# EVALUATION OF ORGANOCHLORINE COMPOUNDS CONTENT AND RADIOCESIUM LEVEL IN SELECTED VEGETABLES FROM THE WARMIA AND MAZURY REGION

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**Abstract:** Organochlorine compounds are very persistent compounds. Considering the harmfulness of these substances, the goal of the study presented in this article was to evaluate the content of organochlorine compounds in selected vegetables. The highest content of lindane were detected in carrot. Accumulation of γ-HCH in cauliflower was more than five times lower. The presence of ΣDDT was detected in all tested vegetables at quantities not exceeding the MRL value. The lowest mean content of ΣDDT was observed in broccoli and spinach, while a three times higher quantity of this compound was detected in carrot. Chlorinated hydrocarbons were detected in all the tested vegetable samples. It was observed that vegetables raised in north-eastern Poland persistently contain numerous foreign chemicals and, as such, should be included in a programme to monitor the levels of harmful chemicals. Contamination of environment and food by artificial isotopes cause receiving radiation doses by people, that can be taken by inhalation of isotopes from the air or the oral route. From the point of view of radioactive contamination of the environment, the most dangerous are the isotopes $^{134}$Cs and $^{137}$Cs, which concentrations are used as an indicator of environmental pollution. In accordance with the Decree of the Minister of Health of 15.01.2003 year, $^{137}$Cs may be present in various products, seeing that is used for irradiating vegetables to inhibit sprouting (in potatoes, onions, garlic), the elimination or reduction of pathogenic microorganisms (bacteria, mold, fungi) and parasites. Radiation also helps to extend the storage life of fresh fruit and vegetables The necessity to monitor the content of radiocesium results from its toxicity, therefore the aim of the study was to analyze the content of radiocesium in chosen vegetables [carrots, cauliflower, broccoli, green peas, green beans, spinach] from area of Warmia and Mazury. The content of $^{137}$Cs in investigated

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vegetables show that the aboveground parts of plants accumulate considerably more radiocesium compared to the root vegetables.

**Key words:** organochlorine compounds, levels, vegetables, γ-HCH, DDT, radiocesium

## INTRODUCTION

Chloroorganic compounds are one of the largest groups of compounds manufactured by industry. They account for about 45% of gross world product [Bonenberg 2003], as they can be found, e.g. in organic solvents, dielectric materials, monomers for the production of plastics, and intermediates for organic synthesis. Chloroorganic compounds are even better known for their use in agents used to eliminate insects dwelling on crops, humans and animals, as well as within buildings [Starek 1996]. Due to the widespread use of these substances, different scales of their harmful emissions, impact range and environmental persistence [Wasiela and Dutkiewicz 1994], their presence in the human environment is inescapable, posing hazards to human health.

Chlorinated hydrocarbons are very stable, persistent compounds that poorly decompose under both atmospheric and biochemical conditions. Some representatives of this class of compounds are considered very persistent and very bioaccumulable [Różański 1992], e.g. DDT (1,1,1-trichloro-bis(4-chlorophenyl)ethane), which is considered one of the most persistent chloroorganic compounds, along with its metabolites [Eichler 1989]. The toxicity of chloroorganics is due to the presence of chlorine atoms [Starek 1996] affecting the toxicological, physical and chemical properties of compounds [Biziuk 2001]. These substances are characterized by high affinity to fats; at the same time, their bioaccumulative potential, as well as persistence in organisms, is a result of active uptake from the environment [water, food, air] and is combined with biological magnification of concentrations in food chains [Struciński et al. 2002a i b]. Considering the above, as well as taking into account the food webs, lifespans and the fact that humans are the last links in the food chains, one should expect that the largest accumulation of chloroorganic compounds in human tissues occurs in human tissues [Różański 1992, Gertig 1996, Góralczyk et al. 1996 , Góralczyk et al. 1998, Struciński et al. 1995, Wierzbicki et al. 1997].

The most important representatives of the class of chloroorganic compounds, besides the already-mentioned DDT, are lindane (γ-HCH) and methoxychlor (DMDT), successively withdrawn from use since 1970 due to their strong toxicity and persistence [however, literature data show that they continue to be in use in tropical countries, from where they can be transported over considerable distances in air or water [Biziuk 2001].

The main metabolites of DDT include DDE (dichlorodiphenyldichloroethane) and DDD (dichlorophenyldichloroethane). Anaerobic conditions accelerate the transformation of DDT into DDD, while aerobic conditions favour its transformation into DDE [Kawano et al. 2000]. γ-HCH (lindane) is one of 9 spatial isomers of HCH, and is characterized by strong insecticidal properties, which accounted for their household use as an agent to eliminate ants, cockroaches and other insects, as well as a wood protecting agent. Lindane is characterized by a somewhat higher toxicity than DDT, which led to

cases of intoxication with the pesticide. Lindane is better absorbed from the alimentary tract and undergoes faster metabolic transformation compared to DDT [Eichler 1989].

