as well as with soil clay (Zn and Cu). Total concentration of all metals studied correlated significantly with their available concentrations.