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GRAVEYARD – POINT SOURCE POLLUTION OF NATURAL WATER BY PESTICIDES

MOGILNIK – PUNKTOWE ŹRÓDŁO ZANIECZYSZCZENIA WÓD NATURALNYCH PESTYCYDAMI

Abstract: The objective of the paper is to evaluate the state of water and soil in the vicinity of the pesticide graveyard in Folwarki Tylwickie and to present a study on the possibility of reducing the migration of pesticides from deposited wastes by using waste sorption agents. Water samples from bored wells, dug wells, piezometers, and soil samples from the vicinity of the graveyard were examined. About 47 biologically active pesticide substances were chosen for monitoring.

In the examined water and soil, among the identified pesticides, dominated the most durable chloroorganic insecticides and their metabolites. Stabilized sewage sludge from a dairy wastewater plant after compost stabilization was used as sorbent. The use of Freundlich's, Langmuir's and BET's isotherms proved that sewage sludge compost has sufficient sorption properties in relation to chloroorganic insecticides. Due to the properties they can be used to construct a sorption shield around the graveyards. In the future, this would allow to apply a sorption screen around the pesticide burial area which reduces pesticide migration into the environment.

Keywords: pesticide graveyard, heavy metals, pesticide, soil, water, sorption isotherm

Pesticides, as toxic compounds, are cancerogenic, teratogenic, embryotoxic and mutagenic. They are detected in all environmental compartments: atmosphere, hydrosphere, geosphere, flora, fauna, and of course, man. Outdated or not used pesticides become very dangerous wastes, that when inappropriately stored, penetrate into the natural environment making a threat for all life forms [1–7]. The past left tens of thousands tons of accumulated pesticide wastes that have been storing continuously since 1950's. Those reserves grew, among others in 1970's when, due to ecological and toxicological reasons, many of these means were withdrawn from the market and agricultural application. Also wrong management, distribution and uncontrolled import of plant protection means have contributed. Part of means was remained at the stores, another part was placed in graveyard buildings which were started in 1970's in a form

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of wells of 3–4 meter deep made of concrete circles of 1–3 meter diameter or built as brick constructions that were buried with 0.5 m thickness soil layer after filling [1, 2].

Previous designing procedures did not take into account the long-term effects of the graveyard exploitation. Neither hydrological conditions, land characteristics, nor environmental conditions were taken into account, and no geological investigations were performed at localizing these objects, which resulted in their building on geological forms with great permeability and sometimes even on water-carrying layers. Supervision made by Sanitary and Epidemiological Stations revealed that 1/3 of graveyards did not meet localization conditions. They were closer than 300 m from water intake points, water reservoirs and agricultural areas. At least 75 graveyards were situated near rivers and lakes, 100 were near drinking water intakes and about 140 of them near residential areas. Among 16 pesticide stores in Podlasie province, 7 of them are localized within Upper Narew river area, and the remaining at the direct neighborhood of other surface flows. Chambers of majority of graveyards are leaky, which is proved by soil and water analyses due to supervisions [1, 6, 7]. There is also possibility to worsen the construction condition along with the occurrence of corroding the concrete bunkers and wells, the outdated pesticides are deposited, and in consequence, a toxic leakage. The leakage can be transported by underground water and then in a form of so-called underground inflow, it is caught by a network of surface waters. Accumulation of outdated pesticides, even after removal, will be a potential source of a threat and natural environment pollution for many years. Accumulation of toxic substances at one place along with confirmed pesticide emission into the underground water make a serious hazard for people. A graveyard contains a variety of substances that reacting to one another can produce often more toxic and mutagenic compounds than the substrates. Although local penetration of poisons into the water or ground may have no direct and significant effects on inhabitants, short filtration way (often through light, permeable and with low sorption capacity soils) makes a great threat for quality of surface water that transports toxins to a considerable distance. Mean flow rate of underground water near the graveyards in Podlasie province is about $80\text{--}100\text{ m} \cdot \text{yr}^{-1}$, which means that in the case of any constructional damage, a constant supply of pollution into the open waters will be happening for many years. Therefore, there is a necessity to search for the solutions to reduce the pesticide migration in an environment as well as to introduce new concepts. Thus, it seems to be purposeful to undertake studies upon application of sorption process using selected natural and waste adsorbents as a screen for pesticides in order to reduce their migration from other graveyards, stores and contaminated soils and concrete [8–13].

