

Dedicated to Professor Apolodor Aristotel Răduță's 70th Anniversary

HEAVY METAL ACCUMULATION AND TRANSLOCATION IN DIFFERENT PARTS OF *BRASSICA OLERACEA L*

C. RADULESCU¹, C. STIHI¹, I.V. POPESCU^{1,2,5}, I.D. DULAMA³,
E.D. CHELARESCU^{2,4}, A. CHILIAN³

¹ Valahia University of Targoviste, Faculty of Science and Arts, Targoviste 130082, Romania
E-mail: radulescucristiana@yahoo.com, cstihi@yahoo.com, ivpopes@yahoo.com

² Horia Hulubei National Institute for Physics and Nuclear Engineering, P.O.Box MG-6, RO-077125
Bucharest-Magurele, Romania

³ Valahia University of Targoviste, Multidisciplinary Research Institute for Science and Technologies,
Targoviste, 130082, Romania

⁴ University of Bucharest, Faculty of Physics, Doctoral School, Bucharest 050107, Romania

⁵ Academy of Romanian Scientists, Spl. Independentei nr. 54, sector 5, 050094 Bucharest, Romania
Correspondence authors: C. Stihi, I. V. Popescu, E.D. Chelarescu, dana_chelarescu@yahoo.com

Received June 10, 2013

The aim of this study was to quantify the concentration of seven heavy metals including (Cd, Fe, Mn, Cu, Zn, Pb, and Ni) in soil and to investigate the bioavailability of heavy metals from soil to different parts of *Brassica oleracea L. var. capitata*. The mobility of heavy metals from soil into the food chain and their bioaccumulation in cabbage has increased from safety point of view. The metal concentrations were determined by Flame Atomic Absorption Spectrometry technique. In this study the highest concentration of copper and iron in soil were obtained. This can be a consequence to the using excessively the fertilizers, pesticides and copper sulphate as treatment for cabbage protection. The manganese, nickel, zinc and cadmium concentrations in soil not exceed the normal values according with the Romanian Regulation. The bioaccumulation factor (BF) of seven heavy metals in cabbage revealed that this vegetable was a poor accumulators of Fe, Ni, Cu, Cd, and Pb (BF <1), and good accumulator of Mn (BF >1). Obviously, only with BF is no possible to establish if the cabbage may be considerate as accumulator species for a certain metals and from this reason the translocation factor (TF) was calculated.

Key words: *Brassica oleracea L. var. capitata*, heavy metal, flame atomic absorption spectrometry, accumulation factor, translocation factor.

1. INTRODUCTION

In Romania, from the point of view of cultivated land, *Brassica oleracea L. var. capitata* ranks the second place, which means approximately 21% of the total

cultivated area with vegetables. Therapeutic properties of cabbage are known from antiquity and many peoples used this vegetable. The nutritional value [1] of the cabbage is emphasized by the high vitamins content, such as, vitamin A (5 μ g/100g) vitamin C (37 mg/100g), vitamin E (0.2 mg /100g), vitamin B6 (0.1 mg/100g), vitamin B3 (0.2 mg/100g), vitamin K (76 μ g/100g) and vitamin U. This vegetable has lower levels of saturated fat and cholesterol and is a good source of thiamin, calcium, iron, magnesium, phosphorus, potassium, dietary fiber, folate (vitamin B9) and manganese as well. In this respect the cabbage is a usefully food for the people of the whole world. From a traditional point of view, in many Eastern European countries, cabbage in the form of sauerkraut is one of appreciate traditional foods. A real matter of serious concern is the fact that the cabbage can be a prolific accumulator of heavy metals from soil, providing an easy entry into food chain of these toxic metals. It is well known that heavy metals appear in the soil in soluble form, as well as in combined forms. Certainly, only soluble exchangeable and chelated metal species in the soils are mobile and therefore available to the plants [2, 3]. However, metal can be accumulated in plant depending on vegetable species, growth stages, soil composition, geographic and atmospheric conditions, and type of metal [4-6].

The aim of this study was to investigate that *Brassica oleracea L. var. capitata*, can accumulate some soluble form of heavy metals from soil in different edible parts which can be a direct pathway for metals incorporation into the human food chain.

2. EXPERIMENTAL PART

2.1. SITE DESCRIPTION

The investigated area is one of the old villages from Southern of Dambovită County, namely Puntea de Greci, with traditional activities in agriculture and vegetable farming. In this area is cultivated especially cabbage and potatoes.

As pollution sources can be mentioned auto traffic (*i.e.* the highway A1 and other district roads – Figure 1), fertilizers and domestic wastes.

2.2. SAMPLING

The basic plant material of *Brassica oleracea L. var. capitata* used for investigation was obtained by sampling from seven well-established points (Fig. 1 and Table 1) which represent the most cultivated sites of Puntea de Greci village. The global positioning system (GPS) was used in recording the coordinates and geographical information system (GIS) was used to locate the map of the investigated sites (Table 1). The cabbage was collected according with [7] and [8].



Fig. 1 – Vegetable farming area Puntea de Greci, Dambovită County.

Table 1

Geographical information system (GIS) and sampling codes of cabbage and soil

| Sampling points | GIS coordinates | | Altitude [m] | Soil sample | Component parts | Cabbage sample |
|-----------------|-----------------|--------------|--------------|-------------|---|--|
| | N | E | | | | |
| P1 | 44°38'54.73" | 25°18'11.12" | 168 | S1 | Outer leaf Interior leaf Core Interior stem Exterior stem Root | V1 V2 V3 V4 V5 V6 |
| P2 | 44°39'01.33" | 25°18'02.02" | 174 | S2 | Outer leaf Interior leaf Core Interior stem Exterior stem Root | V7 V8 V9 V10 V11 V12 |
| P3 | 44°38'57.97" | 25°18'21.90" | 170 | S3 | Outer leaf Interior leaf Core Interior stem Exterior stem Root | V13 V14 V15 V16 V17 V18 |

Table 1 (continued)

| | | | | | | |
|------------|--------------|--------------|-----|----|---|--|
| P4 | 44°38'58.71" | 25°18'04.19" | 173 | S4 | Outer leaf Interior leaf Core Interior stem Exterior stem Root | V19 V20 V21 V22 V23 V24 |
| P5 | 44°38'54.61" | 25°18'13.42" | 165 | S5 | Outer leaf Interior leaf Core Interior stem Exterior stem Root | V25 V26 V27 V28 V29 V30 |
| P6 | 44°38'55.10" | 25°18'16.95" | 172 | S6 | Outer leaf Interior leaf Core Interior stem Exterior stem Root | V31 V32 V33 V34 V35 V36 |
| P7 (Blank) | 44°38'23.97" | 25°18'29.93" | 164 | S7 | - | - |

Each cabbage samples were coded from P1 to P6 and then were selected in component parts such as: outer leaf, interior leaf, core, interior stem, exterior stem and root, coded from V1 to V36 as well (*e.g.* Table 1). All the samples were washed with deionized water and dried at 60°C in 72 hours. Then samples were powdered and weighed in order to determine the heavy metals concentrations by atomic absorption spectrometry. The sampling and preparation procedure of soil (*i.e.* S1–S7) were achieved according with [9, 10].

