Effect of the waste products storage on the environmental pollution by toxic organic compounds

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Vplyv odpadových produktov na znečistenie životného prostredia toxickými organickými zlúčeninami

A permanent deposition of industrial wastes is a method of its neutralization. A storage yard for toxic materials must meet specific site and construction conditions. The storage place region of toxic organic waste materials has to be monitored. The environmental impact of this waste on the groundwater quality, especially the migration of persistent organic pollutants, was discussed on the example of a chemical plant.

Key words*: chemical waste, pesticides, environmental pollution, groundwater monitoring*

Introduction

A common method of the managing of waste materials, including the hazardous and toxic ones, is their controlled storage – mostly on surface but also underground (Jasiński, 2003; Macuda, 1997; Lewkiewicz-Małysa, 1988; Stępniak, 2002; Wołkowicz, 2000). To eliminate or at least minimize their environmental impact, definite storing conditions have to be met, including the remediation of the area (Janigacz, 2001; Kazimierski, 2000; Kowal, 1999; Tyrała, 2000). The chemical industry produces wastes which in most cases are dangerous and of different degree of environmental hazard. In 2003 above 4,5 Mt of such waste was produced in Poland, and almost half of it was neutralized by a storing method, used for managing of about 114 Mt of waste (Statistical Yearbook of Poland, 2004).

The highest risk waste contains the so-called persistent organic pollutants (POP) with the chlorine products of aromatic hydrocarbons playing the most important role. A variety of pesticides that are synthesized to fight pests belong to this group. They are toxic by nature. Owing to the fact that they are slowly biodegraded by the soil microorganisms, they stay in the environment for a quite long time (Bączkowski, 1998, Bodzek, 1999, Gałuszka, 2000, Migaszewski, 1999, Testard, 1996).

The ultimate criterion of evaluation of a good storing place are the positive environmental monitoring results (Guz, 2003, Hordejuk, 2000). Generally, in 1997–2003, the state of the lowest quality water in Poland was observed to improve slightly. However, almost 20% of the groundwater samples meet the standards for the poorest quality water (Statistical Yearbook of Poland, 2004).

Environmental characteristics of chemical waste storages

The evaluation of the state of environment in which the chemical waste is disposed was made on the example of a chemical plant "Organika". This plant has been continuously operational since 1918. The production line changeding several times during these years. Throughout decades, a number of products or intermediate products have been made, e.g. artificial fertalizers and organic products, especially a variety of pesticides. This company produced or used such substrates throughout its history as DDT ((1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane)), HCH (mixed isomers of 1,2,3,4,5,6-hexachlorocycloheksane), mainly Lindane (γ-HCH), Fenitrothion ((O,O-dimethyl-O-(3-methyl-4-nitrophenyl)phosphorotioate)), Dichlorvos (2,2-dichlorovinyl dimethyl phosphate), Methoxychlor ((1,1,1-trichloro-2,2-bis(4-methoxyphenyl)kethane)), Tetradifon (4-chlorophenyl 2,4,5-trichlorophenyl sulphone), Chlorfenvinphos ((2-chloro-1-(2,4-dichlorophenyl)-vinyl-diethyl phosphate)) and Atrazine (2-chloro-4-ethylamino -6-isopropylamino-1,3,5-triazine).

The post-production waste has been gathered in a central storing place for years. The storing place is adjacent to the plant premises, covering an area of about 10 ha. The storing place is located in the stream basin mainly of quaternary sediments, in the form of sands of varying grain-size, 2.3 to 16.8 m of thickness. These permeable beds are connected with two principal water-bearing horizons, belonging to the main carboniferous groundwater reservoir, which are of fracture-porous type. The quaternary waters flow

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to the west, towards the stream. The sandstone strata are underlied by clay or silt beds of varying thickness, ranging from 0 to 24.7 m (Technical Documentation, 1998).

The storing place is made up of seven objects I – VII. The oldest ones (I and VII) were reclaimed and now are a recovered. Presently the waste is safely disposed in the reinforced concrete objects III and IV. The remaining are gradually subjected to reclamation works. The whole place is drained with troughs and closely monitored. The localization and documentation scheme of the central storing place is presented in Fig. 1.

The total amount of stored waste is assessed to be over 150 000 ton, and over a half of it make hazardous organic and inorganic substances. Individual objects II – VI may have different environmental impact, both quantitative and qualitative, if a contamination would occur (Table 1). Potentially most dangerous are old inactive objects, (e.g. II).

