IDENTIFICATION OF IMPACTS AND HUMAN HEALTH RISKS PRODUCED BY THE PRESENCE OF PESTICIDES IN THE ENVIRONMENT
I. PESTICIDES BEHAVIOUR IN THE ENVIRONMENT

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Abstract. *The need to ensure the protection of plants and various areas affected by the presence of pests and pathogens imposed the use of chemicals to help in diminishing crop damages, namely pesticides. As Persistent Organic Pollutants (POPs), pesticides are resistant chemicals to bio(degradation), their residues being difficult to be removed from the environment. This papers discuss the state of investigations on the presence of pesticides in the environment, their behavior determined by their characteristics, types of pesticides used, the sources from which the pesticides can come. Also some threats that pesticides can generate in the environmental compartments (water, air, soil, sediments) are discussed in correlation with some specific properties of pesticides. A distinct section is dedicated to the presence and behavious of pesticides in fruit and vegetables, the residues found in some plant products according to European Food Safety Authority (EFSA). This analysis generates the support for the identification and characterization of impacts and risks on human health generated by the consumption of plants containing pesticide residues.*

Keywords: absorption, air, bioaccumulation, long distance transport, persistence, soil, volatilization, water

https://doi.org/10.56082/annalsarsciphyschem.2022.2.83

1. Introduction

In recent decades, along with the growth of the global population and its needs, there has been a considerable increase in the production of various synthetic substances and articles, the composition of which includes a series of chemical compounds, which, during manufacture and use, present a great danger to the health of people and the environment. The rapid development of the chemical and agro-chemical industry in the last century led to the discharge into the environment of a very large number of chemical compounds [1, 2]. Since the

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middle of 20th century, the application of pesticides in agriculture was enhanced significantly to provide protection against pests and diseases, which also generated toxic effects on all living beings. Regardless of their advantages to capitalize on the yield of agricultural crops, the effects of the pesticides use are thoughtful, beause most of these chemicals are toxic both for the environment and humans [3, 4].

This is still very topical, although some pesticides have been banned as a result of their high toxicity and persistence in the environment, properties that generate historical pollution of some sites or areas where pesticides have never been applied. Although these pesticides have been banned, they can still be found in water, soil, sediments even after a number of years, due to their high half-life, stability and long-distance transport. It is already known that the pollution caused by organochlorine pesticides (DDT, aldrin, dieldrin, endrin, heptachlor), which are among the most toxic and persistent, represent a great threat to the environment and human health, as a consequence of their accumulation in the food chain [3, 5].

Due to their negative impacts, the use of pesticides in agriculture needs long-lasting monitoring mainly to minimize the risks to human health [6]. In spite of regulations and good practice about the application of pesticides in agriculture, at present a few actions were developed to monitor and end the improper and illicit uses of pesticides [1, 7]. Humans can be exposed to pesticides in several ways whether through inhalation, dermal contact or food consumption, food products have been recognized as the main route of exposure to pesticide residues [8]. Fruits and vegetables are sources of vitamins, minerals, fiber and antioxidants, and according to the World Health Organization, the average food intake consists of 30% of fruits and vegetables.

In addition to their nutritional value, these products can be a source of toxic substances, i.e. pesticide residues. In addition, fruits and vegetables are commonly consumed raw or semi-processed and, consequently, they contain higher levels of pesticide residues than other food groups [9, 10]. In this context, this paper discusses some aspects regarding the presence of pesticides in the environment, their behavior depending of their class, structure and properties, and threats the pesticides can generated for environment and human health, mainly due to pesticide residues remanent in fruit and vegetables.

2. Status of research on the presence of pesticides in the environment and in fruits and vegetables

2.1. The use of pesticides

Pesticides are substances or mixtures of substances used to prevent, reduce and eliminate pests (insects, mites, nematodes, weeds, rodents) that may occur in agricultural crops [3]. Pesticides are also used to limit the transmission of some diseases through insects, in housing, animal care, maintenance of green areas and in industry [11].

The Food and Agriculture Organization of the United Nations (FAO) defines pesticides as "*any substance or mixture of substances intended for the prevention, destruction or control of any pest, including vectors associated with human or animal diseases, of unwanted species of plants and animals that cause damage in during or interferes with the production, processing, storage, transportation or marketing of food, agricultural products, wood and wood products or animal feed, or substances that can be administered to animals to control insects, arachnids or other pests in or on their bodies*". This class of organic compounds embraces substances envisioned for use as a plant growth regulator, defoliant, desiccant, or applied before or after harvest to protect the products during storing and transportation [8, 12].

According to the United States Environmental Protection Agency (USEPA), pesticides contain both active ingredients used to prevent, destroy a pest or plant regulator, defoliant, desiccant or nitrogen stabilizer, and inert ingredients (stabilizers, solvents, vegetable oils) that are important to product performance and utility [13, 14].

The use of pesticides dates back to the era of Sumer. The evolution of pesticides uses and discoveries is succinctly presented in Figure 1. Pesticides are of great importance in plant protection, increasing productivity and quality of agricultural products. Every year, more than 140,000 tons of pesticides are applied to agricultural crops in the European Union alone. Fruits and vegetables, especially grapes, citrus fruits and potatoes, are among the most vulnerable plant products to be contaminated with pesticides. If pesticides were not used to eliminate pests, then the production losses in the case of fruits, vegetables and cereals would be quite high, respectively, 78% in the case of fruits, 54% in the case of vegetables, and for cereals a percentage of 32% [3].

Although plant protection is absolutely necessary to obtain quality products in sufficient quantities to meet food needs, the use of pesticides leads to negative effects on the environment (water, soil and air pollution) and on human health (headaches, abdominal pain, vomiting, coma, difficulty breathing, coma, cancer)

[15]. In this context, it is necessary to impose measures to reduce the occurrence of risks to human health caused by pesticides used for the protection of vegetables and fruits against pests [1, 16].

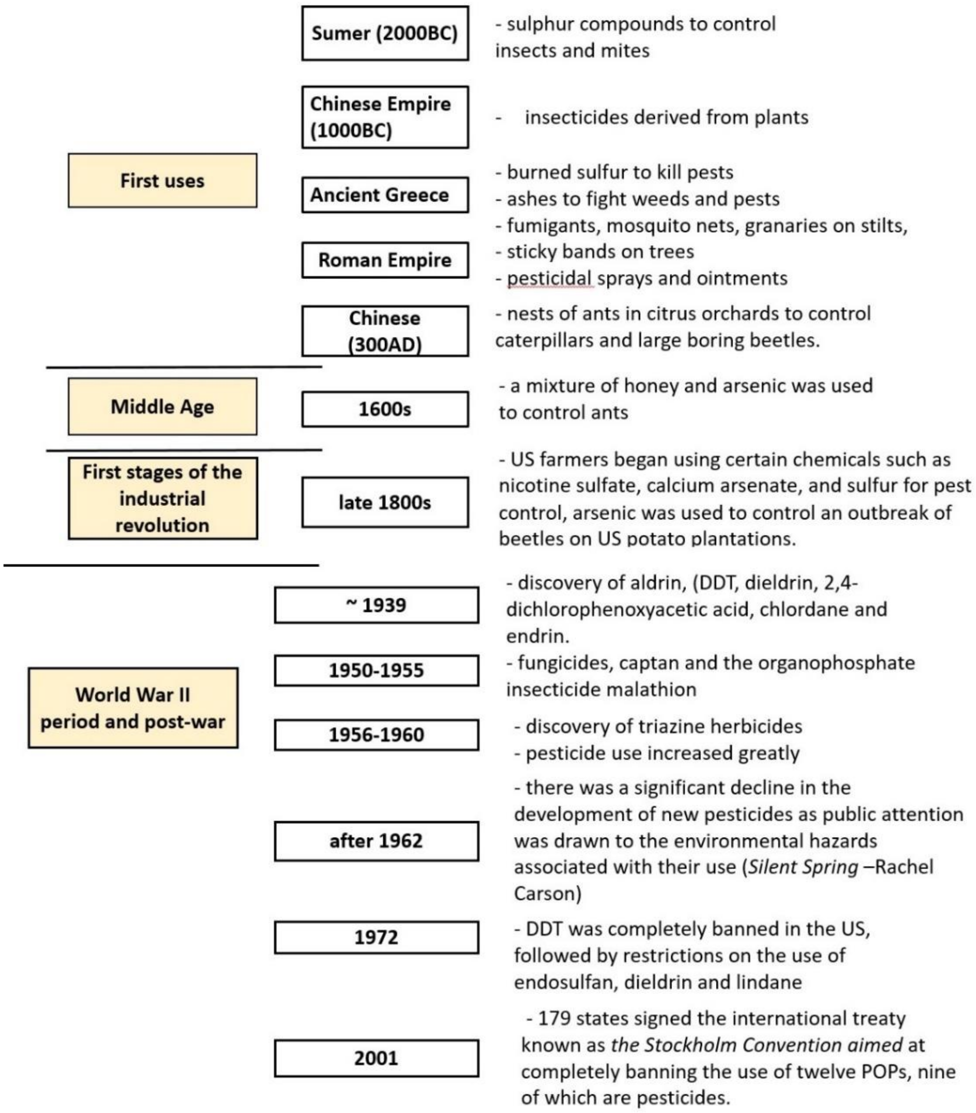

Fig. 1. Short history of the use of pesticides.

