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KATARZYNA MAJEWSKA-NOWAK*,
MAŁGORZATA KABSCH-KORBUTOWICZ*,
MONIKA DODŹ*, TOMASZ WINNICKI*

PESTICIDES – A SERIOUS HAZARD TO THE ENVIRONMENT IN POLAND

The objective of the study was to pinpoint the potential threats to natural environment, which may result from the use of pesticides. Consideration was given to the mechanisms and pathways of their migration in air, water, soil, with emphasis on the non-negligible toxicity of the pesticides, as well as the ease with which they penetrate animal and human organisms. Another major objective was to present the results of monitoring obtained for pesticide concentrations in surface and ground waters in the context of drinking water supply. The problem of admissible pesticide concentrations in potable waters, as well as related legal aspects were also analyzed. It was emphasized that a quick and effective disposal of useless pesticides in graveyards had taken on a sense of urgency.

1. INTRODUCTION

It is a well established fact that where there are intensive anthropogenic operations, these may be paralleled by an increased pollution of both surface and ground waters. Of the various micropollutants detected in watercourses, pesticides deserve special attention as they contain substances of a high biological activity.

Agriculture, forestry and sanitary services are amongst the major uses where pesticides are applicable. They have found wide acceptance in pest control (to protect agri-, horti- and pomicultural crops), in sanitary and veterinary hygiene, as well as in the control of fungi and insect growth in textiles, plastics and leather goods manufacturing plants. Another handful of applications includes breweries, sugar plants, and dairies, archives, libraries, and museums (to protect and preserve documents, paintings, valuable pieces of art, etc.). Pesticides are also useful when added to open industrial cooling water systems to kill the microorganisms present there [1].

* Wrocław University of Technology, Institute of Environment Protection Engineering, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland.

Two major sources are blamed for continual or episodic environmental contamination by pesticides – effluents from pesticide manufacture and landfills receiving industrial wastes where pesticides are present. The effluents form the manufacture of pesticides and other agrochemical agents display very high concentrations of pesticides, which range form 1 to 1000 mg/dm^3 [2], [3]. Pesticides are also responsible for the contamination of atmospheric air, soil and vegetation. They produce particular threat when leaching form the pits or graveyards where agricultural chemicals are stored [4], [5].

In Poland, most of pesticides migrating through the environment (surface waters, soil, atmosphere) come from agriculture, where masses of crop protection products are in use. For example, in 1999 the volume of the pesticides used for agricultural purposes approached 25,000 tons. Of these, herbicides accounted for as much as 64.1%. Taking account of the predicted development trends in Polish agriculture until 2010, there will be a continuous tendency to increase the crops [6]. It is worth noting that in 1999 the volume of pesticide wastes disposed of on landfills, dumps and in lagoons amounted to approximately 24,000 tons.

Plant protection products are sold in the form of granules, powders (dusting preparations), liquids (sprays) and gases (fumigants). Typically, pesticides are classified as toxic species which – depending on the level of toxicity – become hazardous to humans, bees or fish. Another kind of environmental nuisance, which pesticides are blamed for, comes from their long life and capability of bioaccumulation. High-durability pesticides take from 2 to 5 years until they are degraded with an efficiency of 75 to 100%. The degradation of moderately durable pesticides takes from 1 to 18 months [7].

2. MIGRATION OF PESTICIDES IN THE ENVIRONMENT

It is worth remembering that wherever there was a widespread use of pesticides, this was paralleled by a high environmental risk. Airborne and waterborne pesticides were found to be subject to transboundary transport. What is more, the ease with which they travel throughout the natural environment facilitates the penetration of pesticides into the food chain. The nature and the power of the toxic activity inherent in these species depend on a variety of factors such as chemical structure, dosage, duration and conditions of exposure, as well as the interaction with other compounds. We have to remember that many pesticides accumulated in the adipose tissue of humans and animals, to say nothing of their frequent detection in milk.

