A.3. Soil

Study on the pesticides content in the groundwater in the Republic of Bulgaria: Some problems and recommendations

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Abstract

The Ministry of Environment and Water (MoEW) has made an investigation of the pesticides content in the groundwater during the period 1997 - 2000. The main aim was to determine the groundwater pesticide contamination in previously chosen agricultural areas. In the selected areas, 29 pesticides have been investigated. These included organo-chlorine pesticides, HCH, heptachlor, isomers and metabolites of DDX, aldrin, dieldrin, endrin, isodrin, HCB, triazines, chlordane, endosulphan, metoxychlor and also the organophosphorus pesticides phosalon and phenitrotion. The detected levels have been compared with those criteria that are recently published in the Official Gazette, number 57/2000 in Bulgaria, and also with international standards for drinking water supply.

Keywords

Pesticides, groundwater, and contamination diffusion from agriculture

Introduction

Plant protection products, including pesticides, are one of the most important sources of the diffuse groundwater contamination caused by agricultural activities. Pesticides and their metabolites can leach through the soil with water from rainfall or artificial irrigation and infiltrate into the aquifers. The infiltration depends on some factors such as their persistence, water solubility, migration ability, application rate, as well as aquifer protection. So the problem is very complex and difficult.

The first attempt of an organised systematic investigation by the MoEW for the pesticide content in groundwater was made in 1997 and has been continued in 1998, 1999 and 2000. The number of sampling sites during 1997 was limited because of financial and analytical difficulties (only 32 of the preliminary selected sampling points were analysed and evaluated). During 1998, this number increased to 56 and in 1999 it reached 97. During the spring of 2000, 44 groundwater sampling points have been analysed and evaluated. The number and distribution of the sampling sites in the selected agricultural areas are shown in Table 1. 29 pesticides have been analysed, mainly organochlorine such as alpha-, beta-, gamma-, delta-, epsilon- HCH, hexachlorobenzene, simazine, atrazine, propazine, ametryn, prometryn, terbutryn, heptachlor, aldrin, dieldrin, chlordane, metoxychlor etc., including DDT-isomers and metabolites - op-DDD, pp-DDD, op-DDE, pp-DDE, as well as the organo-phosphorus - phosalon and phenitrotion. The main aim of our investigations was to determine the groundwater pesticides contamination caused by agricultural activities, but in 1999 and 2000 samples have been taken at some hydrogeological points situated nearby obsolete pesticides storages.

As standards, the Bulgarian recommended standards have been used, as well as the EU Directive, WHO, US EPA, US NAS standards for drinking water. We have given an account of the high harmfulness of aldrin, dieldrin and heptachlor. Actually the first Bulgarian recommended pesticides' standards are established in 07.07.2000 by accepting a Regulation for research, use and protection of groundwater with its Annex 3 -"Recommended parameters for groundwater protection from contamination" (Appendix 2). Here are ecological and contamination values established. The ecological value for all pesticides is 0.01 ug/l. The contamination values were different.

Methods

Methods for groundwater investigations

The main principles and sequence of investigations were the following:

- Agricultural areas with intensive treatment of pesticides were determined in the different parts of the country (Appendix 1). Data of the Central Office for Vegetable Protection, Quarantine and Agro-chemistry, of the Ministry of Agriculture and Forests were used.
- Hydrogeological and geomorphological conditions have been determined for every chosen area. The sampling points were chosen on the basis of lithological - stratigraphical, geomorphological conditions and vulnerability of the aquifers. The groundwater sampling sites are shown on Appendix 1; their numbers are shown in Table 1.
- The choice and selection of the sampling sites was mainly from the National Groundwater Monitoring Network, which is maintained by MoEW. This selection was supplemented by suitable groundwater points.
- Sampling sites with high nitrate content were chosen in several cases.
- Points with available data for pesticide contamination (P-71) have been included.
- Samples were collected from 39 sampling sites during the spring of 2000. These samples showed higher pesticides levels exceeding those recorded previously during the period 1997 - 1999. The aim was to compare the results of low and high groundwater table and to follow the pesticides' dynamics in groundwater.
- In case of detecting higher pesticides levels, attempts have been made for sampling additional groundwater points in the same aquifer. For example P-21 and P-113 in Quaternary alluvial deposits.
- During 1999, two samples have been collected from groundwater points situated near facilities of previous agricultural co-operatives (pesticide users and applicators - P-105 and P-108). While during the spring of 2000, samples have been collected from 5 groundwater points situated close to facilities of previous state-owned agricultural co-operatives (P-108, P-109 and P-110, P-111, P-112).

Methods for soil investigations (See also contribution of Valentina Vassileva in this book)

- During 1997, soils have been investigated in potentially agricultural contaminated areas.
- In the next years, a new sampling system has been used. The locality of sampling points is fixed in the crossed points of parallels and meridians at intervals of 20' latitude and 30' longitude (Scale 1: 500 000)
- The analysed pesticides were in accordance with Montreal protocol by Convention on long-range transboundary air pollution.