2.3. ATOMIC ABSORPTION SPECTROMETRY AND SAMPLES PREPARATION PROCEDURES

Approximately 0.2 g of cabbage samples were digested with 8 mL of HNO₃ (65% Merck) and 10 mL H₂O₂ (30% Merck) in a Berghof MWS-2 microwave digestion system. The digestion was carried out at 220°C, at a pressure of 75 MPa for 20 minutes. The clear solutions were filtered and were brought in 50 mL volumetric bottle with distilled deionized water. The metal concentrations were determined by Flame Atomic Absorption Spectrometry (FAAS) technique [11–16]. All concentrations were reported as mg/kg dry weight of material. For the quality assurance, the results were checked by carrying out a triplicate analysis according to certified standard reference materials NIST SRM 1515 (Apple leaves) and was obtained a recovery between 95.9% and 101.2%. A quantity of approximately 0.5 g of soil samples were mineralized with 12 mL HNO₃ (65% Merck), 6 mL HCl (37% Aldrich), 4 mL HF (40% Aldrich) and 1 mL H₂SO₄ (96% Aldrich) according with 3051 EPA standard. Heavy metals concentrations were analysed by Flame Atomic

Absorption Spectrometry (FAAS). To check the analytical precision, randomly chosen samples (about 20% of the total numbers) were measured in triplicate according to International Standard Reference Material: NIST SRM 2709, 2710 and 2711 for soil. Average recoveries ($n = 5$) were between 85 and 99% for analysed heavy metals. Measurements of pH values of soil were carried out in deionized water ratio of 1:2 according to the NF ISO 10390/2005 procedure. pH determination was performed with Consort P501 pH-meter.

3. RESULTS AND DISCUSSION

The results obtained for pH of soil samples and soil reaction as well, are presented in Table 2. The pH values ranged from 6.56 to 7.53 (Table 2).

Table 2

Soil reaction at measured pH values

| <i>Soil</i> | <i>pH</i> | <i>Soil reaction</i> |
|-------------|-----------|----------------------|
| S1 | 7.54 | weak alkaline |
| S2 | 7.43 | weak alkaline |
| S3 | 7.09 | neutral |
| S4 | 7.23 | weak alkaline |
| S5 | 7.21 | weak alkaline |
| S6 | 6.92 | neutral |
| S7 | 6.56 | weak acidic |

These values are in concordance with the pH acceptable range for cabbage cultivation (*i.e.* pH 6.0 - 7.5).

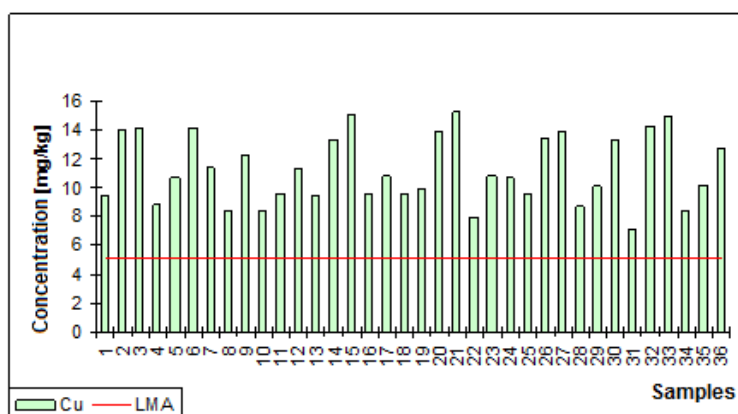
Table 3

Mean of heavy metals concentrations in *Brassica oleracea L.* parts

| <i>Cabbage sample</i> | <i>Component parts</i> | <i>Mean of heavy metals concentrations [mg/kg d.w.]</i> | | | | | | |
|-----------------------|------------------------|---|-----------|-----------|-----------|-----------|-----------|-----------|
| | | <i>Cu</i> | <i>Fe</i> | <i>Mn</i> | <i>Ni</i> | <i>Zn</i> | <i>Cd</i> | <i>Pb</i> |
| V1 | Outer leaf | 9.43 | 226.08 | 78.20 | 2.37 | 22.66 | 0.98 | 1.09 |
| V2 | Interior leaf | 13.90 | 202.24 | 48.45 | 2.24 | 55.76 | 0.82 | 0.92 |
| V3 | Core | 14.09 | 184.49 | 48.84 | 2.06 | 67.60 | 0.61 | 0.88 |
| V4 | Interior stem | 8.80 | 147.71 | 48.05 | 1.79 | 10.92 | 0.34 | 0.89 |
| V5 | Exterior stem | 10.66 | 159.94 | 34.56 | 1.64 | 26.02 | 0.28 | 0.72 |
| V6 | Root | 14.10 | 907.66 | 161.47 | 2.14 | 53.41 | 1.13 | 3.45 |
| V7 | Outer leaf | 11.39 | 194.14 | 64.70 | 2.30 | 25.89 | 0.78 | 1.02 |
| V8 | Interior leaf | 8.41 | 154.83 | 78.99 | 2.40 | 13.66 | 0.56 | 0.79 |
| V9 | Core | 12.27 | 158.57 | 66.05 | 2.21 | 48.85 | 0.41 | 0.82 |
| V10 | Interior stem | 8.44 | 141.99 | 57.10 | 1.99 | 11.23 | 0.36 | 0.98 |
| V11 | Exterior stem | 9.59 | 136.90 | 52.82 | 1.81 | 16.81 | 0.11 | 0.44 |
| V12 | Root | 11.28 | 1013.83 | 515.49 | 2.24 | 30.19 | 0.82 | 2.89 |

Table 3 (continued)