Figure 1 visualizes the migration of pesticides in the environment (soil, water and air), thus enabling the prediction of their behavioural pattern. The reduction of pesticide concentrations in soil and water proceeds via physical (dissolution, sorption, sedimentation), biological (metabolic transformation by microorganisms and plants) and chemical processes (oxidation, reduction, hydrolysis) [4].

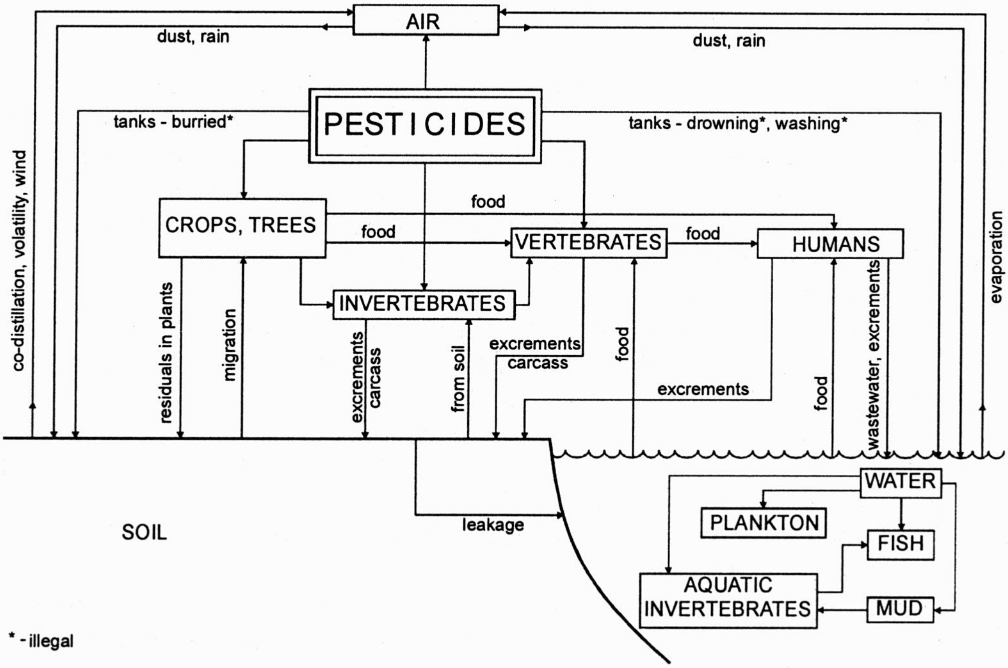

Fig. 1. Migration of pesticides in the environment [4]

Pesticides enter to the atmosphere via spraying and fumigation during protective treatment of the crops. Other mechanisms governing the emission of pesticides into the atmosphere include: (1) oxidation of the pesticide particles following their contact with the soil surface and vegetation, and (2) co-distillation with water vapour following their contact with a water surface or any other wet surfaces. Airborne pesticides come from a variety of sources, e.g., emissions from pesticide manufacturing plants, transport and storage, spraying procedures in agriculture (fields, meadows) and forestry, and domestic applications in towns and villages.

Released into the atmosphere pesticides can travel very long distances, their propagation depending on some major meteorological factors (wind velocity, air mass advection, air humidity, air temperature), method of emission, and topographic parameters (topographic profiles, type of building development, stand density). The decrease in air borne concentrations is influenced by a number of physicochemical processes. Airborne pesticides, together with the products of their transformation in the air, fall down onto soil and water surface after a certain period.

Besides the agricultural use of pest-control agents, soil contamination with pesticides is due to a wide spectrum of other contributing factors, e.g., rainfall, snowfall, deposition of airborne particulates, disposal of wastes from pesticide manufacture, disposal and storage of useless pesticides in graveyards, etc. Increased adsorption on the humic and clayey substances, which are present in the soil, extends the life time of pesticides.

