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MONITORING OF RESIDUES OF DITHIOCARBAMATE FUNGICIDES IN POLISH CROPS DURING 1999–2000

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Abstract: The results of studies on residues of dithiocarbamate fungicides in 13 different crops during 1999–2000 are presented. According to monitoring programme 2,226 samples of fruits and vegetables were collected from the productions sites in the whole country. The samples were analyzed for residue content by a spectrophotometric method. In 11.3% of samples the residues were detected. Residues exceeding Polish MRLs were found in 10 samples (0.5%).

Key words: dithiocarbamate residues, spectrophohotometry, fruits, vegetables, greenhouses

INTRODUCTION

The preservation of the environment and human health from exposure to organic contamination is nowadays a priority objective. Pesticides constitute a very important group of target compounds due to their high toxicity and unavoidable use in agriculture.

The compounds belonging to the group of ethylenebisdithiocarbamate (EBDC) and thiuram disulfide have been used in agricultural practice for a long time. Dithiocarbamate pesticides are widely used on variety of crops as effective fungicides against a broad spectrum of fungal diseases. They are economically important for the plant protection, and can be used as field treatment as well as seed dressings. These pesticides are still in use because of their environmental properties, such as a short field life and relatively low mammalian toxicity. However, ethylenethiourea (ETU) that is formed as a result of decomposition and/or metabolism of EBDC fungicides was found (Khera 1973) mutagenic, cancerogenic and teratogenic, very toxic for animals and human beings.

Since dithiocarbamate fungicides have been applied for long time, their residues have been frequently found on the variety of fruits and vegetables. The amount of ETU in food depends on dithiocarbamate residues in plants. Contamination of fodder with EBDC may cause penetration of ETU to the animal products, e.g. milk (Engst and Schanaak 1979). For that reason the systematic control of dithiocarbamate residues is necessary.

Method for the determination of dithiocarbamates is based on their decomposition to carbon disulfide (Keppel 1971) or ethylenediamine (Newsome 1974). Colometric method elaborated by Cullen (1964) modified by Keppel (1969, 1971) is very common. In order to increase the sensibility and reproducibility of the method, Chmiel (1979) modified Keppel's method and introduced a more stable complex for spectrophotometric determination. The quantity of carbon disulfide can be also determined by headspace gas chromatography with electron capture detector (Mc Lead and Mc Cully 1969), but the method did not find wide application.

The aim of the study was to analyze the levels of dithicarbamates in domestic crops taken from greenhouses and fields in 1999–2000.

MATERIALS AND METHOD

During 1999–2000 vegetation seasons 2,226 samples of fruits and vegetables (Tabs. 1, 2) were collected randomly from the fields and greenhouses in the whole country area by trained staff of Plant Protection Inspectorates. 1,351 samples of greenhouse vegetables, 526 samples of fruits and 349 samples of field vegetables were analyzed for dithiocarbamate residue content by six laboratories of Institute of Plant Protection.

Table 1. Analyzed crops

Analyzed crops	Number of samples	% of samples	
		A[1]	B[2]
GREENHOUSE VEGETABLES	1,351	60.7	
Cucumber	412		30.5
Lettuce	212		15.7
Tomato	590		43.7
Mushroom	137		10.1
FIELD VEGETABLES	349	15.7	
Cucumber	220		63.0
Red beet	33		9.4
Sugar beet	5		1.4
Tomato	91		26.2
FRUITS	526	23.6	
Cherry	98		18.6
Currant	115		21.9
Plum	41		7.8
Raspberry	15		2.8
Strawberry	257		48.9

[1] % of samples of individual crop groups in total quantity of analyzed samples
[2] % of samples of particular crops in the crop groups