Radionuclides are unstable forms of chemical elements that undergo radioactive decay emitting $\alpha$ or $\beta$ particles and X or $\gamma$ radiation [Indulski 1991]. Natural radionuclides generated by the emission of particulate dusts from power plants, volcano eruptions, fires, or natural gas combustion may permeate into groundwater and be absorbed by plants, eventually making their way into animal and human food chains. Of all radioactive decay products, only radionuclides with intermediate or long half-lives that easily enter the food chains are hazardous to humans. Such features are observed for isotopes with chemical and metabolic properties similar to those of elements naturally occurring within the biosphere. These include $^{131}$J, $^{134}$Cs, $^{137}$Cs, $^{89}$Sr and $^{90}$Sr [Eichler 1989, Petrykowska and Rubel 1987].

The pathways of radioactive isotopes within plant and animal organisms, as well as within food chains, are the same as for the stable isotopes of the respective elements, e.g. radioactive iodine is incorporated into thyroid tissue in the same manner as nonradioactive iodine [Koller 1996]; these pathways are similar for all isotopes of all elements characterized by similar chemical properties. Contamination of the environment and food with artificially made isotopes leads to higher radiation doses being absorbed by humans [Haber 1989, Grabowski et al. 2000, Zonenberg et al. 2006].

The harmful effect of radionuclides on living organisms is based on the ionization process leading to the formation of highly reactive free radicals within the cells. Free radicals affect the production of cell components, in particular proteins and nucleoproteins, as well as either partially or completely damaging the cell structure [Schull 1963].

The toxic effects of radionuclides may be categorized into somatic and genomic damage. Somatic damage leads to structural changes within cells and the disturbance of processes responsible for normal functioning of the organism, resulting in acute radiation sickness. The genetic aftermath is much more dangerous. Genetic damage leads to structural changes in the chromosomes within reproductive cells, destroying the system's capability for the proper transmission of genetic traits [NCRP 1989].

The excretion of radionuclides is a slow process [Moskalew 1963]. Therefore, the resistance of the organism to genetic damage is reduced, leading to increased incidence of cancer [Mück 2002]. Lymphoma and malignant tumours are believed to be caused by the interaction of radionuclides with the DNA of individual cells or organs [Haber 1989] Due to the different sensitivities of different organisms, no threshold dose has been established for radioactive radiation. Radiation is most dangerous for cells that undergo rapid proliferation, and therefore small children are at the highest risk of harmful effects (cf. the explosion within the nuclear power plant in Chernobyl, leading to an increase in the number of births of children with Down syndrome (trisomy 21) in Germany) [Zonenberg et al. 2006].

From the standpoint of environmental pollution, the most dangerous radioisotopes include $^{134}$Cs and $^{137}$Cs; levels of these isotopes are used as indicators of environmental pollution. Pursuant to the Ordinance of the Minister of Health dated 15 January 2003, $^{137}$Cs may be present in various products, as it is used for the irradiation of vegetables to inhibit germination (potatoes, onion, garlic), and to eliminate or reduce pathogenic microbes (bacteria, moulds, fungi) and parasites that cause their decomposition. Irradiation with Cs-137 contributes to extension of the storage life for fresh fruit and vegetables [Rozp. Ministra Zdrowia z dn. 15 stycznia 2003 r.].

Considering the harmfulness of these substances, the goal of the study presented in this article was to evaluate the content of chloroorganic compounds in selected vegetables. The need to monitor radiocaesium content is due to its toxicity as described above; therefore, the objective of this study was to analyze the contents of radiocaesium in selected vegetables (carrot, cauliflower, broccoli, green peas, common bean, spinach) from the Warmia and Mazury area.

## MATERIALS AND METHODS

Our research consisted in the analysis of the content of chlorinated hydrocarbons $\gamma$-HCH and $\Sigma$DDT and radiocaesium in selected vegetables (carrot, cauliflower, broccoli, green peas, common bean and spinach).

The study material consisted of vegetables supplied by different producers from north-eastern Poland. Vegetables were produced mainly by individual farmers who had signed appropriate collaboration agreements and who were partially using seedlings delivered by Chłodnia Olsztyn. The sizes of individual plantations were varied. Study samples of 1 to 2 kg, originating from randomly selected producers, were collected immediately after the delivery of vegetables for initial storage. Next, the study material was transferred to the laboratory and stored in -18°C in a Gorenje ZOS3167C laboratory freezer until the analyses. The analyses were conducted at the University of Warmia and Mazury. Evaluation of radiocaesium in vegatables were conducted during 10 days. The investigations were carried out on the defrosted samples of vegetables.