Results and conclusions

The number and distribution of groundwater sampling sites and the types of investigated pesticides in each region are presented in Table 1 and Appendix 1.

Table 1. Number and distribution of the groundwater sampling sites in the selected agricultural regions and the investigated pesticides in the period 1997-2000.

Name of agricultural area	1997	1998	1999	The spring - 2000
I. Northwest Bulgaria	12/23+ DDX	10/15+DDX	10/6+DDX	12/14+DDX
II. Centralnorth Bulgaria	4/23+ DDX	2/15+DDX	16/6+DDX	3/6+DDX
III. Northeast Bulgaria	No sampling sites	7/11+DDX	26/8+DDX	6/8+DDX
IV. Southwest Bulgaria	No sampling sites	2/15+DDX	8/16+DDX	4/14+DDX
V. Trackian Lowland	16/5+DDX	28/8+DDX	26/6+DDX	17/9+DDX
VI. Sliven-Straldza valley, Yambol and Bourgas areas	No sampling sites	7/14+DDX	9/12+DDX	2/14+DDX
VII. Central Rhodophian area	No sampling sites	No sampling sites	2/6+DDX	No sampling sites

Note: number of sampling sites / number of analysed type of pesticides

Information about the depths of the aquifers and their thickness in the various regions are given in Table 2.

Table 2. Depth and thickness of aquifers

Name of agricultural area	Aquifers	Depth of aquifer [m]	Thickness of aquifer [m]
I. Northwest Bulgaria	1. Quaternary rivers Tcibritza and Ogosta; Kozloduy lowland	from 2-4 to 8-10	3-18
	2. Plio-pleistocene massif between rivers	25-35	3-6
	3. Pliocene	from 5-10 to 50-150	50-100
	4. Sarmatian	10-300	50-80
	5. Upper Cretaceous	5-15	10-20
	6. Jurassic-Cretaceous (Callovian - Barremian)	0-5	
II. Centralnorth Bulgaria	1. Quaternary - rivers Vit, Osam, Yantra, Djulyunitza	from 2-4 to 8-10	4-14
	2. Sarmatian	5-30	4-10
	3. Upper Cretaceous	2-5	4-10
III. Northeast Bulgaria	1. Quaternary	1-10	3-15
	2. Sarmatian	from 1-4 to 80-100	3-60
	3. Lower Cretaceous - Hauterivian Barremian	2-150	80-100
	4. Lower Cretaceous - Valanginian	0-1000	600-800
IV. Southwest Bulgaria	IV a - 1. Quaternary	4 - 25	15-20
	IV a - 2. Pliocene	4 - 150	100-120
	IV b - 1. Quaternary	2-4	from 20 to >50
V. Trackian Lowland	1. Quaternary	2-3	10-90
	2. Pliocene	2-3 to 100	30-100
	3. Paleogene - Upper Eocene	5-30	30-100
	4. Upper Cretaceous - carbonate flysh	1	>500
VI. Sliven-Straldza valley, Yambol and Bourgas areas	1. Quaternary	2-5	10-80
	2. Upper Neogene (Pliocene)	5-10 to 100	30-100
	3. Upper Eocene	0-	>50
	4. Upper Cretaceous	0-	>500
VII. Central-Rhodophian area	1. Precambrian	0-	>500

The following represents conclusions about groundwater from the investigated areas together with some comparisons with other soil investigation results:

Regions in Northwest Bulgaria

Groundwater has been sampled in Quaternary and Neogenic aquifers and at 2 springs draining Upper Cretaceous and Valanginian limestone. During 1997, 7.2% of all results exceed the ecological value for groundwater. (See appendix 2). The highest contributions have pp'-DDE, which is above an ecological value, in 91.7% of the all sampled sites and metoxychlor in 83.3 % of all investigated points. (Appendix 1 and Figure 1). There are rare cases where op'-DDE, aldrin and mirex exceeded the permissible ecological value.