| | | | | | | | | |
|---|---------------|---------|---------|---------|---------|---------|-----------|---------|
| V13 | Outer leaf | 9.43 | 304.36 | 78.99 | 2.60 | 20.07 | 1.06 | 2.89 |
| V14 | Interior leaf | 13.37 | 201.79 | 44.65 | 2.31 | 40.08 | 0.92 | 1.89 |
| V15 | Core | 14.97 | 201.82 | 56.00 | 2.40 | 45.38 | 0.78 | 0.93 |
| V16 | Interior stem | 9.62 | 136.75 | 48.40 | 1.77 | 12.33 | 0.83 | 0.94 |
| V17 | Exterior stem | 10.77 | 143.89 | 26.38 | 1.88 | 15.51 | 0.76 | 0.57 |
| V18 | Root | 9.56 | 5767.02 | 1615.1 | 1.36 | 44.09 | 1.25 | 4.67 |
| V19 | Outer leaf | 9.87 | 213.28 | 110.57 | 2.74 | 22.84 | 1.10 | 2.11 |
| V20 | Interior leaf | 13.86 | 206.34 | 59.63 | 2.28 | 43.33 | 1.02 | 1.05 |
| V21 | Core | 15.20 | 229.77 | 70.38 | 2.43 | 65.01 | 0.89 | 1.03 |
| V22 | Interior stem | 7.90 | 151.05 | 34.20 | 1.91 | 9.89 | 0.88 | 0.95 |
| V23 | Exterior stem | 10.80 | 235.59 | 45.83 | 1.73 | 33.31 | 0.53 | 0.79 |
| V24 | Root | 10.70 | 2543.56 | 1180.52 | 1.50 | 47.19 | 1.35 | 3.49 |
| V25 | Outer leaf | 9.46 | 214.96 | 140.85 | 2.79 | 43.80 | 1.43 | 2.56 |
| V26 | Interior leaf | 13.48 | 204.04 | 96.29 | 2.39 | 52.60 | 1.16 | 1.88 |
| V27 | Core | 13.84 | 202.14 | 78.42 | 2.28 | 91.75 | 0.87 | 1.56 |
| V28 | Interior stem | 8.73 | 172.79 | 50.15 | 1.71 | 18.82 | 0.74 | 0.92 |
| V29 | Exterior stem | 10.08 | 145.27 | 25.95 | 1.49 | 63.88 | 0.65 | 0.81 |
| V30 | Root | 13.33 | 963.61 | 362.18 | 2.13 | 108.13 | 2.19 | 3.21 |
| V31 | Outer leaf | 7.07 | 195.43 | 53.86 | 2.40 | 13.72 | 1.01 | 1.84 |
| V32 | Interior leaf | 14.23 | 179.76 | 44.81 | 2.20 | 38.55 | 0.84 | 1.05 |
| V33 | Core | 14.90 | 193.25 | 61.60 | 2.28 | 54.00 | 0.76 | 0.84 |
| V34 | Interior stem | 8.40 | 217.18 | 60.37 | 1.76 | 9.21 | 0.57 | 0.93 |
| V35 | Exterior stem | 10.21 | 168.93 | 27.61 | 1.71 | 23.34 | 0.38 | 0.77 |
| V36 | Root | 12.76 | 957.66 | 148.67 | 1.91 | 30.62 | 1.74 | 3.22 |
| MAL for fresh or congealed vegetables / raw vegetable leaves (Ord. 975/1998 and JECFA 2005) | | 5.0 | - | - | - | 15.0 | 0.1 / 0.2 | 0.5 |
| RSD [%] | | 1.0-3.4 | 2.3-7.8 | 1.4-5.6 | 0.3-1.1 | 2.4-5.3 | 0.1-0.5 | 0.1-0.7 |

Fig. 2 – Copper concentration in *Brassica oleracea L.* samples.

The mean of heavy metals concentrations in *Brassica oleracea L.* parts are presented in Table 3. Usually copper is an essential element for the plant growing. This microelement reaches into the composition of many enzymes in plants, but the interval of positive actions being limited it may become very toxic in high concentrations. In this respect, it was analyzed copper concentrations in different parts of cabbage. From Table 3 and Figure 2 it can be seen that the copper concentration exceeded the maximum admitted limit (MAL) according with MAL (Ord. 975/1998 from Romanian legislation [18] and JECFA 2005) for fresh or congealed vegetables/raw vegetable leaves (5 mg/kg) in all analyzed samples. The highest levels were recorded on the interior and outer leaves, and this is a consequence of the application of foliar fertilizers with high copper content. A high concentration was found in the interior stem as well (Table 3). Lowest concentration of copper was found in the exterior stem of cabbage samples.

Iso-concentration curves (Figure 3) can be relevant for copper accumulation in different parts of *Brassica oleracea L. var. capitata*.

Therefore, Fig. 3a shows that the outer leaf collected from site P2 has a highest content of copper comparative with the other outer leaves. This can be explained by the using of fertilizers and treatment with copper sulphate near to the sampling period. Highest concentration of copper in core can be observed from Figure 3b for samples collected from P3, P4 and P6 sites. These samples accumulate copper from soil due to the treatments with copper sulphate applied to the cabbage to comb the disease called "fall seedlings". In these sites the copper concentrations in soil samples exceeded the MAL according with Ord. 956/1997 from Romanian Regulation. From Figure 3c it can be seen that the root collected from P1 site presents the highest concentration of copper comparative with the other roots collected from P2, P3, P4, P5 and P6 sites. However, the soil sample presents the lowest concentration of copper (Table 3). The explanation is the same: treatment with copper sulphate near to the sampling period.

Cadmium is a non-essential nutrient, and together with selenium, cesium, silver, lead and mercury, doesn't yet have a well-established biological role, being poisons for plants depending to the concentrations. Cadmium accumulation in plants depends by species and genus, as well as by the soluble form in soil. It is well-known the high cadmium bioavailability for plants and from this reason it can explain that the cadmium concentrations is so high in all cabbage samples (except V11 - exterior stem and V24 - root) comparative with MAL from Commission Regulation (EU) 1881/2006 [17] and Ord. 975/1998 from Romanian legislation [18] (Figure 4). The highest concentrations of cadmium were in V30 and V36 samples (*i.e.* root) (Table 3).

Zinc is a good nutrient for vegetable, which helps the chlorophyll formation in cabbage leaves. The zinc concentration is exceeded the MAL value according with Ord. 975/1998 and JECFA 2005, in most of the samples (except V4, V10, V16, V22, V28, V34). A highest concentration of zinc was found in root and core cabbage samples (Table 3 and Figure 5).

