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ASSESSMENT OF THE QUALITY OF THE ENVIRONMENT IN THE VICINITY OF A PESTICIDE BURIAL SITE*

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Abstract

Biologically active substances of plant pesticides deposited on pesticide burial sites can be a source of toxic substances threatening underground and surface waters and consequently drinking water. Mercury usually makes up about 0.7% of the total waste content, copper - 4.3%, zinc – 4%, and chloroorganic compounds – 29.9%. The aim of the work was to evaluate the quality of the environment in the vicinity of a pesticide burial site in Podlasie, Poland. The study was carried out in September-November 2009. The burial site comprised three containers consisting of concrete circles insulated with roofing paper and cement. Samples for determinations were collected from the immediate surroundings of the pesticide burial site. Soil samples were also taken from three holes made to the depth of 0.2-0.4 m and situated 15 m away from the burial site depth and from two sites under the concrete well (0.5 m and 1.0 m). Moreover, water samples from two piezometers and samples of plants growing up to 30 m distance (pine needles, grasses, mushrooms, birch and alder leaves and twigs, cabbage, and maize) were collected as well. Copper, mercury and zinc were determined in samples of waters, soils and plants. The metal content in soils corresponded to the natural levels; the concentrations in plant samples indicated no accumulation and the water samples were not determined to contain elevated concentrations of the above metals. It has been proven that the concrete wells were hermetic and the environment around the pesticide burial site has not been polluted.

Key words: dump, metals, pesticide, water, soil, plant.

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OKREŚLENIE JAKOŚCI ŚRODOWISKA NATURALNEGO W POBLIŻU MOGILNIKA PESTYCYDOWEGO

Abstrakt

Biologicznie aktywne substancje pestycydów składowanych w mogilnikach mogą być źródłem substancji toksycznych migrujących do wód podziemnych, powierzchniowych, a w konsekwencji do wody pitnej. W przeciętnym mogilniku ilość rtęci wynosi 0,7% masy wszystkich odpadów, miedzi 4,3%, cynku 4%, zaś związków chloroorganicznych 29,9%. Praca przedstawia jakość środowiska otaczającego mogilnik pestycydowy na Podlasiu. Badania prowadzono w okresie wrzesień-listopad 2009 roku. Mogilnik zbudowany jest z betonowych kręgów studziennych izolowanych lepikiem. Próbki do badań pobierano w bezpośrednim sąsiedztwie mogilnika. Próbki gleby pobierano z głębokości 0,2-0,4 m w odległości do 15 m od mogilnika, próbki gleby spod studni z głębokości 0,5 oraz 1,0 m pod dnem. Próbki wody pobierano z dwóch piezometrów, zaś roślin w promieniu 30 m od mogilnika (igły sosny, trawy, grzyby, dynie, brokuły). W próbkach wody, gleby i roślin oznaczono miedź, cynk i rtęć. Gleby cechują się naturalną zawartością tych pierwiastków, stężenia metali w próbkach roślinnych można określić jako akumulację małą, a rośliny jako nie zanieczyszczone, nie zanotowano także zwiększonej ilości pierwiastków śladowych w wodach podziemnych. Może to świadczyć, że ten mogilnik jest szczelny, a środowisko wokół niego nie jest zanieczyszczone.

Słowa kluczowe: mogilnik, metale ciężkie, pestycydy, woda, gleba, rośliny

INTRODUCTION

Dumps leaking to soil and water have been one of the most difficult problems to solve for years; they make an extreme hazard for people as well as the natural environment. Pesticides past the expiry date or unused, often containing heavy metals compounds, become very dangerous waste that, when inappropriately stored, penetrate the natural environment uncontrollably, which poses a serious threat to all life forms (BAGIŃSKA at al. 2008, BIZIUK 2001, CONESA et al. 2007). The Ministry of the Natural Environment Protection estimates that the total weight of pesticide waste in Poland could be as high as 60 000 tons. Recent supervision of the technical condition of p[esticide burial sites has revealed that the situation is the worst in eastern Poland. In total, there are 10 pesticide burial sites (including 5 liquidated ones) and 13 storage sites with pesticide waste in the Province of Białystok (IGNATOWICZ 2009). Previously binding design and construction procedures did not take into account effects of long-term exploitation of pesticide burial sites. Pesticide waste stored at former state farms is the most severe threat because of the disastrous technical condition of those burial stores. Besides, many burial sites are unsealed ground dumps. They are a source of toxins and poisons emitted into the natural environment: soil, water and air. The ground- and surface water, especially underground water reservoirs near dumps, is contaminated (IGNATOWICZ 2007).