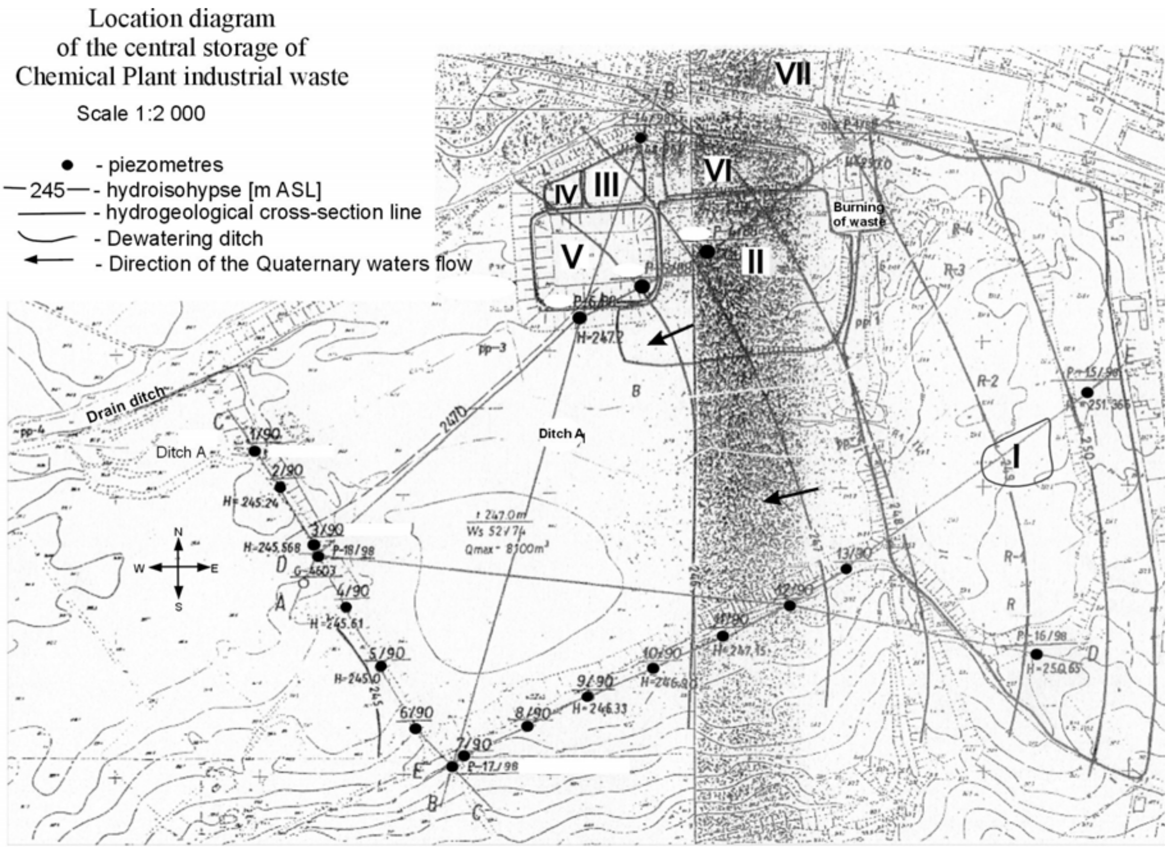


Fig. 1. Location diagram of the central storage of the chemical plant industrial waste

Tab. 1. Total ballast of the operative objects II – VI collected industrial waste

Object	Kind of waste – % ratio:		
	hazardous waste	neutral waste	hazardous waste in total ballast of object
II	84,36	24,25	77,67
III	0,29	1,39	17,26
IV	0,00	1,68	0,00
V	3,30	72,68	4,34
VI	12,05	0,00	100
	100	100	

Owing to the degree of noxiousness of the stored waste, both in the past and nowadays, a suitable security and prevention measures are applied. Seepages from the storing place are directed to the treatment plant, and the efficiency of the applied protection is checked out through the groundwater monitoring. Filled landfills are reclaimed. The plant has its waste treatment department and a modernized waste combustion furnace, which increases the efficiency of pesticides removal and the degree to which the waste gases can be cleaned. The global production of hazardous substances is reduced. For the needs of environmental monitoring, encompassing both hydrogeological properties of the area and the degree of contamination of the infiltrating waters, a dozen of observations were drilled.

