Pol. J. Environ. Stud. Vol. 21, No. 2 (2012), 321-329

Original Research

Contents of Heavy Metals, Nitrates, and Nitrites in Cabbage

Anna Czech[1]*, Marek Pawlik[2], Elżbieta Rusinek[1]**

[1]Department of Biochemistry and Toxicology, Agricultural University in Lublin, Akademicka 13, 20-950 Lublin, Poland
[2]Norman B. Keevil Institute of Mining Engineering, University of British Columbia, 517-6350 Stores Road, V6T 2K8, Vancouver, BC, Canada

Received: 2 March 2011
Accepted: 27 September 2011

Abstract

The contents of lead, cadmium, zinc, copper, iron, manganese, nitrites, and nitrates were determined in six species of cabbage of the cruciferous family obtained from different areas of Poland. The results were analyzed and compared in terms of the effect of local industrial (southern Poland, Katowice) or agricultural (southeastern Poland, Lublin) activities on the amounts of heavy metals in the tested vegetables. While the levels of cadmium, lead, and manganese correlated well with the different industrial levels of the locations, the concentrations of copper, iron, and zinc in the vegetables were not very different between the two cities. All the vegetables could generally be characterized by low levels of cadmium and lead (less than 0.1 mg·kg^{-1}), and relatively high levels of zinc, iron, and manganese (3-10 mg·kg^{-1}) regardless of location. Among the tested vegetables, Chinese cabbage (*Brassica pekinensis Rupr*) from Katowice consistently gave higher levels of all the analyzed elements (except zinc) than the same vegetable from Lublin, while the other specimens produced variable data. Red cabbage turned out to contain the highest levels of all contaminants compared to other vegetable species. Nitrate levels in all the Lublin samples were approximately equal, suggesting that the extensive fertilization in the Lublin area produces a uniform background level of these anions. On the other hand, the Katowice samples exhibited quite variable and extreme levels of nitrates and nitrites.

Keywords: heavy metals, nitrates, nitrites, cabbage, contamination

Introduction

The content of heavy metals, nitrate, and nitrite in plants depends on the location of their growth and harvest, as well as on the capacity of the plants to accumulate various substances from soil (fertilization), water (sewage, fertilizers) and air (dust, particulates, fumes). Lead and cadmium, due to their strongly toxic properties and harmful effects on living organisms, are classified among the most important contaminants of vegetables, and the contents of these metals should be under strict control and monitoring. In the case of nitrites and nitrates, even though nitrates are of relatively mild toxicity, nitrites produced as a result of the microbiological reduction of nitrates are highly toxic [1, 2].

Cabbage is widely cultivated in Poland and analysis of the contents of heavy metals, nitrite, and nitrate in each variety of these vegetables [3, 4] is of primary importance to understanding the accumulation capabilities of these plants toward both nutrients and contaminants [5, 6].

Southern areas of Poland are the most industrialized parts of the country. Essentially the country's entire heavy industry, with the vast majority of operational mines and smelters, is located in Upper Silesia with the city of

*e-mail: annaczech@poczta.fm
**e-mail: elzbieta.rusinek@up.lublin.pl

Katowice being the industrial center of Poland. Southeastern parts of Poland are primarily agricultural, with some of the best quality and most fertile soils in Europe. The city of Lublin and the Lublin Voivodship are the main administrative units of that area. However, several large industrial sites such as chemical plants in Pulawy, Pionki, Nowa Sarzyna, and Tarnobrzeg are also located in that part of the country.

Considering these geographical factors, the main objective of this study was to determine the contents of heavy metals (lead, cadmium, zinc, iron, copper, manganese) and nitrate and nitrite in selected cabbage vegetables obtained from market places in the cities of Lublin and Katowice. Additionally, the results obtained from those two locations could be compared in order to verify a working assumption that the vegetables from the Lublin area would be characterized by increased levels of nitrates from the extensive use of agricultural fertilizers, while the vegetables collected in the Katowice area would show markedly higher levels of heavy metals. Recently, a deficiency of various metallic trace elements in the food products of plant origin has been reported for the Lublin area [7].

Materials and Methods

The focus of this research was on cabbage belonging to the cruciferous family (Brassicacae=Cruciferae): white cabbage (*Brassica oleracea L. var. capitata f. alba*), red cabbage (*Brassica oleracea L. var. capitata f. rubra*), savoy cabbage (*Brassica oleracea L. var. Sabauda*), Chinese (suchoy) cabbage (*Brassica pekinensis Rupr*), cauliflower (*Brassica oleracea L. var. botrytis*), and broccoli (*Brassica oleracea L. var. botrytis italica*).