On an average dumping site, mercury makes 0.7% of total waste, copper 4.3%, zinc 4%, and chloroorganic compounds 29.9% (BIZIUK 2001, IGNATOWICZ 2009). In the past, heavy metals were also a component of pesticides. Those compounds, as toxic ones by definition, are cancerogenic, teratogenic, embryotoxic and mutagenic. They are detected in all elements of the natural environment: atmosphere, hydrosphere, geosphere, flora, fauna, and even in human bodies. Water, soil and air near dumps are very rarely monitored, hence the present study comprised analyses of water, soil and plants samples collected near pesticide burial sites in order to find out whether pesticides past the expiry date and stored in leaky and corroded concrete containers could migrate into the environment. The paper presents results of analyses of environmental samples collected from near operating, unsealed and corroded concrete burials localized in Podlasi, performed in order to assess the risk of migration of heavy metals, which are pesticide components. It is an important issue because pesticides and some metals (Cd, Pb, Hg, Ni), as stated by the European Parliament Directive 2008/105/WE on environmental quality norms for water policies, are among priority substances. The aim of the research was to assess the quality of the environment in the vicinity of pesticide burial sites.

MATERIAL AND METHODS

The study was carried out from September to November 2009 near an operating pesticide burial site, which comprised three containers consisting of concrete circles insulated with roofing paper and cement (Figure 1). The estimated amount of stored waste (according to an inventory made in 2009 by the Regional Directorate for the Environmental Protection in Białystok) was 3.39 Mg. The burials were set on varied and medium-grain sands, which are highly permeable (the filtration coefficient k = 10^{-7} ms^{-1}). Any of the stored hazardous substance can easily migrate from leaky containers along with rainfall water. The burial is built at the level of about 1.6-3.0 m, while the groundwater lies 3.0-5.0 m deep. The burial site lies close to an arable cultivated field, 20 m away from crop plantations (maize, carrot, broccoli, cabbage) and 100 m from a fruit orchard.

Samples for determinations were collected from the immediate surroundings of the pesticide burial site (Figure 2). Soil samples from the depth of 0.2-0.4 m were gathered by making three holes (S8, S9, S10) at a 15-meter distance; additionally two samples under the concrete well (0.5 m and 1.0 m) were taken (St. 3). Moreover, water samples from two piezometers (S8, S9) and samples of plants growing up to 30 m away from the burial site (pine needles, grasses, mushrooms, birch and alder leaves and twigs, cabbage, and maize) were collected.