The present research was aimed at searching for a possibility to reduce the migration of deposited pesticide wastes by applying natural and waste sorption substances that would make a barrier for plant protection means against penetration to the hydrosphere. It would protect ground and surface waters that are often the source of drinking water for people and animals. In future, it would allow for applying the sorption screen around pesticide burial area, which reduces pesticide migration into the environment, and grown energetic plants – through phytoremediation – would prolong the sorbent vitality and remove pesticides accumulated in aboveground parts by means of combustion.

Material and methods

Experimental area

The size of pesticide migration disposed in graveyard was evaluated on selected objects localized in Podlasie province in Folwarki Tylwickie (53°00' 23°26'). It is an active graveyard consisted of three containers made of ferroconcrete well circles isolated with tar-board and cement (1.26, 1.8 and 1.8 m³ capacities). In total, 5000 kg of expired pesticides and 10 kg of chemicals from Sanitary Station are deposited. The dump was localized on fine and medium sands that have good filtration properties. All dangerous substances leaking from leaky tanks may easily migrate along with rainfalls. Burial ground is set at about 1.6 m depth, whereas underground water is at the level of 2 m. Surface water intake is situated at the distance of about 4.5 km, groundwater about 1 km (bored well 1000 m, dug well 800 m). River Malynka flows nearby (about 1.5 km). Graveyards are localized among brushwood directly in cultivated field, and near protected area and congested housing.

Materials

Determinations of natural water and soil qualities in that area and near the graveyard were carried out. Samples of natural water and soils around the burial ground were collected for analyses. Physicochemical parameters were determined in water samples taken from groundwater near graveyard (piezometers), dug wells (farm wells, bored wells) of surrounding farms, surface water and soil from 1 m depth layer. Analyses of soils, ground and surface waters were carried out in spring, summer and autumn (2006–2008) during rainfalls. Collected water and soil samples were analyzed for remains of pesticides from chloroorganic, phosphoorganic, pyrethroids, nitrophenols, triazines, and phenoxyacids groups being components of the most disposed chemicals. Moreover, heavy metals and other properties influencing on pesticide conversions were determined in water.

Table 1

The characteristic of compost

Sorbent	Properties						
Compost	Manurial [% in d.m.]						
	Ca	Mg	Total N	NH ₄ ⁺ -N	Total P	K	
	5.61	0.46	1.39	0.009	1.47	0.45	
Compost	Metal [mg · kg ⁻¹ d.m.]						
	Pb	Cu	Cd	Cr	Ni	Zn	Hg
	7.0	22.7	0.63	9.9	5.8	210	2.5
Compost	Other [%]						
	pH	Hydration		Dry mass		Organic matter	
	6.7	67.5		34.2		67.5	

On a basis of literature data and own studies, chloroorganic pesticides that most often occurred near the graveyards at the highest concentrations were selected as representative sorbats [1–7]. Individual pure active substances (HCH, DDE, and aldrin) were applied. Sewage sludge compost achieved directly from dairy treatment plant in Sokolka. The characteristic of the compost are given in Table 1.

Sorption procedure

Studies under static conditions were performed in accordance with methodology applied in Belgium, Germany, France, Italy, England, USA, and Poland [8–11, 13, 14]. They were aimed at plotting the adsorption isotherms due to which it is possible to compare the sorption capacities of different adsorbats on different adsorbents. Sorption experiments were carried out by adding a known mass of compost (0.001; 0.002; 0.005; 0.01; 0.025 g per 100 cm³ solution) to glass flasks filled with pesticides aqueous solution. Flasks were shaken in an isothermal water bath shaker at 130 rpm and 20 °C for 24 hours, and were left for 24 hrs in order to reach a sorption equilibrium. Freundlich's and Langmuir's isotherms [8–11, 13–16] were plotted on a base of achieved results applying Statistica software in order to analyze the processes.

Analytical procedure

Pesticide concentrations were determined in collected samples in accordance with an obligatory methodology using gas chromatograph coupled with mass spectrometer (GC/MS/MS 4000) as well as gas chromatograph AGILENT6890 equipped with ECD1 and NPD2 columns. Moreover, after sample digestion according to EPA 3015 procedure using microwave digester Mars 5, also metals concentrations were determined by means of ICP-AES technique, except of mercury determined by means of CV-AAS technique [17, 18].

Results and discussion

In total, 108 of water samples and 54 of soil samples were analyzed. Results are presented in Table 2. The analyses were carried out for 47 biologically active substances from different chemical groups: chloroorganic, phosphoroorganic, pyrethrins, triazines, and others (Table 2).

From the regional point of view, the graveyard is located on a slight morphological slope. Water level corresponds to the area surface. It is a couple of meters deep next to the graveyard. The direction of underground water flow is consistent with the terrain morphology.