Table 2. Analyzed crop groups in each province

Province	Greenhouse vegetables			Field vegetables			Fruits			% of all analyzed samples
	Number of samples	% of samples		Number of samples	% of samples		Number of samples	% of samples		
		A[1]	B[2]		A	B		A	B	
Total	1,351		60.7	349		15.7	526		23.6	
Dolnośląskie	58	4.3	2.6	20	5.7	0.9	21	4.0	0.9	4.4
Kujawsko--Pomorskie	93	6.9	4.2	20	5.7	0.9	35	6.7	1.6	6.6
Lubelskie	120	8.9	5.4	50	14.3	2.2	71	13.5	3.2	10.8
Lubuskie	52	3.8	2.3	11	3.2	0.5	16	3.0	0.7	3.5
Łódzkie	96	7.1	4.3	14	4.0	0.6	33	6.3	1.5	6.4
Małopolskie	111	8.2	5.0	14	4.0	0.6	34	6.5	1.5	7.1
Mazowieckie	177	13.1	8.0	48	13.8	2.2	91	17.3	4.1	14.2
Opolskie	76	5.6	3.4				24	4.6	1.1	4.5
Podkarpackie	103	7.6	4.6	21	6.0	0.9	26	4.9	1.2	6.7
Podlaskie	53	3.9	2.4	23	6.6	1.0	29	5.5	1.3	4.7
Pomorskie	49	3.6	2.2	14	4.0	0.6	33	6.3	1.5	4.3
Śląskie	78	5.8	3.5				16	3.0	0.7	4.2
Świętokrzyskie	22	1.6	1.0	30	8.6	1.3	50	9.5	2.2	4.6
Warmińsko--Mazurskie	94	7.0	4.2	2	0.6	0.1	4	0.8	0.2	4.5
Wielkopolskie	125	9.3	5.6	71	20.3	3.2	24	4.6	1.1	9.9
Zachodnio-Pomorskie	44	3.3	2.0	11	3.2	0.5	19	3.6	0.9	3.3

[1] % of samples in individual crop groups
[2] % of samples in the total number (quantity) analyzed

The residues were determinated using Chmiel procedure. The sample was heated with hydrochloric acid and tin (II) chloride to release carbon disulfide, which was distilled off and collected in a solution of potassium hydroxide in methanol. Under these conditions CS_2 form potassium xanthate, which was then heated with zinc acetate. On acidification of the reaction medium the precipitate of zinc sulfide release hydrogen sulfide. This compound reacted with p-dimethylaminoaniline and iron (III) to afford methylene blue. The quantity of the colored complex was determined by measurement of its absorbancy at 662 nm. Concentration of dithiocarbamates was calculated and expressed as mg CS_2/kg. Assignment of dithiocarbamate residues in plant material to a specific compound is impossible. Only the quantification of the whole dithiocarbamates group is possible by this method. The maximum residue levels (MRLs) for dithiocarbamates are expressed as CS_2 and established for the whole group of compounds (mancozeb, maneb, metiram, thiuram, zineb).

Pesticide free fruit and vegetables samples were used as blank and spiked for recovery assay. Quantitative determinations were performed using a calibration curve. The recoveries obtained from spiked samples with different concentrations were in 78–98% range. The relative standard deviation did not exceed 4%. Limit of determination of the method for different crops was established as follows: mushroom – 0.05 mg/kg, lettuce – 0.2 mg/kg, others – 0.1 mg/kg.

RESULTS AND DISCUSSION

Since for many years dithiocarbamate fungicides have been used in Poland. Institute of Plant Protection carried out the regular studies on their residues in samples of fresh fruits and vegetables collected in the whole country. The pesticide residues are frequently found in fresh fruit and vegetable samples, which makes conducting such a control very important. Nowadays, the number of samples with dithiocarbamate residues is relatively low in comparison with the number of contaminated samples detected in the seventies-eighties, when the formulations based on EBDC were extensively used (Dąbrowski 1978).

2,226 samples of fruit and vegetables were analyzed for dithiocarbamate residues during 1999–2000. The residues were detected in 11.3% of samples. The data on the residues in particular crops are presented in table 3.

The traces of dithiocarbamates were the most often found in fruit samples (22.5%), rarely in samples of field vegetables (12.1%). In the group of greenhouse vegetables the lowest percentage of samples contained residues (6.8%) (Tab. 4).

The residues were the most frequently detected in black currant (37.4%), field tomato (34.1%) and raspberry (33.3%). The frequency of residues occurrence in each individual crops is shown in figure 1.

The percentage of samples containing residues exceeding Polish maximum residue limits (MRLs) was relatively low (0.5%) and almost the same for fruits, field

Table 3. Residues of dithiocarbamate on each individual crop

Crop	Number of analyzed samples	Samples with residues		Range of residues found mg/kg	Limit of determination mg/kg	MRL	
		Number	%			PL[1]	EU[2]
GREENHOUSE VEGETABLES							
Cucumber	412	3	0.7	0.2–0.3	0.1	1	0.5
Lettuce	212	10	4.7	0.5–27.5	0.2	5	5
Tomato	590	59	10.0	0.1–2.3	0.1	1	3
Mushroom	137	20	14.6	0.05–0.3	0.05	2	0.05
FIELD VEGETABLES							
Cucumber	220	11	5.0	0.1–0.2	0.1	1	0.5
Red beet	33	0	0		0.1	2	–
Sugar beet	5	0	0		0.1	2	–
Tomato	91	31	34.1	0.1–1.5	0.1	1	3
FRUITS							
Cherry	98	9	9.2	0.1–1.0	0.1	2	1
Currant	115	43	37.4	0.1–3.9	0.1	2	5
Plum	41	5	12.2	0.1–0.4	0.1	2	1
Raspberry	15	5	33.3	0.2–0.6	0.1	2	–
Strawberry	257	56	21.8	0.1–1.7	0.1	2	2
TOTAL	2,226	252	11.3	0.05–27.5			

