Prace przeglądowe

IMPACT OF CROP PROTECTION CHEMICALS ON PLANTS AND ANIMALS

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Abstract

Crop protection chemicals are chemical compounds of high biological activity and are used on a large scale in agriculture. Their influence on crop planning and storage quality is mostly positive. Crop protection chemicals, on the other hand, may cause environmental pollution. Due to errors in agronomic practice, such chemicals may occur in various ecosystems, causing threat to people, animals and plants. Adverse effects of these products are attributed to their inappropriate use, decomposition time and the ability to accumulate in the environment. Their long-lasting presence has a negative effect on living organisms, including humans. Biocides enter the human body mainly through the digestive tract, causing life-threatening disorders, which, in some extreme cases, may be fatal.

Key words: crop protection chemicals, plants, animals, human.

WPŁYW ŚRODKÓW OCHRONY ROŚLIN NA ROŚLINY I ZWIERZĘTA

Abstrakt

Środki ochrony roślin to związki chemiczne o dużej aktywności biologicznej, powszechnie stosowane w rolnictwie. Wywierają one przede wszystkim pozytywny wpływ na plonowanie roślin oraz jakość przechowywanych płodów rolnych. Środki ochrony roślin mogą

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być także przyczyną zanieczyszczenia środowiska przyrodniczego. Preparaty te w wyniku nieprawidłowych zabiegów agrotechnicznych przedostają się do różnych ekosystemów, zagrażając ludziom, zwierzetom i roślinom. Negatywne działanie tych substancji jest związane z ich niewłaściwym stosowaniem, trwałością oraz zdolnością do kumulowania w środowisku. Ich długotrwałe zaleganie wpływa negatywnie na organizmy żywe, w tym człowieka. Biocydy przedostają się do organizmu ludzkiego głównie drogą pokarmową, powodując zaburzenia w funkcjach życiowych, a w skrajnych przypadkach śmierć.

Słowa kluczowe: środki ochrony roślin, rośliny, zwierzęta, człowiek.

INTRODUCTION

Crop protection chemicals have been used since ancient times, when people understood the importance of combating plagues and epidemics. Copper sulphate, for instance, was first applied as a fungicide in ancient Egypt and Babylonia. The earliest studies on crop protection chemicals are associated with the work of Alexis Millardet, who in 1895 used the Bordeaux mixture, a combination of copper sulphate and lime milk, to control downy mildew. Major development in for crop protection chemicals occurred after World War Two, for example large-scale production of DDT began in 1946 (BZIUK 2001, PRACZYK, SKRZYPCZAK 2004).

Chemical crop protection provides a basis for agricultural practices and measures aimed at generating the highest yields of best-quality farm products. Intensive agricultural production as well as mass occurrence of pests and weeds encourage increased use of crop protection chemicals (WYSZKOWS-KI, WYSZKOWSKA 2004a). Pest organisms can cause yield losses ranging from 20 to 90%, depending on crop types (BANASZKIEWICZ 2003). Herbicides and insecticides are crucial chemicals applied in agriculture, as they can effectively control weeds and pests, thus increasing the quantity and quality of harvested crops (MICHALCEWICZ 1995, NOWAK et al. 1999, WYSZKOWSKI, WYSZKOWSKA 2004b). Crop protection chemicals are applied in agriculture not only to control pest organisms but also to disinfect storage space and to protect animal feeds, foods, plant raw materials and products (BANASZKIEWICZ 2003).

Biocides also play an important role in the protection of human life. BZIUK (2001) reported that the use of crop protection chemicals in the winter of 1944 allowed to curb a typhus fever epidemic, which nevertheless caused a large death toll in and around Naples. Crop protection chemicals have also been used to control malaria.

The basic component of any given crop protection chemical is a biologically active substance, also referred to as an active component. Biologically active substances are characterized by high biological activity against specific organisms (BANASZKIEWICZ 2003, PRZYBULEWSKA 2004). At present, 10,000 active compounds, components of crop protection chemicals, are known and applied throughout the world (BIESZCZAD, SOBOTA 1993).