The vegetables were collected in 2009 from major marketplaces in the cities of Lublin and Katowice. The vegetables of the same variety were obtained from four individual producers (6 varieties × 10 producers × 2 marketplaces), so in total – 120 samples were collected. The specimens were first prepared by removing major particulate impurities, rinsing with water and air-drying, and grinding into smaller fragments. From the material so obtained, 10-gram samples were weighed and submitted for the determination of heavy metal contents, whereas smaller 5-gram portions were used for assaying nitrates and nitrites. In order to determine the lead and cadmium contents, the pre-weighed samples were ground and subsequently burnt in a muffle furnace at a temperature of 450ºC. The resulting ash was diluted with 5 cm^3 of 6N spectra pure HCl (Merck). The acidified samples were transferred quantitatively to 100 cm^3 measuring flasks and filled with water to the mark. Deionized water prepared in a deionizer Direct Q5 was used throughout. The contents of lead, cadmium, copper, zinc, iron, and manganese in the analyzed vegetables were assayed by the Central Apparatus Laboratory, University of Life Science in Lublin. This analytical facility and their quality control system are certified under ISO 9001:2000. The lead and cadmium concentrations were determined by flameless atomic absorption spectrophotometry (AAS) using a Varian Spectra AA 880Z spectrometer with a deuterium background correction. Copper, zinc, iron, and manganese were assayed by flame AAS. Lead was determined at a wavelength (λ) of 217 nm, cadmium at λ=228.8 nm, copper at λ=324.8 nm, zinc at λ=213.9 nm, iron at λ=248.3 nm, and manganese at λ=279.5 nm. The measuring analytical ranges were 0-50 $\mu g \cdot l^{-1}$ for lead, 0-5 $\mu g \cdot l^{-1}$ for cadmium, 0-1 $mg \cdot l^{-1}$ for copper, 0-2 $mg \cdot l^{-1}$ for zinc, 0-10 $mg \cdot l^{-1}$ for iron, and 0-1 $mg \cdot l^{-1}$ for manganese. Oriental tobacco (CTTA-OTL-1, Poland) was used as a certified reference material (CRM) for calibration and validation of the analytical procedure. The analysis of nitrates and nitrites was performed following the colorimetric procedure according to PN-92/A-75112 (Polish standard) [8], and measuring the intensity of the color produced through the reaction between nitrite ions with the Griess reagent. Nitrates were earlier reduced to nitrites with the use of powdered cadmium [8]. All the chemical analyses were made as duplicates.

The statistical significance of the obtained results was analyzed using the program Statistica ver. 5. The significance of differences was established with the single-factor variance analysis ANOVA, assuming a significance level p of less than 0.05.

Results and Discussion

The lead contents in the analyzed vegetable samples are presented in Table 1. It can be seen that none of the samples, regardless of location, exceeded the acceptable lead levels as prescribed in the national standard (0.3 $mg \cdot kg^{-1}$ of fresh mass) [9]. In the vegetable samples coming from the Lublin market, the highest average content of lead was found in cauliflower and in red cabbage, while the lowest levels of this element were found in Savoy cabbage and broccoli. In the remaining vegetables the lead content was at a similar level.

Substantially higher concentrations of lead were obtained in all the vegetables collected in the Katowice market, except perhaps cauliflower. The average lead contents in red, Chinese cabbage and broccoli were similar but higher by about 50±10% compared to the content of this element in cauliflower, Savoy, and white cabbage. The obtained results are comparable with the results reported by other authors [10] for vegetables collected from other parts of Poland. All the cabbage examined (except cauliflower) that came from the marketplace in the Katowice center were characterized by a significantly higher average concentration of lead compared with the samples obtained from the market in Lublin. No other data on the lead content in cabbage from the Katowice area have so far been reported.

This elevated level of lead most likely originates from the higher accumulation of lead in the soils in the Katowice region compared to other parts of Poland, as shown in the work of Terelak et al. [11]. These authors found that the average lead content in the soils of the Katowice voivodship (50.9 $mg \cdot kg^{-1}$) was four times higher than the countrywide average. According to a compilation of field data by

Table 1. Lead content in cabbage from Lublin and Katowice.

Vegetable	Lead content (mg·kg^{-1} of fresh mass)		Lead content (mg·kg^{-1} dry product)		Average	
	Lublin	Katowice	Lublin	Katowice	mg·kg^{-1} of fresh mass	mg·kg^{-1} of dry product
Chinese Cabbage	0.026^{a}±0.014	0.056^{b}±0.015	0.24^{a}±0.13	0.51^{b}±0.14	0.041±0.014	0.37±0.13
White cabbage	0.020±0.006	0.031±0.013	0.18±0.054	0.28±0.12	0.025±0.009	0.23±0.09
Savoy cabbage	0.016^{a}±0.006	0.034^{b}±0.012	0.14^{a}±0.053	0.30^{b}±0.11	0.025±0.009	0.22±0.08
Red cabbage	0.030^{a}±0.012	0.067^{b}±0.021	0.27^{a}±0.11	0.60^{b}±0.19	0.048±0.016	0.43±0.15
Broccoli	0.019^{a}±0.008	0.055^{b}±0.035	0.17^{a}±0.073	0.50^{b}±0.32	0.037±0.021	0.33±0.2
Cauliflower	0.036±0.016	0.04±0.021	0.30±0.14	0.34±0.18	0.038±0.018	0.32±0.16

a, b – values in the same rows marked with different letters differ significantly at $p \leq 0.05$.

Table 2. Cadmium content in cabbage from Lublin and Katowice.

Vegetable	Cadmium content (mg·kg^{-1} of fresh mass)		Cadmium content (mg·kg^{-1} of dry product)		Average	
	Lublin	Katowice	Lublin	Katowice	mg·kg^{-1} of fresh mass	mg·kg^{-1} of dry product
Chinese Cabbage	0.034±0.015	0.047±0.022	0.31±0.14	0.42±0.20	0.04±0.02	0.36±0.17
White cabbage	0.030±0.012	0.035±0.010	0.27±0.11	0.32±0.09	0.03±0.01	0.30±0.10
Savoy cabbage	0.032^{a}±0.017	0.057^{b}±0.015	0.28^{a}±0.15	0.51^{b}±0.13	0.04±0.02	0.40±0.14
Red cabbage	0.046^{a}±0.022	0.075^{b}±0.031	0.41^{b}±0.20	0.88^{a}±0.30	0.06±0.04	0.65±0.17
Broccoli	0.021^{a}±0.010	0.065^{b}±0.022	0.19^{a}±0.09	0.60^{b}±0.20	0.04±0.02	0.40±0.15
Cauliflower	0.030±0.012	0.037±0.016	0.25±0.10	0.32±0.14	0.03±0.01	0.29±0.12

a, b – values in the same rows marked with different letters differ significantly at $p \leq 0.05$.

