## DETERMINATION OF HEAVY METAL DISTRIBUTION IN THE ENVIRONMENT OF THESSALONIKI, GREECE BY MEANS OF NUCLEAR MICROANALYSIS

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### INTRODUCTION

In the framework of the CRP "Determination of heavy metal distribution in the environment of Thessaloniki" three main subjects have been investigated:

1) The distribution of toxic elements in road-side dust of the area of Thessaloniki (This study has finished and results obtained have been published [1]).

2) Toxic element concentrations in an urban and rural site of the area of Thessaloniki (the study is continued).

3) Toxic element distribution in vegetables grown in the area of Thessaloniki (the study is continued).

Although the study of the third subject was not included in the final aims of the CRP, it became necessary after the findings that road-side dust in the area of Thessaloniki is polluted with As, Pb, Cd and Cr.

As there are many vegetable production sites in the area of Thessaloniki, even inside the industrial zone, we had to examine the toxic element content of the main species of vegetables grown.

This paper presents the first evaluations obtained from the analysis of 7 vegetable species (cabbage, carrot, celery, endive, leek, lettuce and spinach ) for As, Sb, Pb, Cd, Mn, Cu, Cr, Zn, Fe, Br, Ca and Mg. Vegetable samples were collected from 4 production sites, as shown in Fig. 1. Three of them (Diavata, Magnesia and Sindos) are located in the industrial area, whereas the forth (Redestos) is in an agricultural region.

The main activities in the industrial area of Thessaloniki are fertilizer and cement production, manganese ore treatment, iron and steel manufacturing, non-ferrous metal smelting processes, etc.

## EXPERIMENTAL

Composite samples from 7 vegetable species (cabbage, carrot, celery, endive, leek, lettuce and spinach) were collected from the selected sampling areas in March 1990. Samples were washed with tap water as normally in the kitchen. Then, they were reduced, oven-dried at 700°C for 3 days, and ground by using a food processor with stainless steel cutter.

The determination of As, Sb, Zn,Cr and Br in ground samples were performed by INAA combined with high resolution V-ray spectroscopy. The samples were activated at the 5 MW swimming pool-type research reactor of the N.R.C.P.S. "Democritos"/Athens, at a neutron flux of $2 \times 10^{13}$ $n \cdot cm^{-2} \cdot s^{-1}$ for 30 min. The counting was performed after a cooling time of 3 days at the Chemical Dept. of the University of Thessaloniki by using an Ge - $\gamma$-ray detector (efficiency 20% compared to 1" x 1" NaI (Tl) detector, energy resolution 1.8 KeV for the 1.332 MeV $^{60}$Co-line). The detector was connected to a 4 K Multichannel Analyser (CANBERRA S-35 Plus). The counting time was optimized in order to get information about all possible elements of interest. The IAEA Soil-7 and pepperbush reference materials were used for results validation.

Lead, cadmium, copper, iron, manganese, magnesium and calcium were determined by AAS after acid digestion of the dried samples with $HNO_3$ and $HClO_4$. Reagent blanks and pepperbush reference material were treated similarly.

Digested samples were analysed for Cu, Fe and Mn by direct flame-AAS versus acid-matched standard solutions. Strontium chloride was used as a spectrochemical buffer for Ca and Mg determination.

Cadmium and lead were extracted from the digested samples in butylacetate as mixed chelate complexes with N, N-hexamethylenedithiocarbamic acid, hexamethylene-ammonium salt (HMDTC-HMA) and pyrrolidinecarbodithiotic acid, ammonium salt (APDC) [2]. Metals extracted were determined by electrothermal AAS using a Perkin-Elmer 2380 G AA spectrophotometer equipped with an HGA400 graphite atomizer and a deuterium background corrector. Uncoated graphite tubes, pretreated with multiple additions of Ce(IV) were used.

## *RESULTS AND DISCUSSION*

Results obtained from the analysis of vegetable samples either by INAA or AAS are presented in Fig. 2-6.

