Pol. J. Environ. Stud. Vol. 21, No. 6 (2012), 1703-1712

Original Research

Monitoring Study of Pesticide Residues in Cereals and Foodstuff from Poland

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Received: 29 November 2011
Accepted: 28 June 2012

Abstract

The aim of our study was to investigate the amount of 110 pesticide residues in cereals and foodstuff from Poland as a part of official control. A total of 89 samples were collected in 2009-10. In 84.2% of the samples no residues were found: 15.8% of samples contained pesticide residues below the maximum residue limit. Pirimiphos-methyl was the most frequently found pesticide.

The results show that occurrence of pesticide residues in cereals and feeding stuff could not be considered serious threats to human and animal health. Nevertheless, an investigation into continuous monitoring and tighter regulation of pesticide residues in food and feed is recommended.

Keywords: pesticide residues, pirimiphos-methyl, cereals and feeding stuff, monitoring

Introduction

Pesticides are broadly used in farming for their economic benefits in fighting crop pests and reducing competition from weeds, thus improving yields and protecting crop quality, reliability, and the price of production. The widespread use of these compounds has resulted in contamination of environmental compartments such as surface water, groundwater, soil, and air [1-4]. In addition, agricultural plants used for feeding livestock may be contaminated and, consequently, pesticides may become exposed to human consumption via animal feed. In recent years, increasing attention has been paid to the risks posed to consumers by chemical contaminants or residues in foodstuff [5]. Therefore, rules on undesirable substances in these matrices are needed to ensure agricultural productivity and sustainability and to guarantee public and animal health, animal welfare, and environmental protection. In this sense, maximum residue limits (MRLs) in cereals and feeding stuff, among other compounds, have been established by the European Union in Directive 32/EC [6].

Among the major groups of pesticides, organochlorines (OCPs) are more potent due to their persistence and stability. Universally important organochlorine pesticides (OCPs) are p,p' DDT, BHC, chlordane, heptachlor, aldrin, dieldrin, and endrin. Due to the lipophilic nature of these pesticides,

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milk and other fat rich substances are the key items for their accumulation. These toxicants enter the human body through the food chain and cause serious health problems. Residue concentrations have decreased in monitored foods since these chemicals were banned in most countries, although trace levels are still detected in many foodstuffs.

Organophosphorus pesticides (OPPs), used mainly as insecticides, are esters of phosphoric acid with different substituents [7]. OPPs have widely varying physico-chemical properties such as polarity and water solubility [8]. Since these substances act through inhibition of acetyl-cholinesterase, they also represent a risk to human health [9].

Carbamate pesticides (CBs), or N-substituted carbamic acid esters, are used for broad-spectrum insect control around the world [10]. Exposure to carbamate pesticides acting as acetyl-cholinesterase inhibitors can lead to reversible neurologic disorders [9], and some are suspected carcinogens and mutagens [11]. CBs are thermally unstable compounds. Synthetic pyrethroid pesticides (PYRs) are effective broad-spectrum insecticides with low mammalian toxicity and short-term environmental persistence [12]. Pyrethroids are non-polar to low-polarity lipophilic compounds [13]. Owing to their metabolism in animals, they tend to bioaccumulate in lipid compartments, becoming a potential source of human exposure through foodstuffs [3]. Triazines (TRZs) are among the most widely-used herbicides in agriculture. Most of them are derived from s-triazine (1,3,5-triazine), but a few are based on 1,2,4-triazine [14]. The triazines are degraded by chemical and biological processes in their respective hydroxytriazines [10]. s-Triazines and their degradation products are weakly basic, poorly water-soluble compounds with low polarity and are stable in the environment and therefore persistent. 1,2,4-Triazines have similar physico-chemical properties but are more polar [14]. These herbicides are suspected of causing cancers, birth defects, and disruption of hormone functions [15]. Other pesticides, such as benzoylureas, quinoxalines, amines, and fluorides, have been evaluated for analytical purposes in foods of animal origin.

Cereals and foodstuff, when contaminated, act as the main source of entry of pesticides into the animal body. Once the animal body is contaminated with pesticide residues, not only does it affect the animals directly but it also exerts indirect effects on human health through food of animal origin such as milk and meat. Therefore, unless residues in cereals and foodstuff are controlled, pesticides are likely to accumulate in animal body tissues and then be excreted in milk. Most of the residue-monitoring programmes are concentrated on food crops, fruits, and vegetables.

The available literature offers few reports about the pesticide residues in cereals and foodstuffs are available from Poland [16, 17] and abroad [18, 19].