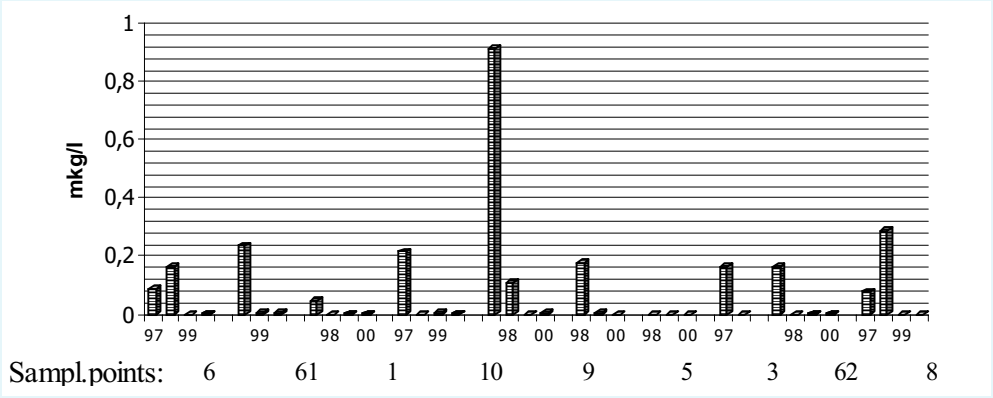


Figure 1. pp'-DDE content in groundwater of Northwest Bulgaria

During 1998, 14.8% of the analysed pesticides in groundwater samples exceeded the ecological value. Most frequently they exceeded 0.01ug/l atrazine in 70% of sampling points and propazine at 70% of the points (Figure 3). There are a few cases where heptachlor, dieldrin, metoxychlor, simazine and some DDX isomers exceeded the ecological value. At 3 Neogene sampling points, organophosphorus pesticides exceeded the value of 0.01 ug/l.

During 1999, 1.7% of analyses exceeded the ecological value. Atrazine exceeded 0.01 ug/l in 31.3% of the sampling points, while in the spring of 2000, a.m. percentage for atrazine recorded 41.7. Heptachlor recorded 0.002 ug/l during spring 1999 at point 66 (Upper Cretaceous).

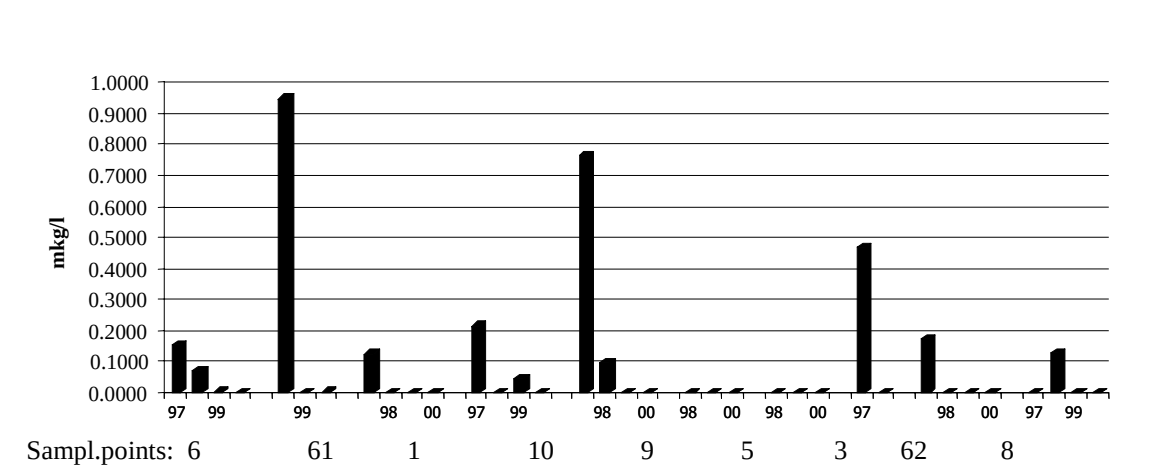


Figure 2. Metoxychlor content in groundwater in Northwest Bulgaria
(Note: mkg/l means ug/l)

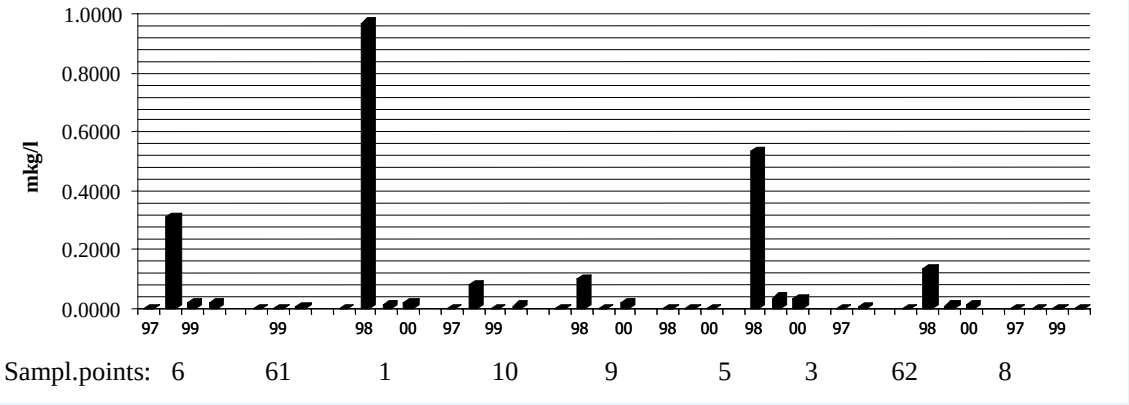


Figure 3. Atrazine content in groundwater of Northwest Bulgaria

An attempt has been made to compare the groundwater results with pesticides content in soils (27 soil samples nearby groundwater sampling sites). In the soil samples, DDX (sum)) exceeded the MAC (Maximum admissible concentration) of 1.5 mg/kg in 63% of soil samples for the whole period from 1997 to 1999. The abovementioned percentages were respectively 59% for op'pp'-DDT; 26% for op'pp'-DDD; 59% for op'pp'-DDE (MAC - 0.5 mg/kg). Hexachlorobenzene values ranged between 0.025 mg/kg (preventive value) and 0.25 mg/kg (MAC) in 56% of samples. HCH (sum) exceeded the MAC (0.01mg / kg) in 22% of sampling points while metoxychlor was determined in 26% of samples between 0.307 and 9.636 mg/kg. High values for heptachlor, cis-heptachlor- epoxyd, aldrin, dieldrin and endrin, and phozalone were rarely determined.