2.2. Short characterization of pesticide classes

Pesticides are substances that can have toxic properties, can accumulate in organisms, are resistant to degradation and can be transported by air and water over transboundary distances. Pesticides contain both active ingredients and "inert" ingredients that work to control pests, which also can induce threats for the environment and human health [14, 17]. Active ingredients are the chemicals in a pesticide product. The active ingredients must be identified on the pesticide product label, along with its percentage by weight. The categories of active ingredients are [17]: conventional, antimicrobials, biopesticides. Inert ingredients can increase pesticide performance, hinder their inactivation due to exposure to sunlight, facilitate application, improves safety for the applicator.

Pesticides are classified following some criteria [18, 19]: chemical structure (organochlorine pesticides, organophosphorus pesticides; carbamates; pyrethroids); toxicity; combated target; mode of action. Some pesticides (e.g. organochlorine compounds) are classified as persistent organic pollutants (POPs) and are substances of concern due to their potential for long-range transport, persistence in the environment, ability to bioaccumulate in ecosystems, and significant adverse effects on human health and the environment [20, 21]. The Stockholm Convention on Persistent Organic Pollutants is an international treaty signed in 2001 and adopted in May 2004 by EU legislation through Regulation 850/2004 which requires the countries involved to make and implement plans and strategies for the reduction and elimination of 12 of these substances, 9 of them being pesticides (aldrin, endrin, chlordane, dieldrin, DDT, heptachlor, mirex, toxaphene, hexachlorocyclohexane), in order to protect human health and the environment [5, 22].

2.2.1. Organochlorine pesticides

Organochlorine pesticides were the first pesticides used in agriculture and public health, being very stable and persistent, with high potential for bioaccumulation [18]. The first synthetic organic pesticide was DDT (dichlorodiphenyltrichloroethane) which, in the first phase, due to its effectiveness in combating insects, low cost and ease of application, was widely used, including in combating some diseases (malaria during the second world war), but considering its negative effects on the environment and human health, DDT and other organochlorine compounds were banned. However, due to their high stability (30 years or more) these pesticides may still be present in the environment [23].

Representative examples of organochlorine pesticides are: DDT, lindane, endosulfan, aldrin, dieldrin and chlordane, and their chemical structures are shown in Figure 2.

2.2.2. Organophosphorus pesticides

Organophosphorus pesticides are most widely used in agriculture, especially as insecticides and acaricides for vegetable crops, fruit trees, cotton. They are derivatives of phosphoric acid, they act on the central nervous system by inhibiting acetylcholinesterase, an enzyme that regulates the levels and quantity of the neurotransmitter – acetylcholine (Figure 3). Contrasting with organochlorine compounds, organophosphorus insecticides are less stable in the environment, being potentially degradable biochemical and biological reactions. Some of the widely used organophosphorus insecticides are parathion, malathion, diazinon [18, 24].

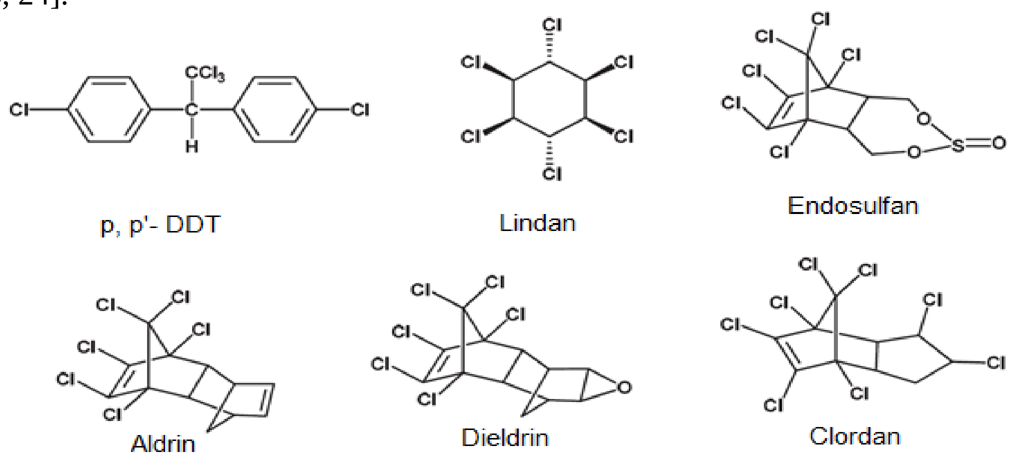

Fig. 2. Organochlorine pesticides.

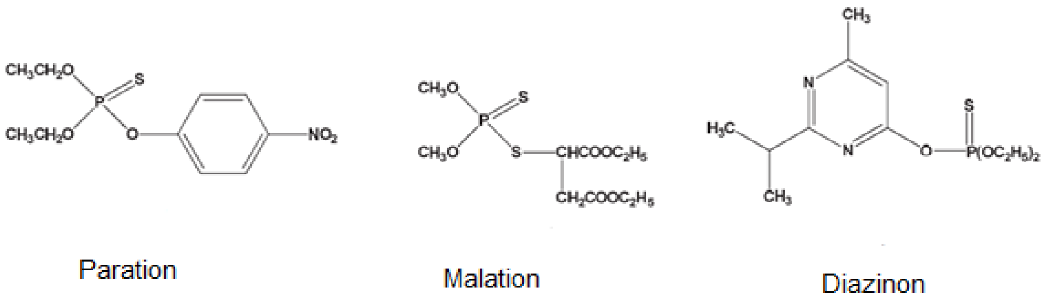

Fig. 3. Organophosphorus pesticides.

2.2.3. Carbamates

Carbamates are derived from carbamic acid and are less persistent than organochlorine and organophosphorus pesticides (Figure 4). They are used to eliminate insects, fungi, nematocides [18]. Some of the widely used insecticides within this group include carbaryl, carbofuran and aminocarb [19].

2.2.4. Pyrethroids

Pyrethroids can also be obtained naturally by extracting pyrethrin from chrysanthemum flowers, later they were chemically synthesized and manufactured in large numbers (Figure 5). Pyrethroids are recognized for their rapid effect against insects, low mammalian toxicity and easy biodegradation. The most widely used synthetic pyrethroids include permethrin, cypermethrin, and deltamethrin [16].

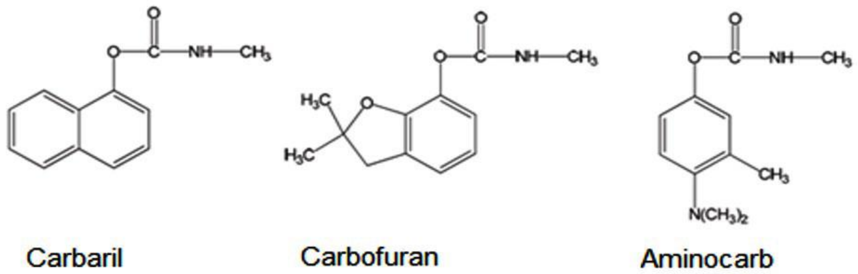

Fig. 4. Carbamic pesticides.

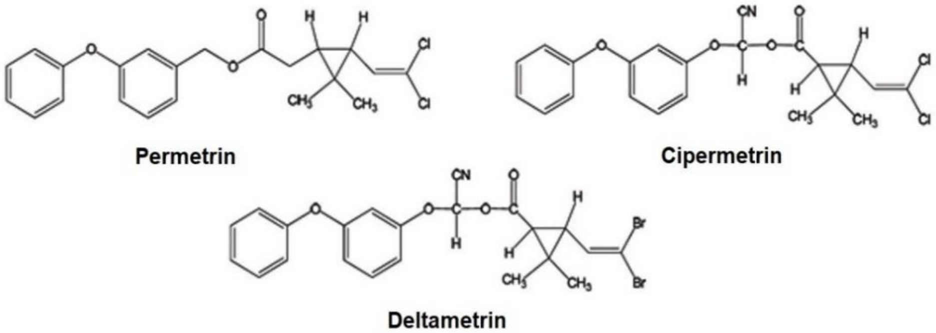

Fig. 5. Examples of pyrethroids.

2.3. Pesticides toxicity

Before manufacturers can distribute pesticides, Environmental Protection Agencies must evaluate them to ensure they meet standards for protecting human health and the environment. Claimants must produce data necessary regarding: identity, composition, potential adverse effects and fate in the environment [6, 16]. These data make possible the appraisal of the individual pesticide, its potential for harm of non-target organisms and endangered species [25]. Table 1 presents a classification of pesticides according to toxicity.

Table 1. Toxicity of pesticides*

Type	***Level of toxicity***	***LD $_{50}$ rats (mg/kg body weight)***	
		Oral	***Dermal***
Takes	Extremely toxic	<5	<50
Ib	High toxicity	5-50	50-200
yl	Moderate toxicity	50-2000	200-2000
III	Reduced toxicity	> 2000	>2000
u	It is unlikely to have an acute effect	5000 or >5000	

*LD_{50} - the dose required to kill half of the members of a tested population after a specified period; * from WHO [26] under CC Creative Commons (Attribution-NonCommercial-ShareAlike 3.0 IGO (CC BY-NC-SA 3.0 IGO))*

Depending on the degree of toxicity assigned, each pesticide has specified on the label precautions that must be taken, according to Regulation (EC) No 1272 [27].

2.4. Pesticides by target

Pesticides aid mainly as plant protection products, but not exclusively, and can destroy pests such as insects, weeds, anumals, birds, nematodes, microbes, algae, mites, plant pathogens etc., [16, 28]. Figure 6 shows the types of pesticides according to the target.