Therefore, the present investigation was undertaken to analyze cereals and foodstuff samples collected from different areas of Poland during 2009-10 for persistent pesticide residues.

The usefulness of cereal grain for consumption and fodder processing is determined by its biological value and commercial quality. Cereal grain is considered to be healthy for animals and people if its color is typical for a given type, is free from foreign smells, mycotoxins, contaminations with live pests, and the concentration of active substances of pesticides does not exceed the maximum residue limits (MRLs). Plant protection products used by the producers can be found in feed in the form of residues and, in such case, they constitute hazardous chemical contaminants. In addition to biological contamination, they are the most frequently reported chemical pollutants.

The aim of the study was to determine the presence of pesticide residues used for plant protection purposes in cereal grain and foodstuff using the accredited analytical multiresidue method (MRM) and to demonstrate their harmfulness to humans and animal health.

The research material consisted of samples of plant origin from various areas of Poland, presented in Fig. 1. In total, the research program included 110 active substances of plant protection products (Table 1), including: insecti-

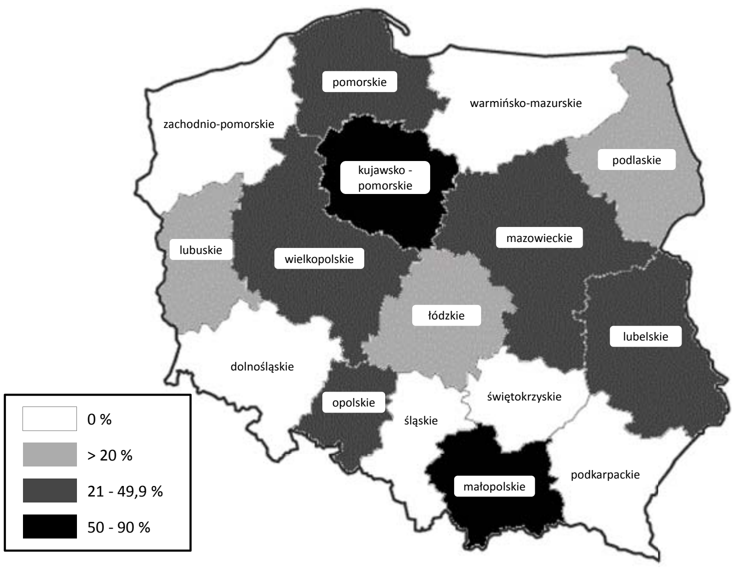

Fig. 1. Origin of samples of the examined cereal and feed containing residues of plant protection chemicals.

Table 1. Determined active substances of plant protection products.

Species of pesticides		Active substances (a.s.)
Group (by biological activity)	Chemical class (number of a.s.)	
Acaracides	Organochlorine (1)	Dicofol
Fungicides	Carbamate (2)	Carbendazim, Thiophanat-methyl
	Other (35)	Azoxystrobin, Benomyl, Bitertanol, Bromoconazole, Bupirimate, Captan, Chlorothalonil, Cyprodinil, Cyproconazole, Dichlofluanid, Difenoconazole, Dimethomorph, Dithiocarbamate, Fenarimol, Fenhexamid, Flusilazole, Folpet, Iprodione, Kresoxim-methyl, Metalaxyl, Myclobutanil, Pirimethanil, Oxadixil, Procymidon, Propiconazole, Quintozene, Tebuconazole, Tecnazene, Tetraconazole, Tolclofos-methyl, Tolylfluanid, Triadimefon, Triadimenol, Trifloxystrobin, Vinclozolin
Insecticides	Organochlorine (14)	Aldrine, o,p' DDT, o,p' DDT, p,p' DDE, p,p' DDT, Dieldrine, Endrine, HCB (hexachlorobenzene), α-HCH, β-HCH, γ-HCH (lindane), Heptachlor, Heptachlor-epoxide, Metoksychlor
	Organophosphate (21)	Azinphos-ethyl, Azinphos-methyl, Chlorofenvinphos, Chlorpyrifos, Chlorpyrifos-methyl, Diazinon, Dichlorvos, Dimethoate, Fenitrothion, Formothion, Fozalon, Heptenophos, Izofenphos, Malathion, Mecarbam, Methidathion, Omethoate, Parathion-ethyl, Parathion-methyl, Pirimiphos-methyl, Triazophos
	Carbamate (5)	Carbaryl, Chlorpropham, Monocrotophos, Pirymicarb, Propoxur
	Pyrethroide (11)	Acrinathrin, Alpha-cypermethrin, Beta-cyfluthrin, Bifenthrin, Cypermethrin, Deltamethrin, Esfenvalerate, Fenpropathrin, Fenvalerate, Lambda-cyhalothrin, Permethrin
	Other (6)	Bromopropylate, Buprofezine, Endosulfan (sum of endosulfan α, β and sulfate), Ethopropfos, Fipronil, Tetradifon
Herbicides	Assorted (15)	Atrazine, Dichlorprop, Lenacil, MCPA, Mecoprop (MCPP), Metribuzin, Napropamide, Nitrofen, Pendimethalin, Promethryn, Propachlor, Propyzamide, Simazine, Trifluralin, 2,4-D