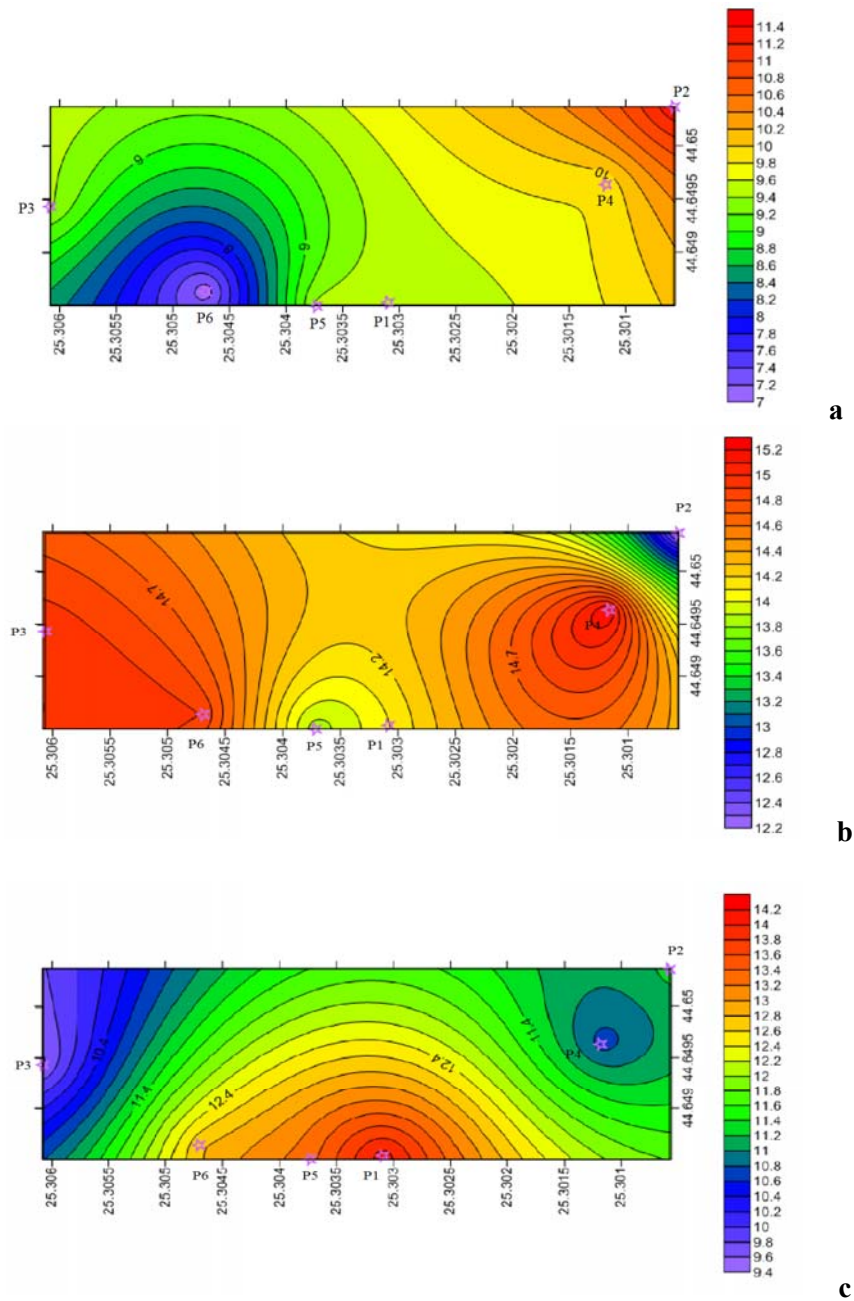


Fig. 3 – Copper concentration in *Brassica oleracea* L: outer leaf (a); core (b); root (c).

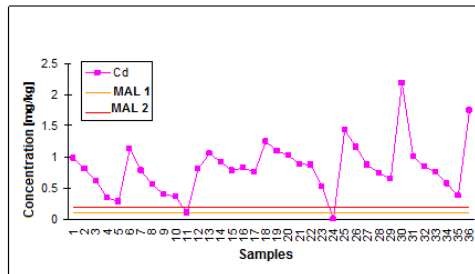


Fig. 4 – Cadmium concentration in *Brassica oleracea L.* samples.

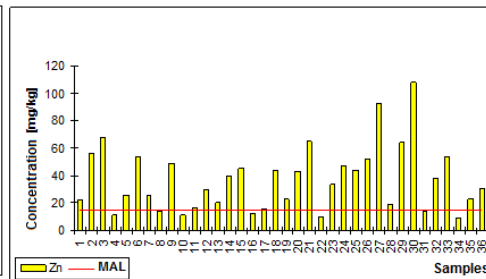


Fig. 5 – Zinc concentration in *Brassica oleracea L.* samples.

Lead is a toxic element for life and environment. The highest concentration of lead (Table 3 and Figure 6) was observed in all analyzed cabbage samples (except V11). The most important and alarming aspect was the highest concentrations of lead in all root samples which exceed by up to nine the MAL in Romanian legislation (*i.e.* 0.5 mg/kg) [18] and European Regulation (*i.e.* 0.3 mg/kg) [17]. It can be due by the historical pollution with lead provided from auto traffic (*e.g.* highway A1 and other county roads). In Romania the use of leaded petrol was banned completely only science January 2012.

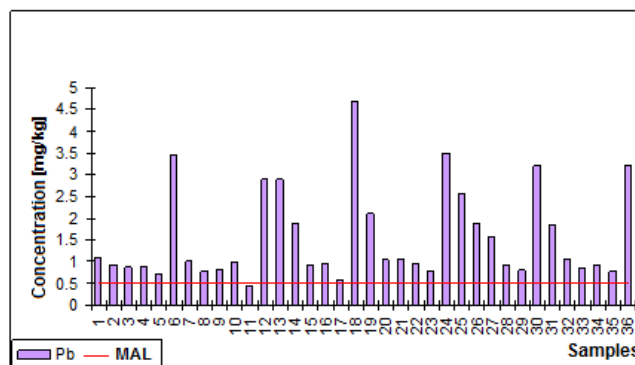


Fig. 6 – Lead concentration in *Brassica oleracea L.* samples.

The manganese is one of the most nutrients for vegetables and from this reason all fertilizers contain important quantities of manganese sulphate. In Romanian legislation is not specified the MAL for manganese in vegetables (*e.g.* 400 ppm of manganese are toxic for *Zea mays L*; 5 ppm of manganese is a toxic concentration for peanuts). In Table 4 are presented the obtained concentration of heavy metals in substrates comparative with the reference values from Romanian Regulation (Ord. 756/1997) [19] for heavy metals in soil.

Table 4

Heavy metals concentration in substrates of cabbage samples, comparative with the reference values from Romanian Regulation (Ord. 756/1997).

| Soil sample | Mean of heavy metals concentrations [mg/kg d.w.] | | | | | | |
|-------------------------|--|-----------|---------|---------|---------|---------|---------|
| | Cu | Fe | Mn | Ni | Zn | Cd | Pb |
| S1 | 350.65* | 7502.75** | 420.99 | 9.52 | 299.66 | 4.33 | 10.64 |
| S2 | 420.43* | 6690.55* | 402.23 | 5.59 | 353.93 | 3.78 | 8.44 |
| S3 | 462.83* | 8123.75** | 578.68 | 9.23 | 368.80 | 4.47 | 19.35 |
| S4 | 550.82** | 6578.64* | 413.75 | 8.38 | 280.85 | 4.68 | 9.21 |
| S5 | 706.64** | 6546.10* | 401.60 | 16.79 | 282.14 | 5.03* | 10.60 |
| S6 | 532.26** | 7969.47** | 354.54 | 16.17 | 242.75 | 3.02 | 14.68 |
| S7 (Witness) | 261.35* | 8603.45** | 535.36 | 8.08 | 343.83 | 2.85 | 6.44 |
| RDS | 1.2-6.2 | 1.0-7.8 | 1.4-4.6 | 0.5-1.1 | 1.2-3.7 | 0.1-0.9 | 0.3-1.3 |
| Normal value (VN) | 20 | 3000 | 900 | 20 | 100 | 1 | 20 |
| Maxim value (PM) | 250 | 4500 | 2000 | 200 | 700 | 5 | 250 |
| Intervention value (PI) | 500 | 7000 | 4000 | 500 | 1500 | 10 | 1000 |