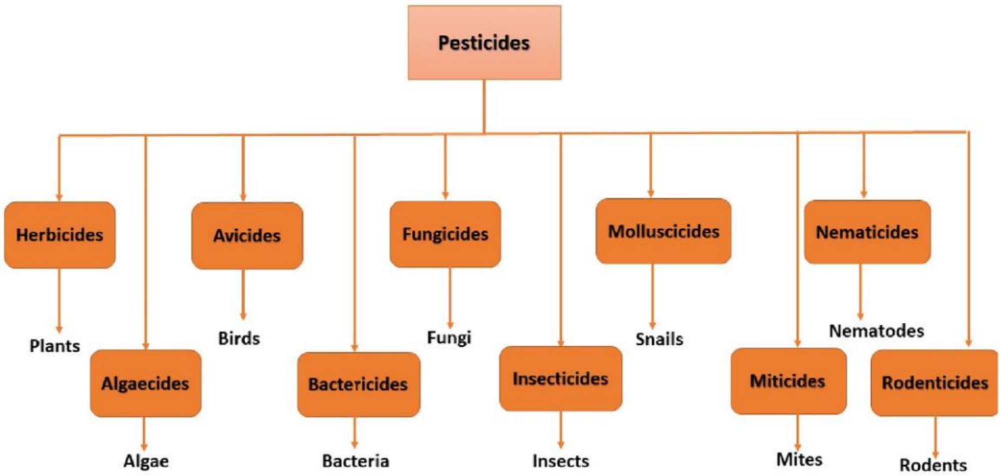

Fig. 6. Classification of pesticides by target (reused from Muhammad et al. [29], under Creative Common under the CC BY-NC-ND license)

2.5. Pesticides - mode of action

According to the mode of action, pesticides can be as systemic and non-systemic (contact). Systemic pesticides can successfully enter the plant tissues to produce the anticipated outcome. Non-systemic pesticides do not penetrate the plant tissues, but only produce their wanted consequence when they come into contact with the target pest [19, 30].

3. Properties of pesticides

3.1. Physico-chemical properties

3.1.1. Solubility

The importance of pesticide solubility in the environment derives from the fact that a pesticide that is highly soluble in water will not tend to accumulate in the soil or ecosystem because it will degrade through hydrolysis [19, 31].

3.1.2. Vapor pressure

The vapor pressure of a substance is the measure of the degree of volatilization and transformation into gaseous state. Pesticides with high vapor pressure have a high volatilization capacity and can produce environmental contamination [32]. Pesticides with a low vapor pressure have a low volatilization capacity and can accumulate in water when water soluble. Otherwise, the pesticide can accumulate in soil or ecosystems [19].

3.1.3. Henry's constant

It expresses the tendency of a material to volatilize from aqueous solution into air. The importance of the Henry’s law constant is that a pesticide with a high value of the constant will be volatilized from solution into the air and distributed over a large area [33]. Conversely, a pesticide with a low constant value tends to persist in water and may be adsorbed to soil [19].

3.1.4. Octanol/water partition coefficient - K_{ow} (log K_{ow})

Octanol/water partition coefficient K_{ow} is considered a good indicator of the bioaccumulation of pesticides in organisms and food, but also of the mode of action of a pesticide. Pesticides with low $K_{ow\ values}$ (≤2) indicate pesticide translocation into the transvascular system of plants. K_{ow} values are generally influenced by the polarity of the pesticide and general physical factors. Polar pesticides tend to be more soluble in water and therefore have low K_{ow} values. K_{ow} increases with increasing molar volume, molecular mass and density [19, 34].

3.1.5. Lethal dose LD_{50}

In toxicology, the median lethal dose, LD_{50} (lethal dose 50%) or LC_{50} (lethal concentration, 50%) is a measure of the lethal dose of a toxin or pathogen and is the dose required to kill 50% of the members of a tested population after a certain period of time. $LD_{50\ values}$ are used as a general indicator of the acute toxicity of a substance. In the present case for pesticides used in agriculture, a low $LD_{50\ value}$ indicates increased toxicity [35].

3.2. Specific properties of POPs

The behavior of pesticides as persistent organic pollutants (POPs) in the environment is determined by the following characteristics of POPs [28, 36]:

- *persistence:* in the environment: resistance to degradation through chemical, physical, biological processes, which determines the long life of these substances and long-distance transport (thanks to this property, POPs can exist in regions where they have never been used);

- *semi-volatility:* volatility is the property of chemical compounds to vaporize in the air. POPs are semi-volatile chemical substances. After their release into the environment, they go through several cycles of evaporation, air transport and condensation.

- *long-distance transport:* is evidenced by the measurements of chemical substances in biotopes located at great distances from the emission source; POPs are transported across international borders influencing air quality in neighboring states.

- *bioaccumulation:* POPs have low solubility in water, but have high solubility in fats (in the tissues of living organisms), which determines their concentration in adipose tissues. Substances with this property bioaccumulate in the fatty tissues of living organisms, through the environmental factors water, air, but also through food.

- *toxicity*: the property of the chemical substance to cause damage to humans and the environment.

POPs pesticides are toxic substances for humans and animals, aquatic life and other organisms, in some cases at low concentrations, producing imbalances of the immune, reproductive, nervous system and have carcinogenic and genotoxic effects.

3.2.1. Persistence

Pesticides are considered to be persistent in a given environment, since they cannot be easily degraded by physical, chemical and biological processes [20]. The persistence in the environment can be measured by the half-life time in the environment (half-live), which represents the measurement time required to reduce the concentration of a substance by 50% in a specific environment - it is noted TD_{50} - as well as by the time of the disappearance of 90% of the product (TD_{90}). Since pesticides have long persistence times in water, soil or sediments, they have a high potential for accumulation in the environment and also in living organisms. The soil acts as a receptor and reservoir of pesticides. Pesticides degrade in the soil, but can generally persist long after application.

The main factors, on which the persistence of pesticides in the soil depend are [37]:

- *the physico-chemical characteristics of the pesticide* are mainly solubility in water and fats, volatility. Related to the physico-chemical characteristics, it was found that organochlorine pesticides are more difficult to degrade in the soil than organophosphorus pesticides. TD_{50} for organochlorine pesticides can vary from a few days to a few years [35, 38].

- *the quantity and physical condition in which it is administered:* for example, the application of a pesticide in the form of granules leads to an increase in TD_{50} compared to the situation when it is applied in the form of a solution or emulsion;

- *the physico-chemical characteristics of the soil* are also important: organic matter content , texture, humidity, temperature, pH etc. TD_{50} has higher values for a soil with a high content of organic matter, low humidity and temperature, neutral pH;

- *the presence and number of microorganisms in the soil*, given their ability to degrade organic substances;

- *the climatic conditions of the area*: abundant precipitation as well as high air temperatures favor the migration and decomposition of pesticides in the soil.

All persistent organic pollutants have half-lives with high values in water and soil, for some POPs such as DDT and mirex, the half-lives have the highest values, of the order of years (Table 2).

Table 2. Half-life values in water, soil, sediments for some POPs*

Substance	***Water***	***Soil***	***Sediments***
Aldrin	760 days	>20 days	
Dieldrin	>1460 days	>175 days	
chlordane	7.6 years	>20 years	
DDT	>4380 days	>15 years	>1100 days
Mirex		>600 years	>600 days
toxaphene	20 years days	20 years	
hexachlorobenzene	<1 days	>986 days	
Endrin	>112 days	>1460 days	
2,3,7,8 TCDD	>380	10 years	>365 days

** from Bețianu and Gavrilescu [36], with permission of EcoZone Publishing House, Iasi, Romania*

3.2.2. Bioaccumulation and bioconcentration

Bioaccumulation is a measure of the potential of chemical substances to concentrate in the tissues of living organisms. The use of pesticides, everywhere in the world, without restrictions, resulted in the contamination of the entire biosphere with these substances. Today, traces of pesticides and other POPs are found in air, soil, sediments, in living tissues (animals or plants), all over the planet. The degree of danger is amplified by the fact that very large losses occur at the time of administration. Thus, on average, of certain insecticides and fungicides applied, about 97% are lost in the soil, on plants or other organisms and only 3% perform their true role for which they were manufactured. The extremely long persistence of some of the pesticides, the possibility of accumulation in microorganisms and in plants, in invertebrates and in vertebrates, register pesticides and other POPs in the biosphere [2, 7].

The bioaccumulation of these toxic substances becomes more and more dangerous, with the consumption of these substances by small animals. Once pesticided accumulate in the fatty tissues of these small animals, each successive predator will consume a large amount of toxins (Figure 7) [39]. Along the food chains, a rapid process of increasing the concentration of pollutants takes place, by *bioconcentration*. Due to this phenomenon, there have been decreases in the number of eagles, pelicans, hawks, predatory fish and other species at the top of the pyramid of long food chains [37].

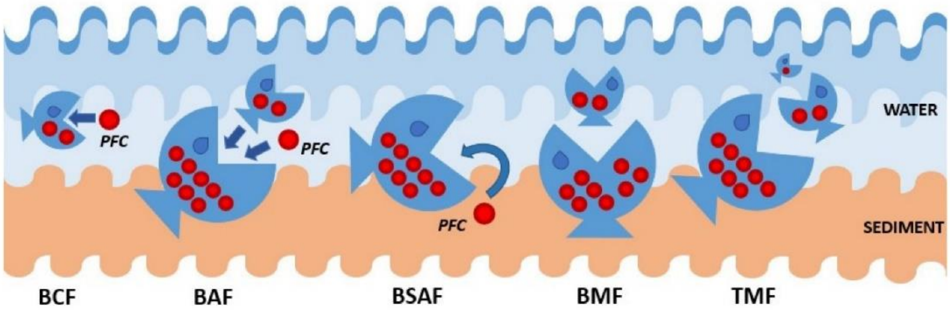

Fig. 7. Illustration of bioaccumulation processes ([39], under the terms and conditions of the Creative Commons Attribution (CC BY) licens).