cides (organochlorine – 14, organophosphorus – 21, pyrethroid – 11, carbamate – 5 and others – 6), fungicides (37), herbicides (15), and acaricides.

Materials and Methods

Samples and Reagents

In this study, 89 samples of plant origin, including 57 cereal samples (12 wheat, 4 oat, 15 barley, 5 triticale, 1 rye and 20 maize samples), and 32 foodstuff (13 cereal mixtures, 7 bran, and 12 ground grain samples) from various areas of Poland have been investigated (Fig. 2).

Samples (1 kg) were collected as a part of the national monitoring program for pesticide residues. The sampling was performed by authorized personnel from the food control authorities (Main Inspectorate of Plant Health and Seed Inspection and the Main Veterinary Inspectorate). The samples were mainly taken at importers and wholesaler's warehouses in different parts of the countries. All samples transported to the laboratory and stored at 4ºC until being analyzed.

Pesticide-free cereal samples were used as blank to spike for the validation process. All reagents used were analytical grade. Acetone, n-hexane, and methanol for pesticide residue analysis were provided by J.T. Baker (Deventer, Holland) Florisil (60-100 mesh) was supplied by

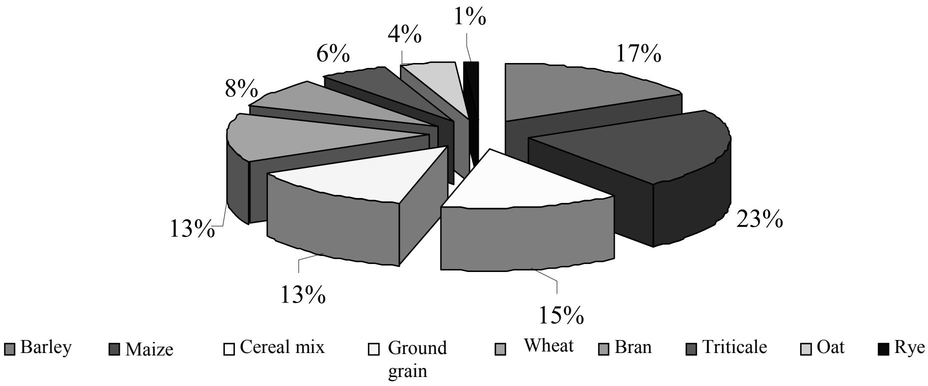

Fig. 2. Share of individual examined samples of cereal and foodstuff.

J.T. Baker (Deventer, Holland), and sodium sulphate anhydrous was from Fluka (Seelze-Hannover, Germany). Silica gel was obtained from Merck (Darmstadt, Germany). All sorbents were activated at 600ºC.

Standards

Pesticides were obtained from the Dr. Ehrenstorfer Laboratory (Germany) and are listed in Table 1. Pesticide standard stock solutions (purity for all standards > 95%) of various concentrations were prepared in acetone and stored at 4ºC. Standard working solutions were prepared by dissolving appropriate amounts of stock solution with a hexane/acetone mixture (9:1).

Sample Preparation

A representative portion of the sample was blended. 2.0 g of a sample was put in a mortar with 4.0 g of the solid support – florisil and was manually mixed together using a pestle to produce a homogeneous mixture. The mixed material was transferred to the glass column (1.5 cm i.d. × 40 cm length) containing a piece of glass wool, anhydrous sodium sulphate (5.0 g) and silica gel (2.5 g). The analytes were eluted using 25 ml of a mixture of acetone/methanol (9:1). The extract was dried by evaporation at about 40ºC. The eluate was concentrated in a vacuum rotary evaporator to approximately 1 ml at 40ºC (ca. 30 min). Then the eluate was diluted to 2 ml volume of a mixture of hexane/acetone (9:1). One millilitre of the final solution was put into a GC vessel and placed on the rack of the autosampler.

