ARCHIVES OF ENVIRONMENTAL PROTECTION
vol. 35 no. 4 pp. 69 - 77 2009
PL ISSN 0324-8461

OCCURRENCE STUDY OF AGRO-CHEMICAL POLLUTANTS IN WATERS OF SUPRAŚL CATCHMENT

KATARZYNA IGNATOWICZ

Białystok Technical University, Department of Technology in Engineering and Environmental Protection
ul. Wiejska 45a, 15-351 Białystok, Poland
e-mail: izoplana@wp.pl

Keywords: Herbicides, pesticides, Supraśl catchment, agropollutants, biogenic, rural catchments.

Abstract: The paper presents the results on the studies on determination of concentrations of four phenoxyacetic herbicides, four triazine herbicides, seven insecticides and other pollutants in the Supraśl catchment. The samples were collected over a period of two years, from May 2003 to April 2005. This work will be a precious source of information about the occurrence of agropollutants in the surface water. The residues of herbicides active ingredients were determined using chromatography methods – GC with ECD and NP detection. The maximum residues of herbicide in surface water were detected in spring and autumn – up to 120 μg/dm^3 for phenoxyacetic acid (2,4-D, MCPA, MCPP). The most important fact noted during the research is that in surface water used for drinking significant amounts of crop protection substances were detected, which, in the light of the new law concerning the quality of drinking water, must undoubtedly be removed in the treatment processes.

INTRODUCTION

The river Supraśl basin consists of relatively poorly industrialized areas of typically agricultural character as well as large forests. Wide fragments of river Supraśl valley are characterized by high peat index with great percentage of organic soils. This area is distinguished by high contribution of arable lands (from 61.0 to 63.6) and woodlands (from 30.3 to 33.2) of total area (Fig. 1). The agricultural area in the basin covers about 22 073.7 ha, including 3 937.8 ha of arable lands and 18 135.9 ha of green lands [15]. These areas are potentially threatened by river water pollution due to wastes from agrotechnical operations associated with fertilization and using the plant protection means. The pollutants penetrate into the water not only with surface runoff, but also through melioration ditches and drainage filters, because soils are meliorated in 80.

Individual farms with mean area of about 10 ha dominate within the river Supraśl basin. Mineral fertilizers are applied at amounts much lower than in the rest of the country. In total, about 62 kg of pure NPK/ha were used in the river Supraśl basin in 2004 [6]. N : P : K ratio is 1.3 : 1.0 : 0.8, which gives:

N – 62/3.1 × 1.3 = 26 kg/ha,
P_2O_5 – 62/3.1 × 1.0 = 20 kg/ha,
K_2O – 62/3.1 × 0.8 = 16 kg/ha.

According to Sapek [11], nitrogen, phosphorus and potassium losses due to washing out are: nitrogen – 6, phosphorus – 0.4–0.5, and potassium – 21–25. About 573.9