Regions in Centralnorth Bulgaria

Groundwater has been investigated in Quaternary, Sarmatian (P-73) and Lower Cretaceous (P-12) sediments. During 1997, 6.9% of the groundwater analyses exceeded the ecological value for heptachlor, endrin, metoxychlor, pp'-DDE and mirex. In 1998, the a.m. percentage was 4.8 % due to atrazine and propazine content that recorded up to 0.056 ug/l at P-12 (Aptian aquifer). At P-74 (Quaternary), heptachlor at a level of 0.084 ug/l was detected

During 1999, the detected levels of the investigated pesticides did not exceed the ecological values. During spring of 2000, only 3 high levels of DDX (sum) exceeding the ecological value were recorded at P-110, P-111, and P-112 nearby obsolete pesticides storages. A comparison among analyses from 10 soil sampling points in the vicinity of groundwater points was made. The MAC of 1.5 mg/kg has been exceeded for DDX (sum) in 50% of soil samples during the whole period from 1997 to 1999. The abovementioned percentages were respectively 50% for op'pp'-DDT; 33% for op'pp'-DDD; and 50% for op'pp'-DDE (MAC - 0.5 mg/kg). Single higher values for each of HCB, cis-heptachlor- epoxyd, atrazine, propazine and phozalon were detected.

Regions in Northeast Bulgaria

Groundwater samples were collected from Sarmatian aquifers, Aptian (3 points) and Valanginian limestone. During 1998, the ecological value was exceeded for 11.8% of the groundwater analyses. Above this value are cis-heptachlor-epoxyd in 57.1% of sampling sites, metoxychlor in 57.1% of monitoring points (Appendix 1), op'-DDE in 42.9% of sampled hydrogeological points. Single exceedings were determined for gamma-HCH and organophosphorus pesticides.

During 1999, in 1.04% of pesticides analyses the ecological value has been exceeded. Heptachlor in Sarmatian P-86 and P-89 has exceeded the ecological values. At P-80 (Qal+K1ap), DDE isomers levels ranging from 0.251 up to 0.274 ug/l were detected. The groundwater sampling campaign in spring 2000 did not show exceedings.