Pesticides in the soil move in both horizontal and vertical (20 to 60 cm) directions. Because of the variety of physical, chemical and biological reactions between the liquid and solid components of the soil environment, it is very difficult to define the directions of movement and the method of accumulation for the pesticides which have entered the soil. Their long-lasting residence in the soil environment enables these nuisant species to penetrate into crops and thereafter (with or without conversion) into animal and human organisms.

Pesticides are also detected in aquatic environments. From there, they move either to the atmosphere or settle in the bottom and bank sediments. Some of the pesticides which have reached the atmosphere or settled in the bottoms have a longer life time than those residing in the soil. Pesticides persisting in an aquatic environment may be transported over distance of more than a dozen kilometers. The concentrations of waterborne pesticides decrease as a result of physical (dissolution, sorption, sedimentation), chemical (electrolytic dissociation, hydrolysis, oxidation) and biological processes (accumulation in aquatic organisms).

The extent of migration from soil to crop depends on the type and concentration of the pesticide and on the type of soil. Because of their high affinity for humic substances, long-life pesticides show a greater ease to penetrate crops and watercourses from sandy than from humus soil. Pesticides enter human and animal organisms via different pathways – to reach the circulatory system; from there they are distributed throughout the body. Pesticides can get in a human body due to: (1) direct consumption of contaminated water, (2) adsorption via direct pesticide–skin contact, (3) consumption of contaminated fodder by farm animals, (4) inhalation of contaminated airborne particles, and (5) consumption of contaminated farm produce, fish or meat [8]. Pesticides enter human organisms via digestion, inhalation and adsorption through skin. Depending on the time of exposure and the dose received, the pesticides accumulate in the suprarenal gland, kidney, liver, brain, lungs or spleen. They are also able to pass through the blood–placenta barrier and cumulate in the organs of the foetus, and this includes the cerebral tissue.

3. TOXICITY OF PESTICIDE – ENVIRONMENT INTERACTIONS

Many pesticides present a serious threat to water reservoirs (natural and impoundment lakes, ponds) and streams (creeks, rivers, canals) when their admissible concentrations are exceeded (c_a = 0.0001 mg/dm^3). This holds particularly for chlorfenvinfos, fenitrothion, malathion, trichlorofon, carbaryl, propoxur, γ-HCH, DMDT, DDT, toxafen, parathion, and metyloparathion, and is also true for 2,4-D, MCPA, 2,4,5-T, atrazine, linuron, dichlorfos, trichlorofon, DNOC, and DNRB (their admissible concentrations being $0.0001 < c_a < 0.01$ mg/dm^3). The table gathers the half-life periods for the pesticides of choice [9].

Table

Half-life for pesticides residing in water and soil [9]

Pesticide	Half-life period	
	In water, days	In soil
DDT	n.d.a.	3 – 10 years
DMDT	1.39 – 29.36	200 days
Chlorfenvinfos	4.05 – 9.02	60 days
Carbaryl	1.16 – 2.67	8 days
2,4-D	5.14 – 14.62	10 – 30 days
MCPA	5.62 – 20.62	30 – 180 days
Atrazine	2.72 – 3.21	300 – 500 days
Simazine	2.37 – 3.84	200 – 400 days
Linuron	5.90 – 7.12	120 days
Aldrin	n.d.a.	1 – 4 years
Dieldrin	n.d.a.	1 – 7 years

Note: n.d.a. – no data available.

On comparing the WHO recommendations for safe pesticide concentrations in potable water with relevant values measured in the water supply systems of many Polish municipalities, it has been found [9], [10] that there is a threat to human health from triazine-based herbicides (simazine, atrazine), phenylacetic acid derivatives (MCPA,MCPP, 2,4-D, 2,4-DP, dicamb), urea-based herbicides (linuron, monolinuron), phosphoorganic insecticides (chlorfenvinfos, fenitrathion, malathion), and chlorinated hydrocarbons (metoxychlor, lindane).