Water flows from the graveyard in the direction of Malynka and Suprasl valley. Many toxic substances accumulated in one place and confirmed leaks of pesticides to underground waters pose a serious threat to the environment and local inhabitants. The largest amounts of biologically active substances remains (25.4 %) were found in soil samples. Presence of six of 16 studied chloroorganic compounds was determined. They

were the most stable and the least environmentally degradable agents. Achieved results of soil analyses indicate that large area is polluted with pesticides originating most probably from leaky chambers in the dump. Moreover, phosphoorganic compounds, pyrethrins and herbicides were found. Pesticide levels found are not very high, but their presence indicates the spreading of pollutants within the soil. The highest values were recorded for DDT ($0.927 \text{ mg} \cdot \text{kg}^{-1}$) and atrazine ($0.710 \text{ mg} \cdot \text{kg}^{-1}$) (Table 1). Wolkowicz [7], who studied water and soil near burial grounds achieved similar results in Mlynów, Wagów and Poznań as well as Stobiecki [6] and Morzycka [4] in Wasocz in Podlasie province.

Table 2

List of substances determined by gas chromatography in water and soil samples

Active substance	Method of detection	LD Soil	Conc. Soil	LD Water	Concentration				
					Farm wells	Bored wells	River	Piezometer	
					[mg · kg ⁻¹]		[mg · dm ⁻³]		
H	Atrazine	GC-NP	0.01	0.710	0.0001	0.0022		0.0032	
	Chlorpropham	GC-NP	0.01		0.0006	0.0025		0.0015	
	Dichlorprop	GC-EC	0.08		0.0038				
	Dinoseb	GC-NP	0.03		0.0015	0.0049		0.0040	
	DNOK	GC-NP	0.02		0.0010				
	MCPA	GC-EC	0.10		0.0020	0.0330		0.0025	
	Mecoprop	GC-EC	0.10		0.0033	0.0109		0.0161	
	Simazine	GC-NP	0.02		0.0001				
	2,4-D	GC-EC	0.02		0.0010				
	Trifluraline	GC-NP	0.001	0.016	0.0003				
IC	Carbaryl	GC-NP	0.50		0.0030				
	Carbofuran	GC-NP	0.050		0.0004				
	Pirimicarb	GC-NP	0.008	0.015	0.0001				
	Propoxur	GC-EP	0.050		0.0005	0.0002	not detected	0.0001	
OC	Chlorfenson	GC-EC	0.020		0.0002				
	p,p'-DDD	GC-EC	0.004		0.0002	0.0036			0.0020
	o,p'-DDT	GC-EC	0.001	0.927	0.0002	0.0025		0.0035	0.0030
	p,p'-DDE	GC-EC	0.0004	0.275	0.0001				0.0005
	p,p'-DDT	GC-EC	0.005	0.139	0.0002	0.0016		0.0010	0.0020
	Dieldrine	GC-EC	0.001		0.0010				0.0010
	DMDT	GC-EC	0.002		0.0010				
	Endrin	GC-EC	0.001	0.012	0.0010				0.0020
	α-β Endosulfan	GC-EC	0.007		0.0001				
	Endosulfan – sulfate	GC-NC	0.009		0.0001				
	HCB	GC-EC	0.002	0.056	0.0001				
	α-HCH	GC-EC	0.001		0.0001	0.0136			0.0010
	β-HCH	GC-EC	0.008		0.0002				0.0002

Table 2 contd.

Active substance	Method of detection	LD Soil	Conc. Soil	LD Water	Concentration			
					Farm wells	Bored wells	River	Piezometer
					[mg · kg ⁻¹]		[mg · dm ⁻³]	
γ-HCH	GC-EC	0.003	0.033	0.0001	0.0016	not detected	0.0018	0.0090
δ-HCH	GC-EC	0.004		0.0001	0.0217			0.0004
Methoxychlor	GC-EC	0.003		0.0001			0.0003	0.0002
OP	Bromfenvinfos	GC-EC	0.06		0.0004	not detected		
	Chlorfenvinfos	GC-EC	0.02		0.0003			
	Chlorpyrifos	GC-EC	0.05		0.0002			
	Chlorpyrifos – methyl	GC-EC	0.1		0.0002			
	Diazinon	GC-NP	0.08		0.0001			
	Dimethoate	GC-NP	0.01		0.001			
	Fenthion	GC-NP	0.01		0.0002			
	Fenitroton	GC-NP	0.01		0.0002			
	Heptenophos	GC-NP	0.02		0.0004			
	Izofenphos	GC-NP	0.01	0.045	0.0001			
	Methidation	GC-NP	0.01		0.0052			
	Parathion	GC-NP	0.01		0.0001			
	Thiometon	GC-NP	0.02		0.0001			0.0003
	Triazophos	GC-NP	0.01		0.0002		0.0008	
P	Cypermethrin	GC-EC	0.05		0.0004			
	Deltamethrin	GC-EC	0.02		0.0005			
	Fenprothrin	GC-EC	0.01		0.0003			