Kowalska-Pyłka et al. [12], it is rather clear that the city of Lublin, in great part, is not excessively polluted with heavy metals. However, as a result of the progressive urbanization and expansion of the city, the overall accumulation of heavy metals in soil and plants gradually reaches alarming levels. The data presented in Table 1 for cabbage correlate well with these general trends reported by other researchers for various parts of Poland. In this context, it is interesting to compare the data from Table 1 with the results reported by Rai and Tripathi [13] on the lead content in Indian cabbage (*Brassica oleracea*) grown on soil with a lead content of 18-19 mg·kg^{-1}. The levels of lead in cabbage reported by Rai and Tripathi [13] were on the order of 800 mg·kg^{-1} (dry mass), which is several orders of magnitude higher than what was found in any of the samples from the Katowice area, even though the lead content in soil in the Katowice area was reportedly more than two times higher [11] than that of the Indian location – Lohta village whose soil was irrigated with water recycled from a sewage treatment plant. These discrepancies highlight the importance of the bioavailability of contaminants, and not just their absolute contents in soil, to the accumulation mechanisms of heavy metals in vegetables [1, 2, 6].

Irrespective of the location from which the specimens were obtained, Chinese and red cabbages were consistently characterized by the highest level of lead accumulation, cauliflower and broccoli showed intermediate levels, and white and Savoy cabbages exhibited the lowest lead concentrations.

It can be seen from Table 2 that among the vegetable samples collected from the market in Lublin, the highest average content of cadmium was found in red cabbage and the lowest in broccoli. The content of this metal in the other varieties of the analyzed cabbage vegetables was constant.

Similarly to the trends in lead concentrations, substantially higher amounts of cadmium (25±12%) were found in all the vegetable samples from the Katowice market compared to the Cd levels obtained for the Lublin specimens. The highest level of cadmium was noted in red cabbage and broccoli, about 25±7% higher than the Cd levels detected in Chinese and Savoy cabbages. Out of all the investigated vegetables, the lowest concentration of cadmium was noted in white cabbage and cauliflower. Comparing the cadmium contents in the vegetables obtained from Lublin and Katowice regions, it is worth noting that broccoli, red, and Savoy cabbages showed the highest differences in the con-

Table 3. Copper content in select cabbage varieties from Lublin and Katowice.

Vegetable	Copper content (mg·kg^{-1} of fresh mass)		Copper content (mg·kg^{-1} of dry product)		Average	
	Lublin	Katowice	Lublin	Katowice	mg·kg^{-1} of fresh mass	mg·kg^{-1} of dry product
Chinese cabbage	0.56±0.14	0.70±0.14	5.10±0.37	6.37±1.36	0.63±0.14	5.73±0.86
White cabbage	0.67±0.03	0.45±0.23	6.03±0.27	4.07±2.07	0.56±0.13	5.05±1.17
Savoy cabbage	0.64±0.04	0.40±0.15	5.71±0.35	3.60±0.98	0.52±0.09	4.65±0.66
Red cabbage	1.05±0.16	0.67±0.33	9.42±0.53	6.03±2.95	0.86±0.24	7.72±1.74
Broccoli	0.88±0.04	0.94±0.20	8.01±0.36	8.60±1.82	0.91±0.12	8.31±1.09
Cauliflower	0.61±0.02	0.50±0.17	5.21±0.22	4.30±1.44	0.55±0.10	4.75±0.83

Table 4. Zinc content in select cabbage varieties from Lublin and Katowice.

Vegetable	Zinc content (mg·kg^{-1} of fresh mass)		Zinc content (mg·kg^{-1} of dry product)		Average	
	Lublin	Katowice	Lublin	Katowice	mg·kg^{-1} of fresh mass	mg·kg^{-1} of dry product
Chinese cabbage	10.3^{b}±1.42	7.13^{a}±2.49	95.13^{b}±13.01	64.8^{a}±7.66	8.72±1.95	79.9±10.33
White cabbage	8.77^{b}±2.93	6.0^{a}±2.25	78.93^{b}±26.37	54.3^{a}±20.36	7.38±2.6	66.6±23.36
Savoy cabbage	8.0±2.36	7.06±2.41	71.2±21.0	63.19±21.57	7.53±2.38	67.19±21.28
Red cabbage	12.74±2.02	10.02±1.79	114.0±18.08	90.18±16.11	11.4±1.91	102.1±17.1
Broccoli	12.61±2.32	9.29±0.82	115.0±21.11	85.5±17.54	10.95±1.57	100.25±19.32
Cauliflower	11.6^{b}±1.63	5.22^{a}±2.40	98.6^{b}±13.85	44.63^{a}±20.52	8.41±2.01	71.6±17.18

a, b – values in the same rows marked with different letters differ significantly at $p \leq 0.05$.

tent of Cd for these specimens purchased in the Katowice marketplace versus those coming from the Lublin region.

It may be suggested that the elevated accumulation of heavy metals in the vegetables purchased in the Katowice region was caused by higher environmental contamination from the metallurgical industry [1, 6, 14].

Regardless of the harvest place of the cabbage, the average cadmium level statistically remained at a similar level except for red cabbage, for which the Cd content proved to be the highest (Table 2). The acceptable cadmium content in the analyzed samples (0.05 mg·kg^{-1}) [9], as required by Polish standards, was generally not exceeded except red and Savoy cabbages and broccoli obtained from the Katowice region. Similar results were noted by Huang et al. [2] in a peri-urban region.

The results on the cadmium levels obtained in this research work were higher by about 80±10% compared to those reported by Liu et al. [15]. Different data were also presented by Karavoltsos et al. [16], and they appeared to be higher by about 40-60% for broccoli and cauliflower than those of the present study. However, the presented results showing a relatively low cadmium content in cauliflower agree well with the observations of Huang et al. [2].