Such a bioconcentration process was observed in the Black Sea. The cell of a contaminating microscopic alga contains a tiny amount of such persistent pollutants, but the zooplankton animals (small crustaceans, fish larvae) that feed on the contaminating algae will store in their body a greater amount than that of a microalgae. Following the concentration of POPs in animals located at the upper levels of the food chain, its value increases by several orders of magnitude, which means that organochlorine substances have a high potential for bioconcentration in the food chain. The concentration of DDT measured in the body of two dolphins from the Black Sea was 50-100 times higher than the values recorded in the body of cetaceans from the North Sea, the Atlantic Ocean and the Baltic Sea [40, 41].

A similar study was carried out on Clear Lake in California, located about 150 km from the city of San Francisco, where diluted solutions of DDD (pesticides from the same chemical group as DDT) were applied in order to combat mosquitoes, which created discomfort in the surroundings of the lake [42]. After about 3-4 years of repeated use, the mosquitoes developed resistance, and at the same time strange effects began to appear, the most serious being the massive death, almost to the point of extinction, of some water birds spread in the area (*Western grebes*) and reduction of the fish population. Suspecting that the repeated application of pesticides was the cause of producing these effects, biologists measured the concentration in DDD of the different components of the lake's ecosystem and found a dramatic concentration of pesticides along the trophic chain [37].

The bioaccumulation property is expressed by the bioconcentration factor (BCF=organism concentration/concentration in the environment) or bioaccumulation factor (BAF).

3.2.3. Long distance transport

Pesticides are among the most persistent and mobile substances, which are conferred by the structure of the molecules and often associated with a high degree of halogenation. The physico-chemical properties of these compounds determine their volatilization and therefore they are present in high concentrations in the atmosphere. The potential for the transport of these substances over long distances can be indirectly appreciated through the persistence time in air, water, soil or by volatility.

The long distance transport of pesticides has caused their distribution around the world, usually in places where they have never been produced or used (e.g.: the Arctic area) (Figure 8). Low solubility in water, high solubility in the fatty tissues of living organisms, high stability in the environment, are characteristics that favor the transport of pesticides over long distances [43, 44]. In tropical countries there are much higher annual temperatures than temperatures in temperate countries and Polar Regions of the globe. The use of pesticides in agricultural production in tropical areas, during very hot seasons, can facilitate their spread in air and water [45]. The large proportion of use of pesticides in tropical countries has led to their dispersion in the atmosphere and their transport over long distances, usually reaching the Polar Regions, where they are deposited and volatilized. The characteristics of polar ecosystems intensify the problems of contamination with pesticides. The cold climate, the reduced biological activity, the temporary lack of sunlight, result in the increased persistence of these substances. Chemical substances are transported from regions with lower temperatures to temperate zones at lower rates due to lower temperatures [44].

An example of long-distance transport of pesticides was observed in Midway Island, a coral island located in the North Pacific Ocean between North America and Asia. The island is located 1,150 miles from Honolulu, 2,400 miles from

Tokyo and 3,100 miles from Los Angeles, so it is a remote region from any major industrial area. With all_these, DDT, PCBs, dioxins and furans, were detected in the body of local birds, in significant quantities [43].

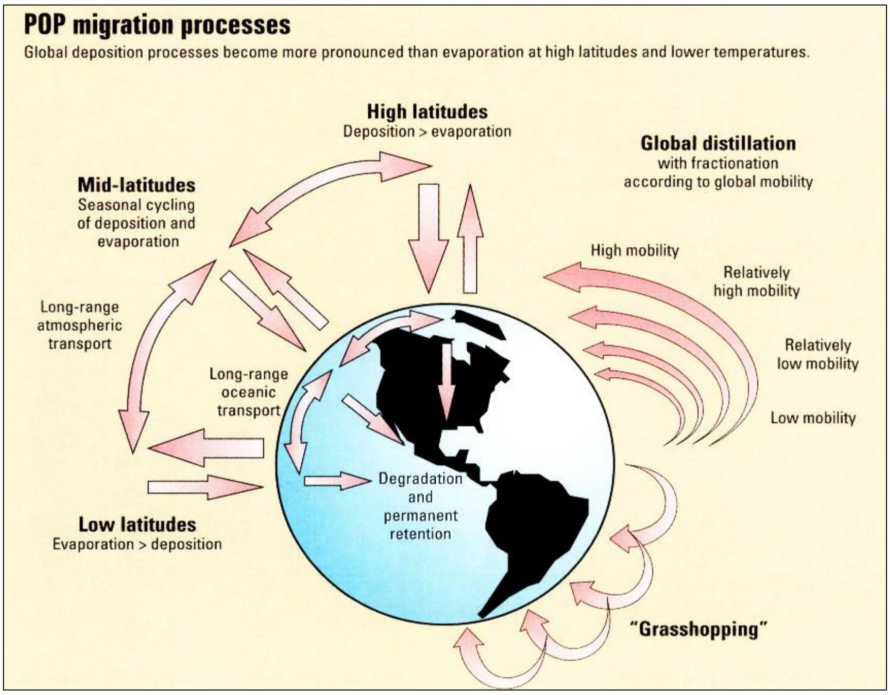

Figure 8. Pesticides POPs migration process (with permission from Wania and MacKay [44], Copyright 2013, American Chemical Society)

3.2.4. Semi-volatility

Semi-volatility is a property correlated witg long distance transport that gives pesticides a high degree of mobility in the atmosphere, which allows a large amount of substances to enter the atmosphere and be transported to large distances from the source. Substances with this property are strongly halogenated compounds, with molecular mass M=200-500 g/mol and vapor pressure less than 1000 Pa [46].

Volatilization occurs when pesticides separate from the solid or liquid phase and turn into a gas phase. With the volatilization of the substance, it can diffuse into the environment, assuming a risk for the environment. Volatilization depends on the size, structure and properties of POPs. High temperatures intensify the volatilization of POPs in the environment, while humidity can affect the degree of volatilization. Volatilization occurs on the surface of plants and soil, following the application of POPs used as pesticides [43].

3.2.5. Toxicity

Most pesticides are considered dangerous due to their toxic action. Scientific evidence suggests that some have a high potential to cause negative effects on human health and the environment, both locally, regionally and globally, by transporting pollutants over long distances. In the decades of the last century, pesticides were almost non-existent in the environment. However, there was a dramatic increase in pesticides following the Second World War [47].

Thus pesticides were identified in water, air, soil, in the body of the human and animal population. People can be exposed to the action of pesticides, through breathing, dermal contact, inhalation of concentrations of pesticides from contaminated air, dust by residents of areas close to the storage of hazardous waste containing POPs, through the consumption of certain foods (pesticides were detected in food: eggs, meat, etc.), daily consumption of products or meat from animals that graze on contaminated pastures, consumption of food produced on contaminated soils, consumption of fish from contaminated waters, consumption of contaminated water, consumption of breast milk by newborn children (pesticides bioaccumulate in breast milk and are transmitted from mother to child through feeding) [43, 45, 48].

The widespread use of pesticides, followed by their penetration into the biogeochemical circuit of ecosystems, could not fail to affect the human body as well. Human exposure to pesticides can be acute or chronic, professional or extra-professional, deliberate or involuntary, or the result of an accident or incident and can be oral, respiratory or cutaneous [49].

Frequently, massive poisoning with pesticides is caused by negligence, direct contact with pesticides by factory workers, workers handling pesticides, children playing near storage areas, consumption of unwashed fruit immediately after spraying etc. As a result of massive poisoning with pesticides, death often occurs. The most affected population segment are children under 10 years old (half of deaths caused by pesticides in the world affect this group), then agricultural workers who handle pesticides and harvesters treated with pesticides [37]. Pesticides can accumulate in fate tissues, in biological fluids that contain lipids (eg milk), with milk they are transmitted to the child and incorporated into the body. A unique aspect of POPs is that they enter the food chain, being able to pass from mother to child through the placenta and breast milk. Exposure of workers to pesticides, during waste management, is an important source of occupation that poses a very high risk to people [11]. Exposure to high concentrations of some pesticides has resulted in illness, even death. Obstacles arising from the use of pesticides at the workplace, in agriculture, are mainly due to the lack of safe equipment for use, due to inadequate working conditions, the lack of instructions for use and protective equipment.

Signs and symptoms of poisoning with different pesticides can be the following: dizziness, headache, nausea, vomiting, visual disturbances, abdominal pain, convulsions, cough, trembling, irritability, delirium. Numerous studies have shown that exposure and long-term use of pesticides can cause effects on the immune system, the reproductive system, the nervous system, can cause hormonal disorders, dermatological effects, can cause cancer (generally cancer of the liver and bladder biliary) [8]. An example report of exposure to pesticides in SE Turkey: food poisoned with hexachlorocyclohexane, which resulted in the death of 90% of the affected segment, and 10%_they showed diseases such as liver cirrhosis, neurological, arthritic. In another study it was detected an increase in the mortality of workers involved in the production of DDT. The study included workers employed for a minimum of 6 months prior to December, 1964. Effects of exposure to DDT detected were: liver cancer, gallbladder cancer, cerebrovascular disease [45].