Explanations: H – herbicides, IC – carbamate insecticides, OC – organochlorine insecticides, OP – organophosphorus insecticides, P – pyrethrins, LD – limit of detection, Conc. – concentration.

It was discovered that in the burial grounds there were mixtures of various substances which were products of mutual changes, which gave new molecules of unknown toxic properties. The leak from the burial ground chambers is transported by underground waters and after several tens of meters it is intercepted by a network of surface waters. Average groundwater flow from the burial ground was approx. 80–100 m · yr⁻¹. Water from bored wells localized near burial grounds in land holding, from farm wells in Folwarki Tylwickie and from Malynka river was subjected to analysis for pesticides remains.

In the graveyard in Folwarki Tylwickie most stable chloroorganic insecticides and their metabolites were dominant. Very characteristic was the presence of isomer γ-HCH which is the least degradable of all HCH isomers. These are highly toxic compounds having long periods of half decomposition. Presence of 10.64 % among 47 studied active substances was recorded in water samples. Surface water sample from Malynka river – presence of MCP (25 μg · dm⁻³), MCPA (23.4 μg · dm⁻³), simazine (161 μg · dm⁻³) and water samples from dug wells were the most polluted. High level of

herbicide in river may be also explained by the surface runoff from fields after autumn agrotechnical operations. Studies of pesticide agents in water samples collected in bored wells did not confirm any of 47 analyzed pesticide. Instead, it confirmed the suggestion that graveyard caused the pollution of the first water bearing layer and surface water. Measurements of physicochemical parameters and heavy metals contents were determined in collected water samples (Table 3). In general, achieved results did not show the presence of elevated values and concentrations of those parameters (pH, conductivity, TOC), nor any heavy metal (in spite of Mn).

Table 3

List of metals determined in water samples

Parameter	Concentration in water		
	Farm wells	Bored wells	River
pH	7.94	7.28	7.88
Conductance [$\mu\text{S} \cdot \text{cm}^{-1}$]	527	477	596
TOC [$\text{mg} \cdot \text{dm}^{-3}$]	23.46	21.10	25.28
Metal [$\text{mg} \cdot \text{dm}^{-3}$]			
Al	0.02585	< 0.01	0.076
Cd	< 0.0005	< 0.0005	< 0.0005
Cr	< 0.002	< 0.002	< 0.002
Cu	< 0.002	< 0.002	< 0.002
Fe	0.2526	0.0381	0.0834
Hg	0.00018	0.00002	0.00025
Mn	0.32813	0.05487	0.0044
Ni	< 0.002	< 0.002	< 0.002
Pb	< 0.00027	< 0.00027	< 0.00027
Zn	0.11858	1.4257	< 0.020

Characteristics of applied sorbents (Table 1) indicate that both meet requirements of compost for natural applications. The adsorption process is described using Freundlich's, Langmuir's or BET's formulae:

$$\begin{aligned} \text{Freundlich} & \quad A = kc^{1/n} \\ \text{Langmuir} & \quad A = a_m kc / (1 + kc) \\ \text{BET} & \quad A = ac / (1 + c)(1 + kc) \end{aligned}$$

Following curves were achieved $A_F = 24378.4 c^{2.16}$ for compost at correlation coefficient of $R = 0.973$, $A_L = 951 c / (1 + 4.4508 c)$ at correlation coefficient of $R = 0.957$, and $A_{\text{BET}} = 1005c / (1 + c)(1 + 4.627c)$ at correlation coefficient of $R = 0.956$.

Constants k and $1/n$ were estimated by means of the least squares by Gauss-Newton and Levenberg-Marquardt method applying Statistica software, and then the errors for these constants were evaluated. Figure 1 present adsorption isotherms for studied pesticides on applied compost adsorbents as a function of adsorbate amount adsorbed by adsorbent weight unit (x/m) vs. adsorbate's balance concentration (c_0).