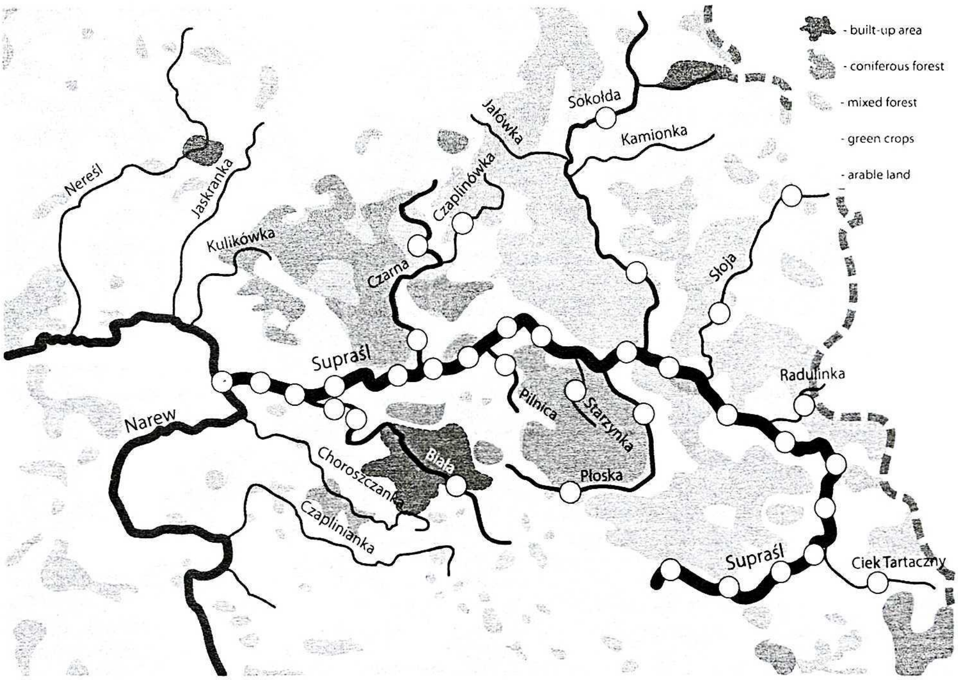

Fig. 1. The map of sampling points in the Supraśl catchment

Mg of pure nitrogen (26 kg N/ha × 22 073.7 ha), 441.5 Mg of phosphorus P_2O_5 (20 kg/ha × 22 073.7 ha) and 353.2 Mg of potassium K_2O (16 kg/ha × 22 073.7 ha) are applied in fertilizers annually. Theoretically, 34.4 Mg of nitrogen (573.9 Mg × 6%), 11.0 Mg of phosphorus (22 073.7 ha × 0.0005 Mg/ha) and 88.3 Mg of potassium (353.2 Mg × 0.25) may be washed out every year.

The amount of pesticides applied was estimated on the base of screening studies upon selected plants in 2004 in Białystok community, including the river Supraśl valley. The studies were carried out by the Department for Plant Protection and Sowing at Regional Inspectorate in Białystok. It reached 2 716.54 kg of biologically active substance of pesticides that may be partially washed out into the river. Pesticides are applied exclusively on arable lands. In general, 10 times less pesticides are used in Poland than in former EU countries.

Performance of the river Supraśl valley also includes the utilization of river water for drinking purposes for Białystok city [5, 6]. EU regulations and those currently binding in Poland precisely define the quality of surface water for drinking as well as they characterize sampling frequency and measurement methods along with permissible limits of pesticide residues in water. Directives [3, 4], Ordinance of November 7, 2002 [9] and Ordinance of August 20, 2008 [10] lists maximum chosen pesticide levels.

Because north-eastern region of Poland is typically agricultural and phenoxoacetic and triazine herbicide utilization is high, there is a serious threat of an excessive penetration of these substances into the surface water. The available literature data does not present their current concentrations in Podlasie region waters. Only the measurements of DDT content (that has not been applied for tens of years) and its metabolites have been conducted for several years. Therefore, undertaking the study upon the agrochemical pollution occurrence within the river Supraśl basin seemed to be advisable, because of the fact that the river is a source of drinking water.

MATERIAL AND METHODS

The river Supraśl basin is apparently asymmetric. The river has 18 tributaries, including 11 right and 7 left ones. The right tributaries irrigate 70% and left only 30% of the area. The major right-side tributaries are rivers: the Słoja, the Sokołda and the Czarna, and left-side: the Płoska, the Biała and the Pilnica [6]. The characteristic flow of chosen rivers in the Supraśl catchment is presented in Table 1, and the morphology parameters of the Supraśl tributaries are presented in Table 2. The study area (Fig. 1) besides the river Supraśl (19 points for water sampling), also consisted of its tributaries (14 points): the Słoja, the Pilnica, the Czarna, the Biała, the Radlinka, the Dzierniakówka, the Starzynka, the Płoska, and the Sokołda.