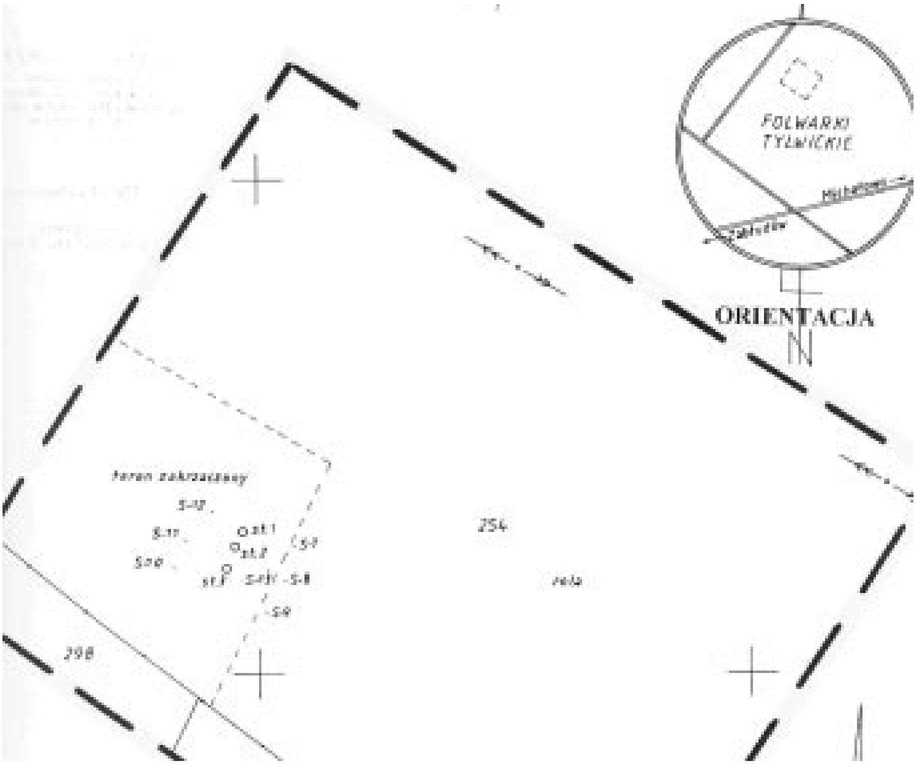

Fig. 1. Location of the pesticide burial site and the sampling points in Folwarki Tylwickie.
st 1, st 2, st 3 – three containers; S-7 - S-13 – sampling point

The analyzed metals included copper, mercury and zinc. Soil was mineralized using a microwave system Mars 5 according to the EPA 3015 and EPA 3051 procedures. Determinations of copper and zinc were made with the ICP-AES technique, while mercury was analyzed with the CV-AAS technique in an AMA-254 analyzer (SIEPAK 1995, SIEPAK et al. 2008).

Fig. 2. A view of the pesticide burial site in Folwarki Tylwickie

RESULTS AND DISCUSSION

The content of the heavy metals determined in the soil samples is presented in Table 1. The values ranged from 22.76 to 41.76 mg Cu kg^{-1} (mean 31.42), 23.94 to 39.53 mg Zn kg^{-1} (mean 31.59), and less than 0.0005 to 0.025 mg Hg kg^{-1} (0.009, on average). The content of available and extractable trace elements in soils did not exceed permissible values set in the Ordinance of the Minister for the Environment of 9.09.2002, and the soils were classified as group B soils. With respect to the Ordinance of the Minister for the Agriculture and Rural Development of 21.03.2002, the analyzed soils were light ones, i.e. containing up to 20% of the finest fraction. Comparing the determined concentrations of the heavy metals with the limit values given by KABATA-PENDIAS (1999), it can be concluded that the soils near the burial site did not contain elevated levels of these contaminants. Their amounts were described as natural for group A soils with the zero contamination level. These soils can be used for agricultural production. These findings may be explained by the fact that the examined pesticide burial site lies on light sandy soil, low in sorption capacity. Ion such soils, trace elements are more easily available. However, in general, most of trace elements are eluted from such soils and penetrate to the ground- and surface water. The determined concentrations of copper were several-fold higher than the geochemical background. Therefore, copper concentrations were elevated in relation to the average levels present in soils. This was probably due to some leakage of pesticides containing copper. Copper forms hardly mobile bonds with organic matter, sulfates or carbonates in soil (WIATER, ŁUKOWSKI 2010), and therefore it is accumulated in soil layers beneath the burial site, where they can be transported with groundwater. The presence of heavy metals around the pesticide burial site has been confirmed. Out of all the biosphere elements, soils are not only the main medium where many chemicals accumulate, but they also act as some kind of a protective filter for both components migrating to water and for volatile elements (KABATA-PENDIAS 1999, WITCZAK, ADAMCZYK 1995). Artificial fertilizers and some plant protection chemicals are an important source of trace elements in soils, especially in their topmost layers. Long-term application and storage of pesticides can lead to significant concentrations of As, Cu, Hg, and Pb in soils (KABATA-PENDIAS 1999, WIATER, ŁUKOWSKI 2009).

It has been found that the Zn and Hg content was higher directly under the well chamber and decreased with the soil sampling depth (Table 1). This can be attributed to constant leakage of the metals from the unsealed well. Considering the fact that zinc is one of the most mobile metals, it is probably further transported in light soils alongside the groundwater runoff.

Table 1

Content of Cu, Zn ad Hg in soil

Sample	Soil around burial site			Soil under burial site		NDS for group B soil*
Depth (m)	0.2	0.3	0.4	0.5	1.0	
Cu (mg kg^{-1})	26.55	31.61	35.40	22.76	41.76	100
Zn (mg kg^{-1})	23.94	39.53	25.85	38.58	30.03	350
Hg (mg kg^{-1})	<0.005	<0.005	<0.005	0.025	<0.005	3

*The Ordinance of the Minister for the Environment of 9.09.2002 classifies the examined soil as group B soils.

