MANUAL FOR SAFE HANDLING AND USE OF PLANT PROTECTION PRODUCTS

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FOREWORD

The manual, whose foreword you are currently reading, is the result of the work of the authors who have been dealing for years with the registration of plant protection products, control of plant protection products after the registration and control of plant protection product residues in food, plant pests, pathogens and weeds, as well as the measures for their control, storage, safe handling and proper application of plant protection products and equipment for their application.

The aim of the authors is to gather in one place the training material, which shall be included in the training of professional pesticide users, distributors and advisers in accordance with Annex I of Directive 2009/128/EC. Since this is a multidisciplinary field, unified training material on safe handling and application of pesticides has so far not been available in one place, in one book, manual or other publication.

The manual is intended for all users of plant protection products, distributors of plant protection products, as well as for the advisors in the sales of plant protection products and advisors in food production. The manual is mainly intended for institutions authorised for training implementation and authorised lecturers in order to achieve a harmonised training system with a purpose of avoiding that the authorised institutions and lecturers have different interpretations of the areas that shall be included in training.

The manual is written in a simple and understandable manner, even when it deals with quite challenging topics. The manual is richer in content than necessary for certain categories or subcategories of persons subject to training, but also poorer in content for the purposes of certain subcategories of persons subject to training. For example, a professional user of pesticides does not need to be acquainted with the system of registration of plant protection products, but what they need to know is that the plant protection product used shall be registered. Furthermore, the professional user of pesticides using plant protection products intended for professional use (e.g. for seed treatment or fumigation) shall know more than the content of these areas included in the Manual.

Therefore, the authorised institutions are expected to adjust their publications and training materials to the target group, and authorised lecturers are expected to determine the importance of individual thematic units and to adjust their presentations and lectures to a targeted group of persons subject to training.

The Ministry of Agriculture published the Manual on the website of the Ministry (http://www.mps.hr/) and thus ensured that the Manual is available to everyone free of charge.

The establishment of the training system in the Republic of Croatia began somewhat later than planned due to a lack of administrative capacity of the Ministry in the field of the sustainable use of pesticides. This is a long-term problem, which we inherited and resolved in May this year through an internal reallocation of employees. In order to initiate the training system as soon as possible, this version of the Manual has not been proofread. After proofreading is complete, the Ministry shall release a new version of the Manual.

I would like to thank the authors, reviewers and all those who assisted in the preparation of this manual in any manner.
1.1 Placement of plant protection products on the market

The placement on the market of plant protection products includes any form of keeping of a plant protection product for the purpose of sale, including offering for sale or any other form of transfer, with payment or free of charge, as well as the sale, distribution and other forms of transfer, but not returning to the previous seller. The release for free circulation represents the placement on the market. The process of releasing the goods into free circulation is the process by which foreign (imported) goods acquire the status of domestic goods, and customs supervision over it is terminated.

The placement of plant protection products on the market in the Republic of Croatia is regulated through the Act on the Implementation of the Regulation (EC) 1107/2009. The subject Act has been in force since 1 July 2013 and it allows for direct implementation of the Regulation (EC) No. 1107/2009 in the Republic of Croatia. The regulations are legal acts of the European Union, the provisions of which may not be transferred into the national legislation of the Member States of the European Union by creating a new regulation. Member States shall ensure direct implementation of the regulations in their territory. For the implementation of certain regulations, Member States are not required to prepare any legal act, but are required to implement European law directly on the basis of the Treaty of Accession to the European Union. In case of failure to implement the regulations, the European Commission may initiate a misdemeanour procedure against the Member State, which fails to implement the *acquis communautaire*. Certain regulations, such as Regulation (EC) No. 1107/2009, require from the Member States of the European Union to develop a national regulation, which shall ensure direct implementation of regulations and stipulate the competent authorities for the implementation of the regulations, the tasks of the competent authorities, the offenses for violation of the provisions of the regulations and similar. Through the Act on the Implementation of the Regulation (EC) No. 1107/2009, direct implementation of the Regulation has been ensured in the Republic of Croatia and the competent authority, the tasks of the competent authority, authorised professional institutions and their tasks, inspection and administrative supervision and penalty provisions in case of violation of the provisions of the Regulation have been regulated. Pursuant to Regulation (EC) No. 1107/2009, the European Commission adopted a number of implementing regulations, which are directly applicable in the Member States of the European Union and which regulate in more detail the placement on the market of plant protection products, approval of active substances, safeners, synergists, co-formulants, adjuvants, low-risk substances, basic materials, zonal system of registration, candidates for replacement, hormonal disruptors, comparative risk assessment, parallel trade, extension of registration for small crops and small applications, placement on the market of treated seeds, data protection and other. In order to facilitate the implementation of Regulation (EC) No. 1107/2009 and implementing regulations adopted on the basis of this Regulation, the European Commission adopted a number of guidance documents.

Until 2005, the placement of plant protection products on the market in the Republic of Croatia was regulated through the Plant Protection Act and by-laws adopted thereunder.