4. The impact of pesticides in the environment

Pesticides can contaminate surface water, reach surface water through runoff from plants and treated soils. Soil contamination with pesticides can lead to the decline of beneficial microorganisms populations present in the soil and can cause damage to various plants. Pesticides have negative effects on non-target species and affect animal and plant biodiversity as well as aquatic and terrestrial ecosystems. Approximately 80% - 90% of applied pesticides can volatilize within days of application and thus can harm other organisms [13]. The uncontrolled use of pesticides leads to the decline of several terrestrial and aquatic species of animals and plants. Insecticides are considered the most toxic pesticides, while fungicides and herbicides are placed on the second and third position on the toxicity list.

The penetration of pesticides in natural ecosystems depends on their solubility in water. The pesticides soluble in water can contaminate groundwaters, surface water bodies. Besided, fat-soluble pesticides generate the biomagnification process in the body of animals, being involved in the food chain [8, 13].

Small concentration of pesticides can enter the body of the grasshopper (primary consumer). Rodents (secondary consumers) eat many grasshoppers and therefore the concentration of pesticides will increase in their bodies. If the top predator, such as the owl, eats the rodent, the concentration of pesticides in its body increases [13]. The accumulation of pesticides can affect in a direct manner predators and scavengers. Indirectly, pesticides can diminish populations of weeds, shrubs and insects needed to feed the higher orders and declines of rare animal and bird species [13].

4.1. Pesticide threats to aquatic biodiversity

Water contaminated with pesticides is a great threat to aquatic life. It can affect aquatic plants, decrease dissolved oxygen in water (80% of dissolved oxygen is provided by aquatic plants and is needed to support aquatic life), and can cause changes in fish populations. In general, pesticide levels are much higher in surface water than in groundwater [50, 51]. Amphibians are affected by pesticide-contaminated surface waters (e.g. carbaryl is toxic to several amphibian species, low concentrations of malathion affect plankton) [13, 52].

Pesticides can generate impacts and risks on the aquatic environment through direct and indirect effects on the organisms in this environment as discusses above (Figure 9) [52]. The direct action of pesticides, which depends on the concentration of substances, affects the physiological functions of organisms. The indirect effects address the biotic community [2, 7]. There are other factors that influence the occurrence and magnitude of the adverse effects of pesticides in the environment, such as: maturity of exposed organisms; the exposure time and history of exposures that can determine the increase of tolerance or sensitivity; type of pesticides; cumulative effects of pesticides; density and structure of the ecological population; solubility of pesticides in water; distance from the place of application to a body of water; weather conditions; soil type; method used for pesticide application [16].

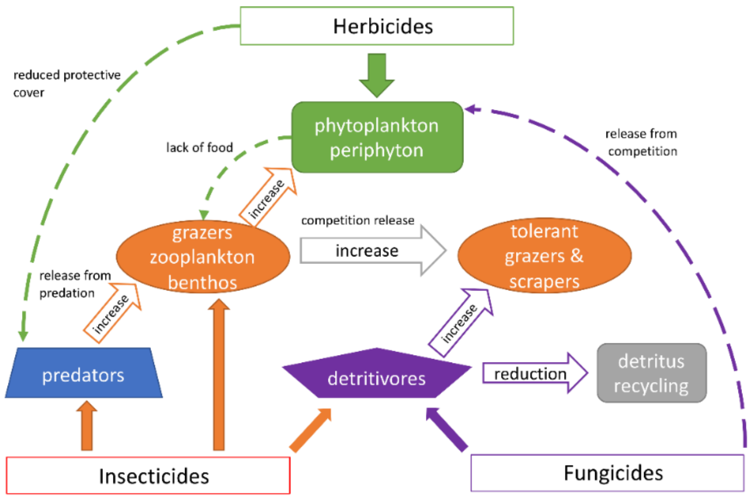

Fig. 9. Indirect effects of pesticides on aquatic ecosystems are indicated by hollow and dashed arrows and direct effects by solid arrows (from Sánchez-Bayo [52], under the terms and conditions of the Creative Commons Attribution (CC BY) license).

Pesticides applied to crops can undergo several transformations and can be transferred to other environments. Toxic residues reaching aquatic systems can eliminate aquatic species, reduce biodiversity and compromise the functioning of aquatic ecosystems, and some toxic substances even in low concentrations are bioconcentrated and can act on sensitive species. Organophosphorus compounds can persist for days/weeks in water and can be accumulated by crustaceans and fish [53]. Pesticides can get into water in several ways. When sprayed, they can move outside the contaminated area, percolate or leach through the soil layers, and soil erosion can also lead to the transport of pesticides into water [16, 54].

A highly water-soluble chemical will tend not to accumulate in soil or biota due to its strongly polar nature. This suggests that it will degrade by hydrolysis, which is the favored reaction in water. A chemical with a high solubility and vapor pressure will generally vaporize and become airborne. The distribution coefficient is an indicator of the environmental fate of a chemical because it gives a general idea of how a chemical will be distributed in the environment. In general, a high value means that a chemical tends to be in an organic medium (non-polar) and not in water (polar). This means that it will have low solubility in water [55].

4.2. Pesticide threats to terrestrial biodiversity

Exposure to pesticides can also cause negative effects on terrestrial plants. The herbicide glyphosate increases plant susceptibility to disease and reduces seed quality. Even low doses of sulfonylurea herbicides, sulfonamides and imidazolinones have a devastating impact on the productivity of non-target crops, plants and wildlife.

Populations of beneficial insects such as bees can be significantly reduced by the use of insecticides (neonicotinoid insecticides such as clothianidin and imidacloprid are toxic to bees). At the beginning of the 21st century, the sudden disappearance of honey bees was observed due to the use of neonicotinoid insecticides. The honey and wax obtained from the hives contained a mixture of neonicotinoid pesticides in a significant proportion. Every year since 2006, bee populations have declined by 29%-36%. Numerous problems were detected on arthropods when exposed to pesticides [52, 56] (Figure 10).

Accumulation of pesticides in the tissues of bird species leads to their death. Eagle populations in the US have declined primarily due to exposure to DDT and its metabolites. Fungicides can indirectly reduce bird and mammal populations by killing the earthworms they feed on [13].

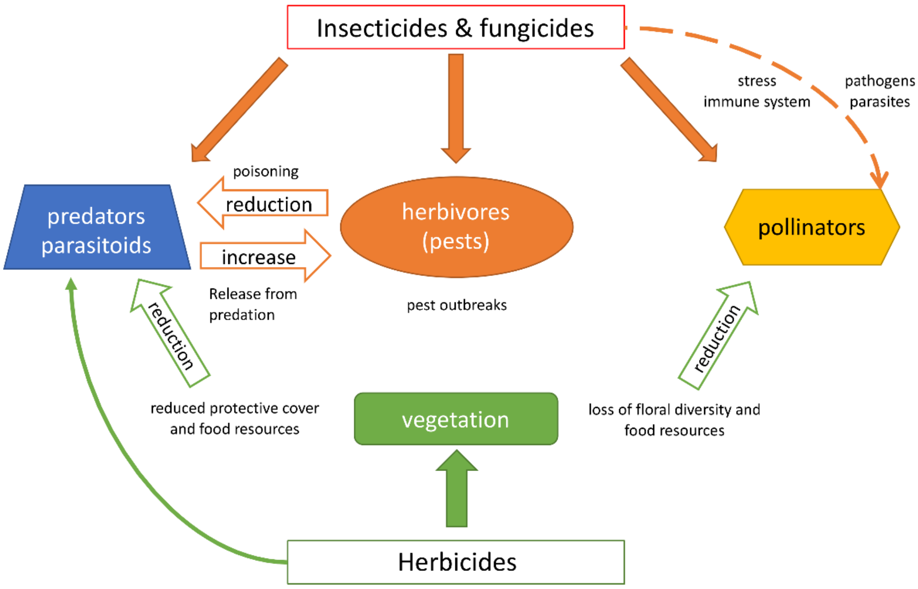

Fig. 10. Indirect effects of pesticides on terrestrial arthropods are indicated by hollow and dashed arrows and direct effects by solid arrows (from Sánchez-Bayo [52], under the terms and conditions of the Creative Commons Attribution (CC BY) license).

4.3. Pesticides in atmosphere

During pesticide application, a significant proportion is dispersed into the atmosphere by spraying or volatilization of the pesticide. Pesticides move in the atmosphere (atmospheric transport) and can be deposited outside their emission zone. The fate of pesticides is influenced by their partitioning between the gas phase and the particle phase. Given the low volatility of most commonly used pesticides, they are often adsorbed on the surface of atmospheric particles. They can undergo various processes that result in the generation of by-products that could be even more dangerous than the pesticides originally released [57].

Volatilization of pesticides after application to soil or crops is an important source of atmospheric emissions and then for pesticides dry or wed deposition (Figure 11) [58]. Volatilization rates range from 0% of the applied dose to more than 90% for highly volatile substances such as lindane. The degree of volatilization is highly variable because it depends not only on the physico-chemical properties of the substance, but also on weather conditions and processes taking place in and on the soil or crops. Fumigants are often highly volatile and are therefore major sources of atmospheric emissions. Numerous studies have shown that volatilization from plants can be to a greater extent than volatilization from soil, vapor pressure can give a first indication of the volatilization potential of a substance [59].