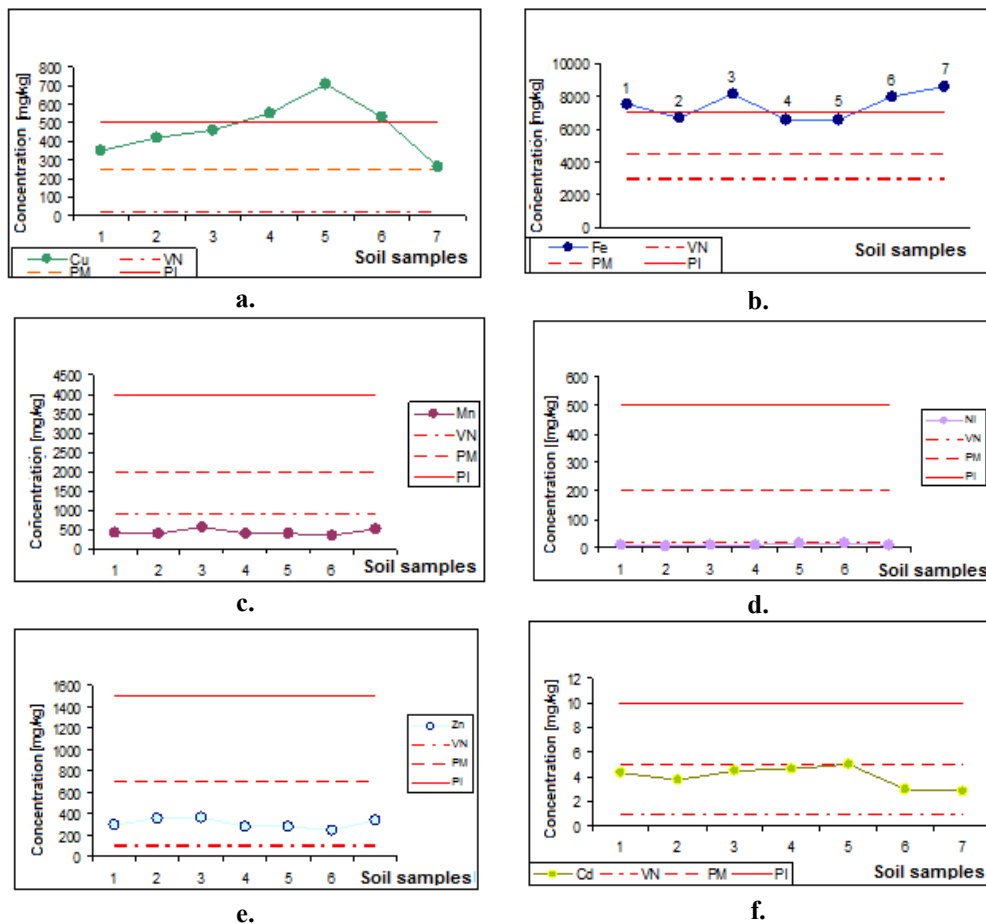
* Values which fall in the intervention threshold; ** Values which exceed the intervention threshold.

Naturally without pollution, the copper concentration in soil is 20 ppm. This content is due to the presence of copper in minerals which can be released only by very slow disintegration processes. However this concentration of copper can increase significant under anthropogenic activities including non-ferrous metal processing, using the substances for plant protection and so on. Table 4 and Fig. 7 show that in all soil samples the copper concentration exceeded the maximum level to intervention threshold according with Romanian Regulation (Ord. 756/1997) [19]. The high concentrations of copper in soil are a consequence to use excessively the fertilizers, pesticides and copper sulphate as treatment for cabbage protection.

The manganese and nickel concentrations in soil not exceed the normal values according with Ord. 756/1997 such as 900 mg/kg and 20 mg/kg [19], respectively (Figure 7). For nickel, UK SHS (United Kingdom Soil and Herbage Survey) has reported concentrations between 1.16 and 216 mg/kg for rural soils with intensive farming activity, and 7.07–102 mg/kg for urban soils. The availability of nickel in soil increase with pH decrease, and most of nickel compounds are soluble at pH values lower than 6.5. The soils collected from Puntea de Greci village are weakly alkaline or neutral and this can explain the low concentration of nickel in soil. The fertilizers applied during the cultivation period of cabbage are poor in nickel and manganese.

In the case of iron concentrations in soil it can see that all values are situated around the intervention threshold. The soil concentration of samples S1, S3, S6 and

S7 exceed the values of intervention threshold according with Ord. 756/1997. The high concentration of iron for sample S7 (*i.e.* witness, Figure 7) can be explained by pH acid of soil useful for grassland.



VN – normal value; PM – maxim threshold; PI – intervention threshold.

Fig. 7 – Heavy metals concentration in soil samples comparative with reference values:
a. Cu; b. Fe; c. Mn; d. Ni; e. Zn; f. Cd.

The zinc and cadmium concentrations in soil samples are between the normal value and maximum value provided in Ord. 756/1997. Zinc is one of the most available nutrients which can be accumulated by cabbage and then translocated in different parts of this vegetable. It is well-known that cadmium in association with zinc can be accumulated in high concentration by vegetables if the pH of soil is between 5.0 and 7.0, as well as if the pH is higher than 7.0. Thus can be explained the higher concentrations of zinc and cadmium as well.

The bioaccumulation factor (BF) from soil to component parts of cabbage, expressed as the ratio of metal concentration in part divided by the concentration of metal in soil, may be an indicator of the cabbage accumulation behavior. In this study it is estimated and compared the values of the bioaccumulation factor (BF) of Cd, Zn, Ni, Cu, Pb, Fe and Mn (Tables 5) from soil to different part of cabbage.

Table 5

The bioaccumulation factor (BF) of metals from soil to different parts of *Brassica oleracea L*

| Cabbage sample | Component part | Bioaccumulation factor, BF | | | | | | |
|----------------|----------------|----------------------------|-----------|--------------|-----------|-----------|-----------|-----------|
| | | BF_{Cu} | BF_{Fe} | BF_{Mn} | BF_{Ni} | BF_{Zn} | BF_{Cd} | BF_{Pb} |
| V1 | Outer leaf | 0.027 | 0.030 | 0.186 | 0.249 | 0.076 | 0.226 | 0.102 |
| V2 | Interior leaf | 0.040 | 0.027 | 0.115 | 0.235 | 0.186 | 0.189 | 0.086 |
| V3 | Core | 0.040 | 0.025 | 0.116 | 0.216 | 0.226 | 0.141 | 0.083 |
| V4 | Interior stem | 0.025 | 0.020 | 0.114 | 0.188 | 0.036 | 0.079 | 0.084 |
| V5 | Exterior stem | 0.030 | 0.021 | 0.082 | 0.172 | 0.087 | 0.065 | 0.068 |
| V6 | Root | 0.040 | 0.121 | 0.384 | 0.225 | 0.178 | 0.261 | 0.324 |
| V7 | Outer leaf | 0.027 | 0.029 | 0.161 | 0.411 | 0.073 | 0.206 | 0.121 |
| V8 | Interior leaf | 0.020 | 0.023 | 0.196 | 0.429 | 0.039 | 0.148 | 0.094 |
| V9 | Core | 0.029 | 0.024 | 0.164 | 0.395 | 0.138 | 0.108 | 0.097 |
| V10 | Interior stem | 0.020 | 0.021 | 0.142 | 0.356 | 0.032 | 0.095 | 0.116 |
| V11 | Exterior stem | 0.023 | 0.020 | 0.131 | 0.324 | 0.047 | 0.029 | 0.052 |
| V12 | Root | 0.027 | 0.152 | 1.282 | 0.401 | 0.085 | 0.217 | 0.342 |
| V13 | Outer leaf | 0.020 | 0.037 | 0.137 | 0.282 | 0.054 | 0.237 | 0.149 |
| V14 | Interior leaf | 0.029 | 0.025 | 0.077 | 0.250 | 0.109 | 0.206 | 0.098 |
| V15 | Core | 0.032 | 0.025 | 0.097 | 0.260 | 0.123 | 0.174 | 0.048 |
| V16 | Interior stem | 0.021 | 0.017 | 0.084 | 0.192 | 0.033 | 0.186 | 0.049 |
| V17 | Exterior stem | 0.023 | 0.018 | 0.046 | 0.204 | 0.042 | 0.170 | 0.029 |
| V18 | Root | 0.021 | 0.710 | 2.791 | 0.147 | 0.120 | 0.280 | 0.241 |
| V19 | Outer leaf | 0.018 | 0.032 | 0.267 | 0.327 | 0.081 | 0.235 | 0.229 |
| V20 | Interior leaf | 0.025 | 0.031 | 0.144 | 0.272 | 0.154 | 0.218 | 0.114 |
| V21 | Core | 0.028 | 0.035 | 0.170 | 0.290 | 0.231 | 0.190 | 0.112 |
| V22 | Interior stem | 0.014 | 0.023 | 0.083 | 0.228 | 0.035 | 0.188 | 0.103 |
| V23 | Exterior stem | 0.020 | 0.036 | 0.111 | 0.206 | 0.119 | 0.113 | 0.086 |
| V24 | Root | 0.019 | 0.387 | 2.853 | 0.179 | 0.168 | 0.288 | 0.379 |
| V25 | Outer leaf | 0.013 | 0.033 | 0.351 | 0.166 | 0.155 | 0.284 | 0.242 |
| V26 | Interior leaf | 0.019 | 0.031 | 0.240 | 0.142 | 0.186 | 0.231 | 0.177 |
| V27 | Core | 0.020 | 0.031 | 0.195 | 0.136 | 0.325 | 0.173 | 0.147 |