IMPACT OF CROP PROTECTION CHEMICALS ON THE NATURAL ENVIRONMENT

Crop protection chemicals used to remove and destroy weeds, to fight parasites as well as to prevent crop losses during storage, have a negative impact on the environment and threaten many ecosystems (ANDERSON et al. 1994, WYSZKOWSKA 2002, BOJAKOWSKA, GLIWISZ 2005, WG et al. 2005). Due to their common use and environmental persistence, crop protection chemicals may be found in all environmental components, i.e. in water, soil, air as well as in plants, foods and in human and animal organisms (McDONALD et al. 1999) – Figure 1.

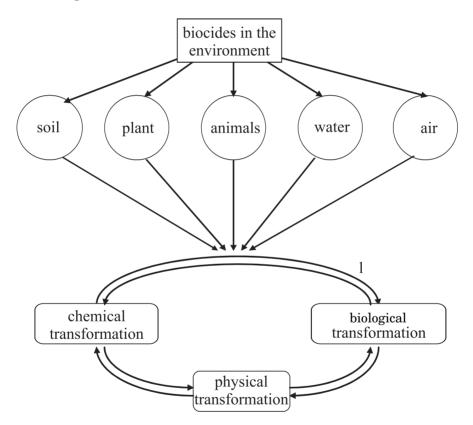


Fig. 1. Biocide transformations in the environment

Biocides are characterized mainly by their selective toxicity and environmental persistence, but they can also be grouped according to bioaccumulation potential and mobility. Many crop protection chemicals undergo bioaccumulation, i.e. they accumulate in living organisms (BZIUK 2001). Bioaccumulation is usually higher in aquatic than in terrestrial organisms. Since crop protection chemicals may accumulate in water and land organisms, their amounts in environment constantly grow and their flow through a food chain accelerates. This is particularly dangerous to organisms at the end of a food chain, such as predators or humans (BOJAKOWSKA, GLIWISZ 2005). Biocide breakdown takes place mainly through biochemical processes, but may also be caused by photochemical and chemical reactions such as oxidation, reduction, hydrolysis and interactions with free radicals. Unfortunately, breakdown products may be more toxic than the original co protection compounds (GRIFFITHS et al. 2001). Many biocides that are no longer used, in particular chloroorganic biocides, remain in soil and water for many years or decades, and their very low water concentrations may multiply biologically in tissues of aquatic organisms (BOJAKOWSKA, GLIWISZ 2005).

Soil, the outermost layer of the Earth, is subject to the effects of chemical compounds, including crop protection chemicals. Due to its properties, soil is a fundamental component of the biosphere, which conditions food production and sustains human and animal life on land. Besides, it is a very diversified ecosystem teeming with a variety of living organisms, which perform many environmentally vital functions (KOBUS 1995, KUCHARSKI et al. 2004, RUSSEL 2005).

Soil fertility and biological activity may be limited if soil becomes contaminated by various toxic substances, including crop protection chemicals (MICHEL 1999). Presence of crop protection chemicals in soil is related to environmentally damaging human activities. Soil contamination by xenobiotics depends primarily on application doses and frequency, as well as on the soil physicochemical properties, sorption capacity, temperature, humidity and pH (Strzelec 1986, Nowak 1996, Michalcewicz 2004, Przybulewska et al. 2004, SWEDRZYŃSKA 2004). Soil is contaminated mostly by compounds whose active substance is characterized by high resistance to soil borne microorganisms (Nowak 1996, Sánchez et al. 2004). All biocides remaining in soil may constitute a danger to organisms living in this environment, primarily to soil microbes (Nowak et al. 1999). As some biocides are toxic to soil microorganisms, quantitative composition and enzymatic activity of microbial populations change, which ultimately lowers soil fertility and causes soil degradation (Megharaj et al. 2000, Das et al. 2003, Durska 2004, Trasar-Capeda et al. 2004).