Instrumentation and Chromatographic Conditions

GC analysis was performed with an Agilent (Waldbronn, Germany) model 7890 A gas chromatograph equipped with ECD and NPD with a non-polar column HP-5 ((5%-Phenyl)-methylpolysiloxane; 30 m × 0.32 mm and film thickness 0.50 μm) and Chemstation chromatography manager data acquisition and processing system (Hewlett-Packard, version A.10.2). For confirmation of residues a mid-polarity HP-35 column ((35%-Phenyl)-methylpolysiloxane; 30 m × 0.32 mm and film thickness 0.50 μm) was used. The operating conditions were as follows: for detectors – injector temperature: 210ºC; carrier gas: helium at a flow-rate of 3.0 ml/min; detector temperature: 300ºC (ECD and NPD); make-up gas: nitrogen at a flow-rate of 57 ml/min (ECD) and 8 ml/min (NPD), hydrogen 3.0 ml/min, air 60 ml/min; for oven – initial temperature: 100°C increase at a rate of 10ºC/min up to 250ºC and held for 25 min, from 250 to 300ºC at a rate of 50ºC/min and held for 5 min at the final temperature (ECD and NPD). The volume of final sample extract injected at 210ºC in splitless mode (purge off time 2 min) was 2 μl injected and the peak height was compared to that of the calibration standards (in matrices) to determine the residue quantitatively.

Method Validation

In this study wheat was selected as a representative commodity for the validation of the method in determining pesticide residues.

Preparation of Calibration Standards

Calibration curves were obtained from matrix-matching calibration solutions. The lowest concentration level in the calibration curve was established as a practical determination limit. Calibration standards were prepared by adding respective spiking solutions to a blank matrix of the wheat, to produce a final concentration of 1^{st} range 0.001-0.05 mg/kg, 2^{nd} range 0.1-0.5 mg/kg, and 3^{rd} range 0.5-2.5 mg/kg.

Recovery Studies

Recovery data was obtained at three range concentrations in the matrix, each day using blank cereal samples (wheat) in accordance with European Commission (EC) guidelines [20]. Blank samples (2.0 g) after homogenization were spiked by the addition of appropriate volumes of pesticide standard mixture in solution: hexane/acetone (9:1) and were left for 1 h (equilibration times) and then prepared according to the procedure described above. Method accuracy and precision were evaluated by performing recovery studies. The precision was expressed as relative standard deviation (RSD). Accuracy can be measured by analyzing samples with known concentration and comparing the measured values with the true values.

LOQ and LOD

The limit of quantification (LOQ) was defined as the lowest concentration of the analyte that could be quantified with acceptable precision and accuracy. The limit of detection (LOD) was defined as the lowest concentration of the analyte in a sample that could be detected but not necessarily quantified. The LOQ and LOD were evaluated as the signal-to-noise ratios (S/N) of 10:1 and 3:1 for the pesticide, respectively.

Results and Discussion

The Laboratory of Pesticide Residues regularly takes a part in proficiency testing schemes organized by the Food Analysis Performance Assessment Scheme (FAPAS; Central Science Laboratory in York) and the European Commission (at the beginning by the University of Uppsala and then by the University of Almeria).

Participation in EC tests is mandatory for all laboratories selected as NRL for pesticides in food of animal origin and commodities with high fat content and, according to Art. 28 of EC Reg. 396/2005 and for all official laboratories undertaking the analysis of these commodities for the offi-

Table 2. Samples of cereal and foodstuff with pesticide residues.

Type	Sample			Active substance	
	total number	with residues		name	Concentration [mg/kg]
	[pcs]	[pcs]	[%]		
Barley	15	1	6.7	Pirimiphos-methyl	0.08
Cereal mix	13	2	15.4	Pirimiphos -methyl	0.01; 0.02
Whey bran	5	5	100	Pirimiphos-methyl	0.01; 0.01; 0.03; 0.05; 0.05
Rye bran	1	1	100	Pirimiphos-methyl	0.01
	1	1	100	Chlorpyrifos	0.05
Wheat	12	1	8.3	Pirimiphos-methyl	0.19
Ground barley	1	1	100	Malathion	0.01
Ground grain	7	1	14.3	Pirimiphos-methyl	0.06
	7	1	14.3	Chlorpyrifos	0.02

Table 3. Pesticide Residues in EU proficiency tests (2008-11).