From 2005 until 1 July 2013, the placement on the market of plant protection products was regulated by the Act on Plant Protection Products and by-laws adopted thereunder. The aforementioned Act and by-laws adopted pursuant to this Act were harmonised with Directive 91/414/EEC. The Directives are legal acts of the European Union, the provisions of which, unlike the provisions in the regulations, shall be transferred into the national regulations of the Member States.

At the European Union level, through the adoption of Directive 91/414/EEC in 1991, uniform criteria for the evaluation of active substances and formulations were established, as well as for the assessment
of risks to human and animal health and the environment. The implementation of the subject Directive was initiated in 1993.

Despite the establishment of a unified legal framework for the evaluation of active substances and formulations, unwanted pesticide residues in soil, water and the environment in general can still be found at the European Union level. Furthermore, in a certain percentage of agricultural products of plant and animal origin, pesticide residues above the maximum residue level (MRL) of pesticides can be found.

For the aforementioned reasons, the "Thematic Strategy on the Sustainable Use of Pesticides" was adopted in 2002 at the European Union level, which establishes a series of measures for achieving the overall objective, reduction of the risk to the environment, human and animal health.

The adoption of the Strategy was followed by a series of regulations aimed at creating the legal basis for achieving the overall objective. In 2005, Regulation (EC) No. 396/2005 on maximum residue levels of pesticides in or on food and feed of plant and animal origin was adopted. Subsequently, Directive 2009/128/EC on Establishing an Action Framework to Achieve the Sustainable Use of Pesticides, Regulation (EC) No. 1185/2009 concerning statistics on pesticides and Directive 2009/127/EC with regard to the machinery safety were adopted in 2009. For the full realisation of the objectives of the Strategy, it was necessary to revise the Directive 91/414/EEC, which was replaced with Regulation (EC) No. 1107/2009.

In Croatia, the provisions of the Act on Plant Protection Products regulated the registration system of plant protection products, which was used to approve their placement on the market, uses, requirements of application, use restrictions, requirements for distributors and users of plant protection products, the requirements for pesticide application equipment, post-registration control of plant protection products, pesticide residues monitoring, inspection and other requirements relating to plant protection products and their use.

The provisions of the Act on Plant Protection Products were harmonised with the provisions of Directive 91/414/EEC, and the aforementioned Act also established the framework for action at the national level in those segments, which were not regulated at the European Union level. The aforementioned Directive was replaced with the Regulation (EC) No. 1107/2009. The application of this Regulation for the European Union Member States began on 14 June 2011, and its direct application in Croatia began on 1 July 2013 on the basis of the Act on Implementation of Regulation (EC) No. 1107/2009. This Regulation establishes higher requirements and standards for the evaluation of active substances used in plant protection products and ensures greater protection of the environment, as well as human and animal health.

Since the area of plant protection products and pesticide residues in food is governed by regulations, legal acts, which are directly applicable through the latest regulations at the European Union level, the following acts that allow for direct application of the Regulations were adopted in June 2013:

- Act on the Implementation of Regulation (EC) No. 1107/2009 concerning the placing of plant protection products on the market and
- Act on the Implementation of Regulation (EC) No. 396/2005 on maximum residue levels of pesticides in or on food and feed of plant and animal origin.


By entry into force of the Act on sustainable use of pesticides, the Act on Plant Protection Products ceased to be valid in its entirety.
1.1.1 Registration of plant protection products

Regulation (EC) No. 1107/2009 concerning the placing of plant protection products on the market was published on 24 November 2009, and its implementation began on 14 June 2011, with many transitional periods. The Regulation establishes new standards with the aim of raising the level of safety to human and animal health, and the environment.

In the Republic of Croatia, the Ministry of Agriculture and two authorised institutions for documentation evaluation and risk assessment participate in the process of registering plant protection products (Figure 1.1).

- **The Ministry of Agriculture** is the main coordinator of all activities regarding the registration of plant protection products and issuing licenses for plant protection products. The Ministry receives applications for the registration of plant protection products or applications for the issuance of certain licences, after which it performs a completeness check of the submitted documentation and, if necessary, requests additional documentation from the applicant. Applications and supporting documentation shall be submitted in three identical copies. Upon determining the completeness of submitted documentation, two identical copies of documentation are sent to the authorised institution for documentation evaluation and risk assessment. If necessary, the authorised institutions request the submission of additional documentation, certain amendments to the request, explanations, etc. Communication with the applicant during all phases of the plant protection product registration procedure takes place through the coordinator in the Ministry of Agriculture. After the authorised institutions have completed the documentation evaluation and risk assessment, the institution that is responsible for coordinating the evaluation procedure submits the proposal for registration to the Ministry of Agriculture. Based on the proposal of the authorised institution, the Ministry of Agriculture issues a decision on the registration of a plant protection product.

- **The Croatian Centre for Agriculture, Food and Rural Affairs - Institute for Plant Protection** performs the documentation evaluation and risk assessment activities in the following areas:
  - evaluation of active substance and plant protection product identity,
  - analytical methods,
  - effectiveness of plant protection products,
  - pesticide residues in food,
  - behaviour in the environment,
  - ecotoxicology,
  - exposure of operators, workers and other bystanders.