**Evaluation of organochlorine compounds**. Determination of chloroorganic insecticide residues was carried out according to a method developed by the National Institute of Hygiene. The method's principle included extraction of chloroorganic compounds from ground samples, purification and condensation of extracts, and determination by gas chromatography with an electron capture detector [Ludwicki et al. 1996]. Thoroughly ground samples of vegetables (50 g) were shaken in 100 mL of hexane on a shaker-stirrer at room temperature. Next, the contents of the flask were filtered, condensed and transferred into a 10 mL volumetric flask. An appropriately prepared, alumina-filled column was washed with n-hexane, which was then discarded. Next, while not allowing the column to dry, the sample (2 mL) was introduced onto the column and extracted with n-hexane. The extract was condensed down to a volume of ca. 2 mL, quantitatively transferred into a 10 mL tube and filled up with n-hexane to 5 mL. The solution (1 mL) corresponded to the extract of 1 g of the sample. The obtained extract was prepared for determinations. Separation and identification of the tested chloroorganic pesticides was achieved by means of gas chromatography. A PU-4600 gas chromatograph with an electron capture detector and a glass column sized 2.1 m $\times$ 4 mm, filled with Supelcoport 100/120 and mobile phase containing 1.5% SP-2250 and 1.95% SP-2401 were used. The carrier gas was argon at a flow rate of 60 mL/min. Separation temperatures were as follows: column 210°C, detector 260°C, sampler 230°C. The accuracy of the method was verified by the addition of standard to the test samples. The recovery rates were 75% for $\gamma$-HCH and 70% for DDT. Compounds were identified on the basis of the retention times of samples and standards (LGC Promochem GmbH, Germany). Areas under peaks were calculated using Unicam 4880 software. The refer-

ence material consisted of powdered spinach from GEMS/Ford – EURO EXERCISE 93/02 interlaboratory studies.

**Evaluation of radiocaesium**. The content of Cs-137 was determined in vegetable samples incinerated at 450$^o$C according to the procedure recommended by the Central Laboratory for Radiological Protection [CLOR]. The method is based on the sorption of caesium from the dissolved ash onto an AMP (ammonium molybdophosphate) bed [CLOR 2004]. Powdered vegetable samples were dried in evaporating dishes at 110$^o$C, and later carbonized and incinerated in a muffle furnace at 450$^o$C. After cooling, the resultant ash was weighed and moistened with distilled water. Next, hydrochloric acid was added (1:1). Following evaporation to dryness, hot distilled water was added and the mixture was filtered. Concentrated nitric acid was added to the filtrate and the mixture was filled up to 150 mL with distilled water. The ammonium molybdophosphate (AMP) bed was prepared as follows: A 50 cm$^3$ beaker was charged with 7 cm$^3$ of ammonium nitrate solution (71.4 g of $NH_4NO_3$ was dissolved in 143.5 cm$^3$ of concentrated $HNO_3$, d = 1.4 g/cm$^3$ and filled up to 1000 cm$^3$), 3 cm$^3$ of ammonium heptamolybdatetetrahydrate (26.5 g of $[NH_4]_6Mo_7O_{27} \times 4H_2O$) was dissolved in 250 cm$^3$ of distilled $H_2O$ at 70$^o$C] and 1 cm$^3$ of ammonium dihydrogen phosphate (3.64 g of $NH_4H_2PO_4$ was dissolved in 500 cm$^3$ of distilled water). The obtained precipitate was heated at 80$^o$C for 20 minutes for recrystallization and then cooled to room temperature and filtered through a radiochemical funnel with a filter made of hard filter paper. The bed was rinsed with distilled water until the disappearance of acidic reaction according to litmus paper. The dissolved ash was vacuum-filtered through a radiochemical funnel with an AMP bed over 20 minutes. The filter paper was transferred to a measuring cuvette, coated with 4% collodion in acetone and allowed to dry. β-Radioactivity was measured using a ZAPKS-1 contamination control and measurement kit (Polon, Warsaw). KCl in an amount 250 mg placed in a measuring cuvette was used as the reference standard. The activity of the KCl standard was compared to that of the $^{137}$Cs standard. The resultant conversion factor of 1.222 was then used to calculate the activity of the test samples.

**Statistical analyses**. All analyses were carried out in triplicate. The obtained results were subjected to statistical analysis with calculation of arithmetical means, standard deviations [SD] and variability coefficients [V]. Bifactorial analysis of variance was performed, and the lowest significant difference [LSD] was calculated according to Tukey's method at a confidence level of 0.05. The results were submitted to statistical analysis to determine significant differences between the contents of individual compounds in the tested vegetables as well as between vegetables supplied by different producers.

The results obtained from evaluation of radiocaesium were subjected to statistical analysis. One factorial analysis of variance was performed, and the lowest significant difference was calculated according to Tukey's method at a confidence level of 0.05. The significant differences between the contents of radiocaesium in the vegetables were determinated.

Calculations and statistical analyses were performed using Microsoft Excel and StatSoft Statistica 10 PL software.

## RESULTS AND DISCUSSION

Table 1 presents average contents of γ-HCH in six vegetable species from 10 different suppliers.