EUPT-C2; 2008		EUPT-C3; 2009		EUPT-C4; 2010		EUPT-C5; 2011	
Active substance	Z-score	Active substance	Z-score	Active substance	Z-score	Active substance	Z-score
alpha-cypermethrin	-0.3	azoxystrobin	0.7	azoxystrobin	-1.9	azoxystrobin	-0.1
azoxystrobin	-1.5	chlorpyrifos	0.2	chlorpyrifos-methyl	-0.6	chlorpyrifos	-0.2
bifenthrin	0.0	cyproconazole	-1.1	deltamethtin	-0.5	deltamethrin	-0.2
chlorpyrifos-methyl	0.5	cyprodinil	0.2	fenitrothion	-0.3	difenoconazole	-0.4
difenoconazole	-0.9	fenvalerate and esfenvalerate	-0.3	fenpropimorf	0.4	epoxyconazole	-0.9
epoxyconazole	-0.7	fludioxonil	0.1	fluchinconazole	-0.4	fipronil	-0.6
iprodione	-0.5	flusilazole	0.0	kresoxim-methyl	0.0	kresoxim-methyl	-0.4
malathion	0.6	lambda-cyhalothrin	1.6	lambda-cyhalothrin	0.7	lambda-cyhalothrin	1.7
prochloraz	-1.1	tebuconazole	1.2	malathion	-0.8	pirimiphos-methyl	0.4
trifloxystrobin	-0.3			pirimiphos-methyl	-0.9	propiconazole	-0.8
				triadimenol	-1.5	tebuconazole	-0.6
						trifloxystrobin	-0.5

cial controls on pesticide residues. Our laboratory is accredited under ISO 17025 and performing multiresidue methods (MRMs) for pesticide residues in official controls. The proficiency tests results (2008-11) are in Table 3. In all cases z-score are below 2.

To be sure about the quality of results when the proposed MSPD analytical method [21] is applied to monitoring analyses, other internal criteria have been established.

The first one is blank extract that eliminates the contamination in the extraction and clean-up processes, instrument or chemicals used. One blank sample was processed in each set of experiments.

The second one is to check extraction efficiency. Recoveries at the second concentration level (0.1-0.5 mg/kg) will be accepted if the majority of recoveries are within 70-120% range.

This study involved examination of 89 plant material samples in total, from 16 provinces (Fig. 1), 14 of which contained residues of plant protection chemicals (15.7 %). All active substances detected, taking into consideration chemical classes, were classified as organophosphorus insecticides (Table 1, Fig. 3). For cereal grains, residues of pirimiphos-methyl were detected in 2 samples, whereas 12 samples of the feed material showed the presence of malathion, pirimiphos-methyl or chlorpyrifos-ethyl (Table 2). A chromatogram of real wheat sample containing pirimiphos-methyl at a concentration of 0.19 mg/kg is shown in Fig. 5.

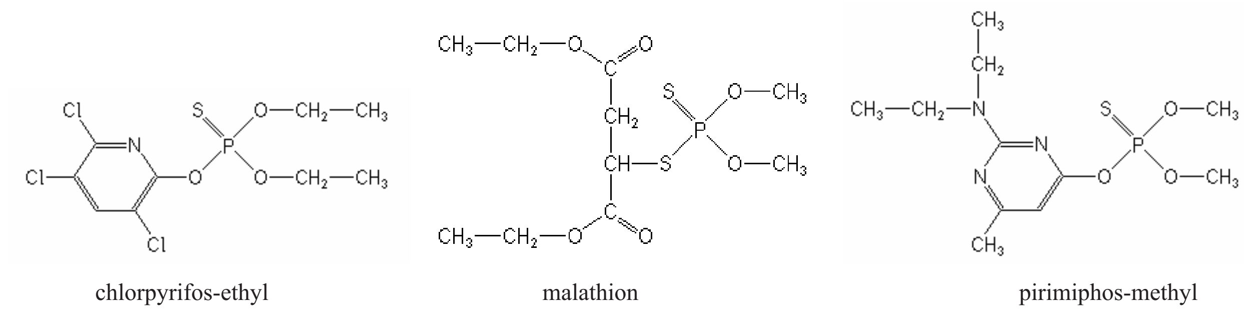

Fig. 3. Structures of detected pesticides in cereals and feeding stuff.

No samples containing more than one compound were found. Malathion was found only in one sample, at a concentration of 0.01 mg/kg, chlorpyrifos-ethyl in two samples, at concentrations of 0.02 and 0.05 mg/kg, and pirimiphos-methyl in 11 samples at concentrations ranging from 0.01 to 0.19 mg/kg. No residues of plant protection products exceeded the MRLs, which for chlorpyriphos is 3.0 mg/kg, and for pirimiphos-methyl and malathion: 5.0 and 8.0 mg/kg, respectively, pursuant to national Polish regulations [22, 23], and since 1 September 2008, pursuant to commission regulations [24].