Table 1. The characteristic flow of chosen rivers located in the Knyszyn Primeval Forest Landscape Park during 1976–1995

River	Płoska	Sokołda	Supraśl
Sampling point	Królowy Most	Sokołda	Załuki
Catchment surface (km^2)	190	464	344
Woodiness (%)	68.1	47.3	53.5
Gauging period	1981–1991	1976–1995	1976–1995
Average flow [m^3/s]	0.92	2.61	1.81
Variability [%].	49.5	54.9	60.6
Low-water flow NNQ [m^3/s]	0.18	0.38	0.34
Variability [%]	39.7	44.2	42.2
Largest flow WWQ [m^3/s]	10.9	40.1	31.2
Variability [%]	97.9	107.9	105.8
WWQ/NNQ	60.6	105.5	91.8
Mean specific runoff [l/(s×km^2)]	4.84	5.62	5.26
[%] underground runoff	75.6	58.2	55.8

Table 2. The morphology parameters of Supraśl tributaries

River	Basin order	River length [km]	Area [km^2]	Mean basin gradient [%]	Mean river gradient [%]	Circular index	Lengthen index
Słoja	IV	19.6	220.6	0.38	1.94	0.66	1.22
Pilnica	IV	10.1	35.0	1.07	3.17	0.49	1.41
Czarna	IV	24.5	199.1	0.73	1.3	0.65	1.23
Biała	IV	29.9	115.4	1.07	2.1	–	–

The study was performed to evaluate the oscillations of agrochemical pollution concentration – biogenic (nitrite, nitrate and ammonium nitrogen, phosphate) and pesticides:

- phenoxyacetic herbicides – 2,4-D (2,4-dichlorophenoxyacetic acid), MCPA (2-methyl-4-chlorophenoxyacetic acid), MCPP (methylchlorophenoxypropionic acid), dichloroprop (2-(2,4-Dichlorophenoxy)propionic acid);
- triazine herbicides – atrazine, metribuzon, prometryn, simazine;
- insecticide – chloropyrifos, endosulfan, parathion.

The data presented here are the result of over 1500 measurements and analytical determinations. The study was conducted between April 2003 and October 2005. Samples were taken once a month. Minimum water sampling frequency during pesticide pollution screening to evaluate the current concentrations and seasonal changes is four times a year with additional measurements during their application and heavy rainfalls [4]. Thus, the assumed sampling rate (once a month) was sufficient.

Gas chromatography (GC) is a preferred method for pesticide determination in surface water ensuring about 25% precision level [9, 10]. Pesticide residue in water samples were analyzed using GC techniques in certified Laboratory of Plant Protection Institute in Poznań. The list of analyzed pesticides is presented in Table 3. Statistical evaluation of GC-EC method is presented in Table 4. Active substances were identified using gas chromatography with specific detectors: electron capture (EC), nitrogen-phosphorus (NP), and mass spectrometer (MS). The content of examined substances was calculated on the basis of water matrix calibration. The main problems of pesticides in water analysis, besides small concentrations, are diversification of their properties and the complexity of the matrix. The analysis of nitro- and phosphoroorganic insecticides was carried out by means of gas chromatography with thermoionic detector (GC-NPD), analysis of chloroorganic insecticides – gas chromatography with electron capture (GC-ECD), and more polar pesticides (phenoxyacids) – after previous esterification, i.e. transforming into volatile derivatives, by means of gas chromatography with electron capture (GC-ECD). Agrochemical pollutants in water from the river Supraśl basin (nitrogen and phosphorus compounds) were determined in the Institute of Engineering and Environment Protection at Technical University in Białystok.

Table 3. List of substances marked by gas chromatography in water (determination and precision level min 25%)

Active substance		Method of detection	LD Water [mg/kg]	Active substance		Method of detection	LD Water [mg/kg]
H	Atrazine	GC-NP	0.0001	I	Chloropyrifos	GC	0.00008
	Metrybuzyna	GC-EC	0.00003		Endosulfan	GC-NP	0.0002
	Prometryna	GC	0.0002		Parathion	GC-NP	0.00035
	MCPA	GC-EC	0.0010		Azynofos	GC	0.0001
	Dichloroprop	GC-EC	0.003		Fenitrition	GC	0.0001
	Mecoprop	GC-EC	0.0010		Fipronil	GC	0.0001
	Simazine	GC-NP	0.0001		Pirymifos	GC	0.00005
	2.4-D	GC-EC	0.0010				