According to literature (ANDERSON et al. 1994, KASZUBIAK et al. 1994, NOWAK 1996, BERGER 1998, JOHNSEN et al. 2001, SŘRENSEN et al. 2003), microbiological and biochemical properties of soil depend on the length of time a crop protection chemical persists in the environmental (half-life). According to BALICKA (1983) and WYSZKOWSKA (2004), the impact of biocides on the growth of microbial populations is reflected mainly by cell metabolism disorders. The effect of these compounds on microbial metabolism is primarily related to their penetration into cells. However, some authors claim that not all metabolic changes impede microbial proliferation. According to KASZUBIAK et al. (1994), crop protection chemicals are not always toxic to microorganisms; in fact some provide nourishment for heterotrophic microbes. Chemical preparations applied as recommended by the manufacturer and at optimal rates have no significant influence on the activity of microbes. Exceeding the optimal dosage may lead to modifications in the biological activity of soil (WEGOREK 1994, FURCZAK, KOŚCIELNA 1997, WYSZKOWSKA, KUCHARSKI 2004). Long-term use of crop protection chemicals affects the persistence time of compounds in soil colloids as well as soil microbial activity (OSTROWSKI 1996).

Soil degradation may also occur as a result of the use of biocides which contain heavy metals such as arsenic, copper and zinc. Heavy metals found in crop protection chemicals are very difficult to remove from soil since they are accumulated mainly in the root system of plants. Elements absorbed by roots penetrate into all parts of plants, pass through a food chain and ultimately reach humans (ZABOROWSKA et al. 2005).

The problem resulting from application of crop protection chemicals on soil surface is that they often block cultivation for many years and generate toxic residues in agricultural products. Non-monitored long-term use of biocides increases the risk of soil contamination with these compounds (DURSKA 2004).

Crop protection chemicals belong to those environmental pollutants that are very often present in surface and underground waters (DUGAN 1969, KOT-RIKLA 1997). They penetrate into surface waters primarily via runoffs from fields and atmospheric precipitations. Maximum concentrations of crop protection chemicals are recorded during melt-water runoffs and following certain agricultural practices. Biocides may also accumulate in bottom deposits and living organisms (BOJAKOWSKA, GLIWISZ 2005).

Crop protection chemicals used intensively to produce high yields may be transported by rainwater and rivers and then filtered down into underground waters. The danger related to contamination with these chemicals increases in regions with high rainfalls during the vegetative growing season. Water contamination with crop protection chemicals is also observed in areas subject to erosion, where chemical compounds are readily transferred from contaminated soil to surface waters. Thus, great caution is advised when using crop protection chemicals as their improper application causes contamination (BLAŻEWICZ 2003).

Herbicides are the main threat to surface and underground waters in Poland and in other developed countries. Crop protection chemicals accumulated in bottom deposits are distinguished by their high toxicity and persistence in aquatic habitats, particularly in bottom deposits, river and lake silt. Biocides may be present in potable water due to insufficient purification of surface waters. They enter a food chain, destroying particular links of this chain. Among the three environmental components: air, soil and water, water is most prone to contamination. Relatively small amounts of crop protection chemicals can deteriorate the organoleptic properties (taste and odour) of water, which disqualifies its use for consumption and household purposes. They can also diminish populations of fish and other aquatic organisms, while higher concentrations result in mass fish mortality and dying out of entire water bodies. Crop protection chemicals, in particular DDT, very often impoverish aquatic herbivorous fauna. Lakes and other water bodies which supply water for municipal purposes are subject to special control and protection.

In accordance with the Council Directive 91/414/EEC of 15 July 1991, the content of crop protection chemicals and substances of similar properties in potable water may not exceed 0.1 cm³ l⁻¹ and 0.5 cm³ l⁻¹ for total harmful compounds.

Due to high vapour pressure, most crop protection chemicals easily escape into the atmosphere from soil, surface waters and waste dumping sites (TOTTEN et al. 2003, SHEN et al. 2005). Research results show that the highest air concentrations of biocides are recorded over areas in which they were produced or intensively used in the past as well as over urbanized areas. Elevated levels of these xenobiotics were also observed over the southern and eastern parts of Europe (JAWARD et al. 2004).