At the request of the Ministry of Agriculture, the Institute for Plant Protection prepares proposals for the registration of plant protection products, proposals for the issuance of certain licences for plant protection products, proposals to extend the registrations, proposals to extend the registrations for small applications and small cultures, expert opinions in the field of plant protection products.

- **The Institute for Medical Research and Occupational Health** performs the documentation evaluation and risk assessment activities in the following areas:
  - toxicology of mammals,
  - exposure of operators, workers and other bystanders.

At the request of the Ministry of Agriculture, the Institute prepares the proposals for the registration of plant protection products, the proposals for the issuance of certain licences for plant protection products, proposals to extend the registrations, proposals to extend the registrations for small applications and small cultures, expert opinions in the field of toxicology.
of mammals and exposure of operators, workers and other bystanders with regard to the plant protection products.

**Figure 1.1:** Schematic representation of the plant protection product registration procedure in the Republic of Croatia (prepared by: V. Novaković)

The main changes introduced by Regulation (EC) No. 1107/2009 in comparison with Directive 91/414 /EEC are the following: additional criteria for the evaluation of active substances (cut-off criteria), comparative risk assessments and candidates for replacement, zonal registration of plant protection products and parallel trade.

There are no significant changes regarding the approval procedure for the plant protection product active substances. Active substances continue to be approved at the European Union level. The industry prepares the necessary studies and tests for the preparation of documentation and selects the Rapporteur Member State (RMS), which represents the company before the European Commission and the European Food Safety Authority (EFSA), which performs the risk assessment in all relevant areas, and the European Commission and Member States, through their representatives in the Standing Committee on the Food Chain and Animal Health - Plant protection products - Legislation, discuss and adopt decisions on the approval of active substances by a qualified majority. Active substances are usually approved for a period of ten years and they are subject to regular re-evaluation, and in the case of new scientific insights, they are subject to re-evaluation even prior to the expiry of the approval period.

In order to further reduce the risk to human and animal health, and to protect the environment against pollution, additional criteria for the approval of active substances have been established. In order to protect human and animal health, active substance classified in certain categories shall not be eligible for approval. These categories are:

- mutagenic substances of 1A and 1B categories,
- 1A and 1B carcinogenic substances and
- 1A and 1B reproductive toxicants.

For the purpose of environmental protection, active substance classified in certain categories shall not be eligible for approval. These categories are:
- persistent organic pollutants (POPs)
- persistent bio accumulative and toxic substances (PBTs) and
- very persistent and very bio accumulative substances (vPvBs).

In addition to the aforementioned categories, the substances that shall not meet the requirements for approval are also those substances, which shall be classified as endocrine disruptors based on uniform criteria. The categorisation of the aforementioned substances is performed in coordination by the European Chemicals Agency (ECHA) in cooperation with the European Food Safety Authority (EFSA).

The use of the substances, which meet the requirements to be classified in one of the above categories shall not be prohibited immediately. Such substances shall become candidates for the replacement and shall be published on the list of candidates for the replacement. The registration of plant protection products containing active substances, which are on the list of candidates for replacement may be revoked and its use may be prohibited if there are more acceptable alternatives for human and animal health, and the environment. If there are no acceptable alternatives, plant protection products containing candidates for replacement shall be issued a registration for a period of up to seven years. The process of searching for and selecting alternatives is called a comparative risk assessment and is implemented at the national level. Each state searches for alternatives within all registered plant protection products, also taking into account non-chemical plant protection measures.

Along with regulating the active substances approval system, Regulation (EC) No. 1107/2009 regulates the approval system of low-risk substances, synergists, safeners, co-formulants and adjuvants. The Regulation stipulates which substances may be considered low-risk substances, and plant protection products containing these substances are considered to be plant protection products of lower risk. Such plant protection products are approved for a period of up to fifteen years, the approval procedure is shorter, and the period of data protection is longer. Safeners and synergists are approved as active substances and are subject to regular re-evaluation. Special requirements for the approval shall be established for co-formulants. Those co-formulants, which do not meet the requirements shall be published on the list of banned co-formulants in plant protection products.

Another novelty is also the basic substances approval system. Basic substances are substances, which have traditionally been used in plant protection (e.g. Equisetum arvense, calcium hydroxide, sucrose, Quassia, vinegar, lecithin ...). The basic substance may be approved only if the substance has not been approved as an active substance in plant protection products. The substances approved as basic substances shall not be used as active substances in plant protection products and shall not be placed on the market as a plant protection product. These substances may be used for the protection of plants against harmful organisms in accordance with Annex I and II of the Review Report or Draft Review Report.

Unlike the active substances approval procedure, where there are no major novelties, the approval procedure for plant protection products as final formulations has been completely amended and is completely new. Pursuant to Directive 91/414/EEC, each state performed a risk assessment in all relevant areas and approved plant protection products at the national level. The active substance shall have been approved at the European Union level or through the temporary registration approval procedure.