Table 3 presents copper contents in the analyzed cabbage. The average copper content in white cabbage, Savoy cabbage, and cauliflower collected in the Lublin marketplace was more or less the same. At the same time, this copper level was nearly two times lower than the copper content in red cabbage. The lowest copper content was found in Chinese cabbage, although the statistical difference of this result in comparison to the other Lublin data in Table 3 is not pronounced. In white cabbage, Savoy cabbage, and cauliflower from the Katowice region, the content of copper was higher by 30±10% in comparison to Chinese and red cabbages. Again, however, considering the statistical distribution of the obtained values, the copper data for the Katowice samples are quite similar. Taking into account the harvest place of the analyzed vegetables, only very small statistically-significant differences were recorded between the Lublin and Katowice samples. Still, it is noteworthy that white cabbage, red cabbage, Savoy cabbage, and cauliflower purchased in the Lublin market on average exhibited a higher copper content (by 30%) when compared to the same vegetable varieties obtained from the Katowice region. This result is quite unexpected since the heavily industrialized Katowice region should promote higher contamination lev-

Table 5. Iron content in select cabbage varieties from Lublin and Katowice.

Vegetable	Iron content (mg·kg^{-1} of fresh mass)		Iron content (mg·kg^{-1} of dry product)		Average	
	Lublin	Katowice	Lublin	Katowice	mg·kg^{-1} of fresh mass	mg·kg^{-1} of dry product
Chinese cabbage	5.55±2.27	7.23±2.06	51.06±20.90	65.80±18.75	6.40±2.16	58.43±19.82
White cabbage	6.24±1.15	4.60±1.76	56.16±10.35	41.60±15.93	5.42±1.45	48.88±13.14
Savoy cabbage	5.82±1.34	4.20±1.09	51.80±11.90	37.60±9.75	5.01±1.22	44.70±10.82
Red cabbage	10.0±3.32	10.0±3.81	89.50±29.70	90.0±24.30	10.0±3.56	89.80±27.0
Broccoli	9.48±3.82	9.18±4.24	86.30±24.80	84.50±29.0	9.33±4.03	85.40±26.90
Cauliflower	6.62±2.33	4.40±2.0	56.20±19.80	37.60±17.10	5.51±2.17	47.0±18.45

Table 6. Manganese content in select cabbage varieties from Lublin and Katowice.

Vegetable	Manganese content (mg·kg^{-1} of fresh mass)		Manganese content (mg·kg^{-1} of dry product)		Average	
	Lublin	Katowice	Lublin	Katowice	mg·kg^{-1} of fresh mass	mg·kg^{-1} of dry product
Chinese cabbage	2.16^{a}±1.18	5.11^{b}±1.12	19.88^{a}±5.85	46.5^{b}±8.4	3.63±1.15	33.20±7.12
White cabbage	2.70^{a}±1.03	4.31^{b}±0.25	24.3^{a}±6.27	39.0^{b}±5.3	3.50±0.64	31.65±5.78
Savoy cabbage	2.35±0.98	3.0±1.34	20.9±8.72	26.8±3.0	2.68±1.16	23.85±5.86
Red cabage	2.58^{a}±0.72	4.37^{b}±1.28	23.1^{a}±5.4	39.3^{b}±8.52	3.50±1.0	31.20±6.96
Broccoli	3.11±1.15	4.17±1.07	28.3^{a}±5.46	38.36^{b}±7.84	3.64±1.11	33.33±6.65
Cauliflower	2.37^{a}±1.09	5.31^{b}±1.39	20.14^{a}±9.26	45.4^{b}±8.88	3.84±1.24	32.77±9.07

a, b – values in the same rows marked with different letters differ significantly at $p \leq 0.05$.

els than those observed, particularly in comparison to the Lublin area. The contamination of Polish soils with copper was shown to be very low with the exception of the areas in close proximity to active copper mines and smelters. Small regions of naturally-high accumulation of copper in host rocks of soil have also been described. Overall, about 99.7% of the total arable land in Poland shows a natural (0º) or slightly elevated copper level (Iº). In the Katowice area, the contribution of such clean soils is equally high (99.8%), which allows for production of high-quality feeds and crops for consumption [11]. Regardless of the place of harvest of the tested vegetables, the highest copper content was recorded in red cabbage and broccoli, whereas the content of this element was 30% lower in Chinese cabbage. The lowest copper level was reported in white cabbage, Savoy cabbage, and cauliflower. According to the studies by Szymczak et al. [17] the average copper content in cabbage vegetables obtained from the Wrocław and Kalisz voivodships amounted to 0.27 mg·kg^{-1} (f.m.), while in the areas presumably not exposed to industrial pollution, the copper level was only slightly lower at 0.23 mg·kg^{-1} (f.m.). The influence of cultivation location (industrial or residential area) on the copper content in the tested vegetables confirms earlier results reported by Yusuf et al. [1].

As can be seen from Table 4, the highest zinc level in cabbage purchased in the Lublin market was observed in red cabbage and broccoli. A slightly lower level (by 15%) was recorded in Chinese cabbage and cauliflower, while the lowest value was found in white and Savoy cabbages. Quite similar trends were observed in the results for cabbage obtained from the Katowice market. Red cabbage and broccoli exhibited the highest zinc accumulation. Averaging the results for a given type of vegetable, the highest capacity for zinc accumulation was exhibited by red cabbage (11.4±1.91 mg·kg^{-1} f.m.) and broccoli (10.95±1.57 mg·kg^{-1} f.m.), with the remaining vegetables showing similar concentrations of zinc considering the statistical scatter of the analytical data.