Large variations of element concentrations were observed regarding both the vegetable species and the sampling sites.

### *Arsenic*

Arsenic is a constituent of most plants as a result of passive uptake from soil with the water flow. Apparently, it is translocated in plants since it can also be determined in the grain. However, with increasing soil As, the highest As concentration were always reported in old leaves and roots. [3].

Another possible source for plant contamination with As is the use of arsenical pesticides.

Arsenic concentrations in vegetables grown on uncontaminated soils are given in Table 1. In general, leafy vegetables concentrate more As than fruits.

Arsenic content in vegetables from the area of Thessaloniki ranged from the detection limit levels up to 1,2 $\mu$g/g d.w. Highest concentrations were found in endive and spinach from Diavata and Sindos, as well as in leek and lettuce from Magnesia. All these locations are in the industrial area. On the contrary, As concentrations in all vegetables from Redestos where below the detection limit indicating lower bioavailability of As in the agricultural area. Considering that the ccnsumption of arsenical herbicides is the same in all the production locations examined, one can suggest that the higher As content of vegetables grown in the industrial area are industrial As emissions. The high As concentration determined in the road-side dust of the industrial area supports this suggestion [1]. Primary As emitting sources located in the industrial are a of Thessaloniki are the fertilizer plant (where about 80,000 ton/year of pyrites are burned for sulphuric acid production), as well as various non-ferrous metal smelters and metal-processing industries [1].

The large variation of As concentration found between vegetables mean that some of them (e.g., endive, lettuce, spinach) are stronger As accumulators. More over, As concentrations in endive from Sindos and Diavata were found to surpass the maximum permissible concentrations of elements in foodstuffs for human consumption (Table 1).

*Chromium*

The Cr content in plants is mainly controlled by the soluble Cr content of soil. Usually a higher Cr content is observed in roots than in leaves or shoots, whereas the lowest concentration is in crains [3].

Common levels of Cr in plants are usually of the order of 0.02 to 0.2 μg/g d.w.; however, a relatively great variation is observed in the Cr content of food plants (Table 1).

Chromium content in vegetables from the area of Thessaloniki ranged from 0.7 to 26 μg/g d.w. From the vegetables examined, leek seems to be the strongest accumulator of Cr. It is noteworthy that all vegetables from Redestos were found to contain relatively higher concentrations. This should be attributed to the fact that Redestos is located in an area rich in chromate deposits [4]. Road-side dust in this area was also found to have a high Cr content (up to 1500 μg/g d.w.) [1]. Although Cr availability to plants is limited even in soils containing significant amounts of Cr several plants can accumulate as much as 0.3% (d.w.) Cr [3].

However, elevated content of this metal implants is significantly associated to anthropogenic sources,since high Cr concentrations (up to 17 ppm d.w.) have been reported for several plants (grass, lichens, mosses, etc) growing within urban or industrial areas [3,5].

The Cr content in vegetables from Diavata, which is the closest location to the phosphate fertilizer Olant, were lower than 5 $\mu$g/g d.w. with the exception of leek that contained Cr up to 15 $\mu$g/g d.w.

*Antimony*

Antimony is easily taken up by plants if present in soluble forms but is considered a non phytotoxic element. Antimony levels in plants are expected to increase in industrial areas (Sb, like As, may be associated with nonferrous ores and is likely to be a pollutant in industrial environments).

Varying concentration of Sb have been reported for edible plants (e.g., 4.3 ng/g f.w. for cabbage, 122 ng/g d.w. for barley roots, 10 ng/g d.w. for barley leaves, etc. [3]).

The Sb content of vegetables from the area of Thessaloniki was found to range from 24 up to 790 ng/g d.w. Highest concentrations were found in carrot, lettuce and spinach from Magnesia, whereas the Sb content in all vegetables from the agricultural area did not exceed 200 ng/9 d.w. This is in agreement with the spatial distribution of Sb concentration in the road-side dust of the area of Thessaloniki [1].