It was found (BZIUK 2001) that over 90% of crop protection chemicals present in the atmosphere are in the gaseous phase. Birds are at higher toxicological risk than humans due to crop protection chemicals released to air because of their more developed respiratory system as well as longer and more intensive exposure to those toxic substances.

IMPACT OF CROP PROTECTION CHEMICALS ON PLANTS

Mass emergence of harmful organisms in arable fields has stimulated increased use of chemicals in agriculture. The method applied most frequently to protect crops and improve their overall health is the use of crop protection chemicals (WYSZKOWSKA 2002, 2004). Despite many advantages, crop protection chemicals may also have a negative impact on plant production, such as inhibition of plant growth and development (KLIMACH, WIECZOREK 1998, SUKUL 2006).

Chemical compounds applied in agriculture often penetrate soil, where they undergo complex transformations leading to their breakdown (JOHNSEN et al. 2001). Biologically active substances contained in biocides are transported deeper into the soil profile and then absorbed by field plants and weeds (SADOWSKI et al. 2001). The amount of absorbed biocides is related primarily to the properties of a given plant species as well as to the chemical structure of active substances (PRACZYK, SKRZYPCZAK 2004). The negative influence of crop protection chemicals on soil properties may also involve inferior nutrient availability to plants, leading to mineral imbalance (Wysz-KOWSKA 2002). Biocides used for agricultural purposes not only contribute to pest and weed control, but also modify plant growth and development, thus changing the technological value of raw materials. Crop protection chemicals are mobile and can accumulate in plants, affecting the physiological, biochemical and nutritional properties of foods (SAWICKA 2004). Disruptions in nutrient uptake by plants lead to yield decline and quality deterioration, which in turn depresses quality of feeds and foods produced from these plants (BRASCHI et al. 2000).

The rate of biocide absorption largely depends on the type and granulometric composition of soil, fertilization levels as well as organic substance content (WYSZKOWSKA 2002, WYSZKOWSKI, WYSZKOWSKA 2004a). Crop protection chemicals penetrate into plants through roots of young seedlings. Absorption takes place mainly through root hairs and phellem cells, which are a fundamental component of the root apex region. Chemical compounds undergo biotransformation under the influence of microorganisms and plant enzymes. These preparations are absorbed by plants similarly to water, together with dissolved nutrients (PRACZYK, SKRZYPCZAK 2004). The response of some plants to herbicides may vary widely, from growth stimulation to yield decrease. Yield decline often results from plant damage caused by spraying with crop protection chemicals (BŁAŻEWICZ et al. 2003). Negative impact of crop protection chemicals may involve morphological changes in plants, including leaf discoloration, turgor loss, leaf wilting and necrosis, plant growth inhibition as well as death of whole plants. Although some plants show no external symptoms, they respond to the use of these preparations by a decline in yield (URBAN 2000). Symptoms of the phytotoxic effects of crop protection chemicals on field plants may be observed during emergence, growth or harvest. Damage may occur to an entire plant or to some of its parts (PRACZYK, SKRZYPCZAK 2004).

By disrupting the physiological processes in cultivated plants, crop protection chemicals may lead to changes in quality and reduce the activity of amylolytic, cellulolytic and proteolytic enzymes (BŁAŻEWICZ et al. 2003, KAWKA et al. 1998). According to WYSZKOWSKI and WYSZKOWSKA (2004ab), biocides exert a considerable influence on the chemical composition of plants, dependent mainly on a plant species and type of an active substance applied. This was confirmed by studies conducted by ROLA and KIELOCH (2001).

SAWICKA (2004) demonstrated that certain active substances in crop protection chemicals inhibit photosynthesis and damage the chloroplast structure. Plants that possess a large surface area relative to their mass absorb a greater amount of biocides, which accumulate mainly in the peel of fruit, particularly citrus fruit (BZIUK 2001).

Research carried out in the year 2000 by the Institute of Plant Protection in Poznań, Poland, has shown that residues of crop protection chemicals can be found primarily in fruits (22.6%), greenhouse vegetables (17.7%) and field-grown vegetables (10.7%). Biocide residues were not found in field crops such as cereals, potatoes and sugar beets. The maximum permissible amounts of biocide residues were most frequently exceeded in greenhouse vegetables (BANASZKIEWICZ 2003).