The obtained results appear to be about 50% higher than the values reported by Huang et al. [2] in their studies on cabbage (Chinese cabbage, cabbage, cauliflower) harvested from Nanjing peri-urban areas. Just as in the case of the copper data, all the vegetables purchased in the Lublin marketplace had an elevated average zinc content compared to the samples obtained from the Katowice market. In the cases of cauliflower, Chinese cabbage, and white cabbage, the differences were statistically most significant ($p \leq 0.05$). Again, however, the exact sources of these surprisingly

Table 7. Contents of nitrate and nitrite in cabbage vegetables from Lublin and Katowice (mg·kg^{-1} of fresh mass).

Vegetable	Nitrate		Nitrite		Average	
	Lublin	Katowice	Lublin	Katowice	Nitrate	Nitrite
Chinese Cabbage	185^{a}±24.6	667.6^{b}±148.6	0.08^{a}±0.01	0.28^{b}±0.04	426.3±76.2	0.18±0.02
White cabbage	70.8^{a}±15.8	128.8^{b}±26.3	0.64±0.04	0.76±0.08	99.8±21.05	0.70±0.06
Savoy cabbage	235.5^{b}±32.4	46.4^{a}±10.2	0.20^{b}±0.03	0.08^{a}±0.01	140.95±21.3	0.14±0.02
Red cabbage	129.5^{b}±21.2	25.8^{a}±7.2	0.58^{a}±0.06	0.80^{b}±0.10	77.65±14.2	0.69±0.08
Broccoli	161.3^{a}±27.6	230.9^{b}±74.4	0.16±0.02	0.28±0.06	196.1±51	0.22±0.04
Cauliflower	151.1±25.7	189±14.2	0.11±0.01	0.23±0.01	170.05±19.95	0.17±0.01

a, b – values in the same rows marked with different letters differ significantly at $p \leq 0.05$.

higher levels of zinc in the Lublin area are not easy to identify. The available literature does not reveal any data concerning the zinc levels in vegetables harvested in the Lublin or Katowice regions. The natural level of zinc in soil around these sites is difficult to define, especially in extensively arable areas and in the immediate vicinity of industrial sites (mainly metallurgical) as the range and extent of soil contamination with metallic dustfall is difficult to assess [11].

Table 5 presents iron contents in the tested vegetable specimens. Most interestingly, the overall iron results follow closely the trends presented for copper and zinc concentrations in Tables 3 and 4. In the samples obtained from the market in Lublin, the highest iron level was determined in red cabbage and broccoli, and these values turned out to be 40±5% higher than for the other studied cabbage. Among the cabbage coming from the Katowice (Silesian) Voivodship as well as from the Lublin area, the highest iron content was found in red cabbage and broccoli. A relatively high concentration of this element was also detected in Chinese cabbage. In the other cabbages the iron content remained at a similar level. Considering the location from which the specimens were collected, only Chinese cabbage from the Katowice region exhibited a 23% higher iron level compared to that recorded in vegetables obtained from the Lublin market. However, the content of this element in white and Savoy cabbages turned out to be 30±4% higher in the Lublin region in comparison to the vegetables from the Katowice market (Table 5). Iron accumulation in red cabbage and broccoli coming from both Lublin and Silesia region was at a similar level. Based on of the obtained results, it may be suggested that the uptake of this element in the vegetables from the Lublin and Katowice markets is proportional to its presence in soil in the forms available for plants. Irrespective of the harvest place, the highest iron content was recorded in red cabbage and broccoli, while in Chinese cabbage it was lower by 40±10%. In the other cabbages the obtained results were quite similar. Ziemlański and Panczenko-Kresowska [18] reported that the presence and amount of iron in plant-based foodstuffs depends on the type of soil and the prevailing climate conditions, which readily leads to varying levels of iron in the same varieties of plants. According to Chiplonkar et al. [19], the iron level in cabbage was higher by about 40% than the data presented in Table 5. In the studies by Cunningham et al. [20], the amount of iron in vegetables harvested in Australia reached 4-6 mg·kg^{-1} in cabbage and cauliflower, and up to 8-10 mg·kg^{-1} in broccoli. In summary, and considering the statistical significance of the presented results, the iron data for the Katowice and Lublin specimens are surprisingly not very different.

Table 6 summarizes the analytical results on the manganese content in the studied specimens. Based on the manganese data in the cabbage vegetables obtained from the Lublin marketplace, it may be noted that the highest level of manganese was recorded in broccoli, whereas the lowest value was observed in Chinese cabbage. In contrast to the copper, zinc, and iron data from the previous sections, it appears that the Katowice data for manganese are on average consistently higher than the results for the corresponding Lublin samples. Within each of these two locations, the manganese contents are very uniform and any differences between the different vegetables are not quite statistically significant. From the location point of view, a significantly lower manganese level (by about 57±2%) was noted in Chinese cabbage and cauliflower purchased in the Lublin market. Similarly, the red and white cabbage samples from the Lublin market exhibited a 40% lower manganese concentration than the same vegetables obtained from the Katowice market. The difference between the Lublin and Katowice results is likely to arise from the industrial emissions in the Katowice area, which in turn increase the concentration of various metals in soil-soluble forms. This observation can be confirmed by a progressive decrease of the concentrations of heavy metals in the upper layers of soil as the distance from industrial areas increases [21]. Regardless of the harvest place and averaging the results for a given type of vegetable, the highest average manganese content was recorded in Chinese cabbage, cauliflower, and broccoli. The amount of this metal accumulated in Savoy cabbage was about 30±5% lower. In red and white cabbage the obtained values were at a similar level. In the studies by Ekholm et al. [22], the contents of manganese in the cabbages obtained from the Finland region, depending on the year of harvest, varied widely between 21 mg·kg^{-1} (d.m.) (broccoli and cauliflower) and 47 mg·kg^{-1} (d.m.) for white cabbage, and were generally similar to those presented in this investigation. The differences in the concentrations of the analyzed elements depend on the plant species, sampling place, soil conditions, anthropogenic factors, or the local agrotechnical practices used for each crop [23].