[1]maximum residue level according to Polish standards

[2]maximum residue level according to EU standards (Council Directives 86/362/EEC and 90/642/EEC with amendments up to 2001/57/EC)

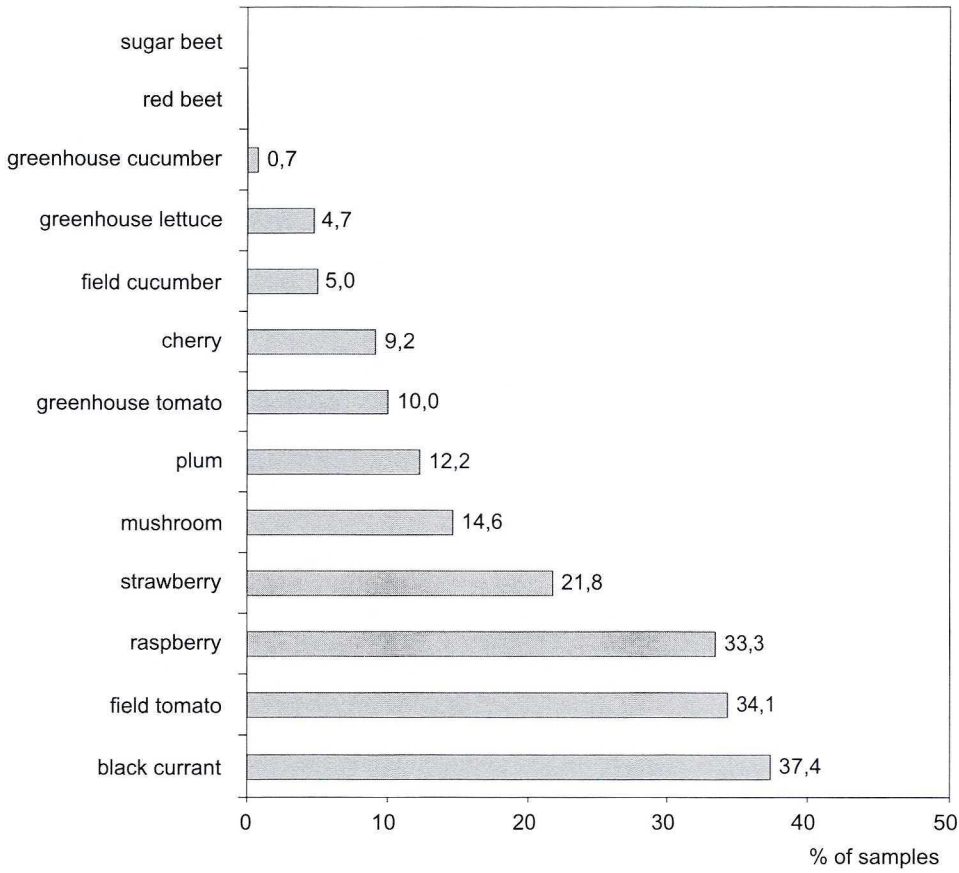

Fig. 1. Frequency of dithiocarbamate residues occurrence in the crops

and greenhouse vegetables (Tab. 4). Violations were found in samples of currant, greenhouse lettuce, and field and greenhouse tomato.

The number of violative samples detected in all crops is two times higher according to the European Union legislation. The table 5 shows the difference in results issued from others levels established for dithiocarbamate residues by Poland and EU.

The highest percentage of samples with residues was found in provinces: Świętokrzyskie (25.5%), Wielkopolskie (21.4%) and Kujawsko-Pomorskie (18.2%); the smallest in provinces: Podkarpackie (2%) and Dolnośląskie (1%) (Fig. 2).

The obtained results indicate that dithiocarbamate fungicides are still in wide use in Poland, in spite of a large choice of fungicides from different chemical groups available in the market. However, their application is not always in agreement with a good agricultural practice and they are sometimes misused. Fortunately, it happens less often today than in the past. This proves that farmers more strictly comply with the rules of good agricultural practice in pesticides application under efficient supervision of the Plant Protection Inspectorates.