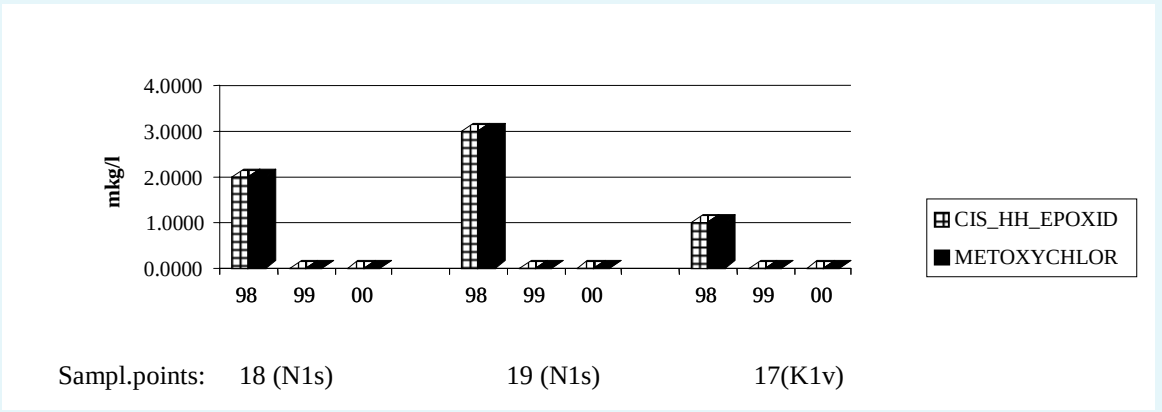


Figure 4. Pesticides content in groundwater in Northeast Bulgaria

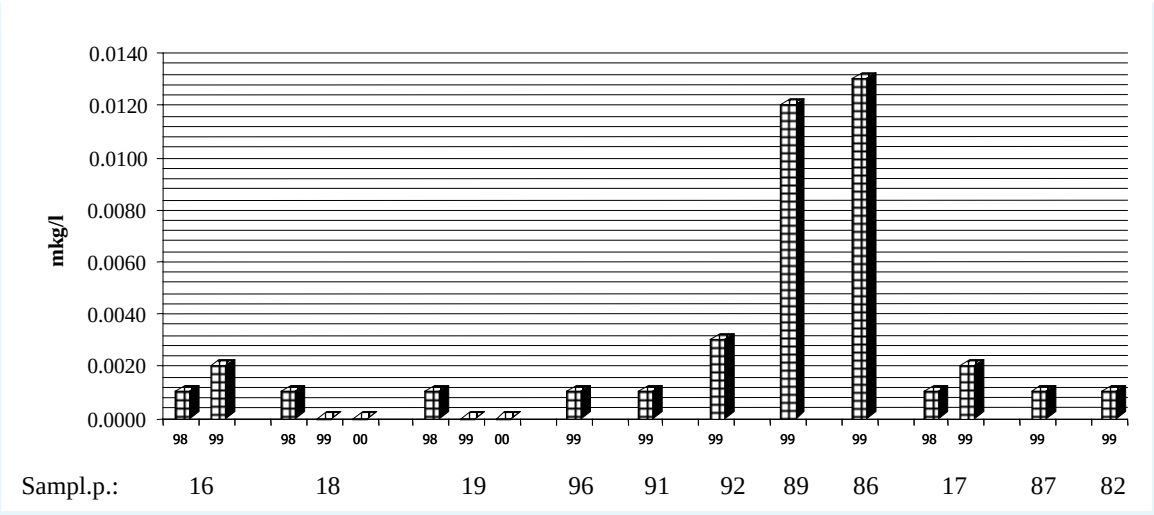


Figure 5. Heptachlor content in groundwater in Northeast Bulgaria

In an attempt to correlate pesticides concentration in the groundwater and soils, the analyses of 20 soil samples in the area have been used. MAC has been exceeded for DDX (sum) in 90% of the soil samples (for the whole period from 1997 to 1999), for op'pp'-DDT in 95%, for op'pp'-DDD in 65% and for op'pp'-DDE in 65% of samples. A few higher values have been measured for heptachlor, cis-heptachlor-epoxyd, aldrin, endrin, metoxychlor and single high value for fenitrition.

Regions in Southwest Bulgaria

Groundwater has been sampled in Quaternary and Pliocene sediments at three Neogenic grabens (valleys).

Area IVa - covers a part of the Sofia valley. The groundwater investigation during 1999 and spring 2000 concluded that the ecological value for triazines in groundwater at P-105 and P-108 had been exceeded (Figure 6). These points are close to facilities of previous state owned agricultural structures (pesticide users and applicators).

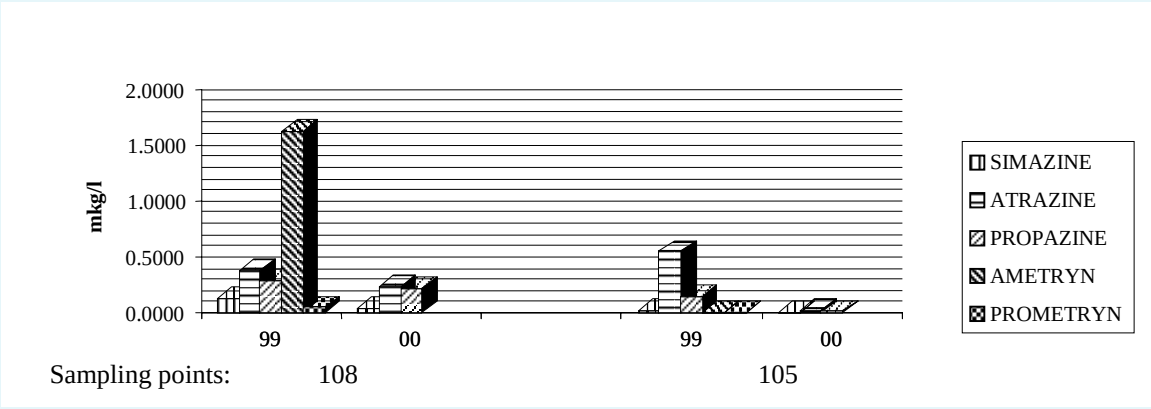


Figure 6. Pesticides contents in groundwater in Southwest Bulgaria

29 soil samples were collected from 12 points situated nearby groundwater monitoring points and analysed. Results concluded that DDX (sum) levels exceeded the MAC (1.5 mg/kg) in 100% of investigated soil samples. These percentages were respectively 100% for op'pp'-DDT; 79% for op'pp'-DDD; 100% for op'pp'-DDE (MAC - 0.5 mg/kg). For HCH (sum), 27.6% have been above the MAC (0.01 mg/kg). A few higher values were recorded for triazines and metoxychlor.

Area IVb covers the Sandansky and Petrich valleys. During 1997, only propazine exceeded the ecological value at point 22 while during 1998, 0.258 ug/l of pp'DDE and 0.129 ug/l metoxychlor were detected in P-21. In order to verify the above-mentioned results, samples were taken from P-21 and P-113 in same Quaternary drift aquifer during the spring of 2000. The isomers DDX exceeded the ecological value at P-113.