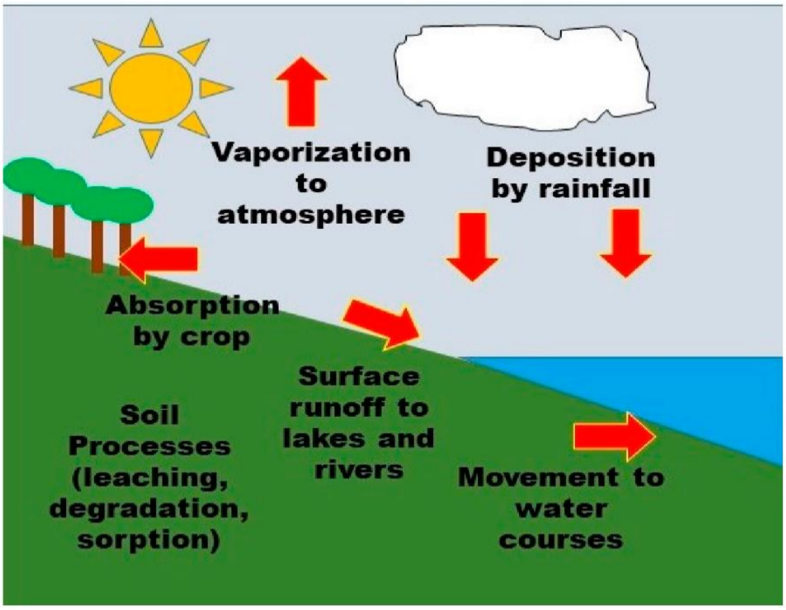

Fig. 11. Pesticide behavior in the natural environment (from Tudi et al. [58], under the terms and conditions of the Creative Commons Attribution (CC BY) license).

4.4. Pesticide treats in soil

Pesticides present in the soil can be absorbed by plants, degraded, reach the groundwater or volatilize. In addition, some of the chemical may become part of the soil structure as residues. Depending on their mobility and persistence, pesticides can migrate into and out of the soil and contaminate water and air [20]. The main pesticide transfer processes are: *a) atmospheric*: by spraying, volatilization and atmospheric transport, followed by re-deposition; *b) led by water*: drainage, surface and underground drains. The importance of each of the processes depends on the conditions of pesticide application, pesticide properties, climatic conditions and soil properties [31, 60].

During the application of pesticides by spraying, a certain portion of the applied amount may reach outside the target area, e.g. on unsuitable soil, plant and water surfaces. Volatilization of pesticides depends on pesticide properties (saturated vapor pressure, Henry's constant, K_{oc} etc.), soil properties (soil structure, water content, organic carbon content, etc.), climatic conditions (wind, temperature etc.) and how to apply pesticides.

Degradation of a pesticide in soil can occur through chemical or microbiological processes. Pesticides in soil are mainly broken down by microbial activity. The higher the microbial activity, the faster the degradation, and soil temperature plays an important role in microbial activity. Through a total degradation of a chemical product, CO_2, salts, water are formed and the harmless components of the chemical end up in the soil humus [60].

Degradation and sorption are causes that affect the persistence of pesticides in soil, which also depends on the chemical nature of the pesticide, the transport from soil to water and in turn to air and food. In Figure 12 the persistence of pesticides in the soil is reported. Some of the pesticides are more persistent and their residues can remain in the soil for days, weeks or years. Numbers indicate the number of compounds for which data are available [31, 53].

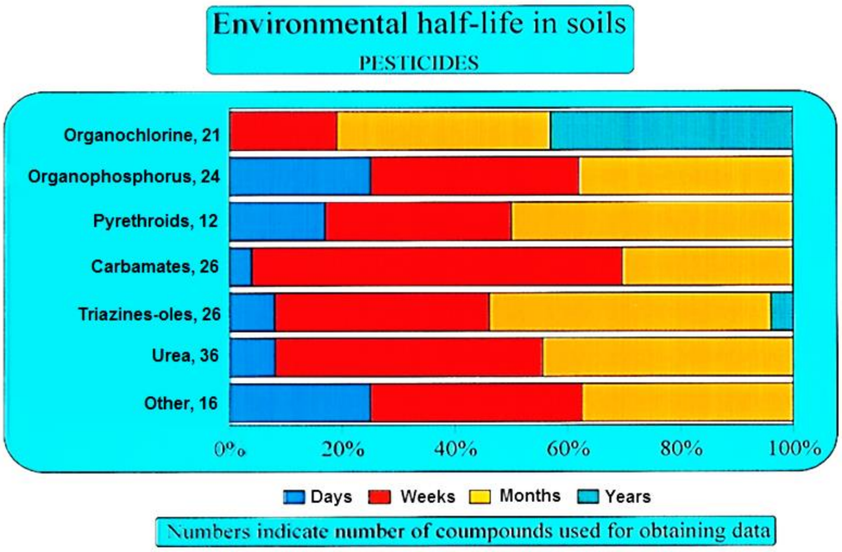

Fig. 12. Persistence of pesticides in soils (duration/half-life) (from Carvalho [53], under the terms of the Creative Commons CC BY license).

4.5. Pesticide in fruits and vegetables

The behavior of pesticides in plants results from the interaction between the properties of the substance and the plant characteristics and the environment. The behavior of a pesticide is the result of its characteristic movement, persistence and fate in the environment [61]. The fate of pesticides in the environment is characterized by a number of complex processes that occur in different components such as: air, soil, surface water and groundwater and plant [62].

4.5.1. Absorption of pesticides in plants

Absorption is the "movement" of chemicals from the surface of plant leaves into their leaves. The absorption of pesticides in plant leaves indicates the way in which we can understand the behavior of pesticides following the interaction of the physicochemical properties of pesticides with the environment [61].

Absorption of pesticides in plants depends on:

- *cuticle structure and properties:* on the surface of plant leaves there is a layer of waxy material known as the cuticle. Although cuticle composition and plant structure varies, it is generally less than 1 μm thick, but can vary from 0.1-20 μm; the outer region consists of epicuticular wax. The aerial parts of the plant are covered with cuticles, and any chemical must pass through the cuticle. The entry of pesticides into the plant requires contact with the surface and compatibility with the cuticle. The compatibility of pesticides and leaf cuticle depends on the interaction of chemical and physical properties. The polarity of the cuticle and pesticide is of major importance, thus the polarity of the cuticle increases from the surface of the leaf towards the pectins in the cell walls and into the aqueous environment of the cell. The outer portion of the cuticle favors the absorption of relatively nonpolar pesticides, and the inner portion of the cuticle favors the absorption of more polar pesticides [61].

- *lipophilicity of pesticides*: lipophilicity is probably the most important property of herbicides related to absorption and is normally described as the octanol/water partition coefficient between the plant cuticle or wax phase of the cuticle and the aqueous phase. Due to the lipoidal nature of epicuticular wax and cuticle, absorption tends to increase with increasing lipophilicity of chemicals [63].

- *pH in the environmental compartment:* most post-emergent herbicides are weakly acidic organic substances, so dissociation depends on the pH of the environment. The degree of dissociation influences the hydrophilic-lipophilic properties of the molecule to remain in a polar phase or to partition into a non-polar phase. The low pH of the solutions produces more undissociated molecules that are more lipophilic, but also with a low solubility in water and could crystallize on the surface of the leaf after drying of the droplets, so they are unsuitable for absorption [63].

- *ambient temperature:* plants are exposed to very different temperatures. On the leaf surface, the temperature can be 10°C higher or lower than the ambient temperature. Temperature is the predominant physical factor influencing cuticle permeability. The coefficients that contribute to permeability are temperature dependent, thus the diffusion coefficient of a molecule increases with temperature and the partition coefficient between the membrane and adjacent phases decreases with temperature. Results from a study involving leaf cuticles reported that cuticular permeability to water increased by approximately a factor of 2 in the temperature range 15°C-35°C; higher temperatures reaching up to 50°C and improving permeability by about an order of magnitude [63].

- *humidity:* several researchers have suggested that absorption and efficacy are affected more by high humidity after spraying than before, so one of the main advantages of high humidity was to prevent herbicide crystallization, which decreases the concentration of the active ingredient in solution, thus reducing penetration into the plant.

- *additives:* an additive or adjuvant is any compound that is included to the pesticide formulation to facilitate mixing, application or effectiveness of the pesticide, increasing the rate of absorption. Adjuvants can be of many kinds (vegetable and petroleum oils, dyes, surfactants, buffer solutes, humectants), but especially surface active agents, can significantly improve absorption effectiveness. They vary depending on the active ingredient and plant species [63].

4.5.2. Chemical behavior of pesticides in plants

The contact of pesticides with plants depends on the method of application (aerial spraying, ground), so most herbicides and insecticides are applied by aerial spraying, and the leaves and stems are the main interception components, and in the case of ground-applied pesticides, the roots are the main components absorbents [61].

Uptake, translocation and persistence of pesticides in plants can lead to high levels of toxic substances that pose a danger to human health and ecosystems [34]. Figure 13 shows the schematic representation of plant-environment interactions (air, water, soil components) with the processes that directly contribute to the absorption or transport of pesticides in plants (half-filled arrows) and the processes that directly contribute to the dissipation of pesticides from plants (solid arrows) [64].

The transfer of chemicals into plants can occur by [65]:

- desorption from the soil, followed by absorption by the roots from the solution applied to the soil;
- transfer from the air by dry and wet deposition of particles on plant surfaces, followed by desorption in the interior parts of the plant.