Residues were detected in two examined groups of crops: in feed cereals – 0.13% (1 sample of barley and 1 sample of wheat), and in cereal products – 37.5% (mixtures, bran and ground grain). Products that most frequently contained residues of the examined compounds included: ground grain (28.65%) and wheat and rye bran (100% each).

The highest number of samples used for the research purposes originated from the province of Warmia-Mazury (26), and 3-6 samples originated from other regions, except Śląskie (1). The highest share of samples with residues of plant protection chemicals was found for: Kujawsko-Pomorskie (75%), Małopolskie (50%), and Opolskie (40%). Between 16% and 33.3% samples with pesticide residue originated from Lubuskie, Łódzkie, Podlaskie, Mazowieckie, Pomorskie, and Wielkopolskie (Fig. 1). Residues of plant protection products were not found in the material originating from the regions of Śląskie, Świętokrzyskie, Zachodniopomorskie, and Warmia-Mazury, from which about 30% of the examined samples originated.

The structures of detected compounds are presented in Fig. 3: malathion 1,2-bis(ethoxycarbonyl) ethyl-O,O-dimethyl-phosphorothioate, parathion-methyl-dimetylo-4-nitrofenylo phosphorothioate, and chlorpyrifos-ethyl-O,O-diethyl O-3,5,6-trichloropyridin-2-yl phosphorothioate.

Residues of chlorpyrifos-ethyl, malathion and pirimiphos-methyl, belonging to the group of insecticides, are active substances (between 15% and 42%) in such preparations as: Actellic 20 FU, Pro Store 157 UL, and Pro Store 420 EC. Actellic 20 FU is used for disinfection of empty storehouses, grain, and fodder silos, in which the content of pirimiphos – methyl is 22.5%. Pro Store 157 UL is used for disinfecting seed and consumption grain, and it contains 15% malathion. Pro Store 420 EC is a product used for both disinfection of empty rooms, as well as for grain intended for seeding and for consumption purposes and has a 42% malathion content.

Plant protection products can be applied at the stage of primary production of plants, as well as during the storage of crops.

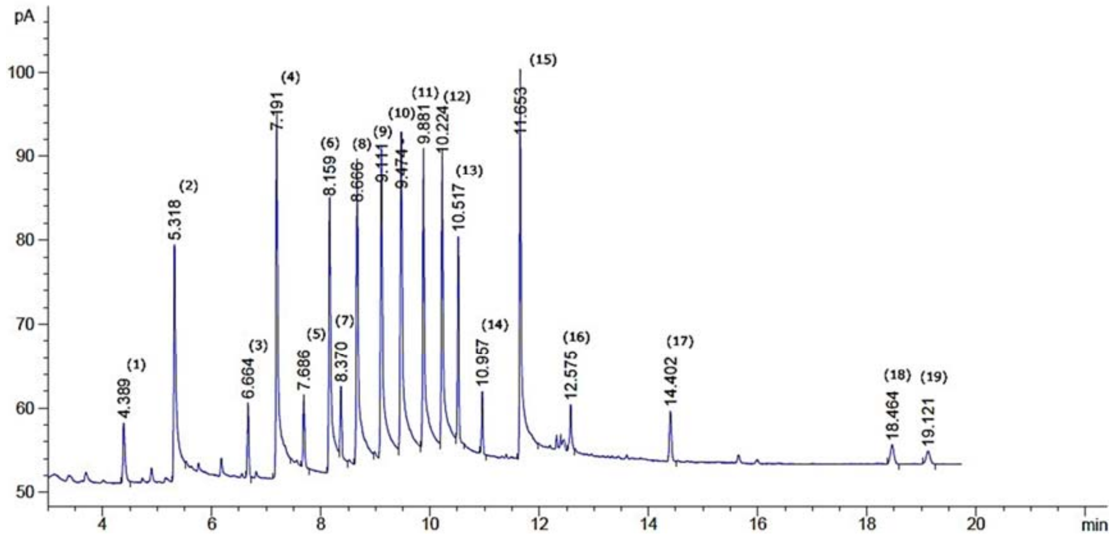

Fig. 4. Chromatogram of the selected standard mixture: 1. propham, 2. heptenophos, 3. simazine, 4. diazinon, 5. pyrimicarb, 6. parathion-methyl, 7. metalaxyl, 8. pirimiphos-methyl, 9. parathion-ethyl, 10. pirimiphos-ethyl, 11. mecarbam, 12. methydation, 13. flutriaphol, 14. bupirymate, 15. triazophos, 16. acetamipiryd, 17. prochloraz, 18. and 19. dimethomorph (GC/NPD).