In order to correlate the groundwater data with soil data, 2 soil samples in the area were used. This correlation showed that the MAC (0.5 mg/kg) for op'pp'-DDE was exceeded.

Regions in Trackian lowland

Groundwater has been sampled in Quaternary and Pliocene sediments. During 1997, 20.1% of all groundwater pesticides analyses exceeded the ecological value. The exceedings were detected for all the analysed pesticides. Aldrin was above 0.01 ug/l in 50% of all groundwater samples. For alpha-HCH, a.m. percentage was 31.3%, for heptachlor recorded 25%. DDX isomers were above 0.01 ug/l in a part of the investigated hydrogeological points.

During 1998, the investigations have shown values above the ecological value for 15.97% of analyses. The most frequent exceedings were for DDX: pp'-DDT in 53.6% of the all the hydrogeological monitoring points; pp'-DDE in 57.1%; gamma-HCH in 21.4%, HCB in 21.4%; and cis-heptachlor-epoxyd in 14.3%. The results for heptachlor and cis-heptachlor-epoxyd are shown in Figure 7.

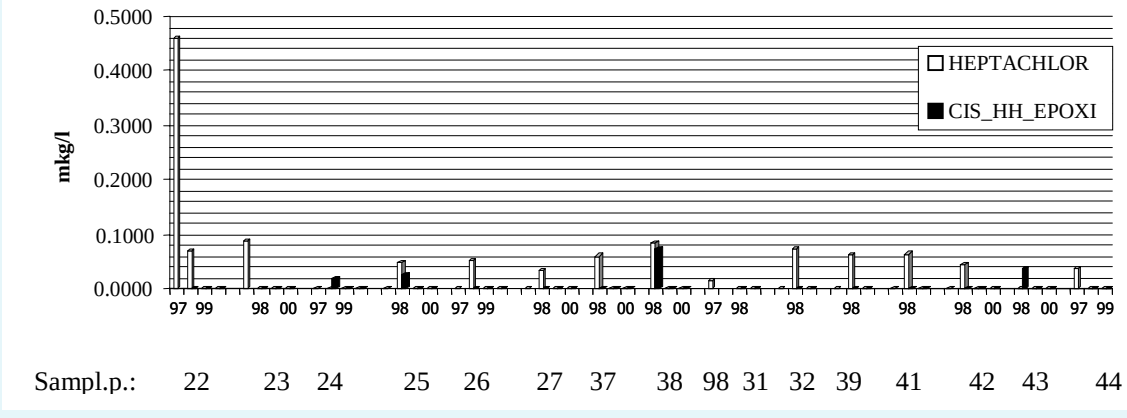


Figure 7. Contents of heptachlor and cis_hh_ep. in groundwater in Trackian lowland

The results from 1999 showed a trend of improvement of the groundwater quality. For only 2.94% of groundwater pesticides analyses, the ecological value was exceeded where pp'-DDT was above 0.01 ug/l in 38.5% of the investigated hydrogeological points. During the spring of 2000, no exceedings have been found.

In order to establish a relation with soil data, 65 soil samples, which have been sampled in the regions where also groundwater is sampled, have been used. DDX (sum) was measured above MAC (1.5 mg/kg) in 74% of all soil samples (for the period 1997-1999). These percentages were respectively, 72% for op'pp'-DDT; 49% for op'pp'-DDD; 74% for op'pp'-DDE (MAC - 0.5 mg/kg) and 24.6% for HCH (sum) (MAC - 0.01 mg/kg). A few higher values have been found for HCB, heptachlor, cis-heptachlor-epoxyd, aldrin, dieldrin, endrin, and metoxychlor.

Regions of the Sliven-Straldza valley, Yambol and Bourgas areas

The investigated sampling sites included drained Quaternary, Neogene, Paleogene and Upper Cretaceous aquifers. During 1998, 5% of the groundwater pesticides analyses exceeded the ecological value. Atrazine and propazine were detected above 0.1 ug/l in Quaternary (P-56) and Neogene (P-55). At P-55, pp'-DDD and pp'-DDE were detected above 0.01 ug/l while, pp'-DDE was detected above the ecological value at P-50, when sampled at springtime (Upper Cretaceous).

During 1999, 1.3% of analyses showed pesticides levels above 0.01 ug/l. Atrazine was determined at P-55 and P-102 (Paleogene aquifer) at level of 0.018 ug/l. During the spring of 2000, DDX (sum) recorded 0.016 ug/l and atrazine showed 0.01 ug/l at P-55. For the establishment of a relation with soil data, 27 soil samples have been used in regions where groundwater was sampled. DDX (sum) was found above the MAC (1.5 mg/kg) in 66.7% of all soil samples (for the period 1997 -1999). These percentages are respectively 55.6% for op'pp'-DDT; 37% op'pp'-DDD; 70% op'pp'-DDE (MAC - 0.5 mg/kg). Single higher values were detected for each of dieldrine and cis-heptachlor-epoxide.

Central Rhodopian massif

During 1999, samples have been taken at 2 springs from Precambrian marbles and did not show any contamination.