The absolute amounts of Cd, Pb, and Zn and their relative proportions found in the tested cabbage vegetables are in a good agreement with the data presented by Furr et al. [24] on heavy metal concentrations in "Golden Acre" cabbage (*Brassica oleracea var. capitata*) grown on soil mixed with industrial sludge ash from 10 different locations in the United States. The ash itself exhibited extremely high levels of these heavy metals, and yet the cabbage grown on such a material turned out to contain surprisingly low levels of these elements. Similar relative proportions of Zn, Cd, Pb, and Cu were reported by Viqar-Un-Nisa and Mohammad [25] in cabbage and cauliflower from the Islamabad area (Pakistan). The amounts of lead and cadmium were low (less than 1 $mg \cdot kg^{-1}$), the level of zinc was on the order of 16-46 $mg \cdot kg^{-1}$, while copper was at an intermediate level (~5 $mg \cdot kg^{-1}$). The same trend in the absolute amounts of Cd, Zn, Cu, and Pb, (Zn>Cu>Pb>Cd) and nearly identical relative proportions were found by Mishra and Tripathi [26] in cabbage from Varanasi (India).

Interestingly, all these concentrations, although in some cases different than those from the present study in terms of absolute values, qualitatively agree with the current data.

As can be seen from Table 7, the lowest accumulation level of nitrates in the vegetables from the Lublin region was recorded in white cabbage and the highest level of nitrates was found in Savoy cabbage. The average nitrate levels in the other varieties of cabbage from Lublin were not statistically different and remained at similar levels. The nitrate results recorded for the vegetables from the market in Katowice turned out to be statistically much more differentiated. The highest accumulation was detected in Chinese cabbage, while a nearly three-fold lower accumulation was measured in broccoli, and an almost 15- to 20-times lower content of nitrates was found in Savoy and red cabbages.

According to a decree of the Polish Ministry of Health from 2003 [9], cabbage belongs to a class of vegetables for which the acceptable nitrate content is 750 $mg \cdot kg^{-1}$ (f.m.), whereas for cauliflower and broccoli this permissible limit should not surpass 400 $mg \cdot kg^{-1}$ (f.m). From analyzing the data in Table 7 for the studied vegetable samples obtained from markets in Lublin and Katowice, it should be noted that the nitrate content did not exceed the acceptable limits in any of the samples.

Ignoring the harvest place of the specimens and averaging the data for a given type of vegetable, it can be found that the highest nitrate concentration was noted in Chinese cabbage, whereas significantly lower amounts of nitrates were detected in broccoli, cauliflower, and Savoy cabbage. The lowest content of these compounds in relation to the other vegetables analyzed was recorded in white and red cabbage. The nitrate content in broccoli and cauliflower appeared lower in comparison to the values given in a study by Leszczyńska et al. [27]. The amounts of nitrates found in Chinese cabbage seem to suggest that the vegetables obtained from the producers from both Lublin and Katowice originated from ecological farms, as the analytical results were similar to the results compiled by Wawrzyniak et al. [28]. According to these authors, the average nitrate content in Chinese cabbage from conventional cultivations around Poland generally remained at a level of 1,045.7±432.2 $mg \cdot kg^{-1}$ (f.m.), while that from ecological farming amounted on average to 552.1±153.5 $mg \cdot kg^{-1}$ (f.m.).

Interestingly, the majority of the cabbages collected from the Katowice market were characterized by a significantly higher nitrate content when compared to the same vegetables from the Lublin region. Only red and Savoy cabbage specimens obtained from the Katowice market showed significantly lower contents of nitrates than the specimens from Lublin. The fact that the nitrate data for the Lublin samples are quite statistically similar does point to the role of the extensive use of fertilizers in the Lublin region in determining the final nitrate levels in cabbage. However, the scattered results from Katowice suggest that some of the vegetables came either from weakly fertilized farms or from areas of increased chemical contamination (most likely due to industrial activities in Silesia).

The DMH [9] did not specify the maximum allowable nitrite content in the cabbage of interest to this study. After analyzing the obtained results with respect to the nitrite level, it can be concluded that in many cases the data seemed to be many times higher than those presented in other relevant Polish works, such as in Wawrzyniak et al. [28]. On the other hand, the field data collected by Szymczak and Prescha [29] were quite comparable to the values presented in Table 7. It can also be seen from Table 7 that the average nitrite content in the analyzed white and red cabbage obtained from the Lublin market was 90% higher than in Chinese cabbage from the same location.

The concentration of nitrite in Chinese cabbage from the Lublin region was similar to that obtained in the study by Wawrzyniak et al. [28], whereas in the vegetable material from the Katowice market the content of nitrites was nearly four times higher. Among the vegetables obtained from the Katowice region, the highest nitrite level was recorded in white and red cabbage and a lower accumulation level (by about 70%) was found in cauliflower, broccoli, and Chinese cabbage, whereas the lowest nitrite content was detected in Savoy cabbage.

Only Savoy cabbage from the Katowice region was characterized by a significantly lower (2.5 times) accumulation level of nitrites in comparison to the same vegetable supplied from the market in Lublin. However, the nitrite contents, similar to the nitrate levels, in the other vegetables turned out to be about 30% lower by 30±5% for the Lublin samples as compared to the vegetables obtained from the Katowice market. Markowska et al. [30] found three times higher nitrate and nitrite accumulation in cabbage obtained from the suburbs of the city of Łódź than in the vegetables from the outskirts of the Łódź Voivodship, which seems to show that rural areas are less contaminated with nitrates compared to large cities.