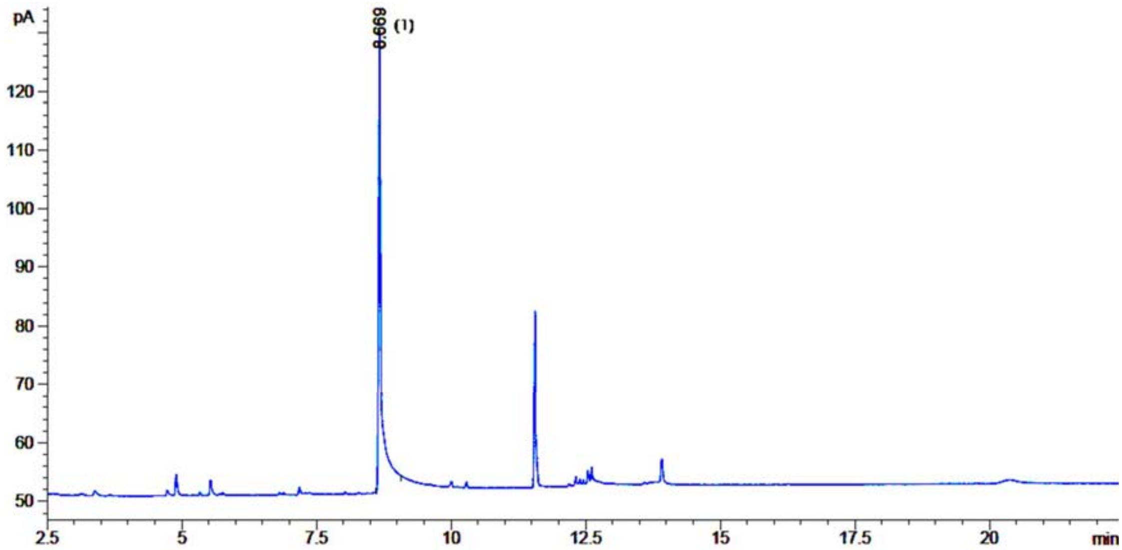

Fig. 5. Chromatogram of the real wheat sample with pirimiphos-methyl (0.19 mg/kg) (GC/NPD).

The problem of crop pest control has emerged along with the changes in crop technologies. Intensive protection against weeds and diseases, together with abundant fertilizing, favours the development of various species of insects. Pests found in crop plants can reduce the grain yield from 2 to 20 dt/ha.

To prevent economic losses caused by storehouse pests, cereal protection most often involves chemical methods: cereal-seed dressing, fumigation, misting, spraying, and dusting. Due to their high efficiency and low costs, many products intended for this purpose are available in Poland. Currently applied preparations include Actellic 20 FU, Actellic 500 EC, K-Othrine 2.5 WP, K-Obiol 02 DP, and their application details are specified on the label – instructions for using a given product.

The percentage of cereals and foodstuff samples that contained pesticide residues, types of detected substances (3 substances out of 110 examined) and level detected (0.01-0.2 mg/kg) of pesticide residues indicate that fodders are much less exposed to contamination of pesticide residue than human food. Nowacka et al. [25] found that pesticide residues in fruit and vegetables occurred in 24.5% of the total examined samples, which involved 43 out of 132 compounds analyzed, at concentration levels of 0.01-2.0 mg/kg. Unlike food intended for people, fodders do not contain residues of forbidden pesticides (1.4%), which certainly results from the fact that fodder crops are large-area cultures and planters have at their disposal a sufficient range of plant protection products.

Pirimiphos-methyl was the most detected in this study (the active substance of a preparation known under its commercial name of Actellic) and has been shown to inhibit acetylcholinesterase. Literature data has established that in research on mammals the level that does not cause any harmful results (determined as NOAEL) is 0.5 mg/kg/bw/d. In the case of humans, no inhibition of cholinesterase was found [26].

The toxicological effect of pirimiphos-methyl, characterized by the LD_{50}, indicates that its toxicity is in category III at a dose of 2,050 mg/kg, and in category II at 1,505 mg/kg. With 90 doses up to 10 mg/kg/day, no delayed neurotoxic effect was observed [27].

Primiphos-methyl did not demonstrate carcinogenic effects in the research carried out in doses up to 300 and 500 mg/kg (the highest test dose) and does not demonstrate teratogenic effects in mice at levels of up to 16 mg/kg/day. The research also indicates that this compound is rapidly expelled, and so far no evidence has been found for its bioaccummulation in the organisms of the examined animals [27].