Table 1. Content of γ-HCH in vegetables [μg/kg of defrosted product] from 10 suppliers
Tabela 1. Zawartość γ-HCH [μg/kg rozmrożonego produktu] w warzywach pochodzących od 10 dostawców

|  | Carrot | Cauliflower | Broccoli | Green Peas | Beans | Spinach | $\overline{X}$ | SD | V |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0,107 | 0,005 | 0,005 | 0,001 | 0,010 | 0,005 | 0,022 | 0,042 | 187,929 |
| 2 | 0,053 | 0,001 | 0,001 | 0,004 | 0,005 | 0,007 | 0,012 | 0,020 | 171,565 |
| 3 | 0,001 | 0,012 | 0,014 | 0,010 | 0,014 | 0,001 | 0,009 | 0,006 | 70,626 |
| 4 | 0,001 | 0,001 | 0,005 | 0,012 | 0,010 | 0,003 | 0,005 | 0,005 | 87,678 |
| 5 | 0,001 | 0,001 | 0,002 | 0,002 | 0,005 | 0,006 | 0,003 | 0,002 | 75,422 |
| 6 | 0,008 | 0,001 | 0,008 | 0,008 | 0,005 | 0,012 | 0,007 | 0,004 | 52,683 |
| 7 | 0,007 | 0,005 | 0,009 | 0,010 | 0,007 | 0,008 | 0,008 | 0,002 | 22,841 |
| 8 | 0,005 | 0,004 | 0,014 | 0,004 | 0,004 | 0,012 | 0,007 | 0,005 | 63,892 |
| 9 | 0,020 | 0,001 | 0,016 | 0,015 | 0,011 | 0,004 | 0,011 | 0,007 | 65,908 |
| 10 | 0,002 | 0,007 | 0,005 | 0,001 | 0,002 | 0,002 | 0,003 | 0,002 | 73,156 |
| $\overline{X}$ | 0,021 | 0,004 | 0,008 | 0,007 | 0,007 | 0,006 | * significance at confidence level of α = 0,05 | | |
| SD | 0,034 | 0,004 | 0,005 | 0,005 | 0,004 | 0,004 | | | |
| V | 167,410 | 95,930 | 66,570 | 74,140 | 51,680 | 63,830 | | | |
| Analysis of variance | | | | | | | | | |
| Factor | $F_{cal.}$ | | $F_{tab}$ | | *p-value* | | LSD | | |
| producer | 0,859 | | 2,096 | | 0,567 | | 0,028 | | |
| vegetable | 1,632 | | 2,422 | | 0,171 | | 0,020 | | |

Table 2 presents average content of ΣDDT in six vegetable species from 10 different suppliers.

Table 2. Content of ΣDDT in vegetables [μg/kg of defrosted product] from 10 suppliers
Tabela 2. Zawartość ΣDDT [μg/kg rozmrożonego produktu] w warzywach pochodzących od 10 dostawców

| No. | Carrot | Cauliflower | Broccoli | Green Peas | Beans | Spinach | $\overline{X}$ | SD | V |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0,062 | 0,017 | 0,003 | 0,003 | 0,032 | 0,013 | 0,022 | 0,023 | 103,766 |
| 2 | 0,004 | 0,007 | 0,003 | 0,003 | 0,004 | 0,010 | 0,005 | 0,003 | 53,939 |
| 3 | 0,003 | 0,021 | 0,004 | 0,003 | 0,003 | 0,009 | 0,007 | 0,007 | 100,005 |
| 4 | 0,039 | 0,006 | 0,003 | 0,014 | 0,046 | 0,008 | 0,019 | 0,018 | 95,356 |
| 5 | 0,047 | 0,004 | 0,018 | 0,006 | 0,010 | 0,004 | 0,015 | 0,016 | 112,033 |
| 6 | 0,003 | 0,005 | 0,003 | 0,010 | 0,003 | 0,008 | 0,005 | 0,003 | 56,458 |
| 7 | 0,022 | 0,011 | 0,011 | 0,012 | 0,021 | 0,007 | 0,014 | 0,006 | 43,331 |
| 8 | 0,016 | 0,015 | 0,003 | 0,012 | 0,012 | 0,006 | 0,011 | 0,005 | 48,048 |
| 9 | 0,016 | 0,008 | 0,015 | 0,020 | 0,022 | 0,013 | 0,016 | 0,005 | 31,958 |
| 10 | 0,016 | 0,013 | 0,004 | 0,006 | 0,010 | 0,010 | 0,010 | 0,004 | 44,754 |
| $\overline{X}$ | 0,023 | 0,011 | 0,007 | 0,010 | 0,016 | 0,009 | * significance at confidence level of α = 0,05 | | |
| SD | 0,020 | 0,006 | 0,006 | 0,006 | 0,014 | 0,003 | | | |
| V | 88,470 | 53,060 | 85,900 | 63,880 | 86,430 | 32,500 | | | |
| Analysis of variance | | | | | | | | | |
| Factor | $F_{cal.}$ | | $F_{tab}$ | | *p-value* | | LSD | | |
| producer | 1,887 | | 2,096 | | 0,079 | | 0,019 | | |
| vegetable | *3,563 | | 2,422 | | 0,008 | | 0,014 | | |

Lindane was detected in all tested materials; however, the detected quantities were not above the maximum residue levels [MRLs]. Despite the ban on the use of DDT and γ-HCH in Poland, these pesticides are present within the environment as deposits in bottom sediments, soils and living organisms, from where they are capable of entering water, air, and even food products and animal feeds, thus posing risks to humans and animals [Biziuk 2001].

Bifactorial analysis of variance revealed no effect of the vegetable species and origin (supplier) on the content of γ-HCH. Tukey's tests [LSD] revealed no significant differences between the average lindane content neither between the tested vegetable species nor between suppliers. The highest content of lindane were detected in carrot (0.021 μg/kg). Accumulation of γ-HCH in cauliflower was more than five times lower.