Pesticides show several types of behavior such as: behavior of pesticides on aerial parts of plants, behavior of pesticides on plant roots and inside the plant [61].

● ***Behavior of pesticides on the aerial parts of plants***

Pesticides that reach the aerial parts of the plant undergo the following processes: absorption, adsorption, volatilization, washing, degradation [61, 66].

- *absorption* (incorporation) - of chemicals into plants is necessary for systemic chemical action, and the degree of absorption indicates the effectiveness of applied treatments.

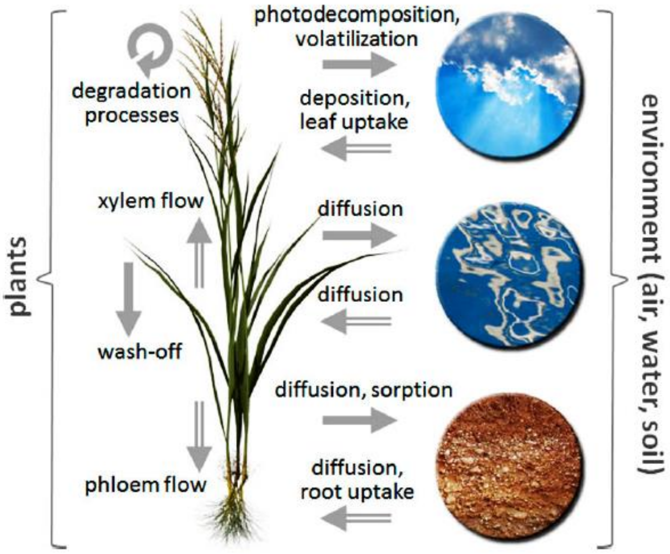

Fig. 13. Schematic representation of plant-environment interactions with processes directly contributing to pesticide uptake or transport in plants (half-filled arrows) and processes directly contributing to pesticide dissipation from plants (filled arrows) (with permission from Fantke and Juraske [64] Copyright American Chemical Society).

- *adsorption* - is the process of retaining a substance (pesticide) on the surface of a body (plant). The degree of adsorption depends on both the size of the leaf and the properties of the pesticide applied.

- *volatilization* - is not very important for substances with a low vapor pressure or a high heat of vaporization, but for some compounds, losses are high. Volatilization causes the substance applied to the crops to go elsewhere, and this reduces the effect of the treatment.

- *washing* - the amount of precipitation leads to a reduction of pesticide residues on plants, this means a decrease in the effectiveness of the pesticides applied and can lead to water pollution.

- *degradation* - is the breakdown of the substance and is important to analyze the effectiveness of the treatment and the impact on the environment. There are three types of degradation: chemical, photochemical and biological (with the help of microorganisms) degradation [20, 61]. The rate of microbial degradation is highly dependent on the amount and nature of pesticides present in the soil, the microbial population in the soil, and soil conditions that favor microbial activities, such as favorable temperature and pH, adequate soil moisture, aeration, and high organic matter content [19, 67].

● ***Behavior of pesticides in plant roots***

The chemicals present on the root as those on the aerial parts of the plant undergo the same processes, but the degree of operation of a process may be different. Pesticides that are soluble in water can be absorbed by the roots and reach other parts of the plant [61].

●***Behavior of pesticides inside plants***

Pesticides reached inside the plant are exposed to the following processes: translocation, storage, metabolism, exudation [61, 68].

- *translocation* - is the movement of substances in plants and is important because the fate of chemicals can vary in different parts of the plant (leaf, stem and root). Translocation takes place on the upper part of the plant in both xylem and phloem; but translocation to roots occurs only in the phloem. Pesticides absorbed on the leaf surface but not reaching other parts of the plant are lost when the leaves fall, and pesticides reaching the roots can reach the soil surface.

- *storage* - the greatest amounts of pesticides are near the point of absorption and where there is intense metabolic activity.

- *metabolism* changes the structure of pesticides, can lead to detoxification or activation, and can occur on both the leaf, stem and root.

- *exudation* is the escape (elimination) of pesticides (as vapors) from within the plant through small plant pores onto the plant surface.

4.5.3. Pesticide residues in plants

A statistic of the cumulative data from 1,074 eggplant samples, 1,201 banana samples, 994 broccoli samples, 1,386 sweet pepper samples and 1,287 table grape samples is presented in an European Union report Report [69].

- eggplants:

During an investigation performed in 2015, a number of 1,074 eggplant samples were analyzed and the results are shown in Figure 14. A comparison with a similar analysis performed in 2012 showed that the global quantification rate is similar, meaning that 32% of samples contained pesticide residues. The most frequently detected pesticides in 2015 were: acetamiprid (9.9%), imidacloprid (6.4%) and cyprodinil (5.9%), while the maximum allowable residual limit was surpassed by 4 different pesticides: acetamiprid, biterethanol, methomyl and dichloran. These exceedances were not detected in 2012 [69].

- bananas

The same statistic from 2015 refers to 1,201 banana samples analyzed. The results are synthesized in Figure 15. Compared to 2012, a 78% decrease in samples containing pesticide residues was observed. The most frequently detected pesticides were: thiabendazole (47.9%), imazalil (45.8%) and azoxystrobin (29.8%).

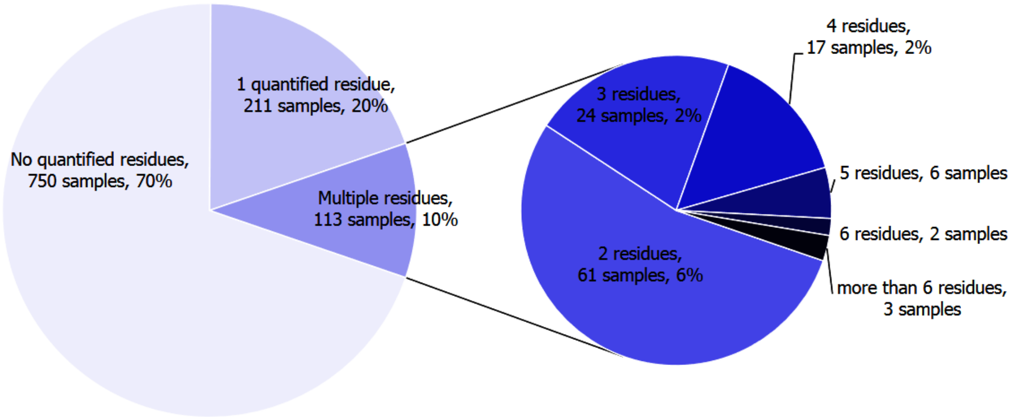

Fig. 14. Number of quantified residues in individual eggplant samples (from EFSA Journal [69] under the under the terms of the Creative Commons Attribution License (CC BY ND).

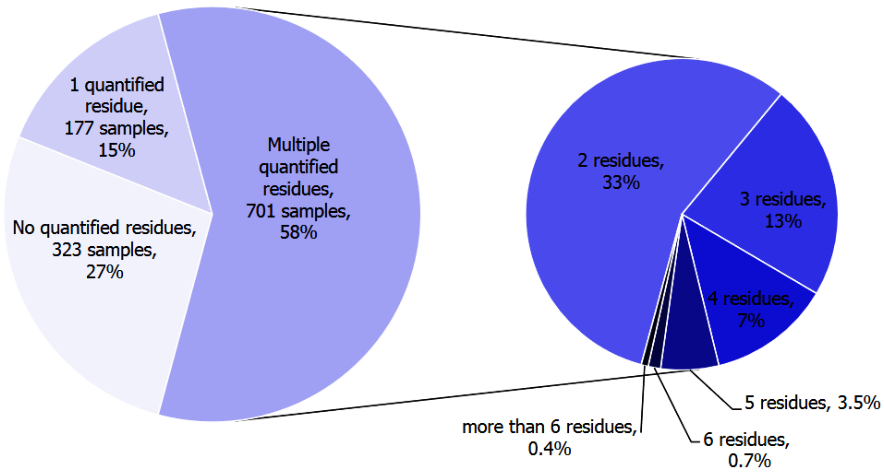

Fig. 15. Number of quantified residues in individual bananas samples (from EFSA Journal [69] under the under the terms of the Creative Commons Attribution License (CC BY ND).

- broccoli

In 2015, 994 broccoli samples were analyzed, from which 54.6% were found with no quantifiable pesticide residues, while in 45.4% one or more pesticides were detected in quantifiable concentrations. Multiple residues were reported for 14.8% of samples and up to 6 different pesticides were reported in one broccoli sample (Figure 16). Compared to 2012, the global quantification rate increased to 31.8%.

A number of 9 different pesticides had exceeded the maximum allowed residual limit. The most frequently pesticides were dithiocarbamates and chlorpyrifos [69].

