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STUDIES ON RESIDUES OF PESTICIDES USED IN RAPE PLANTS PROTECTION IN SURFACE WATERS OF INTENSIVELY EXPLOITED ARABLE LANDS IN WIELKOPOLSKA PROVINCE OF POLAND

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Abstract: Samples of surface waters of intensively exploited arable lands in Wielkopolska Province of Poland were collected in 2006 and 2007. The studies included 13 insecticides used in rape plants protection against pests. All selected pesticides were extracted from water samples by means of solid phase extraction (SPE, carbon black) followed by reverse phase ultra performance liquid chromatography analysis with quadrupole mass detection (RP-UPLC-MS/MS). Totally, 123 samples from lakes, rivers, ponds, field watercourses and drainages were collected (i.e. 79 and 44 in 2006 and 2007, respectively). Of all samples, 36 (29.3%) were contaminated with residues of plant protection products used for protection of rape crops. Contamination with thiametoxam and acetamiprid in 17.1 % and 11.4% of the samples, respectively, were mostly detected, and the highest concentration was determined in sample from filed watercourse taken in spring 2007 containing 1.341 µg/l of acetamiprid. Totally, ten of thirteen studied insecticides were found; however, concentrations of their residues were usually very low. Among all analyzed samples only three exceeded the level of plant protection products established in Directive 2000/60/EC on the level of maximum admissible concentrations (MAC) of harmful substances in water. Although condition of Wielkopolan waters analyzed within the framework of this paper is not alarming, there is a need to take measures directed towards systematic monitoring contamination of water with pesticides used currently in intensive plant production.

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Key words: pesticides, insecticides, water quality, rape, surface water, SPE, UPLC-MS/MS.

INTRODUCTION

Rape is one of the basic industrial plants cultivated in Poland. Applications thereof is not limited to production of edible oils, medications or cosmetics only, but in recent years has become basic component of biofuels. According to the Central Statistical Office of Poland database, the acreage of rape plants in the country amounted to 550,000 ha in 2005 while in 2006 it exceeded 624,000 ha [15]. Wielkopolska Province is most important producer of this material in Poland and the acreage of rape was 72,000 and 88,000 ha in 2005 and 2006, respectively; therefore, both surface and underground waters in the region may be especially affected by the active ingredients of plant protection products (ppp) used in crops protection. It is estimated that 15–50% of losses in rape yield is caused by pests and, when conditions for their development would be favorable, total damage of the crops might occur [11]. It is noteworthy that, up to now, a more effective method of rape protection against pests other than chemical has not been elaborated so far.

In Poland, 19 ppp and 4 seed dressings containing insecticides have been registered for use in integrated agriculture [12]. The above chemicals belong to the following groups: nicotinoids, organophosphorus compounds, carbamates and pyretroids. Unfortunately, besides their high

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effectiveness, they are relatively resistant in the water environment and toxic to the aquatic organisms and animals consuming contaminated water, and finally to humans. People can be exposed to pesticides not only by direct water consumption but also via the respiratory tract and the skin. It is noteworthy and important that some pesticides are potential carcinogens [1].

Waters in Poland, similarly to countries in which intensive chemical protection of the crops is used, are exposed to contamination by pesticide residues [3, 5, 6, 7, 9]. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy, defines the maximum admissible concentrations of pesticide residues in water samples at the level of 0.1 µg/l for single substance, and for the sum of ppp residues at the level of 0.5 µg/l [4].

MATERIAL AND METHODS

Collection of samples. Samples of water were collected in 2006 and 2007 from surface waters in Wielkopolska Province. Investigations included water samples from lakes, rivers, ponds, field watercourses and field drainages. All the above types of reservoirs and watercourses were located on intensively exploited arable lands, mostly close to rape plantations. Samplings were carried out in the environs of Gniezno, Witkowo, Czerniejewo, Pobiedziska, Stęszew, Oborniki Wielkopolskie and Pamiątkowo. All samples taken were analyzed twice and the levels of acetamiprid, imidacloprid and thiametoxam of nicotinoid group, chlorfenvinphos, chloropyrifos, diazinon, phosalone, isofenfos and parathion methyl of organophosphorus insecticides group and carbofuran, carbosulfan, methiocarb and pirimicarb of carbamate group were determined.