Regulation (EC) No. 1107/2009 established a zonal registration system for plant protection products. Member States are divided into three administrative registration zones:

- **Zone A - Northern zone**, which includes Denmark, Sweden, Finland, Lithuania, Latvia and Estonia,
- **Zone B - Central zone**, which includes United Kingdom, Ireland, the Netherlands, Germany, Belgium, Luxembourg, Austria, Slovenia, Slovakia, Czech Republic, Poland, Hungary, Romania,

- **Zone C - Southern zone**, which includes France, Spain, Greece, Italy, Portugal, Bulgaria, Malta, Cyprus and Croatia.

Administrative zones have been established in order to avoid double work. Pursuant to Directive 91/414/EEC, each European Union Member State performed the documentation evaluation and risk assessment with the purpose of registering plant protection products in its territory, and zonal registration system recognises the risk assessment performed by one Member State in the same registration zone or one Member State from any registration zone in case of an interzonal registration procedure. In order to reduce the administrative burden for the industry and for the competent authorities of the Member States, as well as to ensure better consistency and availability of plant protection products, the plant protection product registrations, which are approved by one Member State shall be accepted in other Member States if the agricultural, environmental and climate conditions are comparable.

For the aforementioned reasons, Member States are divided into zones with comparable agricultural, environmental and climate conditions in order to facilitate mutual recognition of risk assessment and approved registrations. However, climate characteristics also differ at the level of individual states, and it is therefore necessary to take those facts into consideration during the registration of plant protection products.

The climate is the average state of the atmosphere (gaseous layer surrounding the Earth) over a certain area observed over a longer period (25 to 35 years). The climate is affected by many factors, such as latitude, ocean currents, the distribution of land and sea, relief and others. The Atlantic Ocean is a major source of humidity for Europe. The humidity is brought by the western winds. Rainfall decreases by moving away from the Atlantic Ocean. In areas closer to the sea, most of the rainfall occurs in winter, and in more remote areas in summer.

The following types of moderate climate are predominant in Europe: moderately warm, moderately continental and Mediterranean climate. Polar and semi-arid climate are less represented. The climate has an immeasurable impact on the distribution of plant and animal species, the possibility of growing certain plant species outdoors, the distribution of pests, plant pathogens and weeds. Plant cover (vegetation) depends on the climate, but human influence is also important. Native vegetation is sparse. Man has destroyed large areas of natural vegetation by building settlements and roads, and turning forests into pastures and farmland.

The European Plant Protection Organisation (EPPO) divided the agro-climatic zones in Europe, Mediterranean and Eurasia (Figure 1.2). These zones have been designed to facilitate international exchange of data on efficiency and phytotoxicity of plant protection products. According to the EPPO division, four agro-climatic zones were established:

1. Mediterranean zone,
2. Maritime zone,
3. North-East zone,
4. South-East zone.
The Mediterranean zone includes the countries or parts of countries around the Mediterranean Sea, including Jordan, Macedonia and Portugal.

The Maritime zone is located north of the southwestern coast of France, through Lyon to the south border of Switzerland and Austria, in the west to the border of Austria and Hungary, further to the west along the border between the Czech Republic and Slovakia, west to the Oder River (the border between Poland and Germany). This zone also includes the entire territory of Ireland, Sweden and the United Kingdom.

The North-East zone includes countries and regions east of the Oder River (the border between Poland and Germany), north of the border between the Czech Republic and Poland, west of the border between Poland and Ukraine, north of the border between Ukraine and Belarus, Russia north of 50° latitude.

The South-East zone includes Bulgaria, Hungary, Serbia, Moldova, Romania, Russia south of 50° latitude, Ukraine, Slovakia, Slovenia, Croatia, Bosnia and Herzegovina, Montenegro and Turkey, except for the Mediterranean coastal areas. These areas indicate that there are different climate characteristics within them in comparison to the zone in which the countries have been classified. In some Member States, for example in France and Croatia, those differences are particularly pronounced. The data on efficiency from one zone may be considered eligible in another zone if the agricultural, environmental, climate and other conditions are comparable.
Climate characteristics and meteorological factors also have an impact on pesticide residues in treated products and soil. The same pesticide amount applied and the same number of treatments may, due to climatic differences, result in different concentrations of pesticide residues.

Due to these differences, two agro-climatic zones have been established for pesticide residues:

1. **Northern Zone** - Northern and Central Europe, which includes Sweden, Norway, Iceland, Finland, Denmark, United Kingdom, Ireland, northern France, Belgium, Netherlands, Luxembourg, Germany, Poland, Czech Republic, Slovakia, Austria, Hungary, Switzerland, Estonia, Latvia, Lithuania, Romania and Slovenia and

2. **Southern Zone** - Southern Europe and the Mediterranean, which includes Spain, Portugal, southern France, Italy, Greece, Malta, Croatia, Serbia, Bosnia and Herzegovina, Macedonia, Montenegro, Kosovo, Albania, Turkey, Bulgaria and Cyprus.

For uses in protected areas (greenhouses), as well as for uses after harvest or picking, one zone is applied. The aforementioned means that for the purposes of registering plant protection products, studies on pesticide residues may be prepared in any zone since the conditions are controlled.

An exception to the zonal system of registration are those registrations whose uses are not related to climate and other relevant conditions of use. Such uses are seed treatment, the use in protected areas, warehouses, silos and similar, and an interzonal registration system has been established for their use.