H – herbicides, I – insecticides, LD – limit of detection

Table 4. Statistical evaluation of GC-EC method

Active substances	Level of fortification [μg/dm³]	N	Recovery [%]	Detectability [μg/dm³]	Limit detection [μg/dm³]
2.4-D	1	4	87.1	1	1
2.4-D	14	4	94.9	0.5	1
MCPA	1	4	89.9	1	1
MCPA	12	4	95.4	0.5	1
MCPP	1	4	68.5	1	1
MCPP	14	4	94.6	0.5	1

DISCUSSION OF RESULTS

Results confirmed the presence of agrochemical pollutants in water of the river Supraśl basin, namely most common plant protection means – phenoxoacetic herbicides (Tabs 5 and 6). Chemical analyses revealed that those herbicides concentrations oscillated within wide range from 10 up to 120 μg/dm³ (Tab. 5). These levels were higher than those found by Żelechowska and Makowski [18] in waters of the rivers Redunia and Reda, as well as by Siepak *et al.* in ground water of the Poznań region [12, 13], but they ranged at similar level as in water of the rivers: Narew, Biebrza and Supraśl in previous years [7]. The Department of Agriculture in Washington [1] discovered that the amount of phenoxyacetic

Table 5. Herbicides analyzed in the Supraśl catchment

Pesticide	Percent of samples with detections				Minimum [μg/dm³]	Maximum [μg/dm³]	Heath value [μg/dm³]
	season	spring	summer	autumn			
Phenoxyacetic herbicide							
2.4-D	37.65	34.1	20	33.3	10	60	30
MCPA	47.05	38	25	44.4	10	50	–
MCPP	64.71	42.5	22.5	55.5	20	120	
Dichloroprop	ND	ND	ND	ND	ND	ND	
Triazine herbicide							
Atrazine	ND	ND	ND	ND	ND	ND	40.0
Metribuzin	ND	ND	ND	ND	ND	ND	100
Prometryn	ND	ND	ND	ND	ND	ND	–
Simazine	ND	ND	ND	ND	ND	ND	20.0
Insecticide							
Chloropyrifos	ND	ND	ND	ND	ND	ND	
Endosulfan	ND	ND	ND	ND	ND	ND	
Parathion	ND	ND	ND	ND	ND	ND	
Azynofos	ND	ND	ND	ND	ND	ND	
Fenitrition	ND	ND	ND	ND	ND	ND	
Fipronil	ND	ND	ND	ND	ND	ND	
Pirymifos	ND	ND	ND	ND	ND	ND	

ND – not detected

acid herbicide in surface waters in Salmonid-Bearing Streams ranged 0.022–19 2,4-D μg/dm^3, 0.012–15 MCPP μg/dm^3 and 0.022–76 MCPA μg/dm^3. Stramer [14] estimated the top value of concentrations 2,4-D in the surface waters in England at 100 μg/dm^3. Thurman [16] estimated the mean value of concentrations of herbicides in Midwestern Reservoir Outflows at 13.6 μg atrazine, 2.1 μg simazine, 0.25 μg metribuzine, and 0.1 μg propazine per dm^3.