Table 4. Residues of dithiocarbamates on crop categories

Crop groups	Number of analyzed samples	% of samples		
		Without residues	With residues < MRLs[1]	With residues >MRLs
Greenhouse vegetables	1,351	93.2	6.4	0.4
Field vegetables	349	88.0	11.5	0.6
Fruits	526	77.6	22.1	0.4
Total	2,226	88.7	10.8	0.5

[1] maximum residue level according to Polish standards

Table 5. Number of samples with residues exceeding MRLs

Crop	Number of analyzed samples	Number of samples with residues>MRL	% of samples with residues >MRL	MRL [mg CS_2/kg] PL	MRL [mg CS_2/kg] EU	Max. residue [mg CS_2/kg]
Greenhouse lettuce	212	2 (PL, EU)	0.9	5	5	27.5
Greenhouse tomato	590	4 (PL)	0.7	1	3	2.3
Field tomato	91	2 (PL)	2.2	1	3	1.5
Black currant	115	2 (PL)	1.7	2	5	3.9
Mushroom	137	18 (EU)	13.1	2	0.05	0.3

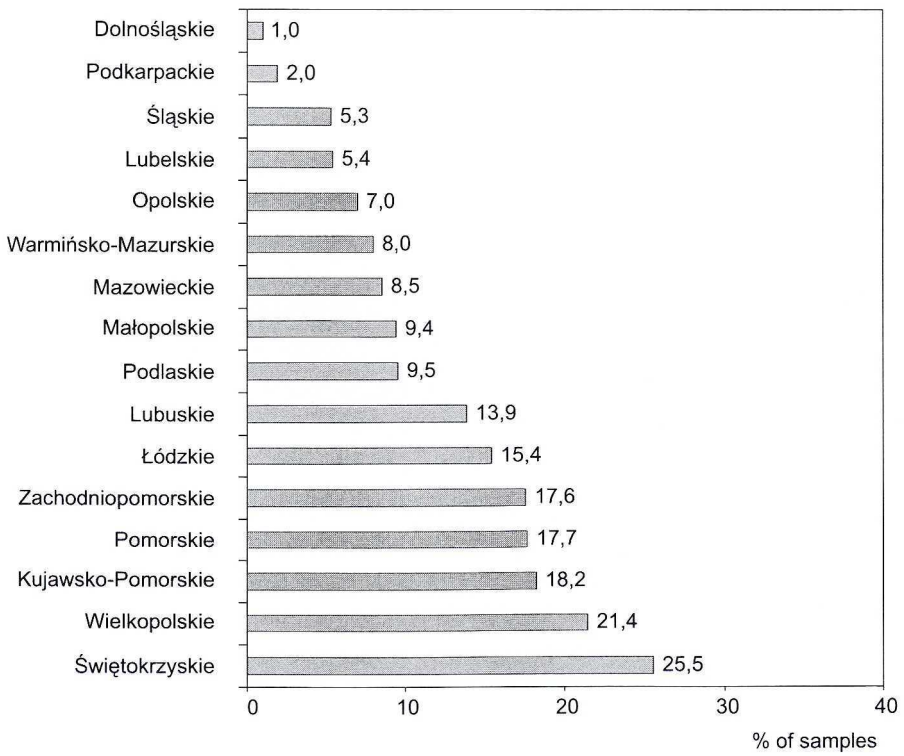

Fig. 2. Frequency of dithiocarbamate residues occurrence in all provinces

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POLISH SUMMARY

BADANIE POZOSTAŁOŚCI FUNGICYDÓW DWUTIOKARBAMINIANOWYCH W PŁODACH ROLNYCH (LATA 1999–2000)

W latach 1999–2000 zbadano 2226 próbek owoców i warzyw na obecność pozostałości fungicydów dwutiokarbaminianowych. Próbki do badań pobierano losowo z miejsc produkcji rolniczej na terenie całego kraju. Pozostałości wykrywano najczęściej w próbkach czarnej porzeczki (37,4%), pomidora gruntowego (34,1%), maliny (33,3%) i truskawki (21,8%).

11,3% badanych próbek zawierało pozostałości, a w przypadku 0,5% próbek stwierdzono przekroczenia najwyższych dopuszczalnych poziomów. W poszczególnych grupach upraw: owocach, warzywach gruntowych oraz warzywach spod osłon udział próbek zawierających niedopuszczalne stężenia dwutiokarbaminianów był podobny i wynosił odpowiednio 0,4%, 0,6% i 0,4%.

Najwięcej pozostałości wykryto w próbkach pochodzących z województwa świętokrzyskiego (25,5%), wielkopolskiego (21,4%) i kujawsko-pomorskiego (18,2%), najmniej w próbkach z województw: podkarpackiego (2%), dolnośląskiego (1%).