The concentrations of the metals determined in the water samples are presented in Table 2. These values were below the detection limit for mercury; for copper, they reached 0.003 mg dm^{-3} for both piezometers (the geochemical background 0.001 mg dm^{-3}), while for zinc they ranged from 0.013 to 0.023 mg dm^{-3} (the geochemical background 0.001 mg dm^{-3}). The concentrations of the heavy metals in samples of underground water collected from the piezometers did not attain increased values. The content of Cu, Hg and Zn did not exceed the permissible levels for potable water as set in the Ordinance of the Minister for Health of 29.03.2007 on potable water quality (Journal of Law, 2006, no 123, item 858). The values were lower than those obtained by the author in a study on natural water contamination around a pesticide burial site (IGNATOWICZ 2010). However, the zinc con-

Table 2

Concentration of Cu. Zn and Hg in piezometer water

Parameters	Piezometr		NDS	
	1	2	groundwater (I class)*	drinking water**
pH	7.41	7.44	6.5-9.5	6.5-9.5
Conductivity (μS cm^{-1})	384	358	700	2500
Cu (mg dm^{-3})	0.003	0.003	0.01	2
Zn (mg dm^{-3})	0.023	0.013	0.05	-
Hg (mg dm^{-3})	<0.00005	<0.00005	0.001	0.001

* The Ordinance of the Minister for the Environment of 23.07.2008 on groundwater quality.
** The Ordinance of the Minister for Health of 29.03.2007 on drinking water quality.

centration in spring 2009 (0.12 mg dm^{-3} in a dug and 1.43 mg dm^{-3} in a drilled well) sugegsts that the analyzed water requires special protection (Zn>0.2 mg dm^{-3}) and treatment before supplied as potable water (Zn>0.8 mg dm^{-3}).

The concentrations of the metals determined in the plant samples are presented in Table 3. All the metals were detected in the collected plant samples (max Cu 0.927, Zn 2.288, Hg 0.02 mg kg^{-1}). According to the Ordinance of the Minister for Health of 27.12.2000 (Journal of Law, 2001, no 9, item 72) and the limit values given by KABATA-PENDIAS (1999), the recorded concentrations can be considered as low accumulation and the plants as not contaminated. Plants growing on metal-contaminated soils develop adaptation or protection mechanisms. On strongly polluted soils, those characteristics weaken and concentrations of metals increase proportionally to their occurrence in the subsoil (TERELAK et al. 2000). Beside the phytotoxic action, excessive amounts of trace elements can pollute the whole feeding chain. The issue requires special attention when elements hazardous to animals and people are involved. In view of the Ordinance of the Minister for Health

Table 3

Content of Cu, Zn ad Hg in plants

Metal	Max content	NDS in food	
		*	**
Cu (mg kg^{-1} d. m.)	0.927	<20.0	-
Zn (mg kg^{-1} d. m.)	2.288	<50.0	-
Hg (mg kg^{-1} d. m.)	0.02	-	0.01-0.05

* The Ordinance of the Minister for Health of 27.12.2000
** The Ordinance of the Minister for Health of 13.01.2003on maximum levels of chemical and biological contaminants allowed in food

of 13.01.2003 on the maximum levels of chemical and biological contaminants allowed in food from, the collected edible plant samples (cabbage, maize and mushrooms) contained excessive levels of mercury, whose concentration reached 0.02 mg Hg kg^{-1}, whereas the permissible value is 0.01 mg Hg kg^{-1}.

Table 4 presents the coefficients of correlation between the analyzed metals in soil and plant samples. For the soil, the strongest dependencies were determined for Hg and Cu as well as Hg and Zn. Among the plant samples Cu and Zn were most strongly correlated.

Table 4

Pearson's correlation coefficients between the metals Cu, Zn and Hg in soil and plant samples (correlation significant at $p \leq 0.05$)

Metal	Soil		Plants	
	Zn	Hg	Zn	Hg
Cu	-0.24	-0.63	0.62	-0.38
Zn		0.55		-0.25

CONCLUSIONS

The determined level of pesticide contamination has demonstrated that the concrete wells did not leak. The determined concentrations of the heavy metals in soil, water and plants proved no pollution of cooper, zinc and mercury originating from the pesticide waste. The soil was characterized by a natural content of these elements and can be used for all agricultural and horticultural crop cultivation. Particular concentrations of the metals in plant samples can be considered as low accumulation and plants were not contaminated. Likewise, the groundwater was not detected to contain higher amounts of the analyzed trace elements.

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