Chlorpyrifos (O,O-diethyl O-3,5,6-trichloropyridin-2-yl phosphorothioate) is a commonly applied insecticide used for pest control in agriculture and industry all over the world [28]. Chlorpyrifos is efficient in controlling the population of many insects, including caterpillars, corn rootworms, cockroaches, larvae, beetles, fleas, flies, termites, red imported fire ants, and lice. It is used as an insecticide in cereal, cotton, fruit, vegetables, and nuts. It has been also registered for direct use in the treatment of sheep, turkeys, horses, and dogs, and for rat extermination in flats, farm buildings, silos, and commercial premises.

The effect of chlorpyrifos on the health and safety of mammals has been assessed in numerous studies [29-32]. Chlorpyrifos is moderately toxic for humans. Poisoning with this compound can affect the central nervous, cardiovascular, and respiratory systems [33].

The estimated risk related to chronic exposure for humans to residues of chlorpyrifos by means of a reference dose (RfD) of cholinesterase (ChE) is low and amounts to 0.03 mg/kg/b.w./d. And while taking into consideration an uncertainty factor related to higher sensibility of organisms with not fully-developed protection mechanisms (as calculated by the USEPA: 0.003 mg/kg b.w./d) [34, 35]. The acceptable daily intake (ADI) for a person was established at the level of 0-0.01 mg/kg b.w./d by WHO/PCS and FAO/WHO JMPR in 1999.

According to the research carried out by [36], chlorpyrifos inhibits development of rats receiving 25 mg/kg b.w./d. [37] found a relationship between the level of chlorpyrifos and low body mass of live-born foetuses. Tian et al. [38] suggested that chlorpyrifos has teratogenic and toxic effects on the mouse embryo in doses lower than assessed in previous research carried out on rats. The effect of chlorpyrifos on human and animal safety is still a current problem investigated by the European Commission and USEPA (http://www.tga.gov.au).

Malathion is a commonly-applied pesticide with a broad spectrum of insecticide effects. It was one of the first organophosphorus insecticides (introduced in 1950). Malathion is used to control the populations of sucking and chewing insects, preying on fruit and vegetables, and agricultural crops. It is also used to control the populations of mosquitoes, flies, home insects, animal parasites, and lice. Malathion is classified as slightly toxic. LD_{50} for rats ranges from 480 to 10,700 mg/kg, and from 775 to 3,321 mg/kg for mice. Severe effects of malathion depend on product purity. Beside malathion, its preparations contain toxic impurities, such as isomalathion (LD_{50} 120 mg/kg for rats) [39, 40], which are produced in commercial manufacturing. Other malathion metabolites are also produced during grain storage [41-44]. The most toxic of those metabolites is malaoxon – a product of oxidation, that is also responsible for the insecticide activity of malathion. Other breakdown products, such as malathion monocarboxylic acids (a) and malathion (b), isomalathin and O,O-dimethyl phosphorodithioate (LD_{50} 26 mg/kg for rats) are produced during hydrolysis, isomerisation of P-S and S-C bonds, and dealkylation [45]. The toxicity of this pesticide also depends on other factors. A strong relationship between malathion toxicity and the amount of protein in the diet of laboratory rats has also been found [46, 47]. In humans, the dose level at which adverse effects were observed, e.g. on the alimentary, neurological, and respiratory systems, was three times higher in women than in men. Among other organophosphorous insecticides malathion, at relatively high doses, can have a negative effect on the immunological system of some species of animals [48, 49].

An inherent element of cereal protection against diseases and pests, besides intensification of crop cultivation and changes in agrotechnology and structure of crops, is the common use of pesticides. In the case of cereal production, they are used both at the stage of primary production and during storage. The application of plant protection chemicals, although highly necessary and effective, can cause the transfer of hazardous substances to the food chain of animals and eventually to humans. Protection of cereals, both in the field and in storage houses, should be carried out in a proper manner, including the pest alert system [50], preserving the principles of good plant protection practice [51], and the amounts of hazardous residues of plant protection products should not exceed the values of MRL, regarded as not causing any adverse effects for human or animal health. Ensuring health safety for grain produced in Poland is an absolute priority in crop production. This study has shown that only a small percentage of the examined cereal and feed material originating from the entire area of Poland (15.7%) contained residues of plant protection chemicals at low concentration levels and did not pose any threat to human or animal safety.

Conclusions

1. This study found that the analyzed grain and feed of plant origin did not contain pesticide residues above acceptable levels.
2. The study did not find any cases of the use of forbidden pesticide, which could be because fodder crops are large-area cultures and the planters have at their disposal a sufficient range of plant protection products.
3. The detected pesticide residues at very low concentrations do not pose any danger for human or animal safety.

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