The reduction in the content of the HCH isomer in vegetables should be associated with the considerable restrictions put on its use in 1988, and the total ban on its use introduced in 1990 [Struciński et al. 1995]. However, these compounds are present in the bodies of humans and animals as they continue to circulate within the ecosystems and are capable of accumulating in animal tissues; humans are most exposed to the harmful effects of these compounds due to magnification of bioaccumulation, as well as low rates of their elimination from the body. [Petrykowska and Rubel 1987]. The most commonly detected chloroorganic compounds include DDT and low quantities of lindane [Garrido Frenich et al. 2003, Mazurkiewicz and Czernecki 2011, Pomianowski et al. 2011].

The presence of ΣDDT was detected in all tested vegetables at quantities not exceeding the MRL value. Differentiation of the ΣDDT content depending on the vegetable species observed, with differences not being statistically significant at the level of $\alpha = 0.05$ for carrot, compared with broccoli, green peas and spinach, with the lowest significant difference [LSD] of 0.014.

The lowest mean content of ΣDDT was observed in broccoli (0.007 μg/kg) and spinach (0.009 μg/kg), while a three times higher quantity of this compound was detected in carrot (0.023 μg/kg).

Mean residues of total DDT in the analysed vegetables were significantly lower than the proposed MRL (0.05 mg/kg). However, the presence of DDT in all the tested vegetable material confirms their persistence and potential for bioaccumulation in the environment and human systems [Zientek-Varga 2005].

As shown by the analysis, the highest contents of both γ-HCH and ΣDDT were detected in carrots. Mean contents of chloroorganic compounds [γ-HCH, ΣDDT] were determined for all six vegetables obtained from different suppliers, but the levels of these compounds were low and did not exceed the maximum residue levels (MRLs) [Góralczyk et al. 1996, Michna and Szteke 2002, Szteke 2001].

The withdrawal of the majority of plant protection agents from the market are due to the fact that these compounds are harmful for human health. Therefore, it is important to monitor the residues of plant protection agents in various food products. The range of such studies should be continuously expanded. Examinations should cover the maximum possible numbers of active substances and species of vegetables, fruit, crops and processed products of plant origin [Gnusowski et al. 2009, Gnusowski and Nowacka 2005].

Table 3 presents the content of radiocaesium in vegetables, including the results of analyses carried out on individual days, and the statistical analyses.

Table 3. Content of radiocesium in vegetables [Bq/kg of defrosted product]
Tabela 3. Zawartość radiocezu w warzywach [Bq/kg rozmrożonego produktu]

| Days | Carrot | Cauliflower | Broccoli | Green Peas | Beans | Spinach |
|------|--------|-------------|----------|------------|-------|---------|
| 1 | 0,510 | 0,400 | 0,62 | 1,300 | 1,210 | 0,900 |
| 2 | 0,500 | 0,400 | 0,61 | 1,300 | 1,210 | 0,920 |
| 3 | 0,520 | 0,410 | 0,61 | 1,300 | 1,210 | 0,920 |
| 4 | 0,510 | 0,400 | 0,60 | 1,300 | 1,210 | 0,920 |
| 5 | 0,510 | 0,410 | 0,60 | 1,310 | 1,200 | 0,910 |
| 6 | 0,500 | 0,410 | 0,60 | 1,300 | 1,200 | 0,910 |
| 7 | 0,500 | 0,400 | 0,61 | 1,300 | 1,210 | 0,900 |
| 8 | 0,500 | 0,400 | 0,61 | 1,300 | 1,210 | 0,920 |
| 9 | 0,510 | 0,410 | 0,61 | 1,300 | 1,210 | 0,910 |
| 10 | 0,510 | 0,400 | 0,60 | 1,300 | 1,210 | 0,920 |
| SD | 0,007 | 0,005 | 0,008 | 0,003 | 0,005 | 0,008 |
| V | 1,290 | 1,290 | 1,100 | 0,220 | 0,410 | 0,920 |

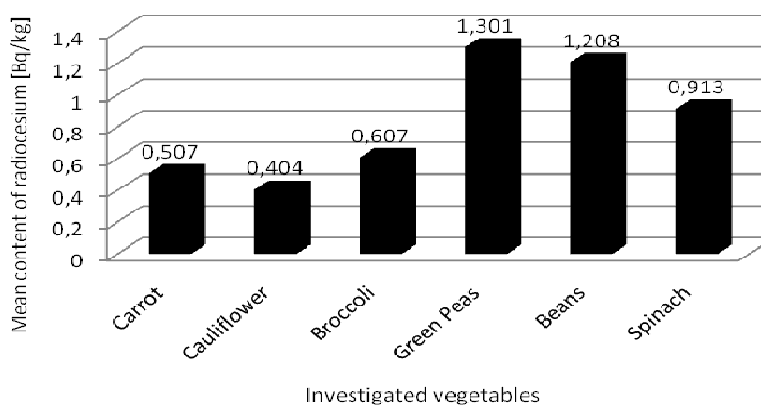$F_{cal}$ 46877,877*       $F_{tab}$ 3,308      LSD 0,007



Fig. 1. Mean content of radiocesium [Bq/kg of defrosted product] in the investigated vegetables
Rys. 1. Średnia zawartość radiocezu [Bq/kg rozmrożonego produktu] w badanych warzywach

Figure 1 presents the mean content of caesium in individual vegetables. The highest content of ^{137}Cs was determined in green peas (1,301 Bq/kg) and beans (1,208 Bq/kg), while the lowest content of ^{137}Cs was determined in cauliflower (0,405 Bq/kg). Similar, low concentrations of radiocaesium were observed in carrot and broccoli.