Table 5 (continued)

| | | | | | | | | |
|-----|---------------|-------|-------|--------------|-------|-------|-------|-------|
| V28 | Interior stem | 0.012 | 0.026 | 0.125 | 0.102 | 0.067 | 0.147 | 0.087 |
| V29 | Exterior stem | 0.014 | 0.022 | 0.065 | 0.089 | 0.226 | 0.129 | 0.076 |
| V30 | Root | 0.019 | 0.147 | 0.902 | 0.127 | 0.383 | 0.435 | 0.303 |
| V31 | Outer leaf | 0.013 | 0.025 | 0.152 | 0.148 | 0.057 | 0.334 | 0.125 |
| V32 | Interior leaf | 0.027 | 0.023 | 0.126 | 0.136 | 0.159 | 0.278 | 0.072 |
| V33 | Core | 0.028 | 0.024 | 0.174 | 0.141 | 0.222 | 0.252 | 0.057 |
| V34 | Interior stem | 0.016 | 0.027 | 0.170 | 0.109 | 0.038 | 0.189 | 0.063 |
| V35 | Exterior stem | 0.019 | 0.021 | 0.078 | 0.106 | 0.096 | 0.126 | 0.052 |
| V36 | Root | 0.024 | 0.120 | 0.419 | 0.118 | 0.126 | 0.576 | 0.219 |

Bioaccumulation factor is calculated with relation:

$$BF = C_p/C_s$$

where: C_p is the mean metal concentration in cabbage sample (mg/kg) and C_s is the mean metal concentration in soil sample (mg/kg). If the $BF > 1$ then the plants can be accumulators; $BF = 1$ is no influences and if the $BF < 1$ then the plant can be an excluder. The bioaccumulation factors (BF) of Cd, Zn, Ni, Cu, Pb, Fe and Mn for cabbage samples are given in Table 5. From this table it can see that in six of the seven elements the accumulation factor has the maximum value in the root samples (*i.e.* 0.04 at Cu and 2.853 at Mn). However, a plant can be considered accumulator if $BF > 1$. In Figure 8 is presented the BF for Mn in root samples of cabbage, because the BF value for Mn exceed in root for samples collected from P2, P3, P4 and P5 sites.

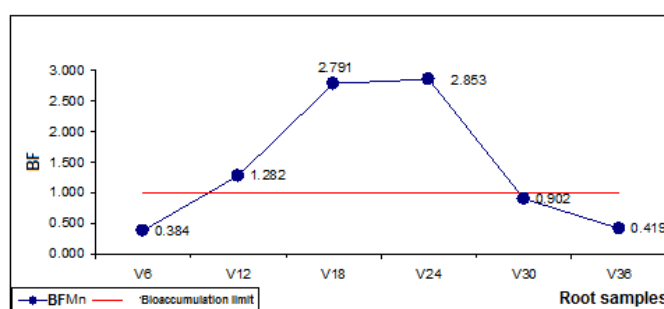


Fig. 8 – Bioaccumulation factor in cabbage root samples.

The root is adapted to carry out the main functions: one for fixing plant in soil and one for absorption water and dissolved minerals. The root contributes to the metabolism of cabbage feeding the whole plant and often serves to store minerals. This ability of roots to accumulate heavy metals is considered to be a

way that the aerial parts of the plant are protected. Adsorption of heavy metals and their transport to the cabbage part depend mainly on the type of metal, in the second on the biological role in cabbage, and the metal ability to form some complexes with the sap components. On the second place is found the outer leaf, being the old leaf, when the accumulation period of heavy metals is much longer than the other leaves. Obviously, the outer leaf is the first which is in contact with fertilizers and pesticides, as well as with acid rain or pollutants from air. Third place in this "ranking" is occupied by the core. It is composed from the youngest leaves of the cabbage. Minerals are found in highest quantity in young leaves in growing, observing some migration of these from mature to the young leaves. The total BF for each cabbage collected from P1-P6 sites were presented in Table 6 and Figure 9.

The $BF > 1$ demonstrates that the manganese is the most assimilated element on *Brassica oleracea L.* In five from six samples, the percentage exceeds value 1. Therefore the root accumulates and stores manganese providing a constant amount required by the plant. In addition, all foliar fertilizers contain manganese in order to stimulate the biosynthesis of phytohormones. Manganese and iron are the most important catalysts oxidoreducătoare for oxido-reducing processes of plant. As a component of the chloroplast, manganese is involved in photolysis of water, having an essential role to donor the electron in photosystem II from photosynthesis process. Thus, after roots, the outer leaves are green and contain the highest quantities of manganese.

Table 6

The amount of bioaccumulation factor for each sample

| Site | BF_{Cu} | BF_{Fe} | BF_{Mn} | BF_{Ni} | BF_{Zn} | BF_{Cd} | BF_{Pb} |
|------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| P1 | 0.202 | 0.244 | 0.997 | 1.285 | 0.789 | 0.961 | 0.747 |
| P2 | 0.146 | 0.269 | 2.076 | 2.316 | 0.414 | 0.803 | 0.822 |
| P3 | 0.146 | 0.832 | 3.232 | 1.335 | 0.481 | 1.253 | 0.614 |
| P4 | 0.124 | 0.544 | 3.628 | 1.502 | 0.788 | 1.232 | 1.023 |
| P5 | 0.097 | 0.290 | 1.878 | 0.762 | 1.342 | 1.399 | 1.032 |
| P6 | 0.127 | 0.240 | 1.119 | 0.758 | 0.698 | 1.755 | 0.588 |

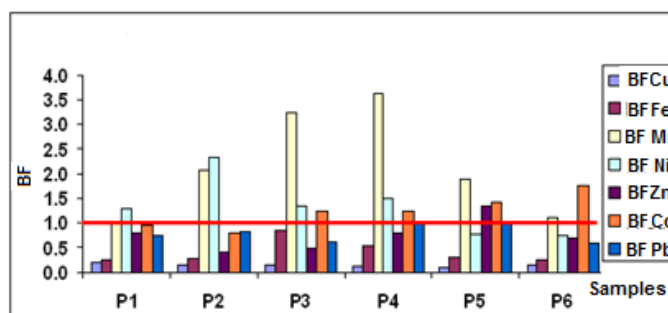


Fig. 9 – Bioaccumulation factor of heavy metals in cabbage samples.