*Bromine*

The natural content of Br in plants does not exceed 40 $\mu$g/g d.w., and some higher values should apparently be related to pollution. The main anthropogenic source of Br is its release from automobile exhausts, while methyl bromide and other Br organic compounds used as fumigants for soils, grain, and fruits may also be serious sources of Br in human diet [3].

Some plant species can accumulate high concentrations of Br (more than 2000 ppm d.w.) in their tissues.

Bromine concentrations determined in vegetables from the area of Thessaloniki ranged from 4 to 82 μg/g d.w. Bromine concentration exceeding 40 g/g were observed only in spinach and endive from Diavata. The lowest Br concentration were determined in cabbage leaves from all locations suggesting that cabbage does not accumulate Br.

*Lead*

Lead occurs naturally in all plants. Although Pb is believed to be the metal of least bioavailability, it is taken up from soils by roots under a process governed by soil and plant factors [3].

Airborne lead is also readily taken up by plants through foliage, and there is likely to be a significant translocation of Pb into plant tissues.

Lead concentration in vegetation has increased in recent decades,owing to man's activities. However, natural Pb in plants growing in uncontaminated and unmineralized areas appears to be quite constant, ranging from 0.1 to 10 μg/g d.w. [3].

The Pb contents of edible portions of plants grown in uncontaminated areas range from 0.05 to 3.0 μg/g d.w. Larger variability-was observed for-the lead content of the vegetables grown in the area of Thessaloniki (0.1 - 9.1 μg/g d.w.) and some species were found to contain more Pb than the maximum permissible for human consumption (Table 2). Highest violations were observed in vegetables grown in the industrial area, such as lettuce from Sindos, cabbage froni Diavata, celery from Diavata and Magnesia. Nevertheless, Pb concentration exceeding the limit of 2.5 μg/g d.w. were also found in leek, endive and spinach from the agricultural area.

This could be attributed to the fact that Pb concentration in plants is strongly dependent on factors such as the distance from traffic and the direction of prevailing winds that can transfer airborne lead [6,7].

Another possible source for vegetable contamination with lead could be the use of organic fertilizers.Organically grown vegetables tend to have a higher Pb content due to the heavy metals that are present in organic fertilizers [8].

*Cadmium*

Cadmium is absorbed by plants by both the root and the leaf system. The soil pH is believed to be the major soil factor controlling Cd uptake. A great proportion of Cd is accumulated in root tissues, even when Cd enters the plant via foliar systems.

Phosphate fertilizers are known as important sources of Cd [3].

In man and animal nutrition, Cd is a cumulative poison, therefore, its content in food and feed plants has been widely studied. Some Cd concentrations determined in vegetables produced under uncontaminated conditions are given in Table 1. These data indicate that leafy vegetables, such as spinach, may have increased Cd content. However, when plants are grown on contaminated soil, Cd is very likely to be concentrated in roots.

The Cd content of vegetables grown in the area of Thessaloniki (Fig. 4) ranged from 0.01 to 0.67 $\mu$g/g d.w. Highest concentrations were observed in leafy vegetables, (lettuce from Sindos, endive from Magnesia and Diavata, etc), as well as in root vegetables such as celery from Diavata and Magnesia. Cabbage, carrot and leek showed a Cd content not exceeding 0.2 $\mu$g/g d.w.

It is noteworthy that some vegetable species grown in the agricultural area had a relatively high Cd content (e.g., endive, celery and spinach from Redestos). As there are no industrial emission sources of Cd in this area, this could be attributed to preferential Cd uptake from soil [1].

*Zinc*

Zinc is essential to plant and animal life. The average daily intake is 12-15 mg [9].

Environmental pollution with Zn greatly influences the concentrations of this metal in plants. In ecosystems where Zn is an airborne pollutant, the tops of plants are likely to concentrate more Zn. On the other hand, plants grown in Zn-contaminated soils accumulate a great proportion of the metal in roots [3].