Table 6. The concentration of agropollutants in the Supraśl catchment

Agropollutants	Residue				
	Mean	Median	Standard deviation	Min	Max
Spring					
2.4-D [μg/dm^3]	25.9	20	11.37	10	50
MCPA [μg/dm^3]	27.6	25	9.71	10	50
MCPP [μg/dm^3]	52	50	16.12	20	100
P-PO_4 [mg/dm^3]	0.56	0.53	0.24	0.25	1.42
N-NH_4 [mg/dm^3]	0.48	0.38	0.40	0.12	1.82
N-NO_2 [mg/dm^3]	0.021	0.014	0.0244	0.005	0.157
N-NO_3 [mg/dm^3]	1.51	1.35	0.79	0.60	5.10
Conductivity [μS/cm]	468	427	130	388	953
Summer					
2.4-D [μg/dm^3]	27.9	30	10.14	10	50
MCPA [μg/dm^3]	29.1	30	8.12	10	50
MCPP [μg/dm^3]	56.3	50	20.49	20	120
P-PO_4 [mg/dm^3]	0.50	0.47	0.14	0.20	0.78
N-NH_4 [mg/dm^3]	0.47	0.34	0.39	0.24	1.8
N-NO_2 [mg/dm^3]	0.039	0.013	0.078	0.007	0.375
N-NO_3 [mg/dm^3]	2.18	2.00	1.09	0.60	5.70
Conductivity [μS/cm]	472	426	142	382	1057
Autumn					
2.4-D [μg/dm^3]	27.9	25	13.19	10	60
MCPA [μg/dm^3]	30.3	30	10.00	15	50
MCPP [μg/dm^3]	61.8	60	18.78	30	100
P-PO_4 [mg/dm^3]	0.76	0.69	0.43	0.08	2.06
N-NH_4 [mg/dm^3]	0.37	0.28	0.35	0.16	2.18
N-NO_2 [mg/dm^3]	0.032	0.011	0.063	0.006	0.310
N-NO_3 [mg/dm^3]	2.35	2.15	0.97	1.10	5.20
Conductivity [μS/cm]	483	439	140	259	954
Research season					
2.4-D [μg/dm^3]	27	25	11.5	10	60
MCPA [μg/dm^3]	29	30	9.3	10	50
MCPP [μg/dm^3]	58	60	19.0	20	120
P-PO_4 [mg/dm^3]	0.63	0.55	0.33	0.08	2.06
N-NH_4 [mg/dm^3]	0.41	0.32	0.34	0.12	2.18
N-NO_2 [mg/dm^3]	0.032	0.013	0.063	0.005	0.375
N-NO_3 [mg/dm^3]	2.06	1.90	0.99	0.60	5.70
Conductivity [μS/cm]	478	436	140	259	1057

The highest amounts of these compounds were observed in summer and in autumn. It is associated with spring agrotechnical operations and washing out of the compounds with thawing snow cover as well as further rainfalls. Strong snow thaws and heavy surface runoffs caused the increase of field pollution losses, which has recently occurred, because winters lasted till the beginning of April in the Podlasie region. Maximum phenoxoacetic acids concentrations were present in June – August and September. Their average concentration in autumn was 61.8 μg/dm³ MCPP (at c_{max} = 120 μg/dm³), 30.3 μg/dm³ MCPA (at c_{max} = 50 μg/dm³). In summer, herbicide contents were: 56.3 μg/dm³ MCPP, 29.1 μg/dm³ MCPA, and 27.9 μg/dm³ 2,4-D (Tab. 6). The temperature drop delays the activity of microorganisms taking part in plant protection means degradation in the soil and water, and thus the rate of compounds in question [2].

Larger amounts of herbicide MCPP ($c_{śr}$ = 58 μg/dm³ at c_{max} = 120 μg/dm³) than MCPA or 2,4-D were found in samples (Tab. 6, Fig. 2). This fact may be elucidated not only by massive application of the compound, but also its highest durability in an environment, as well as by a long half-life in water (to 20 days) and in soil (up to 180 days). The highest concentrations of the studied compounds were recorded at the sampling point on the rivers Czarna and Supraśl (the most distant from river springs). It is probably associated of a constant supply with pollution load from the basin area.