The prerequisite for submitting the application for registration is that the active substance contained in a plant protection product is approved at the European Union level. Until 14 June 2016, it is possible to apply for registration even when the active substance is in the approval procedure. In that case, a **temporary registration** is issued.
The company applying for registration selects one of the Member States within the registration zone as a zonal Rapporteur Member State (zRMS), and the subject state performs the documentation evaluation and risk assessment for the entire registration zone. Other states within the registration zone, in which an application for registration was submitted at the same time, shall refrain from documentation evaluation and risk assessments, and wait until the zRMS completes the documentation evaluation and risk assessment. The documentation evaluation and risk assessment procedure lasts for 12 months until the documentation is complete (Figure 1.3).

After the zonal Rapporteur Member State issues the registration for a plant protection product in its territory, other Member States in which a company applied for registration (concerned Member State - cMS) shall issue the registration within 120 days. When deciding on the requirements for the approval, the cMS may take into account national specificities and requirements (National Addenda) (Figure 1.3).

Figure 1.3: Schematic representation of zonal registration of plant protection products where France (FR) is a zonal rapporteur (zRMS) for Zone C - Southern zone, and the subsequent mutual recognition of registration in Bulgaria (BG) on the basis of registration in Greece (EL) (prepared by: V. Novaković)
In case when all states form a single zone, as with use in warehouses and similar, the company selects one state as an interzonal Rapporteur Member State (izRMS) for the entire European Union and submits the application to all Member States in which it intends to register a plant protection product. After the izRMS issues the registration in its territory, each cMS, regardless of the registration zone, shall issue the registration in their territory within 120 days (Figure 1.4).

The European Union Member State may refuse to issue a decision on the registration of a certain plant protection product for which the zRMS or izRMS has performed the documentation evaluation and risk assessment. Moreover, a Member State may refuse mutual recognition (MR) of a registration from another Member State. In both cases, it shall inform the applicant and European Commission of its decision and provide a professional and scientific explanation for such decision (Figure 1.4).

The applicant may subsequently apply for mutual recognition of registration in a Member State, which was not in the capacity of the cMS at the time of submitting the application for zonal registration. The aforementioned Member State shall accept the registration and issue a decision on registration within 120 days or reject the application for mutual recognition.

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**Figure 1.4:** Schematic representation of zonal registration of plant protection products where the United Kingdom (UK) is a zonal rapporteur (zRMS) for all zones, and the subsequent mutual recognition of interzonal registration in Portugal (PT) on the basis of registration in Spain (ES) (prepared by: V. Novaković)

The Regulation also allows the acceptance of registration from another registration zone if the climatic, environmental, agricultural and other requirements for the use are similar. However, in order to avoid a "domino effect", it is not allowed to accept the already accepted registrations (acceptance of an acceptance).
In accordance with the diagram in Figure 1.5, theapplicant shall submit a letter of intent with brief information on the plant protection product for which it intends to apply for registration to the competent authorities of the Member States in the registration zone. Before the official delivery of the letter of intent, the companies check in advance the possibility of competent authorities assuming the role of the zRMS. The competent authority decides on the acceptance or rejection of the registration application, taking into consideration a number of factors, such as the administrative capacity of the competent authority, the number of applications in the procedure, the issues, which are expected in the registration procedure, alternatives brought by the registration in terms of lower risk to human health and the environment, the plant protection issue, which is resolved through registration and similar. In the event that the competent authority accepts the role of the zRMS, the deadline for the official application submission for the plant protection product registration is agreed. The letter of intent shall be submitted at least 6 months before the expected submission of the application. Before applying for zonal registration, companies may arrange a pre-submission meeting with the competent authorities prior to submitting a formal request. At the subject meeting, the documentation is presented for the plant protection product for which the submission of registration application is planned, the issues in all relevant areas are discussed in detail, the deficiencies in the documentation are determined and the possibilities for their elimination are considered.

The Member States shall check the completeness of the submitted documentation within six weeks from the submission of the application for zonal registration. After receiving a request for registration and documentation (dossier), the competent authority of the zRMS shall perform the documentation evaluation and initial risk assessment within a deadline of 8 months, provided that additional deficiencies in the documentation are established and additional documents are requested as soon as possible and not later than within 6 months from receiving the documentation. In case of any additional documentation deficiencies, the total period of 12 months provided for the registration may be extended for an additional period of up to 6 months (12 months + 6 months). If deficiencies that cannot be eliminated within a period of 6 months are established, such application for registration
shall be rejected. After the expiry of 8 months from receiving the application, the zRMS delivers an initial risk assessment to all Member States, which are listed as cMS. The cMS Member States shall provide their comments on the initial risk assessment submitted by the zRMS within 6 weeks, taking into account their national requirements. After the expiry of the deadline for commenting on the initial risk assessment, within the remaining 2.5 months, out of a total of 12 months provided for the plant protection products registration, the zRMS shall complete the risk assessment taking into account the comments of all Member States from the registration zone and issue a decision on the plant protection product registration in their territory.