Zinc concentrations determined in vegetables grown in the area of Thessaloniki ranged from 11 to 83 $\mu$g/g d.w. Cabbage, carrot and lettuce concentrations didn't show large variation between locations. The lowest Zn content was found in celery, spinach and endive from Redestos. This is in agreement with the lower Zn concentrations found in the road-side dust from this area in comparison to the industrial area [1]. However, leek grown in Redestos was found to contain more Zn than that grown in Diavata, Magnesia and Sindos. Zinc content in cabbage showed a similar pattern.

*Manganese*

Manganese is known to be taken up and translocated within plants rapidly. The soil pH is the major soil factor that governs the uptake. It is essential to plant and animal nutrition. The min human requirement is 3-9 mg daily [9].

Although plant foodstuffs are reported to contain variable amounts of Mn (ranging from 1.3 to 113 μg/g d.w.) its concentration in vegetables does not seem to vary significantly (Table 1).

However, Mn content of vegetable species from the area of Thessaloniki ranged from 12 to 140 μg/g d.w. (Fig. 5). Largest variations were observed between vegetable species rather than between locations. Thus, vegetables from Redestos were found to contain as much Mn as that from the industrial area. This is in agreement with the Mn concentration distribution in road-side dust.

The strongest Mn accumulators among the vegetable examined seem to be endive, spinach and lettuce, whereas cabbage, carrot, celery and leek were found to have a lower Mn content.

*Copper*

The appropriate content of Cu in plants is essential both for health of the plant and for the nutrient supply to man and animals. The concentration of Cu in plant tissues is a function of its level in soil, while elevated Cu content in food plants reflect man-made pollution.

Some Cu concentration in vegetables grown under natural conditions are given in Table 1, whereas higher concentrations have been reported for vegetables grown in contaminated sites (e.g., 64 μg/g d.w. in lettuce growing near a metal processing industry) [3].

The Cu content of the vegetables from the area of Thessaloniki didn't @how large variability ranging neither between locations nor between vegetable species. The highest Cu concentration (18 μg/g d.w.) was found in celery from Diavata, whereas in all the other cases it ranged between 3 and 12 μg/g d.w. Celery and endive seem to concentrate more Cu than the other species.

*Iron*

The appropriate content of Fe in plants is essential both for the plant health and the nutrient supply to man and animals. An adult male requires 10 mg of iron/day [9].

Edible parts of vegetables appear to contain similar amounts of Fe, ranging from 16 to 130 μg/g d.w., with -lettuce being in the upper range and carrot in the lower range (Table 1).

Iron concentrations determined in carrot roots and lettuce leaves from the area of Thessaloniki were found in the same range with the data of Table 1. However, higher Fe concentrations, up to 390 μg/g d.w., were observed in other vegetable species. Spinach, as known, is a strong Fe accumulator, whereas endive and leek can also concentrate great amounts of Fe.

*Calcium - Magnesium*

Calcium and magnesium are major components of plant tissues. The % concentration of these elements in vegetables grown in the area of Thessaloniki is given in Fig. 6.

As can be seen, the Ca content ranged from 0.15 to 0.98% d.w. Carrot, celery and leek were characterized by a relatively low Ca content, whereas endive and lettuce by higher Ca concentrations. The highest Ca concentration (about 1% d.w.) was found in spinach from Redestos.

The Mg content of vegetables from the area of Thessaloniki was fairly similar (ranging from 0.1 to 0.3% d.w.), except spinach which seems to concentrate higher (up to 0.96% d.w.) amounts of Mg.