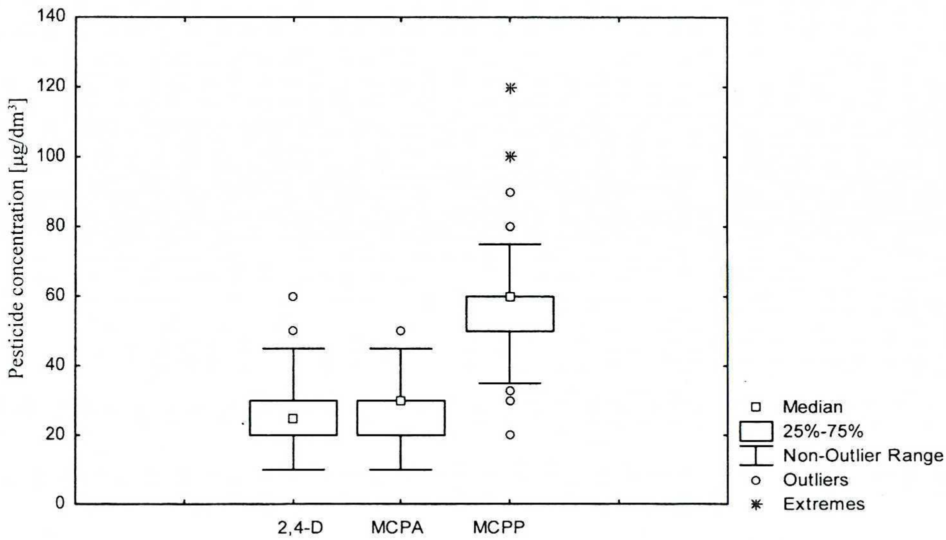

Fig. 2. Mean phenoxyacetic herbicide concentration in the Supraśl River catchment

In studied river, the content of ammonia nitrogen ranged from 0.012 to 2.18 mg/dm³. A typical dependence – low ammonia nitrogen concentration at higher temperatures when it is taken by plants and nitrified, and higher in winter when nitrification process is inhibited – was observed. Because of the fact that winter has been recently delayed even to April in Podlasie region, the lowest mean ammonia nitrogen concentration occurred in spring (0.48 mg/dm³). "Classical" summer is shifted to the end of August and beginning of September, thus the lowest mean ammonia nitrogen contents were recorded in autumn (0.37 mg/dm³). Under aerobic conditions, nitrites are transient and unstable products that are quickly converted into nitrates, which was confirmed by significant correlation dependences. In the examined surface water, the concentration of nitrite nitrogen was from 0.005 to 0.375 mg/dm^3. Its highest contents were recorded in summer ($c_{śr}$ = 0.032 mg/dm^3). Nitrate nitrogen is the biogenic substance that is necessary for aqueous plant's living. Changes of nitrate concentrations occurred analogously to those for phosphates (Tab. 6).

Vervier's opinion on seasonal dependence of biogenic substances occurrence, including pesticides, in rivers of agricultural basins, was here confirmed [17]. The obtained results revealed that there was similar time dependence for nitrogen and phosphorus concentrations in the studied water (Tab. 6). Almost 600 values were analyzed, thus significant dependencies were present just at correlation coefficient 0.25. Calculated correlations led to conclusions about the inter-relation between phenoxoacetic acids and biogenic compounds amounts, namely phosphates. During the study, correlation coefficient between concentrations of various chemical forms of phenoxoacetic herbicides was high ranging from 0.32 to 0.87. Similar dependence may be found between nitrate and nitrite contents (R = 0.68).

CONCLUSIONS

1. The largest amount of pesticide remains was found in surface water in summer; it amounted to 120 μg/dm^3 (2,4-D, MCPA, MCPP).
2. Biogenic concentrations varied through seasons and their largest contents were present in summer and autumn.
3. It was found that the sum of pesticides remains exceeded 5 μg/dm^3, thus a systematic screening of the river Supraśl and its tributaries for these agents should be conducted.
4. Great amounts of plant protection means were found in surface waters often used for drinking. They must be removed during water treatment processes in accordance to a new Decree on the quality of water meant for drinking.

Acknowledgments

Financial support for this research was provided by Ministry of Science and Higher Education within the project W/IIŚ/23/07 and G/IIS/22/07 (N305 070 32/2535).

REFERENCES

[1] Anderson P., R. Jack, Ch. Burke, J. Cowles, B. Moran: *Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams April to December 2003*, WSDA, Washington State, Department of Agriculture, Ecology Publication 04-03-048, 2004.

[2] Dojlido J.R.: *Chemia wód powierzchniowych*, Wydawnictwo Ekonomia i Środowisko, Białystok 1995.

[3] Dyrektywa 75/440/EWG z 16 czerwca 1975 r. dotycząca wymaganej jakości wód powierzchniowych przeznaczonych do pobierania wody pitnej.

[4] Dyrektywa 79/869/EWG z 9 października 1979 r. dotycząca metod poboru i częstotliwości pobierania próbek oraz analizy wód powierzchniowych przeznaczonych do pobierania wody pitnej.

[5] Górniak A.: *Klimat Województwa Podlaskiego*, IMiGW, Białystok 2000.