Summary of results from the investigations

- All the sampling points represent pesticide contamination in groundwater of agricultural areas. Only 5 groundwater monitoring points were in the vicinity of pesticides stores.
- For the period from 1997 to 2000, a positive trend showing the first improvement of groundwater quality was shown. This trend has to be verified during the further monitoring program in the coming years. Certainly will, the measures and control that have been undertaken by MoEW and other responsible authorities have contributed considerably to the positive trend.
- In none of the groundwater analyses in spring 2000, the EC standard of 0,1 ug/l was exceeded. Only single values above the ecological value were detected for simazine, propazine, op-DDT, op-DDD, DDE; for atrazine 38,9% exceeding has been detected. It could be attributed to the natural attenuation by high groundwater levels.
- The attempt to correlate the groundwater pesticides data with concentrations of the pesticides in the soils showed similarity of the results. In some cases, the groundwater investigations have been initiated due to high pesticides concentration in the soils such as area IVa.
- In spite of the fact that Bulgaria banned the application of DDT, aldrin, dieldrin, endrin, heptachlor, chlordane, alpha-, beta-, gamma-HCH etc., at certain locations, concentrations have been found above the ecological value for groundwater.
- When pesticide exceedings were detected in certain aquifers, we try to verify the results by increasing the number of groundwater monitoring points at that aquifer in order to find the source of pollution. For example in area IV b in the Quaternary drift aquifer, the results from P-21 and P-113 during the spring of 2000 confirmed the availability of DDX above the ecological value, which was also detected in 1999 at P-21.
- The executed measurements give information on where local high pesticides concentrations in agricultural areas and in the vicinity of pesticides stores can be found.
- The groundwater pesticides investigations showed that in some cases where local high pesticide concentrations were detected, that drinking water aquifers as shown in the following examples are threatened:

  - Quaternary drift aquifer in area IVb - P-21 is a pumping station for drinking water supply (PSDS). pp'-DDE and metoxychlor were detected above 0.1ug/l.

  - Quaternary and Neogene aquifers in area I - Northwest Bulgaria - P-6 (PSDS), in 1997 metoxychlor - 0.152 ug/l, in 1998, - atrazine - 0.313 ug/l and pp'-DDE - 0.164 ug/l were detected. . At P-61 (PSDS), in 1997, metoxychlor and pp'-DDE were detected above 0.1 ug/l.

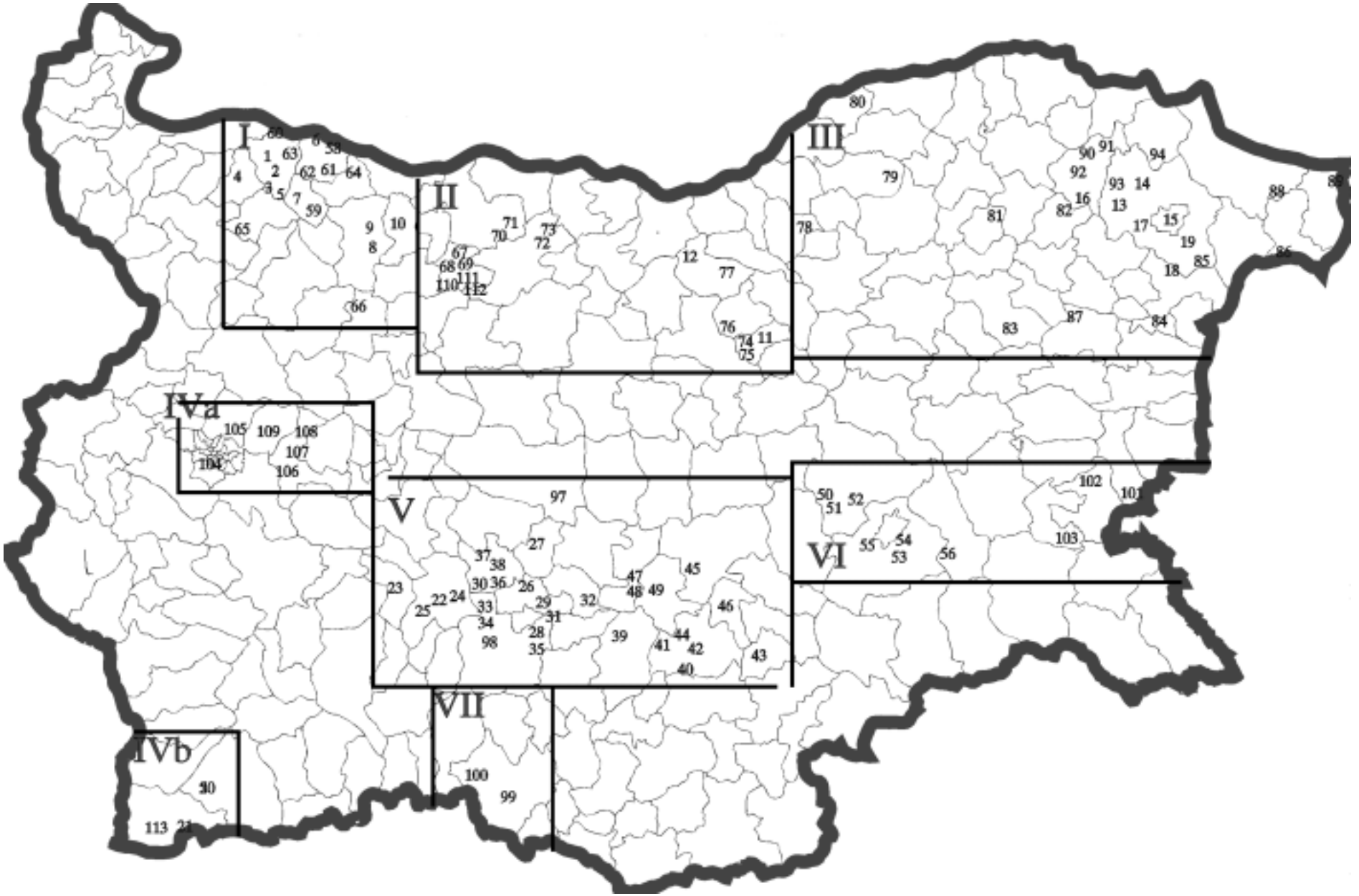
  - Quaternary and Pliocene aquifers in area V - Trackian lowland. In 1998, at P-32 and P-34 (PSDS), pp'-DDT has been found above 0.1 ug/l and heptachlor was detected at P-22 (PSDS) at levels of 0.461 ug/l in 1997 and 0.0682 ug/l during 1998.