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Table 1. Trace element concentrations (µg/g d.w.) in vegetables grown in uncontaminated areas [3].

| Element | Cabbage (leaves) | Lettuce (leaves) | Spinach (leaves) | Carrot (roots) |
|---|---|---|---|---|
| As | 0.02-0.05 | 0.02-0.25 | 0.20-1.50 | 0.04-0.08 |
| Cr | 0.0013[a] | 0.008[a] | | 0.018[a] |
| Sb | 0.043[a] | | | |
| Pb | 1.7-2.3 | 0.7-3.6 | | 0.5-3 |
| Cd | 0.05 | 0.12-0.66 | 0.11[a] | 0.07-0.35 |
| Zn | 24-31 | 44-73 | | 21-27 |
| Mn | 14-28 | 29 | | 8-28 |
| Fe | 42 | 130 | | 16-54 |
| Br | 0.37[a] | 20-22 | | 0.85[a] |
| Cu | 2.9-4.0 | 6.0-8.1 | 1.7[a] | 4.0-8.4 |

a: fresh weight basis

d.w.: air dried or oven dried (up to 70°C) weight basis

Table 2. Maximum permissible concentrations of elements in vegetables for human consumption [10].

| Element | C(μ g/g D.W.) |
|---|---|
| As | 1 |
| Cd | 1[a] |
| Cr | - |
| Pb | 2-2.5 |
| Cu | 50 |
| Sb | 1[a] |
| Zn | 10-50 |

[a]Food in general, excluding fish, vegetables and beverages.

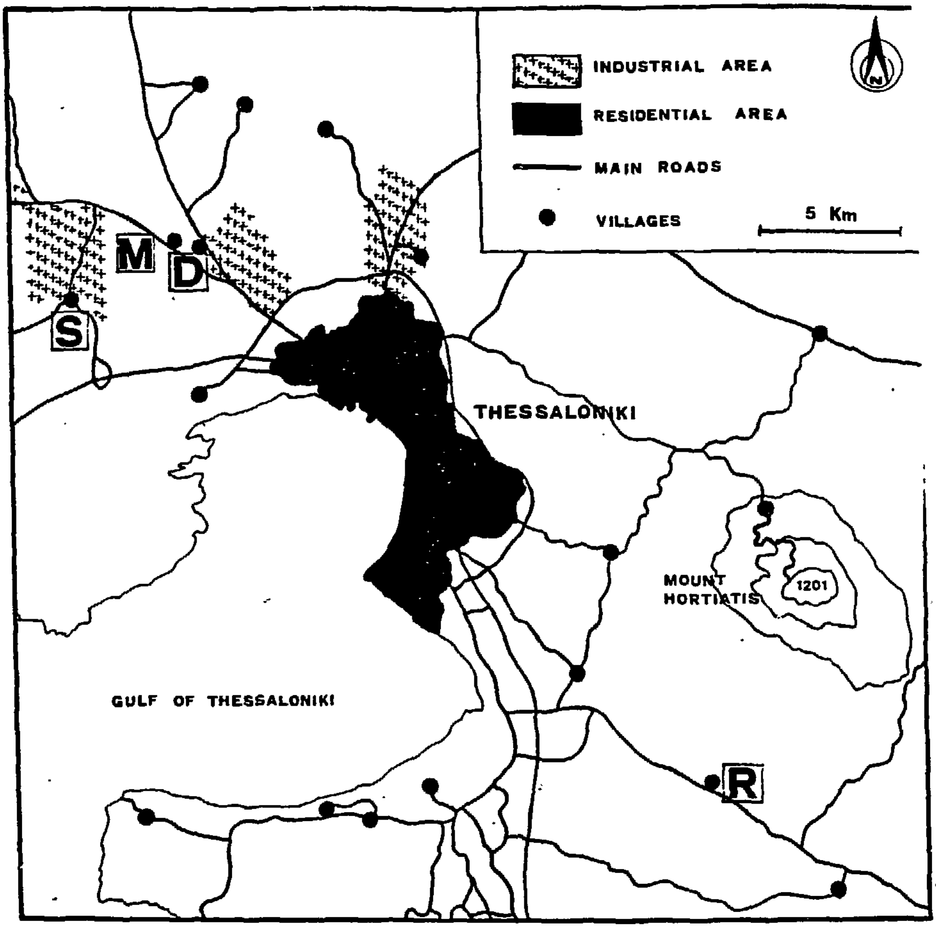


Fig. 1. Map of the sampling area (D: Diavata, M: Magnesia, S: Sindos, R: Redestos).