After the zRMS completes the risk assessment, other Member States listed as the cMS shall issue a decision on registration in their territory within 120 days. The deadline of 120 days also applies in the case of an application for mutual recognition of the registration (the case of Bulgaria: Figure 1.3 and the case of Portugal: Figure 1.4).

Considering the administrative capacity of the Ministry of Agriculture as the competent authority for the plant protection product registration and the capacity of authorised professional institutions, Croatia shall be listed as a cMS for most applications, meaning that we shall issue a decision on registration in the Republic of Croatia within 120 days after the zRMS Member State completes the risk assessment.

For the purposes of research and development in which an unregistered plant protection product is released into the environment, a permit for research and development shall be requested from the Ministry of Agriculture. The permit for research and development shall not be granted for a plant protection product containing genetically modified organisms unless a permission exists pursuant to Directive 2001/18/EC.

In special circumstances, when there are no registered plant protection products for controlling a certain disease, pest, weeds, a permit for emergencies in plant protection may be issued. A permit for emergencies shall be granted for a period of 120 days. The European Commission and all European Union Member States shall be informed on each permit for emergencies, which is issued.

For the purpose of fulfilling the Treaty of the European Union, Regulation (EC) No. 1107/2009 regulates the system of parallel trade of plant protection products. The aim of this system is to prevent large differences in prices of plant protection products among the European Union states. The application for parallel trade may be submitted by any distributor with its seat in the European Union, an association of agricultural producers or the end user. The prerequisites for the approval of parallel trade are that the plant protection product for which the parallel trade is requested originates from one of the European Union states, from the same producer and that is completely equal to the reference plant protection product, which is registered in Croatia. The parallel trade permit is issued for a period in which the registered reference plant protection product has a registration.
1.2 Sustainable use of pesticides

With the adoption of Directive 2009/128/EC and transferring its provisions into the Ordinance on Establishing an Action Framework to Achieve the Sustainable Use of Pesticides, the legal basis was created for the preparation and adoption of the National Action Plan for achieving sustainable use of pesticides in the Republic of Croatia and establishing a system of sustainable use of pesticides to reduce the risks and effects of pesticides on human health and the environment, as well as for encouraging integrated pest management and the use of alternative methods or procedures, such as non-chemical alternatives to pesticides. The provisions of the subject Directive apply only to those pesticides, which are considered plant protection products.

In order to ensure the implementation of regulations from the field of sustainable use of pesticides, it was necessary to establish completely new systems in the Republic of Croatia, which include:

- the establishment of the register of legal and natural persons placing pesticides on the market and the obligation to report the quantity of production, import, procurement of pesticides,
- the establishment of a training system for professional pesticide users, distributors and advisors (persons subject to training), which includes previous authorisation of lecturers and legal/natural persons who shall implement the training, the preparation of manuals for taking exams, keeping records of training, issuance of identification cards,
- the establishment of a mandatory regular inspection system for pesticide application equipment, which includes the implementation of mandatory training for future employees of inspection stations, the establishment and authorisation of inspection stations for the implementation of mandatory regular inspections, keeping records on the performed inspections, issuing the label of performed inspection of the equipment.

It was necessary to align all of the aforementioned systems with the Phytosanitary Information System (FIS), in which all the necessary data are kept.

Despite the fact that the Act on Plant Protection Products contained provisions, which allowed the alignment with Directive 2009/128 EC, it did not contain all the necessary provisions for the complete establishment of the system for sustainable use of pesticides and provisions in case of legal and natural persons failing to meet or violating the provisions of the Ordinance on Establishing an Action Framework to Achieve the Sustainable Use of Pesticides.

The main deficiencies of the previous system were:

- pesticides were available to everyone, regardless of professional qualifications and knowledge they possess. Exceptions were only those pesticides labelled as very toxic (T'), which were not allowed for free sale, as well as a certain number of pesticides, which are intended for seed treatment and fumigation;
- the training program did not include all categories of persons subject to training, but only one part of the advisors in the retail sales of pesticides who did not possess the appropriate professional qualifications. Other advisors in sales were not subject to training if they possessed the appropriate professional qualification, which was prescribed;
- training of professional users, distributors and advisors was not mandatory. The minimum professional qualification was prescribed for responsible persons engaged in placing pesticides on the market and employees. Only those employees who did not possess the lowest prescribed professional qualification were subject to regular basic and additional training;
- to a large extent, the training program was not aligned with the requirements of Annex I of Directive 2009/128/EC, particularly in the part referring to environmental protection, health of the operators, humans and animals and integrated pest management;
lack of categorisation of all entities dealing with placing on the market and the application of pesticides, which shall be covered by the training system, as well as of division of pesticides for professional and non-professional use (for amateur users).

The Government of the Republic of Croatia, at the proposal of the Ministry of Agriculture, adopted the National Action Plan for Achieving Sustainable Use of Pesticides in June 2013. The plan was submitted to the European Commission and all Member States. The states are required to review their plans regularly, at least every five years and report to the European Commission and other Member States on all important amendments.