Natural and artificial radionuclides are found mostly in food of animal origin; in the case of vegetables the uptake of caesium is dependent on soil conditions and the plant species. Literature data suggest that the uptake of caesium into vegetables largely depends on soil conditions and vegetable type, as well as of the mechanisms of isotope binding in soil systems [Chibowski 2000].

Over-ground parts of vegetables were found to accumulate the highest amounts of radioisotopes [Hryńczuk et al. 1997], while studies conducted by many authors [Badran et al. 2003, Grabowski et al. 2006, Królak and Karwowska 2010] confirm that the

pathway of the accumulation of caesium in fruit and vegetables is of a very complex nature.

Markedly lower amounts of radionuclides are found in the roots of the plant materials, while much higher amounts can be determined in the leaves.

The low content of caesium in root vegetables is probably due to the low binding of caesium within the root system. The results of our own study of the content of $^{137}$Cs in carrot are comparable with the mean contents of radionuclides in Poland as assessed by other authors [Zonenberg et al. 2006].

The content of $^{137}$Cs in green peas significantly exceeded the mean concentration of the isotope determined in other vegetables. The obtained results are confirmed by the results obtained by Badran et al. [2003], where the mean content of radiocaesium was 1,74 Bq/kg and the value range was 0,57 to 4,00 Bq/kg [Badran et al. 2003].

The determination of $^{137}$Cs content in food is a part of the monitoring project that has been carried out in Poland since the Chernobyl disaster in 1986 [Grabowski et al. 2000, Grabowski et al. 2006, Grabowski et al. 1993]. Currently, the content of caesium in food samples is mostly due to its concentration in soils [Królak and Karwowska 2010]. In 1992 through 2007 the mean annual activity of $^{137}$Cs in fruit and vegetables in Poland ranged from 0.4 to 0.7 Bq/kg [Grabowski et al. 2006]. However, the value for vegetables alone was as high as 3,89 ± 3,35 Bq/kg [Królak and Karwowska 2010].

On the basis of his studies regarding fruit and vegetables from Lublin region, Chibowski [2000] also observed that accumulation of caesium was higher in the common bean [4,4 Bq/kg] than in red beets [0,7 Bq/kg]. Studies by the same author revealed no presence of caesium in the roots of carrot or celeriac [Chibowski 2000].

The absorption of caesium into plants from the soil is most probably due to the high chemical similarity between caesium and potassium. Therefore, as pointed out by the authors of many studies, although the plant roots absorb radioactive caesium only to a limited degree, they play a mediatory role in the transport of this element from soil to the overground parts of plants [Chibowski 2000, Ban-Nai et al. 1995, Changizi 2010]. This correlation was also observed in our own studies, as the content of $^{137}$caesium in green peas, the common bean and spinach was higher as compared to carrot.


## CONCLUSIONS

1. As shown by the study, there were no statistically significant differences to suggest the impact of the producer on the presence of harmful chemicals. One might assume that vegetable producers (suppliers of frozen food materials) pay attention to the basic rules of plant cultivation.

2. Chlorinated hydrocarbons were detected in all the tested vegetable samples. It was observed that vegetables raised in north-eastern Poland persistently contain numerous foreign chemicals and, as such, should be included in a programme to monitor the levels of harmful chemicals.

3. As shown by the analysis of the results, the highest concentrations of γ-HCH and total DDT were observed in carrot, while the lowest levels of chloroorganics were determined in spinach. One may conclude that chloroorganic compounds are accumulated mostly in root vegetables (carrot).

4. Harmful chemicals being determined were present in the tested vegetables at levels not exceeding the maximum residue levels.

5. As shown by the results of the determination of $^{137}$Cs in the test vegetables, overground parts of tested plants accumulate much more radiocaesium than the root vegetables.

6. Due to the lack of threshold levels of $^{137}$Cs, tests to monitor its content in vegetables are required.

## REFERENCES

Badran, H.M., Sharshar, T., Elnimer, T. (2003). Levels of $^{137}$Cs and $^{40}$K in edible parts of some vegetables consumed in Egypt. J. Environ. Radioact., 67, 181–190.

Ban-Nai, T., Muramatsu, Y., Yanagisawa, K. (1995). Transfer factors of some selected radionuclides (radioactive Cs, Sr, Mn, Co and Zn) from soil to leaf vegetables. J. Radiation Res., 36, 143–154.

Biziuk, M. (2001). Pesticides occurrence, determination and disposal. WNT: Warszawa.

Bonenberg, K. (2003). At random…? Aura 3, 32–33.