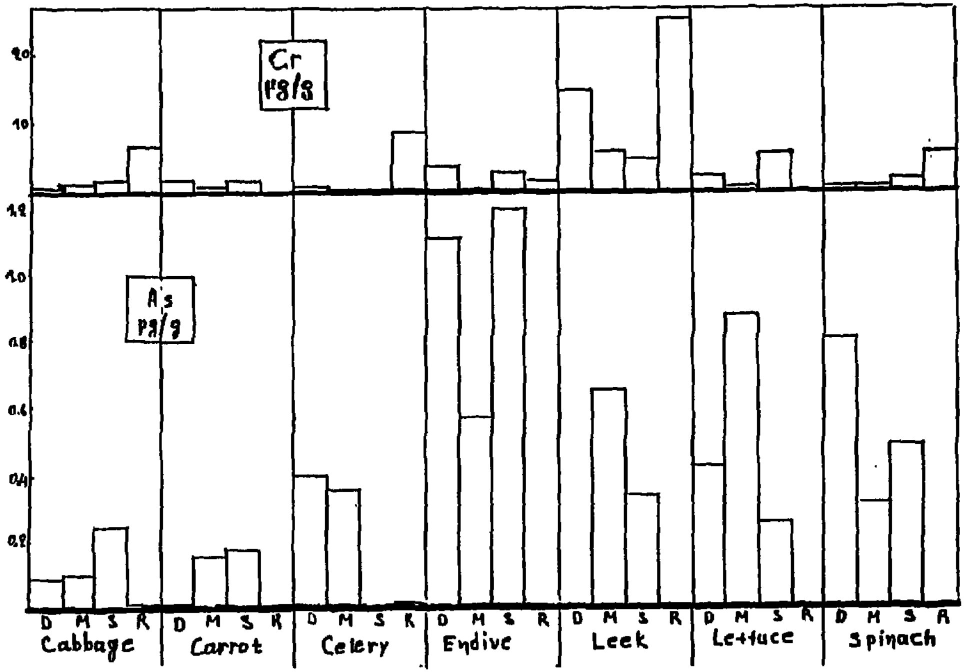


Fig. 2. As and Cr concentrations in vegetables grown in the area of Thessaloniki.