Among the pesticides, which are in use now, there are many species of a carcinogenic or mutagenic activity, with chloroorganic compounds, 2,4-D and chlorophenols as the most hazardous. Another hazardous group of pest control agents includes triazine-based herbicides, which are characterized by a long life time, a great ease to penetrate the aquatic environment, and a carcinogenic activity [9]. According to the Announcement of the Ministry of Food and Agriculture [11], atrazine- and simazine-containing (i.e., triazine-based) herbicides are not allowed within protection areas for water sources and intakes.

4. WATER QUALITY STANDARDS AND ADMISSIBLE PESTICIDE LEVELS

Polish rules and regulations referring to water quality standards generally aim at complying with relevant WHO and EU recommendations, where the admissible concentrations have been established by considering potential health implications.

The Decree of the Ministry of Public Health and Social Welfare of May 4th, 1990 [12], which defined the organoleptic and physicochemical demands made for the water supplied for drinking and household purposes, neglected the fact that in Poland the use of pesticides was changing in terms of both quality and quantity. As a result, the compliance of Polish drinking water quality standards with those of the European Community (80/778/EEC, July 15th, 1980) [13] was very poor.

The draft of a proposal for a new decree, which would determine the quality requirements for potable and household water, as well as those for a safe water supply [14], included a group of 27 pesticides, from among 45 with standard values recommended by the WHO [15].

Presently, this is the Decree of the Public Health Minister of September 4th, 2000 [16] that defines the quality parameters for potable water. According to these regulations, it is necessary to determine the concentrations of such pesticides alone that likely occur as contaminants. The recommended value of 0.1 μg/dm^3 holds for each pesticide which might be detected, except aldrin/dieldrin and heptachlorine epoxide. The highest admissible value of total pesticide concentration is 0.5 μg/dm^3 [16]. Both the values comply with these recommended by the European Union standards for potable water (EU98/83/CE) [17]: 0.1 μg/dm^3 for any single pesticide and derivative product, and 0.5 μg/dm^3 for total concentrations of pesticides and their derivative products.

5. ENVIRONMENTAL CONTAMINATION WITH PESTICIDES IN POLAND

In Poland, the problem of how to store waste pesticides in graveyards without environmental implications has taken on a sense of urgency [8], [18]–[22]. Figure 2 shows the actual amount of pesticides, which have been disposed of, as well as the locations where they have been stored in graveyards. In the seventies, the administration decided to withdraw some of the pest control agents from the market and to construct several hundreds of graveyards for their disposal and for the storage of waste pesticides.

The graveyards in question are concrete bunkers made of tar-insulated disks, which have been buried in the soil. This is where the unserviceable pesticides have been deposited. They generally belong to the chloroorganic, mercury-organic, arsenic and nitrophenolic groups of pesticides, only a small part of them being phosphoorganic or carbamine compounds.