Since more than 70% of the provisions of the Act on Plant Protection Products, as well as numerous by-laws adopted on the basis of this Act were abolished through the aforementioned acts on the implementation of the regulation, and due to the fact that the aforementioned Act did not contain all the necessary provisions for establishing the sustainable use of pesticides, the preparation of the Act on sustainable use of pesticides was initiated in the second half of 2013, and it entered into force in February 2014. This Act fully regulates the system for sustainable use of pesticides and eliminates the existing deficiencies. The new Ordinance on the Sustainable Use of Pesticides is planned to regulate the details necessary for the establishment of a sustainable use of pesticides, such as:

- training of professional pesticide users, distributors and advisors,
- requirements for pesticide distribution and sales,
- regular inspection of the pesticide application equipment,
- special pesticide application procedures and measures for the reduction of risks in specific areas,
- application of the integrated pest management principles and
- other measures for achieving the sustainable use of pesticides.

After publishing the new Ordinance, the current Ordinance on Establishing an Action Framework to Achieve the Sustainable Use of Pesticides shall be abolished.

### 1.2.1 Establishment of a training system

With the entry into force of the Ordinance on Establishing an Action Framework to Achieve the Sustainable Use of Pesticides and the Act on the Sustainable Use of Pesticides, the Ministry of Agriculture undertook to establish a system of training for professional users of pesticides, advisors in the sale of pesticides and advisors in food production, as well as for the distributors.

Professional users of pesticides, distributors and advisors in the sale of pesticides and food production, regardless of their acquired qualifications, shall demonstrate that they possess adequate knowledge of pesticides. The evidence of having the necessary level of knowledge is the certificate on the completed exam and the appropriate identification card issued on the basis of the certificate on the completed exam.

In order to facilitate the acquiring of the necessary knowledge level to persons subject to training, the Ministry of Agriculture authorised the institutions for the implementation of training and taking exams. The training and exam taking are organised by institutions authorised for the implementation of training, and lectures are given by authorised lecturers. The training consists of basic and additional training. Basic training lasts for at least 15 school hours. Following the acquisition of basic education, the persons subject to training shall attend an additional training in the duration of no less than 5 school hours at least every five years. If the person subject to training believes that they possess the appropriate level of knowledge, they may take the exam on the basic and additional training without attending the training, but they shall meet the requirements in terms of the prescribed level of
education for each category of persons subject to training. The exam is taken in written form. The exam is successfully passed by the attendee who achieves 60% of the points. This training does not intend to, nor can it replace the education acquired through the regular education system, therefore, the basic training only complements the knowledge acquired after the completion of standard education.

The list of authorised lecturers and institutions authorised for the implementation of training is published on the website of the Ministry of Agriculture (www.mps.hr).

One of the requirements of the Directive is that the training be adapted to the target group as much as possible. For that reason different modules have been established, and within each of the three modules, training categories and sub-categories have been established, which go up to the level of a certain productive sector (crop farming, fruit growing, viticulture, nursery production, vegetable growing, ornamental plants, olive growing).

Types of training (modules) (Figure 1.6) are as follows:
1. module for professional users of pesticides (basic and additional)
2. module for distributors (basic and additional) and
3. module for advisors (basic and additional).

![Figure 1.6: Schematic representation of persons subject to training for individual modules (prepared by: A. Bokulić)](image)

A **professional user** is a person who uses pesticides intended for professional users in the performance of their professional activities (these are plant protection products for which agricultural pharmacies
are stated as permitted sales locations on the basis of a decision on registration - specialised stores or for which the decision on registration states that the plant protection product is intended for professional users). This information is available on the label of a plant protection product and on the web browser of registered plant protection products (http://fis.mps.hr/trazilicaszb/).

The professional user category also includes a **professional user for professional application** – this is a professional user using pesticides intended for professional applications, which have been approved only for a particular category of professional users, usually service providers, by means of a decision on registration or a decision on the licence.

A **distributor** is a natural person or legal entity that places pesticides on the market, including wholesalers, retailers, vendors and suppliers.

An **advisor** is any person who has acquired adequate competence and advises on plant protection and the safe use of pesticides in the context of their professional capacity or commercial service, including private self-employed and public advisory services, commercial agents, food producers and retailers where applicable.

Persons subject to training apply for basic and additional training and/or taking exams with the institutions authorised for implementation of training via an application form available on the website of the Ministry of Agriculture (www.mps.hr) and on the website of the institutions authorised for the implementation of training, and submit the necessary documents as evidence that they meet the requirements for attending a certain module (e.g. a copy of the relevant diploma or certificate proving the level of education).

Attendance of the training is not mandatory. Only exam taking is mandatory, which proves the possession of the level of knowledge and skills necessary for safe handling and application of pesticides. Only the minimum requirements to be met by the person subject to training in order for them to attend the training and take the exam have been prescribed, as well as the obligation to take the exam.

In accordance with the data on the application form of the legal and natural person authorised for the implementation of the training, it is determined whether a candidate meets the prescribed requirements for attending a certain module for which they have applied, as well as for taking the exam.