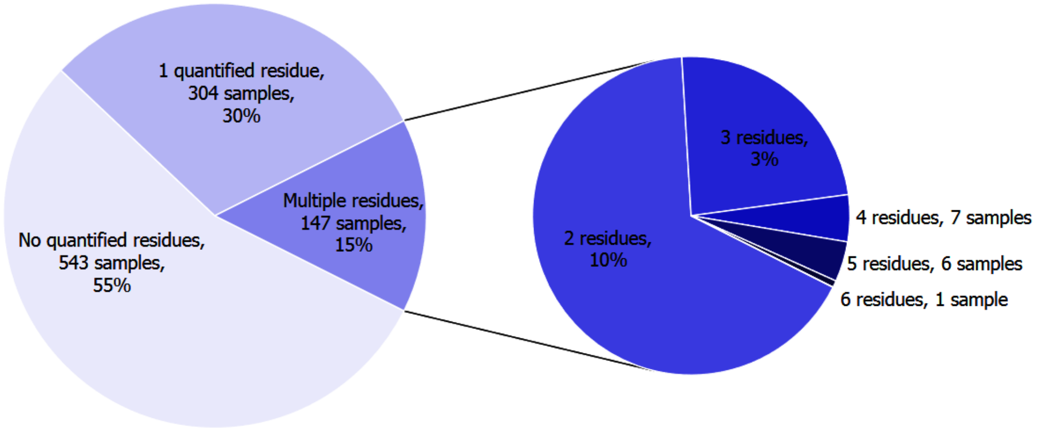

Fig. 16. Number of quantified residues in individual broccoli samples (from EFSA Journal [69] under the under the terms of the Creative Commons Attribution License (CC BY ND)

- *sweet pepper*

The analysis in 2015 for sweet pepper samples showed that, from 1,386 samples analyzed, in 52.2% no quantifiable pesticide residues were found, while in 47.8% one or more pesticides were detected in quantifiable concentrations (Figure 17). The global quantification rate is similar to the period of 2012, where 47.4% of the samples contained pesticide residues. For 9 different pesticides, the maximum allowed residual limit was exceeded. Exceedances of maximum limit values were recorded for the first time for diniconazole, propargite, azinphos-methyl and fenthion [69].

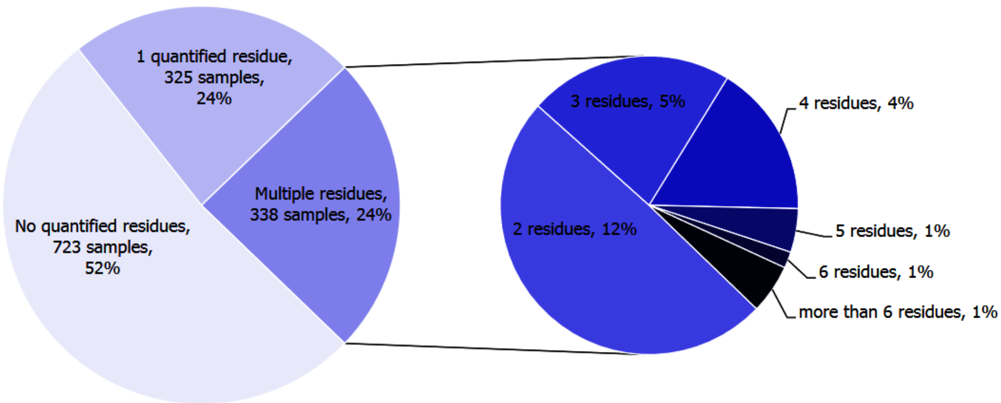

Fig. 17. Number of quantified residues in individual peppers (sweet) samples (from EFSA Journal [69], under the under the terms of the Creative Commons Attribution License (CC BY ND).

- grapes

In 2015, 1,287 samples of table grapes were analyzed; in 22.7% no quantifiable pesticide residues were recorded, while 77.3% contained one or more pesticides in quantified concentrations. Multiple residues were reported in 58.3% of samples (Figure 18). The most common pesticides found are fungicides such as boscalid, dimethomorph, dithiocarbamates and fenhexamid, as well as plant growth regulators ethephon [69].

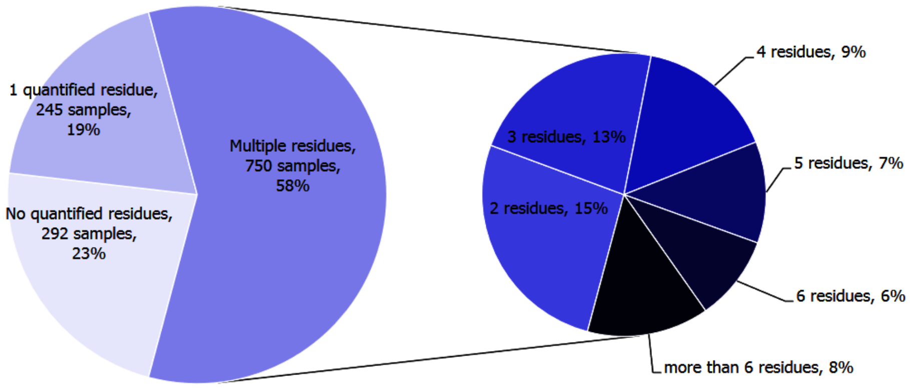

Fig. 18. Number of quantified residues in individual table grapes samples (from EFSA Journal [69], under the under the terms of the Creative Commons Attribution License (CC BY ND).

In Romania, the Ministry of Agriculture and Sustainable Development has the task of monitoring pesticide residues in vegetables and fruits every year through monitoring plans. In 2016, within the Laboratory for the Control of Pesticide Residues in Plants and Vegetable Products in Bucharest, a number of 343 fruit samples and 683 vegetable samples were analyzed (vegetable and fruit samples were taken from warehouses, shops, markets), and the results were as follows [70]:

- *in the case of fruits*: 167 samples showed values below the maximum allowed limit and for 6 fruit samples (4 apple samples, one peach sample and one strawberry sample) they exceeded the maximum allowed concentration, and in the rest of the samples there were no residues found (Table 3) [70].

The most pesticide residues found in fruit samples are tebuconazole (apples, strawberries, cherries, apricots, sour cherries, apricots, table grapes) carbendazim (apples, strawberries peaches, table grapes), cyprodinil (apples, cherries, pears, table grapes), boscalid (apples, strawberries, plums).

- *in case of vegetables:* pesticide residues were detected in 193 samples, 186 samples showed pesticide residues below the maximum allowed concentration and 7 samples (5 salad samples, one parsley sample and one potato sample) exceeded the limit allowed by law (Table 4) [70].

The most pesticide residues detected in vegetable samples are: iprodione (lettuce, peppers, tomatoes, green beans, radishes, potatoes) fludioxonil (lettuce, tomatoes), chlorothalonil (lettuce, green onions, carrots, eggplants, tomatoes), carbendazim (potatoes, beans, cucumbers, peppers, leeks, parsley leaves).

Table 3. Results regarding fruit samples [70]

No. crt.	***Fruit***	***Samples analyzed***	***Samples with pesticide residues***	***Samples without pesticide residues***
1	Apples	67	40	27
2	Plums	48	14	34
3	Wine grapes	40	21	19
4	Table grapes	29	2. 3	6
5	Strawberries	28	17	11
6	Cherries	26	14	12
7	Apricots	24	21	3
8	Watermelon	21	0	21
9	Pears	20	5	15
10	Melon	18	1	17
11	Peaches	17	12	5
12	Cherry	5	5	0
	Total	**343**	**173**	**170**

Table 4. Results regarding vegetable samples [70]

No. crt.	***Vegetables***	***Samples examined***	***Samples with pesticide residues***	***Samples without pesticide residues***
1	Tomatoes	59	27	32
2	Potatoes	54	10	44
3	Salad	51	35	16
4	Pepper	50	16	34
5	Cucumbers	38	15	2. 3
6	Green onion	38	9	29
7	Eggplants	35	4	31
8	Onion	31	1	30
9	Beans	30	3	27
10	Parsley leaves	29	14	15
11	Spinach	29	10	19
12	Cabbage	27	0	27
13	Kidney	25	3	22
14	Green beans	22	7	15
15	Pumpkins	19	5	14
16	Carrot	18	6	12
17	Celery	18	4	14
18	Cauliflower	17	1	16
19	Leek	17	2	15

20	Peas beans	14	3	11
21	Dill	12	9	3
22	Mushrooms	11	2	9
2. 3	Lovage	10	3	7
24	Garlic	7	1	6
25	Parsnip	7	1	6
26	Pea pods	6	0	6
27	Green garlic	5	1	4
28	Broccoli	2	1	1
29	Kohlrabi	1	0	1
30	Beet	1	0	1
	Total	**683**	**193**	**490**

Conclusions

The development of society implicitly led to the development of the pesticide industry, necessary for the elimination of pests present in agricultural crops. In addition to the benefits they bring, they can pose risks to human health, as the population can be exposed to pesticides through inhalation, dermal contact or ingestion.

Although specific groups of pesticides or a certain pesticide are intended to combat a specific pest, relatively significant amounts of pesticides reach other targets than the destination for which they were deliberately released into the environment. The fact that pesticides contaminate water, air, soil regardless of the source from which they come, requires knowledge of their properties and behavior in the environment, as support for evaluating the impact that pesticides induce in the environment and for human health. Also, human health can be threatened by the consumption of fruits and vegetables products, which can contain pesticide residues. In spite to their nutritional value, these products can be a source of toxic substances, represented by these pesticide residues. In addition, fruits and vegetables are commonly consumed raw or semi-processed and, consequently, they contain higher levels of pesticide residues than other food groups. These conclusions are in line with the European Food Safety Authority (EFSA) statistics, based on the investigations of some groups of vegetables and fruits: 1,074 eggplant samples, 1,201 banana samples, 994 broccoli samples, 1,386 sweet pepper samples and 1,287 table grape samples, which were found to contain residues of some pesticides with relevant toxicity.

In this context, studies and research should demonstrate the need to apply less toxic pesticides or biopesticides, easy to be degraded in the environment and encourage practices that abate pesticide use and exposure through diet, while preserving food integrity.

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