While it is perhaps tempting to conclude that higher contents of nitrates and nitrites and heavy metals in the samples from Katowice are due to industrialization of the area, it is also rather obvious that this conclusion does not hold for all the analyzed elements. In fact, in the cases of copper, zinc, and iron levels in the tested vegetables, there are no major statistically-significant differences between the two locations that would conclusively show that the Katowice specimens were more contaminated than the Lublin samples. The trends for nitrites and nitrates are not very clear either, and in some instances the heavy metal or nitrate and nitrite levels in the Lublin samples are actually much higher than those from Katowice. Only lead, cadmium and manganese concentrations follow what could be presumed about the relative contamination of these two testing sites.

It is, however, interesting to observe that among the studied vegetables red cabbage and broccoli tend to most strongly assimilate almost all of the heavy metals of interest to this study regardless of location; the data for the iron and zinc contents are the best illustration of this observation. Red cabbage actually appears to be an exceptional absorber of heavy metals even when other vegetables show low uptakes in the same location. The results for white cabbage, and Savoy cabbage are generally at the lower end of the reported heavy metal concentrations compared to other vegetables. Chinese cabbage (suchoy) and cauliflower give the most inconsistent results in relation to the other specimens. However, Chinese cabbage quite characteristically gives higher metal, nitrate, and nitrite levels in Katowice than in Lublin (with the one exception of zinc). Thus, it seems that Chinese cabbage is actually the only tested vegetable contamination of which was predictably affected by the location of harvest.

The presented results are generally in good agreement with heavy metal data presented by other authors for cabbage vegetables from various locations.

Conclusions

In summary, the tested heavy metals can be divided into two groups with respect to their relative levels in the studied vegetables between the Lublin and Katowice locations. The concentrations of lead, zinc, and manganese give a clear correlation with the industrialization of the sampling locations and with the resulting exposure of the vegetables to metallic contaminants. The levels of these metals in the vegetable samples from the Katowice area are much higher than the levels of these metals in the same cabbage vegetables from Lublin.

On the other hand, the concentrations of copper, iron and zinc do not correlate with the extent of industrial activities in the chosen areas. In several cases, the contents of these metals were actually higher in the Lublin samples than in the Katowice samples, and this rather unexpected trend cannot readily be explained.

The vegetables themselves seem to show variable affinity toward the heavy metals, nitrates, and nitrites. Red cabbage and broccoli most often produced the highest levels of heavy metals, regardless of location. Red cabbage stands out among the tested specimens as a vegetable of the highest capacity to assimilate heavy metals. The results for white cabbage and Savoy cabbage are generally at the lower end of the reported ranges of heavy metal concentrations compared to other vegetables. Although Chinese cabbage (suchoy) and cauliflower give the most scattered results, it is actually the Chinese cabbage that consistently gives higher metal and nitrate and nitrite levels in Katowice than in Lublin (with the one exception of zinc). Overall, Chinese cabbage is actually the only tested vegetable in which the heavy metal levels were clearly affected by the location of harvest. It would thus appear that Chinese cabbage is a good indicator of the level of contamination of an area with heavy metals and nitrates and nitrites.

The nitrate levels did not clearly correlate with location, although the highest nitrate concentrations obtained in this study were found in the Katowice specimens, particularly for Chinese cabbage. The other vegetable species statistically gave rather similar nitrate levels between Lublin and Katowice, although surprisingly the cleanest specimens (Savoy and red cabbage) were also collected in the heavily industrialized Katowice location. It is, however, noteworthy that the extensive use of fertilizers in the Lublin area seems to produce a uniform background level of nitrates in the tested cabbages, while the far more industrialized (and much less agricultural) Katowice area is characterized by rather extreme levels of these anions in the tested specimens.

The nitrite levels appeared to be, on average, slightly higher in the Katowice samples than in the Lublin samples (except Savoy cabbage), although the most extreme values were again observed in the Katowice region. White cabbage and red cabbage were particularly amenable to nitrite uptake in both locations, with the statistical differences for these two vegetables being not so drastic between Lublin and Katowice.

References

1. YUSUF AA, AROWOLO TA, BAMGBOSE O. Cadmium, copper and nickel levels in vegetables from industrial and residential areas of Lagos City, Nigeria. Food Chem. Toxicol. **41**, (3), 375, **2003**.
2. HUANG B., SHI X., YU D., O¨BORN I., BLOMBACK K., PAGELLA T.F., WANG H., SUN W., SINCLAIR F.L. Environmental assessment of small-scale vegetable farming systems in peri-urban areas of the Yangtze River Delta Region, China. Agric. Ecosyst. Environ. **112**, (4), 391, **2006**.
3. CZECH A., RUSINEK E. The heavy metals, nitrates and nitrites content in the selected vegetables from Lublin area. Roczn. PZH, **56**, (3), 229, **2005** [In Polish].
4. OGNIK K., RUSINEK E., SEMBRATOWICZ I., TRUCHLIŃSKI J. Contents of heavy metals, nitrate V and nitrate III in fruits of elderberry and black chokeberry depending on harvest site and vegetation period. Roczn. PZH, **57**, (3), 235, **2006** [In Polish].
5. SZYCZEWSKI P., SIEPAK I., NIEDZIELSKI P., SOBCZYŃSKI T. Research on heavy metals in Poland. Pol. J. Environ. Stud., **18**, (5), 755, **2009**.