The BF for zinc and cadmium registered values less than 1.0 in parts of cabbage, but they amount exceeds this value. This fact depend both by the pH of soil (weakly alkaline or neutral) and the zinc concentration in analyzed soil.

Obviously, only with BF is no possible to establish if the cabbage may be considerate as accumulator species for a certain metals and these can be poisonous for people life. However these data can be used with other data resulted by calculus of translocation factor (TF) using the next formula:

$$TF = C_{\text{cabbage part}} / C_{\text{root}}$$

where: $C_{\text{cabbage part}}$ is mean metal concentration in outer leaf or other parts of cabbage (mg/kg); C_{root} is mean metal concentration in root (mg/kg). Translocation factor were presented in Table 7 and Figure 9.

The iron is a metals which is uniform distributed in all parts of cabbage because the value of TF_{Fe} is less than 1 (*i.e.* 0.024 – 0.249). Translocation factor of copper present values between 0.554 and 1.566. Figure 10a shows that copper migrate from outer leaves to interior leaves and core, as well as from external stem to internal stem and core. The highest value of translocation factor for copper was in core samples. Similar with copper is the compoment of iron (Figure 10c). TF_{Mn} is less than 1 in all samples, and the value gradually decreases from outer leaf to interior leaf, core and stem (Figure 10b). Translocation factor of nickel present values between 0.7 and 1.912. It can observe the same decreases of nickel from outer leaf to interior leaf, core and stem (Figure 10b).

Table 7

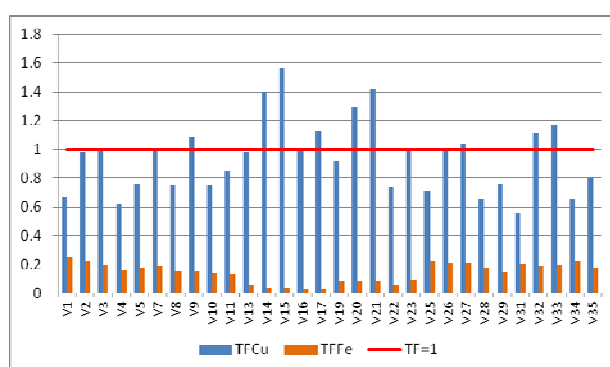
Translocation factor (TF) of metals from root to different parts of cabbage

| Cabbage sample | Component part | Translocation factor (TF) | | | | | | |
|----------------|----------------|---------------------------|-----------|-----------|-----------|-----------|-----------|-----------|
| | | TF_{Cu} | TF_{Fe} | TF_{Mn} | TF_{Ni} | TF_{Zn} | TF_{Cd} | TF_{Pb} |
| V1 | Outer leaf | 0.669 | 0.249 | 0.484 | 1.107 | 0.424 | 0.867 | 0.316 |
| V2 | Interior leaf | 0.986 | 0.223 | 0.300 | 1.047 | 1.044 | 0.726 | 0.267 |
| V3 | Core | 0.999 | 0.203 | 0.302 | 0.963 | 1.266 | 0.540 | 0.255 |
| V4 | Interior stem | 0.624 | 0.163 | 0.298 | 0.836 | 0.204 | 0.301 | 0.258 |
| V5 | Exterior stem | 0.756 | 0.176 | 0.214 | 0.766 | 0.487 | 0.248 | 0.209 |
| V7 | Outer leaf | 1.010 | 0.191 | 0.126 | 1.027 | 0.858 | 0.951 | 0.353 |
| V8 | Interior leaf | 0.746 | 0.153 | 0.153 | 1.071 | 0.452 | 0.683 | 0.273 |
| V9 | Core | 1.088 | 0.156 | 0.128 | 0.987 | 1.618 | 0.500 | 0.284 |
| V10 | Interior stem | 0.748 | 0.140 | 0.111 | 0.888 | 0.372 | 0.439 | 0.339 |
| V11 | Exterior stem | 0.850 | 0.135 | 0.102 | 0.808 | 0.557 | 0.134 | 0.152 |
| V13 | Outer leaf | 0.986 | 0.053 | 0.049 | 1.912 | 0.455 | 0.848 | 0.619 |

Table 7 (continued)

| | | | | | | | | |
|-----|---------------|-------|-------|-------|-------|-------|-------|-------|
| V14 | Interior leaf | 1.399 | 0.035 | 0.028 | 1.699 | 0.909 | 0.736 | 0.405 |
| V15 | Core | 1.566 | 0.035 | 0.035 | 1.765 | 1.029 | 0.624 | 0.199 |
| V16 | Interior stem | 1.006 | 0.024 | 0.030 | 1.301 | 0.280 | 0.664 | 0.201 |
| V17 | Exterior stem | 1.127 | 0.025 | 0.016 | 1.382 | 0.352 | 0.608 | 0.122 |
| V19 | Outer leaf | 0.922 | 0.084 | 0.094 | 1.827 | 0.484 | 0.815 | 0.605 |
| V20 | Interior leaf | 1.295 | 0.081 | 0.051 | 1.520 | 0.918 | 0.756 | 0.301 |
| V21 | Core | 1.421 | 0.090 | 0.060 | 1.620 | 1.378 | 0.659 | 0.295 |
| V22 | Interior stem | 0.738 | 0.059 | 0.029 | 1.273 | 0.210 | 0.652 | 0.272 |
| V23 | Exterior stem | 1.009 | 0.093 | 0.039 | 1.153 | 0.706 | 0.393 | 0.226 |
| V25 | Outer leaf | 0.710 | 0.223 | 0.389 | 1.310 | 0.405 | 0.653 | 0.798 |
| V26 | Interior leaf | 1.011 | 0.212 | 0.266 | 1.122 | 0.486 | 0.530 | 0.586 |
| V27 | Core | 1.038 | 0.210 | 0.217 | 1.070 | 0.849 | 0.397 | 0.486 |
| V28 | Interior stem | 0.655 | 0.179 | 0.138 | 0.803 | 0.174 | 0.338 | 0.287 |
| V29 | Exterior stem | 0.756 | 0.151 | 0.072 | 0.700 | 0.591 | 0.297 | 0.252 |
| V31 | Outer leaf | 0.554 | 0.204 | 0.362 | 1.257 | 0.448 | 0.580 | 0.571 |
| V32 | Interior leaf | 1.115 | 0.188 | 0.301 | 1.152 | 1.259 | 0.483 | 0.326 |
| V33 | Core | 1.168 | 0.202 | 0.414 | 1.194 | 1.764 | 0.437 | 0.261 |
| V34 | Interior stem | 0.658 | 0.227 | 0.406 | 0.921 | 0.301 | 0.328 | 0.289 |
| V35 | Exterior stem | 0.800 | 0.176 | 0.186 | 0.895 | 0.762 | 0.218 | 0.239 |

For cadmium and lead the maximum values of TF are in outer leaves ($TF_{Cd} = 0.915$ and $TF_{Pb} = 0.798$) and minimum values of TF are in stem ($TF_{Cd} = 0.134$ and $TF_{Pb} = 0.122$).