Changizi, V, Jafarpoor, Z., Naseri, M. (2010). Measurement of $^{226}$Ra, $^{228}$RA, $^{137}$Cs and $^{40}$K in edible parts of two types of leafy vegetables cultivated in Teheran province-Iran and resultant annual ingestion radiation dose. Iranian J. Radiation Res., 8, 2, 103–110.

Chibowski, S. (2000). Studies of radioactive contaminations and heavy metal content in vegetables and fruit from Lublin, Poland. Polish J. Environ. Stud., 9, 4, 249–253.

CLOR (2004). Metodyka radiochemicznego oznaczania $^{137}$Cs w próbkach produktów żywnościowych i wodzie, Warszawa.

Eichler, W. (1989). Poisons in our food. PZWL, Warszawa.

Garrido Frenich, A., Martinez Vidal, J.L., Moreno Frias, M., Olea-Serrano, F., Olea, N., Cuadros Rodriguez, L. (2003). Determination of Organochlorine Pesticides by GCECD and GC-MS-MS Techniques Including an Evaluation of the Uncertainty Associated with the Results. Chromatographia 57 (3/4), 213–220.

Gertig, H. (1996). Food and health. PZWL, Warszawa.

Gnusowski, B., Nowacka, A. (2005). Risk assessment of human health hazard by residues of plant protection products in the Polish agricultural crops in 2004. Prog. Plant Prot. 45 (1), 120–126.

Gnusowski, B., Nowacka, A., Walorczyk, S., Łozowicka, B., Szpyrka, E., Sadło ,S. (2009). Pesticide residues in organic food of plant origin in Poland in 2008. Prog. Plant Prot. 49 (4), 1857–1862.

Góralczyk, K., Czaja, K., Ludwicki, J.K. (1996). Biological and environmental monitoring of exposure to chlorinated aromatic hydrocarbons. Roczn. PZH 47 (1), 25–32.

Góralczyk, K., Ludwicki, J.K., Czaja, K., Struciński, P. (1998). Monitoring of pesticides residue in Poland. Roczn. PZH, 49, 331–339.

Grabowski, D., Muszyński, W., Petrykowska, M., Rubel, B., Smagała, G., Wilgos, J. (1993). Radioactive contamination of environmental and food in Poland in 1992. Bibl. Monitoringu Środ., Warszawa.

Grabowski, D., Kurowski, W., Muszyński, W., Rubel, B., Smagała, G., Świętochowska, J. (2000). Radioactive contamination of environmental and food in Poland. Raport CLOR, 143, 30.

Grabowski, D., Kurowski, W., Muszyński, W., Rubel, B., Smagała, G., Świętochowska, J. (2006). Radioactive contamination of chosen environmental components and food items in the years 1986–2005. In: K. Pachocki ed, Czarnobyl – 20 lat później: skażenie środowiska i żywności, wpływ na zdrowie. Energetyka nuklearna w Polsce – za i przeciw. XXI Szkoła Jesienna, Zakopane, 113–124.

Haber K., 1989. Umweltradioaktivität und Trinkwasserversorung. Haberer. – Műnchen; Wien: Oldenbourg.

Hryńczuk, B., Żurawski, H., Hryńczuk, B., Weber, R. (1997). Akumulacja Sr-90 i Cs-137 w zielonce żyta, kukurydzy i peluszki uprawianych na różnych glebach skażonych tymi radionuklidami. Rocz. AR w Poznaniu, 294, 55–61.

Indulski, J.A. (1991). Kryteria zdrowotne środowiska. Wybrane pierwiastki promieniotwórcze. PZWL Warszawa.

Kawano, M., Brudnowska, B., Falandysz, J., Wakimoto, T. (2000). Polichlorinated biphenyls and organochlorine pesticides in soils in Poland. Roczn. PZH 51 (1), 15–28.

Królak, E., Karwowska, J. (2010). Potassium-40 and cesium-137 in the surface layers of arable soils and food supplies. Polish J. Environ. Stud., 19, 3, 599–604.

Ludwicki, J.K., Góralczyk, K., Czaja, K., Struciński, P. (1996). Determination of residues of organochlorine insecticides and polychlorinated biphenyls in foodstuffs by gas chromatography. PZH: Warszawa.

Mazurkiewicz, J., Czernecki, T. (2011). The content of organochlorine pesticides residues in selected frozen vegetables from the Lubelskie market. Acta Agrophysica 17 (1), 151–163.

Michna, W., Szteke, B. (2002). The research of plant materials. The report from monitoring researches of soil, plants, agricultural products and foodstuff in 2001 r. MRiRW, Warszawa.

Moskalew ,J.I. (1963). O uzasadnieniu maksymalnie dopuszczalnych zawartości i skażeń wewnętrznych organizmu izotopami promieniotwórczymi. Post. Techn. Jądrowej, 1, 73, 42–47.

Mück, K., Pröhl, G., Likhtarev, I., Kovgan, L., Meckbach, R., Golikov, V. (2002). A consistent radionuclide vector after the Chernobyl accident. Health Physics 82 (2), 141–156

NCRP – Raport Nr 89 (1989). Skutki genetyczne radionuklidów zdeponowanych w ustroju. Centrum Informatyki i Energetyki, Warszawa, (niepubl.).