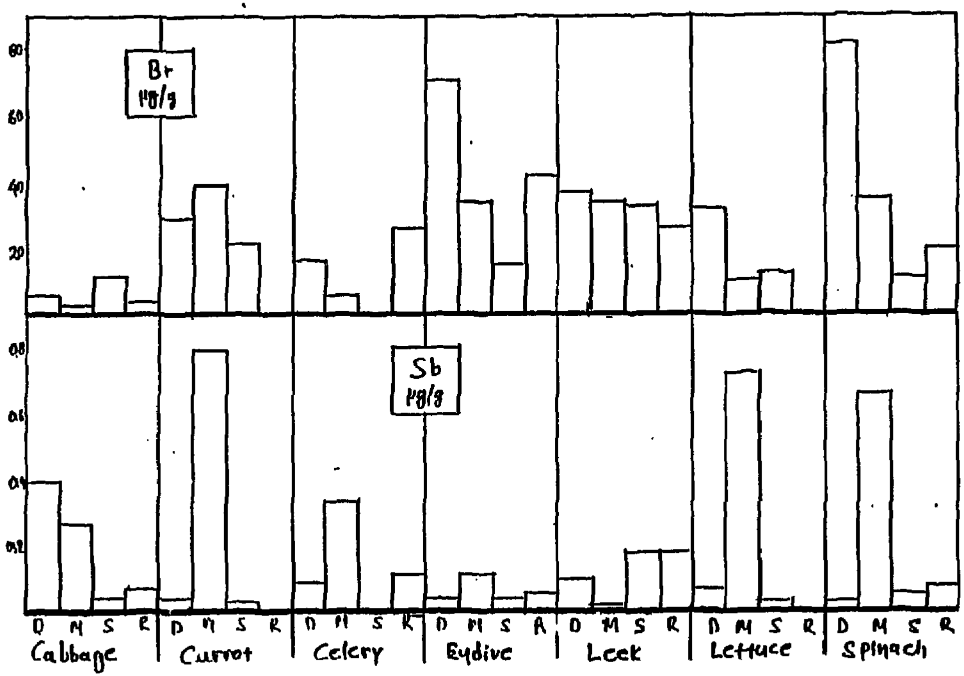


Fig. 3. Br and Sb concentrations in vegetables grown in the area of Thessaloniki.

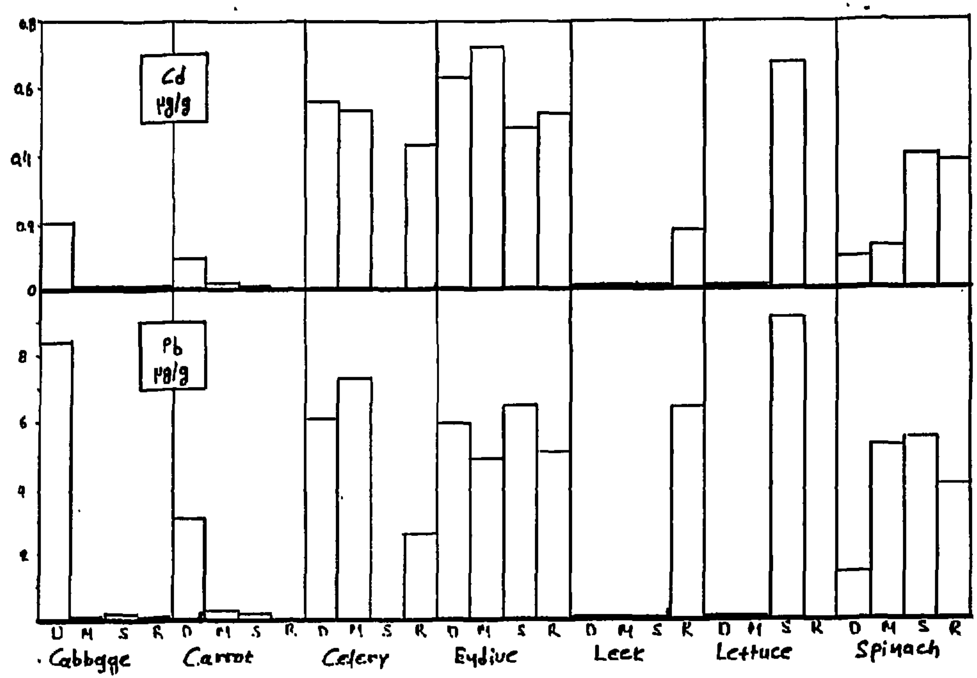


Fig. 4. Cd and Pb concentrations in vegetables grown in the area of Thessaloniki.