6. SHARMA RK., AGRAWAL A., MARSHALL FM. Heavy metals in vegetables collected from production and market sites of a tropical urban area of India. Food Chem. Toxicol. **47**, (3), 583, **2009**.
7. CZECH A., RUSINEK E., BARTOSZEK D. The trace elements content in the selected vegetables from the Lublin area. Roczn. PZH, **57**, (1), 57, **2006** [In Polish].
8. PN-92 A-75112. Fruits, vegetables and derived products. Determination of nitrites and nitrates content [In Polish].
9. DMH J. LAW. No. 37, Item. 326. Decree of Health Minister of the Republic of Poland. **2003** [In Polish].
10. ORZEŁ D., FIGURSKA-CIURA D., STYCZYŃSKA M., BRONKOWSKA M., ŻECHAŁKO-CZAJKOWSKA A. Assessment of heavy metals pollution of food products from emission region of copper foundry "Głogów". Bromatol. Chem. Toksykol. **37**, (4), 323, **2004** [In Polish].
11. TERELAK H., STUCZYŃSKI T., MOTOWICKA-TERELAK T., PIOTROWSKA M. The content of Cd, Cu, Ni, Pb, Zn i S in soils of the Katowice voivodship and Poland. Arch. Ochr. Środ. **23**, (3-4), 167, **1997** [In Polish].
12. KOWALSKA-PYŁKA H., KOT A., WIERCIŃSKI J., KURSA K., WAŁKUSKA G CYBULSKI W. Lead, cadmium, copper and zinc content in vegetables, gooseberry fruits and soil from gardening plots of Lublin. Roczn. PZH, **46**, (1), 3, **1995** [In Polish].
13. RAI PK., TRIPATHI BD. Heavy metals in industrial wastewater, soil, and vegetables in Lohta village, India. Toxicol. Environ. Chem. **90**, (2), 247, **2008**.
14. LIU W., ZHOU Q., ZHANG Y., WEI S. Lead accumulation in different Chinese cabbage cultivars and screening for pollution-safe cultivars. J. Environ. Manage. **91**, (3), 781, **2010**.
15. LIU W., ZHOU Q., SUN Y., LIU R. Identification of Chinese cabbage genotypes with low cadmium accumulation for food safety. Environ. Pollut. **157**, (6), 1961, **2009**.
16. KARAVOLTSOS S., SAKELLARI A., DASSENAKIS M., SCOULLOS M. Cadmium and lead in organically produced foodstuffs from the Greek market. Food Chem. **106**, (2), 843, **2008**.
17. SZYMCZAK J., ILOW R., REGULSKA-ILOW B. Levels of copper and zinc in vegetables, fruit and cereal from areas differing in the degree of industrial pollution and from greenhouses. Roczn. PZH, **44**, (4), 347, **1993** [In Polish].
18. ZIEMIAŃSKI Ś., PANCZENKO-KRESOWSKA B. Mineral components. Nutrition Norms for People. Physiological bases. Wyd. PZWL, Warszawa, **2001** [In Polish].
19. CHIPLONKAR S.A., TARWADI K.V., KAVEDIA R.B., MENGALE S.S., PAKNIKAR K.M., AGTE V.V. Fortification of vegetarian diets for increasing bioavailable iron density using green leafy vegetables. Food Res. Int. **32**, (3), 169, **1999**.
20. CUNNINGHAM J.H., MILLIGAN G., TREVISAN L. Minerals in Australian fruits and vegetables - a comparison of levels between the 1980s and 2000. Food Standards Australia New Zealand, Report, **2005**.
21. KULCZYCKI G., SPIAK Z. Impact of selected industrial works on the content of heavy metals in soil and plants. Zesz. Probl. Post. Nauk Roln. **471**, 1029, **2000** [In Polish].
22. EKHOLM P., REINIVUO P., MATTILA P., PAKKALA H., KOPONEN J., HAPPONEN A., HELLSTROM J., OVASKAINEN M.L. Changes in the mineral and trace element contents of cereals, fruits and vegetables in Finland. J. Food Compos. Anal. **20**, (6), 487, **2007**.
23. VOUTSA D., GRIMANIS A., SAMARA C. Trace elements in vegetables grown in an industrial area in relation to soil and air particulate matter. Environ. Pollut. **94**, (3), 325, **1996**.
24. FURR A.K., PARKINSON T.F., WACHS T., BACHE C.A., GUTENMANN W.H., WSZOLEK P.C., PAKKALA I.S., LISK D.J. Multielement analysis of municipal sewage sludge ashes. Absorption of elements by cabbage grown in sludge ash-soil mixture. Environ. Sci. Technol. **13**, (12), 1503, **1979**.
25. VIQAR-UN-NISA R., MOHAMMAD AM. Levels of selected essential and toxic elements in the foodstuffs of Islamabad as analyzed by DPASV. Toxicol. Environ. Chem. **87**, (1), 67, **2005**.
26. MISHRA A., TRIPATHI BD. Heavy metal contamination of soil, and bioaccumulation in vegetables irrigated with treated waste water in the tropical city of Varanasi, India. Toxicol. Environ. Chem. **90**, (5), 861, **2008**.
27. LESZCZYŃSKA T., FILIPIAK-FLORKIEWICZ A., CIEŚLIK E., SIKORA E., PISULEWSKI PM. Effects of some processing methods on nitrate and nitrite changes in cruciferous vegetables. J. Food Compos. Anal. **22**, (4), 315, **2009**.
28. WAWRZYNIAK A., HAMUŁKA J., GOŁĘBIEWSKA M. Nitrates and nitrites content in selected vegetables from conventional and ecological cultivations. Bromatol. Chem. Toksykol. **37**, (4), 341, **2004** [In Polish].
29. SZYMCZAK J., PRESCHA A. Content of nitrates and nitrites in market vegetables in Wroclaw in the years 1996-1997. Roczn. PZH, **50**, (1), 17, **1999** [In Polish].
30. MARKOWSKA A., KOTKOWSKA A., FURMANEK W., GACKOWSKA L., SIWEK B., KACPRZAK-STRZAŁKOWSKA E., BŁOŃSKA A. Content estimation of nitrates and nitrites in vegetables from the province of Łódz. Roczn. PZH, **46**, (4), 341, **1995** [In Polish].