Analytical procedures. Solid phase extraction (SPE) method packed with activated carbon (Carbograph 300 mg/8 ml, Alltech, USA) was used for extraction and concentration of targeted compounds in water samples [2]. Extraction of water samples was performed by means of 12-port SPE manifold Visiprep (Supelco, USA), equipped with a vacuum pump (KNF, Germany). Evaporation of organic extract of insecticides obtained after elution from extraction columns in a stream of nitrogen from a Drying Attachment (Supelco, USA) was used. Ultrasonic bath Sonorex Super RK 1034 (Bandelin, Germany) was employed for dissolving the residues obtained after nitrogen drying in injection solvent. An ultra performance liquid chromatograph ACQUITY UPLC system (Waters USA) with column and autosampler thermostats equipped with a tandem quadrupole mass spectrometer Waters Quattro Premier XE, operated by a MassLynx software, Waters ACQUITY UPLC column BEH C_{18} 2.1 × 100 mm, 1.7 µm were used for final LC analysis.

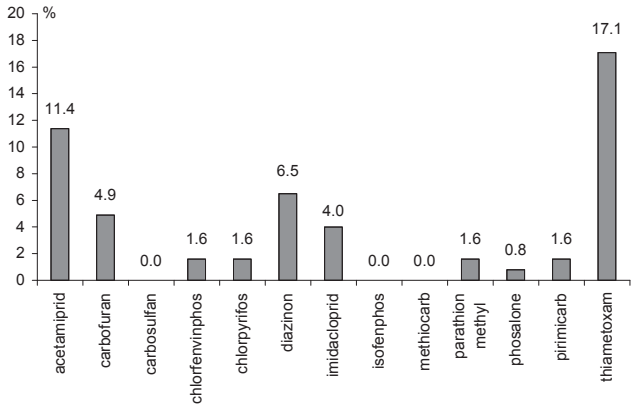

Figure 1. Residues of particular insecticides used in rape plants protection determined in water samples from Wielkopolska Province in 2006 and 2007.

Method validation. All validation procedures were performed using control samples of distilled water. Recoveries were determined for six replicates at two spiking concentrations (0.1 and 0.01 µg/l). Precision was measured by the relative standard deviation (RSD) for the each spiking sample levels (5 spiked samples of each level). Linearity was assessed for analyzed compounds by multi-level standard calibration curves. Water sample spiked with all the pesticides were extracted by applying the SPE. Analytical signal was compared with the signal of a distilled water extract spiked with the target compounds after solid phase extraction.

Recoveries for water samples spiked with a mixture of compounds studied ranged from 80–105% and standard deviations varied between 4–11%. The limits of quantification for all target compounds were determined at the level 0.005 µg/l.

RESULTS

Totally, 123 water samples were collected, i.e. 79 in 2006 and 44 in 2007. Most often, samples from field watercourses, totally 38 (25 and 13 in 2006 and 2007, respectively), and drainages, totally 36 samples (27 and 9 in 2006 and 2007, respectively), were collected. From ponds, 9 samples (3 in 2006 and 6 in 2007) and from lakes, 24 samples (15 in 2006 and 9 in 2007) were taken. Besides, 16 water samples (9 in 2006 and 7 in 2007) were collected from the rivers Cybina, Główna and Mała Wełna. Samplings were performed from May–October 2006 and from April–August 2007. Totally, ten of thirteen investigated pesticide residues were found. Only four times did the determined residues exceed maximum admissible concentration (MAC) for single pesticide demanded by EU Directive [4]. In 2006, thiametoxam was noticed twice, having concentrations 0.117 and 0.144 µg/l and acetamiprid – 0.219 µg/l. In 2007, only acetamiprid at the concentration of 1.341 µg/l was observed once. The second part of the Directive defines the maximum sum of pesticide concentrations that should not exceed 0.5 µg/l;

there was only one case, in the sample collected from a field watercourse in May 2007, where value was higher. Results are presented in Table 1.

In the course of this work, thiametoxam was found most often, and 17.1% of all collected samples were contaminated with residues thereof. Acetamiprid was detected in 11.4%, diazinon in 6.5%, carbofuran in 4.9% and imidacloprid in 4.0% of samples. The remaining active ingredients occurred more rarely while carbosulfan, isophenfos and methiocarb were not detected in any water sample in 2006 or in 2007. The above results are shown in Fig. 1.

Table 1. Residues of insecticides used in rape plants protection determined in water samples from Wielkopolska Province in 2006 and 2007.