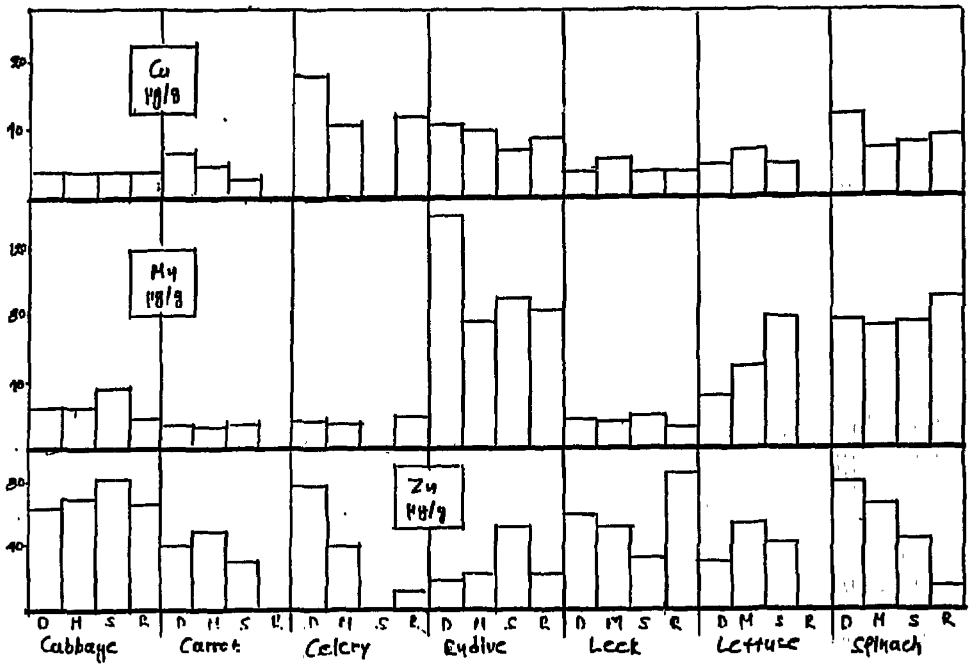


Fig. 5. Cu, Mn and Zn concentrations in vegetables grown in the area of Thessaloniki.

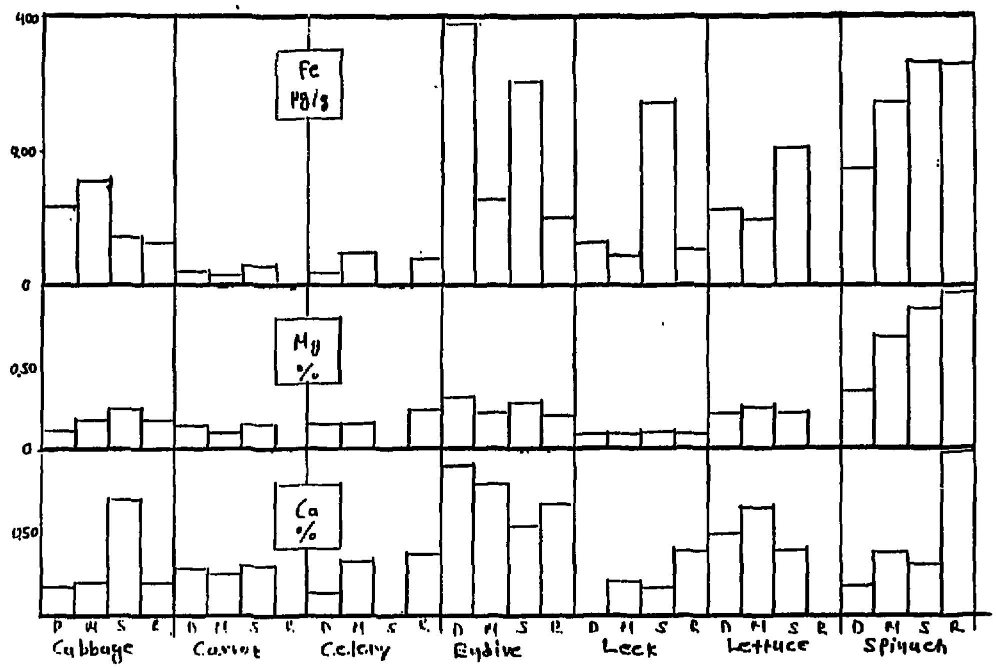


Fig. 6. Fe, Mg and Ca concentrations in vegetables grown in the area of Thessaloniki.