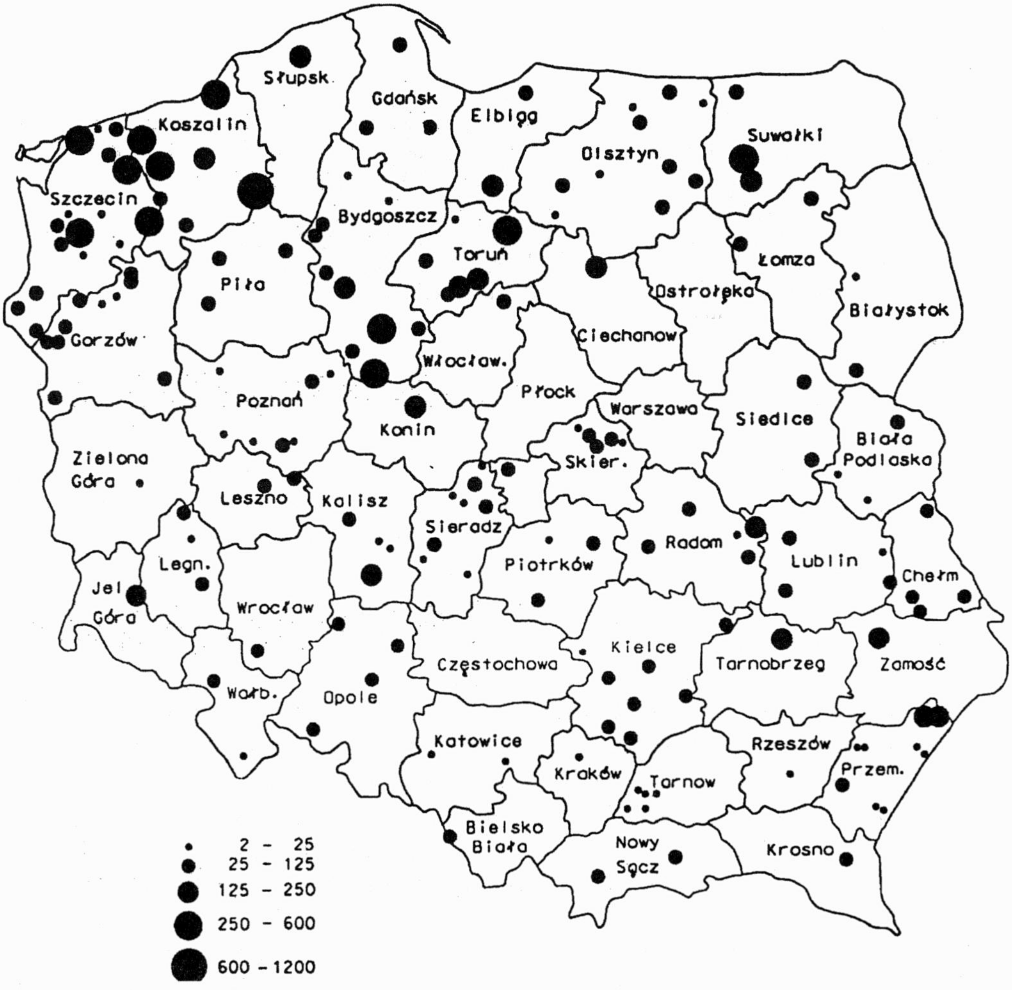

Fig. 2. The amount (in tons) and locations of pesticides stored in graveyards throughout Poland (regionalisation as before January 1st, 1999) [8]

By the end of 1999, the number of graveyards for hazardous wastes totalled 247 (of which 42% were located above the main groundwater reservoirs) [23]. They all contain approximately 10,000 tons of useless pest-control products. The volume of unserviceable pesticides stored on farms or in store-rooms approaches 50,000 tons [22]. Figure 3 shows the proportions of particular pesticide groups deposited in graveyards and store-rooms.

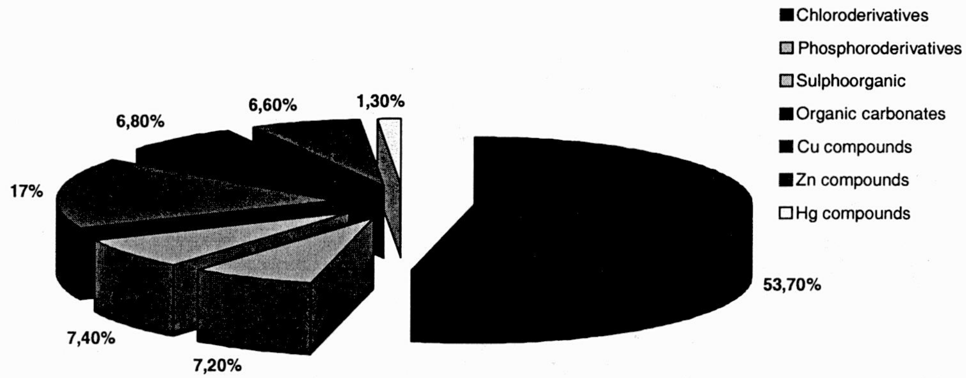

Fig. 3. Proportions of various pesticide groups kept in graveyards and store-room [8]

Sanitary inspections revealed that one-third of graveyards have not been located suitably. They were located less than 300 m apart from the water intakes, water reservoirs, farm land or farm buildings. None of the graveyards was found to be properly protected against leaching of hazardous substances to the environment [8].