Methods of the environmental research and its results

Researches are concentrated on the infiltration of groundwaters in the chemical waste storing area, especially their contamination by organic pollutants made on the basis of chemical and 5-day biochemical oxygen demand (COD and BOD_5) and the pesticides concentration. Water samples came from piezometric wells P-1 ÷ P-18. The distribution of piezometres with respect to the storing place objects is presented in Fig. 1, and their basic technical data are listed in Tab. 2. The piezometer P-14 was situated directly in the storing place, beside the object III in the north; the remaining piezometres were localized in congruence with the direction of the flow of groundwaters. The analysis was made of the results of long term chemical researches continued by the year 2003. The use of piezometres was sometimes limited due to break-downs.

Tab. 2. Basic characteristics of piezometres located in the region of the quaternary water-bearing stage

Object number	Technical data of piezometres:		Object number	Technical data of piezometres:	
	depth [m]	water level depth [m]		depth [m]	water level depth [m]
P-1	9,35	4,55	P-10	9,20	7,55
P-2	9,45	3,30	P-11	9,20	7,05
P-3	9,05	3,35	P-12	9,20	5,70
P-4	9,45	4,75	P-13	9,20	6,50
P-5	9,45	6,25	P-14	15,00	5,00
P-6	9,45	8,86	P-15	15,50	5,30
P-7	9,20	without water	P-16	20,00	9,10
P-8	9,20	8,60	P-17	15,50	without water
P-9	9,20	7,35	P-18	15,00	5,60

The COD and monitored organic substances data for piezometres P-2, P-4, P-5, P-9, P-13 and P-14 are presented in the paper. A full list of analysed components and their concentrations, in which they occurred in individual measuring points, are presented in Tab. 3.

Tab. 3. Results of the underground waters monitoring in the region of the organic industrial waste storage

Organic compound analysed	Range of the toxic organic compounds concentrations for specified piezometres					
	P-2	**P-4**	**P-5**	**P-9**	**P-13**	**P-14**
	mg/dm^3					
COD	29 – 450	2,0 – 853	5,0 – 345	0,0 – 200	4 – 112	23 – 77
BOD_5	0,0 – 33,1	3,5 – 33,8	0,0 – 15,3	0,0 – 21,1	0,0 – 28,2	–
Phenol	0,004 – 0,156	0,004 – 0,46	0,004 – 0,284	0,00 – 0,064	0,00 – 0,068	0,036 – 0,296
Pesticides	µg/dm^3					
DDT	0,0 – 3,6	0,0 – 6,9	0,0 – 2,4	0,0 – 2,6	0,0 – 5,8	0,0 – 5,4
HCH (and isomeries)	0,0 – 14,5	0,0 – 25,0	0,0 – 13,1	0,0 – 6,3	0,0 – 14,1	2,4 – 65,9
Methoxychlor	0,0 – 180,0	0,0 – 31,0	0,0 – 28,0	0,0 – 43,0	0,0 – 20,0	0,0 – 5,0
Chlorfenvinphos	0,0 – 27,2	0,0 – 24,0	0,0 – 69,0	0,0 – 25,0	0,0 – 16,7	4,7 – 56,4
Fenitrothion	0,0 – 25,2	0,0 – 29,1	0,0 – 26,5	0,0 – 23,2	0,0 – 20,0	0,0 – 4,6
Dichlorvos	0,0 – 17,8	0,8 – 7,9	1,2 – 7,1	0,0 – 2,5	0,0	0,0 – 138,8
Atrazine	9,1 – 11,3	4,2 – 20,2	4,2 – 19,5	0,0	0,0	3,2 – 23,0
Tetradifon	0,0 – 2,3	0,3 – 2,0	0,2 – 0,5	0,0 – 0,9	0,0 – 0,5	0,6 – 7,0

The mean annual BOD_5 values and contamination of indexes of selected pesticides throughout the years are graphically exemplified by specific piezometres, see Figs. 2 to 6.