Compound	Total number of samples	Contaminated samples		Range of concentrations
	N	n	%	µg/l
2006				
Acetamiprid	79	6	7.6	0.005–0.219
Carbofuran	79	5	6.3	0.015–0.036
Carbosulfan	79	0	0.0	not detected
Chlorfenviphos	79	1	1.3	0.008
Chlorpyrifos	79	0	0.0	not detected
Diazinon	79	6	7.6	0.005–0.011
Imidacloprid	79	3	3,8	0.005–0.017
Isofenphos	79	0	0.0	not detected
Methiocarb	79	0	0.0	not detected
Parathion methyl	79	2	2.5	0.006–0.015
Phosalone	79	1	1.3	0.014
Pirimicarb	79	2	2.5	0.005–0.006
Thiametoxam	79	15	19.0	0.013–0.144
2007				
Acetamiprid	44	8	18.2	0.005–1.341
Carbofuran	44	1	2.3	0.018
Carbosulfan	44	0	0.0	not detected
Chlorfenviphos	44	1	2.3	0.005
Chlorpyrifos	44	2	4.5	0.005–0.008
Diazinon	44	2	4.5	0.005–0.006
Imidacloprid	44	2	4.5	0.012–0.019
Isofenphos	44	0	0.0	not detected
Methiocarb	44	0	0.0	not detected
Parathion methyl	44	0	0.0	not detected
Phosalone	44	0	0.0	not detected
Pirimicarb	44	0	0.0	not detected
Thiametoxam	44	6	13.6	0.005–0.034

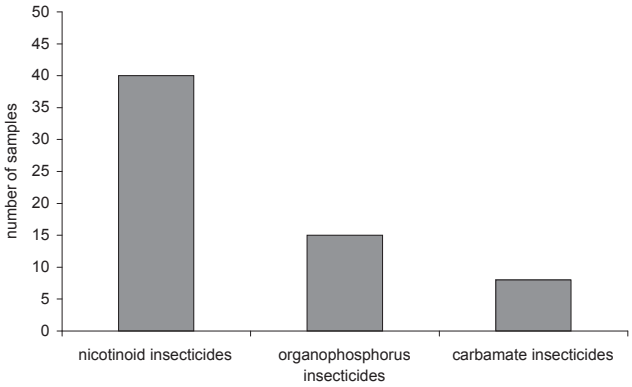

Figure 2. Percentage of particular insecticide groups in water samples in which pesticide residues were determined.

Taking into consideration the groups of chemical compounds of interest in these studies, nicotinoids insecticides were noticed most often and in the highest concentrations, followed by organophosphorus substances, while carbamates occurred rarely. Of 123 collected and analyzed water samples, in 36 there were found residues of nicotinoids, in 15 organophosphorus compounds and in 8 there were found carbamates. Fig. 2 displays distribution of the chemical groups in the samples.

Residues of ppp were searched for in the surface lotic waters (rivers, field watercourses, drendges), as well as in lentic waters (lakes, ponds). It is disputable whether drainages are surface waters or they belong to the underground sort ones. However, taking into account the small depth of drainages, water samples collected from such objects were classed as surface waters. Most often, in the course of the two-year research, insecticides used in rape crops were found in field watercourses and more rarely in drainages, lakes and ponds. No residues were found in samples originating from rivers. In 2006, 79 water samples were collected and 24 of them were contaminated with insecticide residues (30.4%). Taking into consideration the types of waters from which samples were taken, in 11 samples from field watercourses, 8 from drainages and 5 from lakes ppp residues were detected and determined. Fig. 3 presents the distribution of particular kinds of water samples among samples with determined ppp residues in 2006.

In 2007, twelve of all 44 collected water samples (27.3%) were contaminated with residues of investigated ppp. Seven of them were obtained from field watercourses, two each from lakes and drainages, and one from a pond. Graphic presentation of the distribution of particular kinds of water samples among samples with determined ppp residues in 2007 is displayed in Fig. 4.

Due to the chosen analytical methodology (liquid chromatography), pyrethroids were not determined. Compounds of this group are mainly determined by using gas chromatography [10, 13]. The first publications concerning determination of this class of compounds by liquid chromatography have appeared very recently [8].

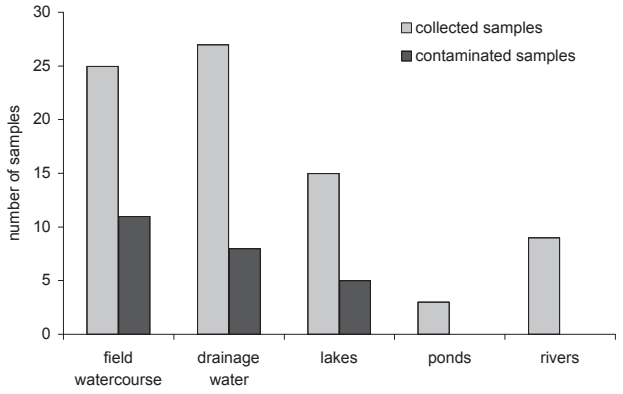

Figure 3. Specification of contamination with pesticide residues depending on water type from which samples were taken in 2006.