IMPACT OF CROP PROTECTION CHEMICALS ON HUMANS AND ANIMALS

Biocides pose a serious toxicological threat. They are toxic by nature, which means that they affect both harmful and beneficial organisms. Along with other properties, such as their environmental persistence and bioaccumulation capacity, they represent one of the most toxic groups of chemicals which humans are in contact with. Practically speaking, all biocides are toxic but their toxicity varies. In Poland, crop protection chemicals are divided into four toxicity classes, depending on the value of LD_{50} , i.e. the lethal dose expressed in milligrams of a toxic substance per kilogram of body weight which results in the death of 50% of the test population of animals following single administration. This pertains to experiments conducted on animals and is related to determining acute toxicity (ACT ON THE Protection of Plants of 18 December 2003, Journal of Laws 2006.171.1225).

Table 1

Toxicity class	Toxicity description	$\begin{array}{c} \text{Acute oral} \\ \text{toxicity } \text{LD}_{50} \\ (\text{mg} \cdot \text{kg}^{-1} \text{ body} \\ \text{weight}) \end{array}$	$\begin{array}{c} \text{Acute dermal} \\ \text{toxicity (rat or} \\ \text{rabbit)} \ \text{LD}_{50} \\ \text{(mg} \cdot \text{kg}^{-1} \ \text{body} \\ \text{weight)} \end{array}$	Acute inhalation toxicity LC_{50} (mg·dm ³ ·4h)
Ι	very toxic	≤25	≤50	$\leq 0.25 - aerosols$ $\leq 0.50 - gases$ and vapors
II	toxic	$25 < LD_{50} \le 200$	$50{<}\mathrm{LD}_{50}{\leq}40$	$0.25 < LC_{50} \le 1 - aerosols$ $0.50 < LC_{50} \le 2 - gases$ and vapors
III	harmful	$200{<}{\rm LD}_{50}{\leq}2000$	$400{<}{\rm LD}_{50}{\leq}2000$	$1 < LC_{50} \le 5 - aerosols$ $2 < LC_{50} \le 20 - gases and vapors$

Classification of crop protection chemical toxicity with regard to mammals according to the Act on the Protection of Plants of 18 December 2003 (Journal of Laws, 2006.171.1225)

Acute toxicity – capacity of the substance to produce a toxic effect in the body following a single exposure or the administration of a single dose.

 $\rm LD_{50}$ – amount of the chemical substance, statistically calculated based on the results of research, that leads to the death of 50% of organisms following its administration in a given manner.

 $\rm LC_{50}$ _ statistically calculated concentration of the chemical substance in an environmental medium leading to the death of 50% of organisms of a given population under certain conditions.

Crop protection chemicals are very toxic to living organisms, with their actual toxicity depending on an organism in question, environmental conditions as well as on the type, form and method of biocide application. The main route of exposure of humans to crop protection chemicals is the digestive tract. Chloroorganic biocides, which the most toxic substances, can enter the human body through the digestive tract, mainly following consumption of fish and crustaceans (BZIUK 2001, BANASZKIEWICZ 2003).

Many crop protection chemicals accumulate in living organisms. Bioaccumulation is usually higher in aquatic than in terrestrial organisms. Biocides may affect living organisms very differently depending on metabolism, toxicity and concentration. Humans are at risk of ingesting residues of crop protection chemicals with food.

Ataniyazova et al. (2001) reported that the concentrations of biocide residues in food products range from 0.1 to 1 mg, compared to 0.1–1 μg in underground waters.

Taking into account the persistence of crop protection chemicals in environment as well as human dependence on food, it has been found that these compounds are mostly accumulated in human tissues (mainly in adipose tissue). These substances often enter the human body through the skin and respiratory system. They may remain in the skin for a few months since exposure. Chloroorganic compounds, including crop protection chemicals, accumulate primarily in fat and milk of animals as well as humans, but they are also found in the brain, liver and kidneys, resulting in malfunction of these organs (MILLER, SHARPE 1998).