Petrykowska, M., Rubel, B. (1987). Po awarii w Czarnobylu. Przyroda Polska, 5, 18–21.

Pomianowski, J.F., Wieczorek, J., Mozolewski, W. (2011). The residues of chlorinated hydrocarbons in ketchups. Bromatol. Chem. Toksykol. 3, 738–741.

Różański, L., 1992. Transformations of pesticides in living organisms and environment. PWRiL, Warszawa.

Rozporządzenie Ministra Zdrowia z dnia 15 stycznia 2003 r. w sprawie warunków napromieniowania środków spożywczych, dozwolonych substancji dodatkowych do innych składników żywności, które mogą być poddane działaniu napromieniowania oraz wymagań w zakresie znakowania i wprowadzania do obrotu. Dz.U. 2003, Nr 37, poz. 327.

Schull, W.J. (1963). Radiation effects on man-hereditary effects. Journal of Occupational Medicine, 5, 6, 329.

Starek, A. (1996). Toxicology of organochlorine compounds in outline. Roczn. PZH 47 (1), 1–12.

Struciński, P., Góralczyk, K., Ludwicki, J.K. (1995). Abiotic and biotic transformation of persistent organochlorine compounds in environment. Roczn. PZH, 46 (3), 279–292.

Struciński, P., Ludwicki, J.K., Góralczyk, K., Czaja, K., Hernik, A. (2002a). Environmental exposure to polychlorinated biphenyls – selected health aspects. Aura 5, 10–11.

Struciński, P., Ludwicki, J.K., Góralczyk, K., Czaja, K., Hernik, A. (2002b). Environmental exposure to polychlorinated biphenyls (2) – selected health aspects. Aura 6, 24–25.

Szteke, B. (2001). Pesticides in edible plant raw materials. Legal considerations. Monitoring of residues. Biul. Nauk. 12, 85–94.

Wasiela, T., Dutkiewicz, T. (1994). Indexed method for the hazard assessment of chemical substances in terms of environment al and occupational exposure. Bromatol. Chem. Toksykol. 27 (2), 91–97.

Wierzbicki, T., Szarkowska, I., Ignatowicz-Owsieniuk, K. (1997). The threat of natural environment pollution by pesticides. Ekoinżynieria 2, 9–13.

Zientek-Varga, J. (2005). Deadly, though are intended to protect. Aura 5, 28.

Zonenberg, A., Leoniak, M., Zarzycki, W. (2006). The effect of Chernobyl accident on the development of non-malignant diseases. Endokrynol Pol 1 (57), 38–44

## OCENA ZAWARTOŚCI ZWIĄZKÓW CHLOROORGANICZNYCH ORAZ POZIOMU RADIOCEZU W WYBRANYCH WARZYWACH Z TERENU WARMII I MAZUR

**Streszczenie**. Związki chloroorganiczne należą do związków bardzo trwałych, tzw. persystentalnych, trudno ulegających rozkładowi zarówno pod wpływem warunków atmosferycznych, jak i biochemicznych, a wśród grup je reprezentujących występują też związki o dużej trwałości i zdolności do biokumulacji. Natomiast zanieczyszczenie środowiska i żywności sztucznymi izotopami powoduje otrzymanie dawki promieniowania przez ludzi. Z punktu widzenia radioaktywnego skażenia środowiska, najbardziej niebezpieczne są izotopy $^{134}$Cs i $^{137}$Cs, których stężenia stosowane są jako wskaźnik zanieczyszczenia środowiska. Mając na uwadze szkodliwość powyższych substancji oraz konieczność monitorowania zawartości radiocezu, ze względu na jego toksyczność, celem zaprezentowanych w pracy badań było sprawdzenie zawartości związków chloroorganicznych oraz analiza zawartości radiocezu w wybranych warzywach (marchew, kalafior, brokuły, zielony groszek, zielona fasola, szpinak] z obszaru Warmii i Mazur. Jak pokazują wyniki badania, nie stwierdzono istotnych statystycznie różnic wskazujących na wpływ producenta na obecność szkodliwych substancji chemicznych. Można przypuszczać, że producenci warzyw mrożonych zwracali uwagę na podstawowe zasady uprawy roślin. We wszystkich badanych próbach warzyw, będących mrożonymi produktami rynkowymi, stwierdzono obecność chlorowanych węglowodorów w ilościach nieprzekraczających najwyższych dopuszczalnych poziomów. Największe stężenie γ-HCH i sumy DDT stwierdzono w marchwi, a najniższym stężeniem związków chloroorganicznych charakteryzował się szpinak. Można zatem stwierdzić, że związki chloroorganiczne są gromadzone głównie w warzywach korzeniowych. Poziomy $^{137}$Cs w badanych warzywach pokazują, że części nadziemne roślin gromadzą znacznie więcej izotopu w porównaniu z warzywami korzeniowymi.

**Słowa kluczowe:** związki chloroorganiczne, poziomy, warzywa, γ-HCH, DDT, radiocez