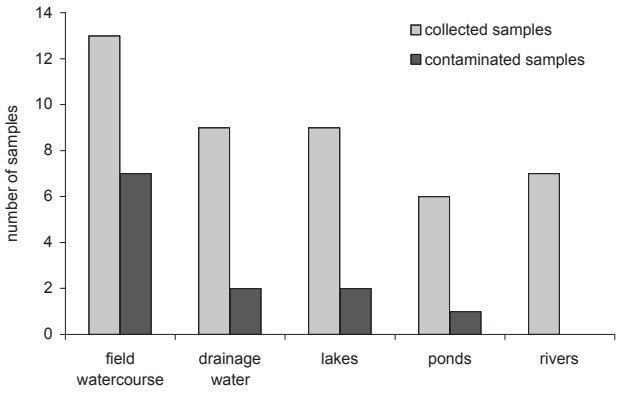

Figure 4. Specification of contamination with pesticide residues depending on water type from which samples were taken in 2007.

DISSCUSION

The above results seem to confirm the validity of such studies as they allow for specification of pesticides used in rape protection able to contaminate the water environment. Ppp introduced to the environment are also a significant problem in Poland where their use is at relatively lower level than in a countries of Western Europe. It is noteworthy that man is the final consumer of water and his health condition depends on its purity. Moreover, chemicals dissolved in water during its conditioning may be transformed to degradation products that may potentially influence its quality [14].

Active substances selected for these studies are not just 'historical' insecticides withdrawn from use, of which residues are still found in waters due to their accumulation in the soil followed by liberation to environment. The investigated compounds are in use in modern protection of rape plantations, and it is highly probable that the residues being found in Wielkopolska Region are a result of current farming [12].

Totally, 123 water samples from field watercourses, drainages, rivers, lakes and ponds in 2006 and 2007 were collected. Thirty-six samples (29.3%) were contaminated with insecticide residues used in rape crops protection. However, taking into account the EU Directive [4] on maximum admissible concentration (MAC) for single compound as 0.1 µg/l, only 3 samples (i.e. 2.4% of all samples) exceeded this value. Regarding the second part of the directive, the sum of all ppp residues in the sample should not exceed 0.5 µg/l and only in the case of one sample (0.8% samples) the value was higher. It can be assumed that Wielkopolska surface waters, even in case of intensive chemical protection of rape plantations, are not at a high risk of contamination with residues of insecticides used in such plant production. It is highly probable that water samples exceeding MAC values are a result of incorrect ppp application, or incorrect equipment used which is inconsistent with plant protection good practice. It is important that types of water reservoirs of high significance to water management, ecology and tourism, i.e. lakes and rivers, are contaminated at a very low levels with pesticide residues. In the case of rivers, residues of investigated compounds were not detected in any sample analyzed, and in water samples from lakes only traces of pesticide residues were found.

Insecticides used in rape plants protection belong to a relatively modern group of ppp active substances and should be characterized by rapid degradation in the environment. Nevertheless, in practice, even insecticides of the nicotinoid group introduced to agriculture recently are able to contaminate both surface and ground waters. It is more probable that residues of other pesticide groups known to be resistant in nature, e.g. triazine herbicides, phenylurea herbicides, phenoxyacetic herbicides or organochlorine insecticides, etc. may be more dangerous to the purity of Wielkopolska waters.

CONCLUSIONS

1. In the course of two-year studies among 123 water samples taken in 2006 and 2007, 36 contained residues of insecticides used in the protection of rape plantations.
2. Pesticides of the nicotinoid group, thiametoxam and acetamiprid were most often detected.
3. In the case of 3 samples, ppp residues exceeded MACs for a single substance as defined in the Directive 2000/60/EC. Only in the case of one sample, MAC for the sum of pesticide residues was higher than that defined in the above-mentioned document.
4. Most often, insecticide residues were found in water samples from field watercourses and drainages, while in samples taken from lakes and ponds, these compounds were confirmed more rarely. No residues of any investigated ppp were found in any sample from rivers.
5. Although the condition of Wielkopolska waters analyzed within the framework of this paper is not alarming, there is a need to take measures directed towards systematic monitoring contamination of water with pesticides used in intensive plant production. However, the national system of

monitoring of water contamination with active substances of ppp used currently in Poland does not yet exist.

6. Analytical methodology used in these studies, liquid chromatography (UPLC-MS/MS), allow for the determination of targeted compounds at the a times lower level than that requested by the above-mentioned UE Directive (0.1 µg/l for single compound and 0.5 µg/l for sum of all pesticides) [4]. Moreover, the use of a quadrupole mass detector allows for qualitative and quantitative determination of the pesticides during the same analytical run.

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