Even low amounts of these xenobiotics may cause negative effects, such as reduction of the reproductive performance of young animals and deterioration of their health. These substances are one of the reasons for developmental disorders in children, which manifest themselves at a later period (JUBERG 2000). Research results show that crop protection chemicals have an enormous impact on the immune (WEISGLAS-KUPERUS et al. 1995) and hormonal systems (BIRNBAUM 1994), and can lead to tumours (MILLER, SHARPE 1998). The group at highest risk of disease resulting from consumption of food and water contaminated with biocides are pregnant women, infants, elderly people as well as people with hypoimmunity (BANASZKIEWICZ 2003). Acute effects of crop protection chemicals may cause many symptoms, from light skin irritation to death. Children that consume relatively large amounts of fruit and vegetables originating from intensive agriculture may be at risk of nervous system dysfunction and disorders caused by toxins (DUGAN 1969, MALLATOU et al. 2002). Additionally, as such toxins can bioaccumulate, they enter a food chain and reach high concentrations in tissues of birds and mammals. The saddest evidence is a continually increasing level of these substances in the human body caused by consumption of crop protection chemicals dissolved in vegetable and animal fat from fish, poultry and beef (NANCY 1999). The highest quantities of these preparations are present in

food products such as cereal grains or vegetables, but primary sources of contamination for humans are milk and milk products, eggs and meat (MAL-LATOU et al. 2002).

In accordance with the Order of the Ministry of Health and Social Care of 15 April 1997, the maximum permissible levels of residues of crop protection chemicals used in the cultivation, protection, storage and transportation of plants (Journal of Laws, No. 43, item 273) may not exceed $0.005 - 0.1 \text{ mg kg}^{-1}$ of food products. The negative effects of crop protection chemicals have gained increasing interest recently, which resulted in the development of environmental monitoring programs, aimed primarily at human health protection (BIESZCZAD, SOBOTA 1993).

SUMMARY

Crop protection chemicals are natural or synthetic substances that are applied primarily in agriculture to fight weeds as well as to control plant diseases and pests. They play a key role in producing high yields, storing farm produce, fighting pests as well as maintaining proper sanitation and hygiene standards. These chemicals have become a very significant part of human life. Aside their advantages, biocides are also known for negative effects. When improperly applied, they pose a serious threat not only to animals, but also to the natural environment. Due to their properties, they possess the ability to accumulate in various ecosystems, resulting in contamination followed by degradation. Crop protection chemicals are capable of impacting all living organisms – including species that are not their target. Beneficial organisms may be destroyed and biodiversity diminished through the use of xenobiotics, which in consequence may upset ecosystem balance.

Intensive use of crop protection chemicals in agriculture, observed nowadays, leads to environmental pollution. However, more and more attention is paid to environment-friendly crop protection practices. The use of chemicals in agriculture requires supervision, monitoring and prevention of potential negative consequences. The range of crop protection chemicals has been changing over the last few decades. Some of them have been withdrawn from the market due to their toxicity, a long half-life as well as the development of resistance in target populations – this pertains in particular to insecticides. The amount of biocides used is increasing drastically, which in many cases makes it very difficult to determine their toxicity. Today a major global problem are disposal sites for hazardous wastes, including crop protection chemicals. These sites have not been properly prepared to store this kind of waste, so pesticides may leak out and cause significant damage to the natural environment. Numerical data concerning this problem are usually difficult to estimate.

There is no doubt that the use of crop protection chemicals should be limited or maybe they should be eliminated entirely. A precise analysis of expected side effects should be performed prior to the introduction of these toxic substances on the market. The threat posed by pesticides may be minimized by strict observance of the relevant regulations as well as by their proper use. The establishment of legal provisions which would regulate all issues related to crop protection chemicals is also very important.

From the ecological perspective, improving agricultural efficiency via chemicalization is a serious mistake, which may have dire consequences in the future. Appropriate steps should be taken to prevent the undesirable side effects of crop protection chemicals on the natural environment.

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