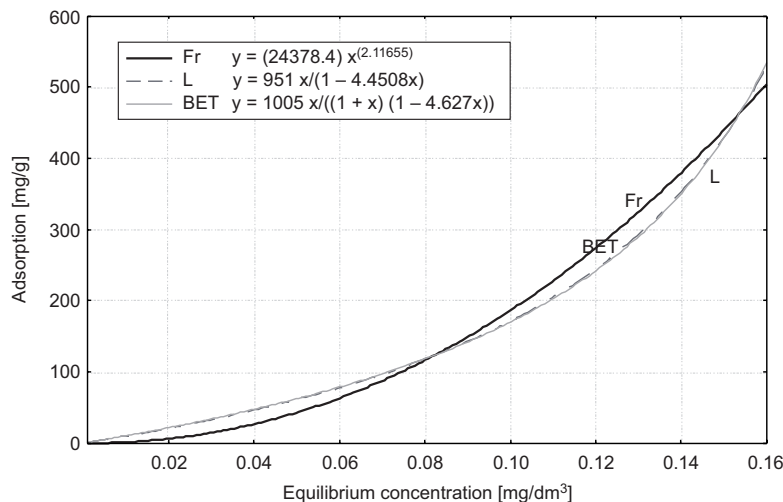


Fig. 1. Sorption isotherms of chloroorganic pesticides on compost

The same group of isotherms according to Giles' classification (S) was achieved for all pesticides [8, 10, 11, 16]. It includes isotherms for systems in which solvent is strongly adsorbed and is competitive for dissolved substance being adsorbed [16]. Isotherm's shape also proves the flat arrangement of adsorbate's molecule at adsorbent's active centers. The isotherms shape testifies also to the fact that the adsorbate particle may be placed vertically or at an angle in the active centre of the adsorbent [9, 16]. Figure 1 apparently shows that, for compost, Freundlich's isotherm does not approach monotonically to limit adsorption within the same balance concentrations range, and it can be predicted as over $500 \text{ mg} \cdot \text{g}^{-1}$.

Knowledge on $1/n$ parameter value in Freundlich's formula allows for assessing the adsorption intensity of a given substance from water phase on adsorbent; value of k constant determines the sorption capacity of an adsorbent at balance concentration in a solution. Higher k value corresponds to higher sorption capacity. In own studies, higher value of k coefficient was achieved for dairy sludge, which proves its usefulness in application as sorption screen around the pesticide graveyard. Constants $1/n$ in Freundlich's formula are directional coefficients of isotherms equal to the tangent of line inclination angle in logarithmic coordinates. Therefore, the higher $1/n$ value, the more intensive adsorption process. Also $1/n$ coefficient for the sludge is two times higher, which proves higher intensity of chloroorganic pesticides retain.

Conclusions

1. It was found pollution of natural water by chloroorganic, carbamate, triazine and phenoxyacetic pesticides and heavy metals.
2. River and dug wells were contaminated with pesticides which was caused by leaking from graveyards.

3. High concentration of herbicide (MCPA, MCPP and simazine) in natural water was caused both by graveyards leaching and surface flow from ploughed fields after agrochemical measures.

4. Sewage sludge compost proved to be the best natural sorbent for the process for migration reduction of chloroorganic pesticides from graveyards.

5. It is indispensable to analyze the Freundlich adsorption isotherm coefficients to get the optimum amount of the sorbent for pesticide detoxication.

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MOGILNIK – PUNKTOWE ŹRÓDŁO ZANIECZYSZCZENIA WÓD NATURALNYCH PESTYCYDAMI

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Abstrakt: W pracy przedstawiono wyniki badań wody i gleby z okolic mogilnika w Folwarkach Tylwických oraz możliwość ograniczenia migracji przeterminowanych pestycydów zdeponowanych w mogilnikach

poprzez zastosowanie odpadowych materiałów sorpcyjnych. Próbki wody ze studni wierconych, kopanych i z piezometrów oraz próbki gleby pobrane w okolicy mogilnika zbadano na obecność 47 biologicznie aktywnych substancji pestycydowych.

W badanych próbkach stwierdzono największe ilości insektycydów chloroorganicznych i ich metabolitów. Do ograniczenia migracji związków chloroorganicznych zastosowano sorbent odpadowy – ustabilizowany osad ściekowy poddany procesowi kompostowania. W celu określenia mechanizmu sorpcji zastosowano równania izotermy Freundlicha, Langmuira i BET. Na podstawie przeprowadzonych badań stwierdzono, że kompost z komunalnego osadu ściekowego może być zastosowany do budowy bariery wokół mogilnika, która ograniczy migrację pestycydów do środowiska.

Słowa kluczowe: mogilnik, metale ciężkie, pestycydy, gleba, woda, izotermy adsorpcji