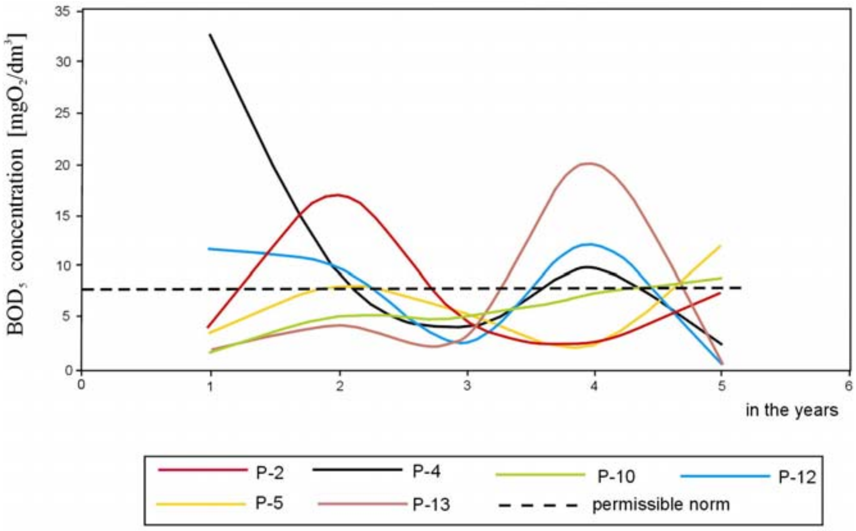


Fig. 2. Average concentrations changes of BOD_5 in the ungerground waters over the years

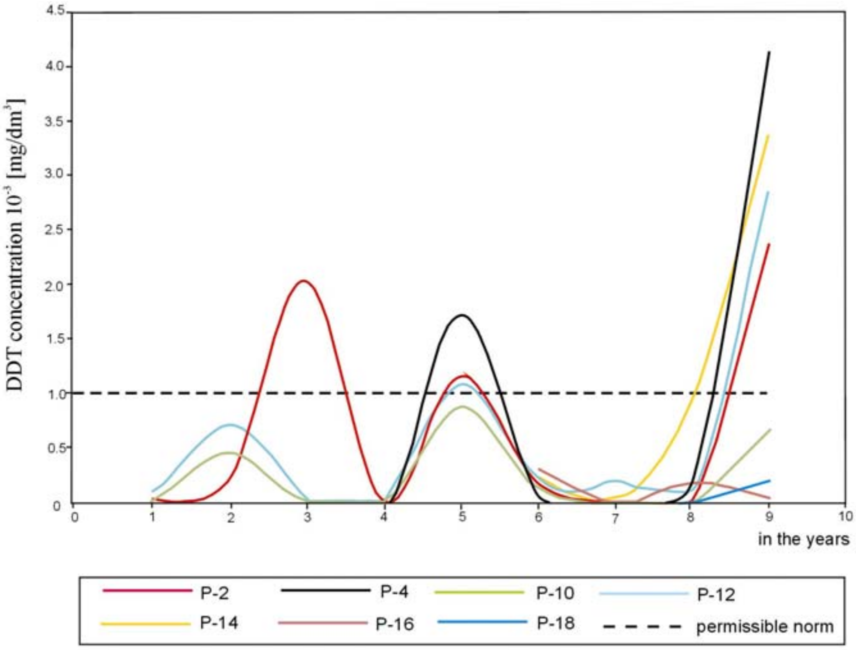


Fig. 3. Average concentrations changes of DDT in the underghround waters over the years

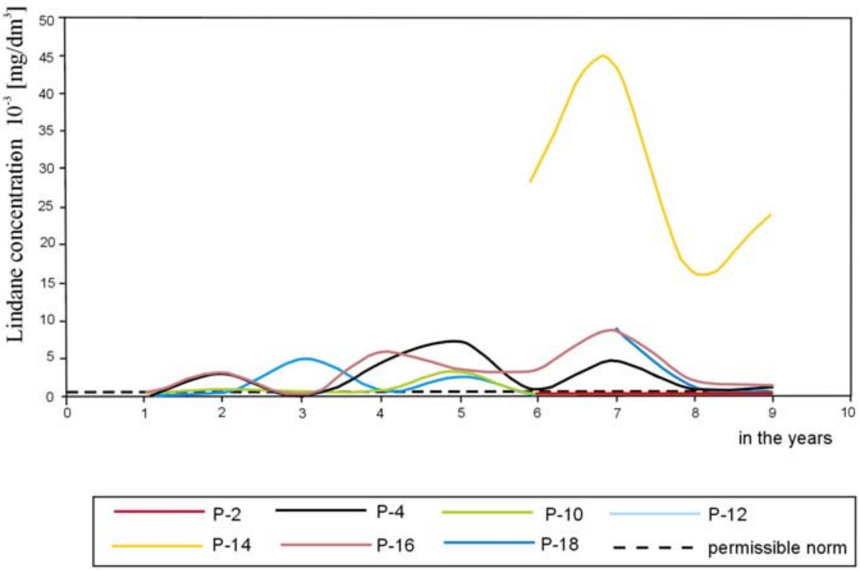


Fig. 4. Average concentrations changes of Lindane in the undergroundwaters over the years