Recommendations for future investigations

1. Connect data for pesticides applications in agricultural areas with type of pesticides, which are going to be investigated in groundwater also as a tool for future groundwater pollution predictions.
2. Verify the results of high pesticides concentrations in groundwater and define the extent of the pesticides contamination, by increasing of a number of investigated points in the same aquifer and by sampling of the same monitoring points in the next month.
3. Increase the number of analysed pesticides. For example - phenoxyacetic acids - 2,4-D, 2,4,5-T, MCPA, which are applied in our country; Also the metabolites of the various pesticides such as desethylatrazine, desisopropylatrazine etc., have to be investigated.
4. Develop tracers or main indicator for pesticides, which could be representative for groups of pesticides, as the number of pesticides is huge and the costs for the analyses could be reduced considerably
5. Sample groundwater for pesticides investigation twice a year, in such manner that it takes into account the time when the pesticides are applied.
6. Undertake groundwater investigations around some obsolete pesticides stores, especially there where the buildings are not in a good condition.
7. Make a risk assessment for groundwater contamination. All physicochemical properties of the particular substances, their transport behaviour in underground, soils, unsaturated zones, and aquifers have to be considered. Further, the retardation factors, sorption, degradation processes, biodegradation should be the basis for groundwater models to be applied at contaminated areas.

Bulgaria is a country with a well-developed agriculture and it is important to continue and extent the groundwater investigations for pesticides contamination. The investigations are an important tool to verify threats as has been shown above and to take the appropriate measures in order to protect humans and environment.

Appendix 1. Groundwater sampling sites for pesticides content



Appendix 2.

Regulation N-1 (7 July 2000)

for research, use and protection of groundwater

Annex 3 - Recommended parameters for groundwater protection from contamination

Parameter	Units	Ecological values	Contamination values
1. Metals			
.....			
2. Other inorganic substances			
.....			
3. Radionuclides			
.....			
4. BTEX			
.....			
5. PAHs			
.....			
6. Chlorinated Hydrocarbons			
.....			
7. Pesticides			
79. Aldrin	ug/l	0.01	0.1
80. Atrazine	ug/l	0.01	0.5
81. DDT/DDD/DDE(8)	ug/l	0.01	0.1
82. Dieldrin	ug/l	0.01	0.1
83. Drins (9)	ug/l	0.01	0.1
84. Endosulphan	ug/l	0.01	0.2
85. Endrin	ug/l	0.01	0.1
86. Carbaryl (1-naphtalenilmetilcarbamat)	g/l	0.01	0.5
87. Carbofuran (2,3-di-hydro-2,2-dimetil-7-benzofuranilmetilcarbamat)	ug/l	0.01	0.5
88. Maneb (manganese- ethylene-byo-di-tiocarbamat)	ug/l	0.01	0.5
89. Methoxychlor	ug/l	0.01	20
90. HCH-compounds (10)	ug/l	0.01	1
91. Propazine	ug/l	0.01	0.5
92. Simazine	ug/l	0.01	0.5
93. Heptachlor	ug/l	0.01	0.2
94. Chlordane	ug/l	0.01	0.2
8. Other organic compounds			
...			

Notes to Annex 3:

...

(8) Sum of the three compounds

(9) Sum of aldrin, dieldrin and endrin

(10) Sum of alpha-HCH, beta-HCH, gamma-HCH and delta-HCH