a

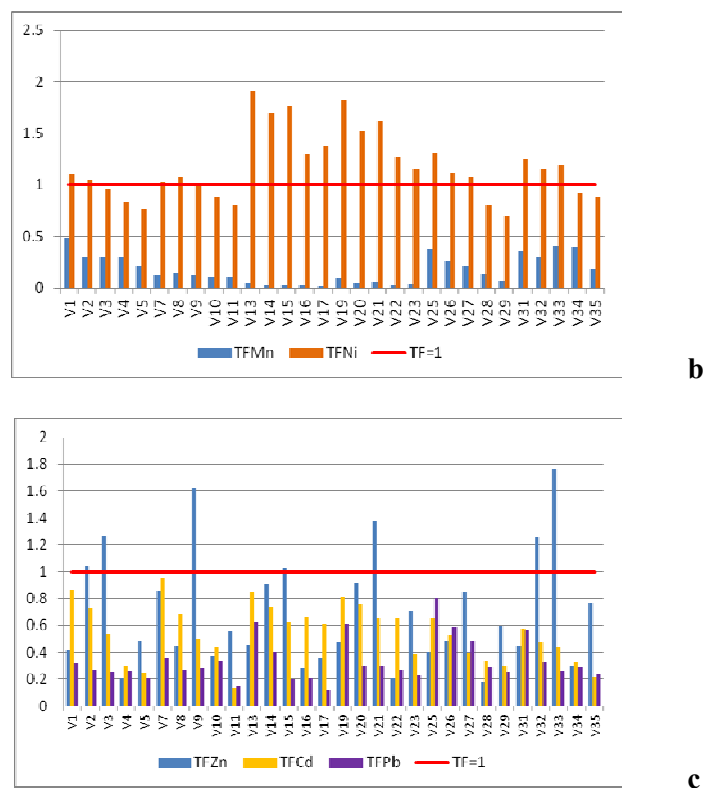


Fig. 10 – Translocation factor of metals from root in other parts of cabbage :
 a. TF_{Cu} and TF_{Fe} ; b. TF_{Mn} and TF_{Ni} ; TF_{Zn} , TF_{Cd} and TF_{Pb} .

4. CONCLUSIONS

Cabbage is interesting from both marketing and dietary points of view because cabbage has many beneficial effects on health. Atomic absorption spectrometry technique of high sensitivity can be successfully applied in the analysis of heavy metals of *Brassica oleracea* var. *capitata*. Cabbage can take up heavy metals by their roots, or even *via* their stems and leaves, and accumulate them in their organs. By this study can concluded that the cabbage take up elements selectively. Accumulation and distribution of heavy metals in the cabbage depends on the component parts, metal type, bioavailability of metal, pH and temperature of soil, and secretion of roots. In conclusion, fresh cabbage from the production area of Puntea de Greci is a good raw material for fresh use and biological fermentation. The climatic and pedological characteristics of the typical and traditional production area favor the production of late cabbage cultivars, suitable for this purpose.

REFERENCES

1. G. Hatfield, Encyclopedia of Folk Medicine: Old World and New World Traditions, ABC-CLIO, pp. 59–60 (2004).
2. S. Singh, M. Zacharias, S. Kalpana, S. Mishra, Heavy metals accumulation and distribution pattern in different vegetable crops, *Journal of Environmental Chemistry and Ecotoxicology*, **4**(10), 170–177 (2012).
3. C. Radulescu, C. Stih, L. Barbes, A. Chilian, E.D. Chelarescu, Studies concerning heavy metals accumulation of *Carduus nutans L.* and *Taraxacum officinale* as potential soil bioindicator species, *Revista de Chimie*, **64**(7), (2013).
4. C. Radulescu, C. Stih, I.V. Popescu, I. Ionita, I.D. Dulama, A. Chilian, O.R. Bancuta, E.D. Chelarescu, D. Let, Assessment of heavy metals level in some perennial medicinal plants by Flame Atomic Absorption Spectrometry, *Romanian Reports in Physics*, **65**(1), 246–260 (2013).
5. I.D. Dulama, I.V. Popescu, C. Stih, C. Radulescu, Gh.V. Cimpoca, L.G. Toma, R. Stirbescu, O. Nitescu, Studies on accumulation of heavy metals in Acacia leaf by EDXRF, *Romanian Report on Physics*, **64**(4), 1063–1071 (2012).
6. C. Radulescu, C. Stih, G. Busuioc, A.I. Gheboianu, I.V. Popescu, Studies concerning heavy metals bioaccumulation of wild edible mushrooms from industrial area by using spectrometric techniques, *Bull. Environ. Contam. Toxicol.*, **84**(5), 641–647 (2010).
7. *** Protocol for Distinctness, Uniformity and Stability Tests. *Brassica oleracea L. var. capitata L.*, UPOV Code: BRASS_OLE_GC, Community Plant Variety Office, CPVO-TP/048/3 (2011).
8. *** Codex Methods of Sampling, General Guidelines on Sampling, CAC/GL 50 (2004).
9. *** Soil Sampling, SESDPROC-300-R2, USEPA Sciences and Ecosystem Support Division (2011).
10. *** SESD Operating Procedure for Field X-Ray Fluorescence (XRF) Measurement, SESDPROC-107, Most Recent Version (2011).
11. G. State, I.V. Popescu, C. Radulescu, C. Macris, C. Stih, Nitescu O., Comparative Studies of Metal Air Pollution by Atomic Spectrometry Techniques and Biomonitoring with Moss and Lichens, *Bull. Environ. Contam. Toxicol.*, **82**(3), 580–586 (2012).
12. G. State, I.V. Popescu, A. Gheboianu, C. Radulescu, I.D. Dulama, I. Bancuta, R. Stirbescu, Identification of Air Pollution Elements in Lichens Used as Bioindicators, by the XRF and AAS Methods, *Romanian Journal of Physics*, **56**(1–2), 233–239 (2011).
13. I.V. Popescu, M. Frontasyeva, C. Stih, Gh.V. Cimpoca, C. Radulescu, G. State, A. Gheboianu, C. Oros, O. Cilicov, I. Bancuta, I.D. Dulama, Atomic and nuclear methods applied in the study of heavy polluting elements, *Romanian Reports in Physics*, **63**, 1205–1214 (2011).
14. I.V. Popescu, M. Frontasyeva, C. Stih, Gh.V. Cimpoca, C. Radulescu, A. Gheboianu, C. Oros, Gh. Vlaicu, C. Petre, I. Bancuta, I.D. Dulama, Nuclear and Nuclear Related Analytical Methods Applied in Environmental Research, *Rom. J. Phys.*, **55**(7–8), 821–829 (2010).
15. C. Radulescu, C. Stih, Metode analitice complementare pentru determinarea concentratiei de metale grele, Ed. Bibliotheca, Târgoviște (2011).
16. I.V. Popescu, C. Radulescu, C. Stih, Gh.V. Cimpoca, I.D. Dulama, Tehnici analitice utilizate in studiul poluarii mediului, Ed. Bibliotheca, Târgoviște (2011).
17. *** Commission Regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs.
18. *** Ord. 975/1998 al Ministerului de Sanatate publica privind limitele maxime pentru metale grele in alimente.
19. *** Ord. 756/1997 pentru aprobarea Reglementarii privind evaluarea poluarii mediului.