It goes without saying that the pesticides in question, which belong to a variety of chemical groups, in most instances powerful poisons, pose exceptional hazard to human being and to the entire environment. During storage in graveyards, pesticide-containing wastes first destroy the package, and thereafter the graveyard construction to penetrate the environment. Analyses of the soil specimens collected in immediate proximity to the graveyards, as well as laboratory tests with groundwater samples, testified to the presence of pesticides. For example, a high-toxicity compound, chlorfenvinfos, was found to occur in water from lake and in farm wells [8]. A major environmental hazard comes from the potentiality for the graveyards to be flooded by vernal snow-melting water, long-lasting rainfall or seasonal inundation, contributing to episodes of high contamination levels in both ground- and surface waters.

It was found [24] that concrete is not a serious hindrance to the pesticides on their pathway from the graveyard to the environment. The experiments revealed that when the amount of cement increased, the pesticides travelled at a slow rate. Metabolites and chemical degradation products were found to penetrate deep into the concrete, and the fastest rate of corrosion was measured when the graveyard received precipitation water or was in touch with groundwater.

The first well-planned actions to eliminate leaky graveyards were taken in August 1996 in Niedźwiady (former Kalisz District) and in 1997 in Sośnicowice (former Katowice District) [20]–[22], [25]. The graveyard of Niedźwiady contained 65 tons of useless pesticides, which were then transported to a temporary landfill. The costs of the operation (building works, transport) totalled 210,000 Euro (excluding the equipment cost) [25]. The removal of the waste pesticides, which had been stored by the

Sośnicowice Department of the Pest Control Institute for many years, was much easier to execute owing to the availability of analytical and technical facilities [22]. It must be emphasized that the two safety measures mentioned have not solved the graveyard problem.

In the period of 1990–1994, the Wrocław Department of the Institute of Meteorology and Water Management carried out surface water monitoring for the concentrations of chloroorganic pesticides [26]. The study revealed that the admissible levels of these compounds were exceeded in 8 out of 49 districts (in those of Chełm, Jelenia Góra, Olsztyn, Płock, Tarnów, Wrocław and Zamość). Exceeded concentrations of pesticides and their derivatives were measured primarily in the upstream and central sections of the Vistula and the Odra rivers.

In the time span of 1993 to 1997, water samples collected in the Odra river reaching the city of Wrocław were analysed for the occurrence of chloroorganic pesticides. Thus, lindane was detected throughout the period investigated, but there were also episodes of water contamination with other pesticides [27]. The highest concentrations (measured in 1997) amounted to 0.642 $\mu g/dm^3$ and 0.127 $\mu g/dm^3$ for lindane and metoxychlor, respectively, the total content of DDT and its analogues being 0.049 $\mu g/dm^3$. In sum, from 1993 to 1997 the Odra river had transported approximately 2000 kg of chloroorganic pesticides.

From 1993 to 1998, investigations were carried out in the Szczecin region to assess the extent of surface water contamination with chloroorganic pesticides [28]. The study led to the following findings: the highest concentrations of the compounds investigated were measured in the Odra river, especially in 1993, and thereafter they tended to decrease, but the maximal concentration values never exceeded 0.037 $\mu g/dm^3$.

The Department of Ecology and Weed Control IUNG, Wrocław, has been monitoring the residues of herbicides in superficial field and well waters in the rural areas in Lower Silesia for many years [29]–[30]. The investigations revealed an increase of herbicide concentrations in the field waters in the time span of 1992–1993. The level of surface water contamination with triazine herbicides was found to increase to over 0.9 $\mu g/dm^3$, and that with 2,4-D and MCPA – to more than 0.3 $\mu g/dm^3$. The concentrations of these compounds followed a seasonal pattern: the highest values were measured in the spring months, and the lowest frequency of occurrence was observed in autumn.