Fig. 5. Average concentrations changes of Clorfen vinphos in the undreground waters over the years

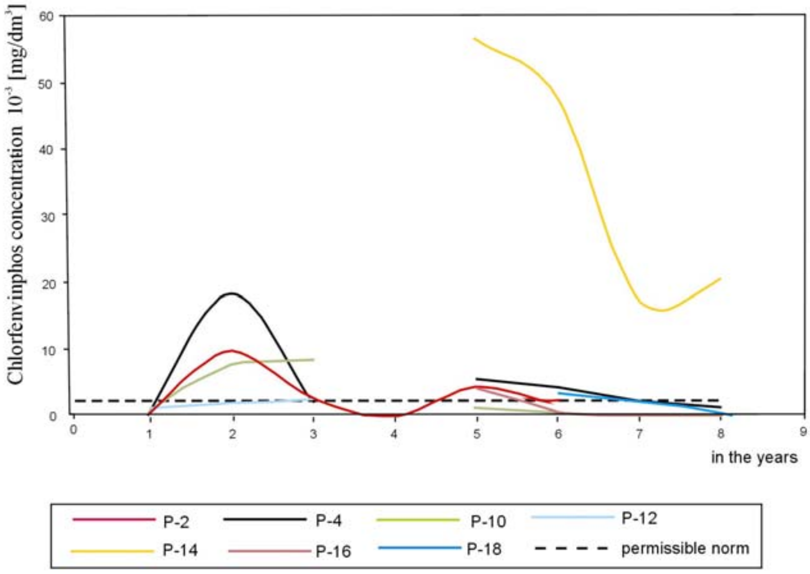
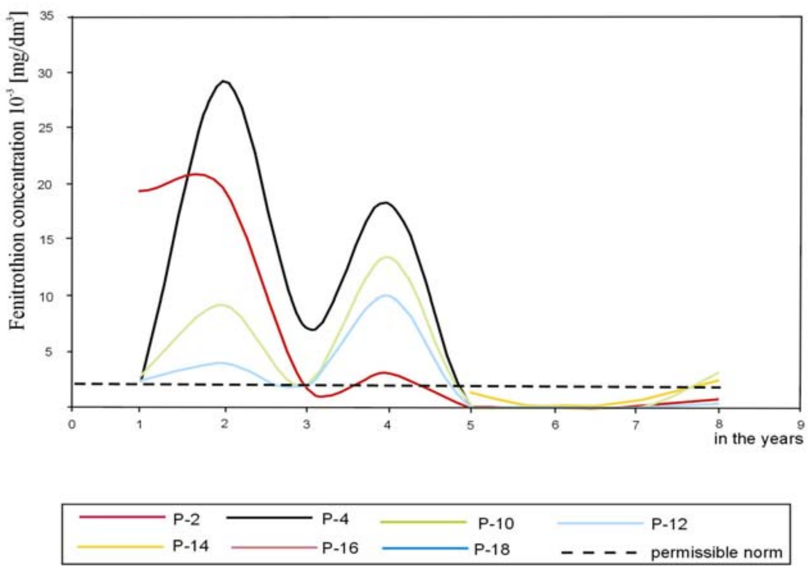


Fig. 6. Average concentrations changes of Fenitrothion in the undreground waters over the years



Discussion of environmental research results

The Chemical Plant has disposed of about 150 000 ton wastes over years. Most of them are hazardous. Their toxicity is caused by the presence of inorganic [Lewkiewicz-Małysa 2004] and organic substances, pesticides including. The environmental pollution can be also caused by the old, non-operational object II. The influence of chemical waste storing place has been assessed on the basis of long term analyses of water samples taken from piezometric wells.