[6] Górniak A.: *Wody Parku Krajobrazowego Puszczy Knyszyńskiej*, IMiGW, Supraśl 1999.

[7] Ignatowicz K.: *Ocena stanu czystości rzeki Białej ze szczególnym uwzględnieniem zanieczyszczeń pestycydowych i biogennych*, Archives of Environmental Protection, **30**, 2, 51–60 (2004).

[8] Ignatowicz K., I. Skoczko: *Occurrence study of Agro-chemical pollutions in chosen waters on marshland and flooding of Biebrza*, Polish Journal of Environmental Studies, **15**, 5, 431–434 (2006).

[9] Rozporządzenie Ministra Środowiska z dnia 27 listopada 2002 r. w sprawie wymagań, jakim powinny odpowiadać wody powierzchniowe wykorzystywane do zaopatrzenia ludności w wodę przeznaczoną do spożycia, Dz. U. nr 204, poz. 1728 z 2002 r.
[10] Rozporządzenie Ministra Środowiska z dnia 20 sierpnia 2008 r. w sprawie sposobu klasyfikacji stanu jednolitych części wód powierzchniowych, Dz. U. nr 162 z 2008 r.
[11] Sapek B.: *Rolnictwo polskie i ochrona jakości wody*, Instytut Melioracji i Użytków Zielonych Falenty, Zeszyt edukacyjny, nr 2/97 (1997).
[12] Siepak J., J. Zerbe, M. Kabacinski: *Wstępna ocena degradacji studni na obszarach wiejskich województwa poznańskiego*, Przyroda i Człowiek, **4**, 117–123 (1993).
[13] Siepak J., J. Zerbe, M. Kabacinski, T. Sobczyński: *Wpływ antropopresji na wody gruntowe na obszarze województwa poznańskiego i miasta Poznania*, Wydawnictwo Sorus, Poznań 1997.
[14] Stamer J.K., W.A. Battaglin, D.A. Goolsby: *Herbicides in Midwestern Reservoir Outflows, 1992–93*, U.S. Geological Survey Open-File Report 134–98, 1998.
[15] Stuczyński T. (red.): *Wdrożenie systemu informacji o rolniczej przestrzeni produkcyjnej w województwie podlaskim*, Instytut Uprawy Nawożenia i Gleboznawstwa, Puławy 2003.
[16] Thurman E.M., D.A. Goolsby, M.T. Meyer, D.W. Kolpin: *Herbicides in surface waters of the Midwestern United States – the effect of spring flush*, Environmental Science & Technology, **25**, 10, 1794–1796 (1991).
[17] Vervier P., A. Pinheiro, A. Fabre: *Spatial changes in the modalities of N and P inputs in a rural river network*, Wat. Res., **33**, 1, 95–104 (1999).
[18] Żelechowska A., Z. Makowski: *Pestycydy w wodach rzek o zlewniach rolniczych zasilających Zatokę Gdańską*, Gaz, Woda i Technika Sanitarna, 2-3, 35–42 (1990).

Received: February 12, 2009; accepted: August 18, 2009.

WYSTĘPOWANIE ZANIECZYSZCZEŃ AGROCHEMICZNYCH W WODACH ZLEWNI SUPRAŚLI

W pracy zaprezentowano wyniki badań dotyczących określenia aktualnych stężeń pozostałości agrochemicznych: herbicydów fenoksyoctowych (4), herbicydów triazynowych (4) i insektycydów (7) oraz innych zanieczyszczeń w wodach zlewni rzeki Supraśli. Okres badawczy trwał dwa lata, od maja 2003 do kwietnia 2005 roku. Pozostałości pestycydów określano metodą chromatografii gazowej GC z detektorem ECD. Największe stężenia pestycydów fenoksyoctowych wykryto w okresie wiosenno-jesiennym (120 μg/dm^3). Najważniejszym jednak spostrzeżeniem jest fakt występowania w wodach powierzchniowych, często ujmowanych do picia, znacznych ilości środków ochrony roślin, które w świetle nowej ustawy o jakości wody przeznaczonej do picia, należy usuwać w procesach uzdatniania.