Nationwide monitoring investigations carried out from 1991 to 1994 showed that both surface and groundwaters were contaminated with triazine derivatives [18]: 19.2 to 44.1% of the water samples analysed in the period contained the compounds mentioned. Of these, atrazine and simazine were amongst the most detected.

In groundwater, pesticides often travel over long distances, varying from several to a dozen or more kilometres [25], and thus create serious contamination hazards to well water [31]. In the time span of 1993 to 1994, the staff of the Institute of Pest and Weed Control, Poznań, analysed water samples collected from 40 wells which had been located in areas with intensive soil cultivation [32]. The highest and most frequently detected concentrations were those of residual atrazine, simazine and their metabolites. Thus, 82% of the samples being analyzed contained residual atrazine and simazine at concentrations higher than 0.1 μg/dm^3. In highly contaminated wells, the concentrations of the two compounds were even as high as 16.8 μg/dm^3 and 18.6 μg/dm^3, respectively.

In Lower Silesia, continuous monitoring of well water was started in 1992 [30]. The IUNG staff (Wrocław) detected that although the contamination of the investigated wells came predominantly from 2,4-D and MCPA (up to 0.35 μg/dm^3), a non-negligible portion should be attributed to triazine residues (up to 0.5 μg/dm^3).

After the flood of July 1997, the contamination of Polish rivers with herbicides increased noticeably [33]. Over 70% of the water samples collected in the autumn of 1997 contained derivatives of triazines; almost 20% of the samples included an active substance of the phenylurea derivatives, and over 55% exhibited more than one active substance. The most frequently detected substances were atrazine, isoproturone and chlorotolurone of the phenylurea group, as well as MCPA and 2,4-D of the phenoxy derivatives. Despite the non-negligible rise in the frequency of herbicides occurrence in the waters investigated, this was not paralleled by the increase in the contamination of the well water.

6. SUMMARY

Owing to their physicochemical properties and potentiality for conversion in the environment, as well as their long live time and capability of biocumulation, pesticides must be subject to continuous monitoring in order to control their concentrations in soil, water and air and to observe the response of the environment.

Of various pesticides monitored in Polish ground- and surface waters, triazine-based herbicides – and atrazine in particular – have come to the forefront. Atrazine concentrations in highly polluted wells were found to be even as high as 16.8 μg/dm^3. The widespread occurrence of atrazine and its derivatives has to be attributed both to the slow conversion of the compounds in the environment and to the common use of herbicides in agricultural and non-agricultural areas.

Presently, the problem of how to store pesticides in graveyards without contaminating the natural environment has taken on a sense of urgency in Poland. The graveyards erected in the seventies for the storage of useless pest and weed-control agents or those withdrawn from the market do not meet the required standards – they are either leaky or have not been located suitably, or suffer from both.

ACKNOWLEDGEMENTS

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PESTYCYDY – POWAŻNE ZAGROŻENIE ŚRODOWISKA W POLSCE

Przedstawiono potencjalne zagrożenie, jakim dla środowiska naturalnego są pestycydy. Omówiono mechanizmy i możliwe drogi przemieszczania się pestycydów w powietrzu, wodzie i glebie. Zwrócono uwagę na szczególną toksyczność pestycydów i łatwość, z jaką przenikają do organizmów zwierząt i ludzi. Podano aktualny stan prawny dotyczący dopuszczalnych stężeń pestycydów w wodzie do picia w Polsce. Przedstawiono wyniki badań monitoringowych stężeń pestycydów w wodach powierzchniowych i podziemnych w Polsce. Podkreślono konieczność szybkiego i skutecznego rozwiązania problemu magazynowania nieprzydatnych pestycydów w mogilnikach.