Based on selected piezometres P-2, P-4, P-5, P-9, P-13 and P-14, a long-term evaluation of groundwater was made (Tab. 3). The assessment was based on the presence and concentration of organic components characteristic of the plant production profile. The total organic matter content was characterized by two indexes COD and BOD_5. A detailed analysis was made for pesticides, including these from the former production, due to their long half live (DDT – 8 years). A special emphasis was put on the production of the plant throughout its whole history. The obtained results were compared with the indexes determining groundwater quality for the classes I to V, in line with the newest classification of underground and an superficial waters state [Regulation of the Minister of Environment in Poland, 2004].

All selected toxic components were found in groundwaters (Tab. 3). Their concentration changed over the years within a wide range from occasionally minimal (even for the water quality class I) to the values typical of the class V. The presence of organic substances in groundwaters can be directly inferred on the basis of an increased COD values to 853 mgO_2/dm^3, and BOD_5 to 33,8 mgO_2/dm^3. The comparison of these values shows that organic compounds present in groundwaters are hardly biodegradable. They do not appear in the characteristics of the analysed water, nonetheless surface waters having a similar characteristic are classified as the quality group V (boundary value COD is above > 60 mgO_2/dm^3).

Therefore, regardless of the COD values, the potential presence of phenol and definite pesticides in groundwaters was analysed. The highest concentrations were within a wide range. For DDT: 2,4 to 6,9 $\mu g/dm^3$, HCH: 6,3 to 65,9 , Methoxychlor: 5 to 180, Chlorfenvinphos: 24 to 69, Fenitrothion: 4,6 to 29,1, Dichlorvos: 2,48 to 138,8, Atrazine: 11,3 to 23,0, Tetradifon: 0,5 to 7,0 $\mu g/dm^3$. According to the ordinance (Regulation of the Minister of Environment in Poland, 2004), no detailed specification of pesticides is required but owing to the specific character of the production of the plant, this measurement has to be done. It can be concluded from the analysis of the values of HCH and its isomers (6,3 to 65,9 $\mu g/dm^3$) and the presented qualitative and quantitative characteristics that the analysed water can represent the lowest class V. This can be true because one of the analysed components is Lindane, and its boundary concentration value for this class is > 5 $\mu g/dm^3$ (in the form of a sum of Dieldrin). The presence of phenols was also observed (to 0,46 mg/dm^3) and this was typical for waters of class V (the boundary concentration for phenols is > 0,05 mg/dm^3).

Based on the specific piezometres, which were operational throughout the successive years without any failure, a possible variant of the contamination expansion in the same hydrogeological conditions was presented. The evaluation was based on the average annual values of BOD_5 and the selected indices of pollution by pesticides. The obtained results were compared with the water quality standards (class I, II and III) for the sake of environmental monitoring (Methodical directions by PIOŚ, 1995¨). It has been stated that the BOD_5 values (Fig. 2) are within the range from 0,4 to 33,8 mg O_2/dm^3, and the admissible concentration for the water quality class I (8,0 mgO_2/dm^3) was exceeded many times. Over long spans of time the contamination of Quaternary waters with organic substances is constant. This evidences the spreading dynamism of organic substances in the past. Recently the BOD_5 values tended to be low, a lower share of biodegradable organic substances.

It has been stated from the behaviour of selected pesticides showing (DDT, Lindane (γ-HCH), Chlorfenvinphos oraz Fenitrothion) (Figs. 3 to 6) that they penetrate groundwaters. Over years their concentrations exceeded many times as compared to the standards for the water representing the quality class I, and which have not been anthropogenically affected. About the year 2000 the groundwater quality was generally observed to have improved. Unfortunately, this favourable trend was not continual and the DDT concentration significantly increases. (Fig. 3). As to the remaining pesticides, the contamination level was observed to rapidly increase in local measuring points.

Conclusions

The analysis of results of long term researches of the groundwater migrating in the vicinity of chemical organic waste storing places indicate that the disposals of substances are environmentally hazardous. Generally, the analysed waters belong to the poor quality class V, what is an evidence of a growing anthropogenic impact.

The migration of organic contamination is a dynamic process, as the type and the direction of the propagation are concerned. The concentration of hazardous components vastly changed. Sometimes even standards for the water quality class I were met. Problems are encountered not only with respect to the presently exploited and well-protected objects III and IV but also the past ones, which have been reclaimed. A constant environmental monitoring of groundwater is necessary for the improving the water ecosystems state at present and for the future.

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