The requirements for the admission into the module for professional users is a completed primary school education in the duration of 8 years. Requirements for the admission into all modules are stipulated by the Ordinance on Establishing an Action Framework to Achieve the Sustainable Use of Pesticides (Figures 1.7, 1.8 and 1.9).
Figure 1.7: Schematic representation of the application requirements for the module for advisors (prepared by: A. Bokulić)

Figure 1.8: Schematic representation of the application requirements for the module for distributors (prepared by: A. Bokulić)
The appropriate identification card is issued on the basis of a certificate on the completed exam. Until the issuance of the identification card or in the case of loss of the identification card, the persons subject to training exercise their rights with the certificate on the completed exam.

The identification card is issued by the Advisory Service on the basis of the certificate on the completed exam, which shall be submitted by the institution authorised for the implementation of training in which the attendee completed the exam.

The types of identification cards are as follows:

1. identification cards for lecturers (authorised lecturer, red identification card)
2. identification cards for advisors and advisors - sellers (authorised advisor or authorised advisor - seller, yellow identification card)
3. identification cards for distributors (authorised distributor, blue identification card)
4. identification cards for professional users (authorised professional user, green identification card)
5. the identification cards for professional users applying the plant protection products intended for professional application (authorised professional user for professional application, green identification card)

For natural persons who acquired the identification card for lecturers, the identification card is valid as if they acquired the identification card for advisors (if they have attended 90 hours of lectures in the field of plant protection and possess an appropriate level of training in the agriculture/forestry profession), distributors (may be the responsible person who has attended 90 hours of lectures in the field of plant protection and possess an appropriate level of training in the agriculture/forestry profession) and professional users (the responsible person may be the professional user for professional application only if they have completed 150 hours of lectures in the field of plant protection and possess an appropriate level of training in the agriculture/forestry profession).

For the natural persons who acquired the identification card for advisors, the identification card is valid also for the distributor and professional user activities (the responsible person may be the professional
user for professional application only if they have completed 150 hours of lectures in the field of plant protection). The identification card for advisors – sellers is valid also for the distributors (but they cannot be the responsible person) and professional users (the responsible person may not be the professional user for professional application). The identification card is not valid as the identification card for lecturers.

For a natural person who holds the identification card for distributors, the identification card is also valid for the professional user (the responsible person may be the professional user for professional application only they have completed 150 hours of lectures in the field of plant protection and possess the appropriate level of education, and they may perform the activities of workers or employees of professional users for professional application if they possess at least secondary school education in the agricultural/forestry specialisation). The identification card is not valid as the identification card for lecturers or advisors.

For a natural person who holds the identification card for the professional user or professional user for professional application, the identification card is valid only for those activities, but not as the identification card for other modules.

The identification card shall bear the name and surname of the person subject to training and is non-transferable to other persons, and it shall be valid for 5 years from the date of issuance of the certificate on completing the exam for the basic module or 5 years from the date of expiry of the identification card in case of additional training.

The identification card is valid together with the personal ID card and with it the person subject to training proves their status and right to engage in a particular activity. Therefore, all persons subject to training and lecturers shall carry the appropriate identification card during the performance of their activities, with which they prove, together with their personal ID card, their right to perform the duties and activities. Upon the expiry of the identification card, a new identification card is issued for a period of 5 years on the basis of a certificate on completing the exam on the additional training.

The deadline by which all persons subject to training shall complete the exam is no later than 26 November 2015 if they wish to continue performing the activities within their professional activities.

Therefore, after the aforementioned date, professional pesticide users shall not be allowed to buy pesticides intended for professional users without the appropriate valid identification card, nor shall the sellers be allowed to sell those pesticides without the appropriate identification cards.

The costs of training do not represent the income of the state budget, but the income of the institutions which organise and implement the training and organise the exams. The costs of training are borne by the persons subject to training themselves. In order to protect the persons subject to training from excessive and unsubstantiated training prices, the Ministry of Agriculture has prescribed the maximum amounts that may be charged for the training costs. The price for primary (first) training amounts to a maximum of HRK 600.00, for taking examinations a maximum of HRK 50.00, and for issuing the identification card a maximum of HRK 40.00. The aforementioned amounts do not include VAT.

Pesticides intended for non-professional users (amateurs) may be purchased and bought by persons without adequate training and without the completed exam.
1.3 Pesticide residues in food

The maximum residue level (MRL) is the maximum legally permissible level of a concentration for pesticide residue in or on food or feed established on the basis of good agricultural practice and the lowest consumer exposure necessary. MRL shall be within allowable limits if a particular pesticide is applied correctly and in accordance with good agricultural practice (provided that there is no contamination from other sources, e.g. pre-existing environmental contamination prior to the application of a certain pesticide).

The level of pesticides in food may not exceed the prescribed level, and the food shall be sanitary correct. The MRL is expressed in mg/kg of product. The lowest limit at which the residues are reported as absolute numbers is the reporting limit and mainly represents the practical limit of determination (LOD). The limit of determination (LOD) is the lowest concentration of pesticide residues that can be measured, i.e. defined and published as a result of routine monitoring with validated control methods. The name limit of quantification (LOQ) is also used in order to avoid confusion with the limit of detection (LOD also), which is always less than the limit of determination, and means that pesticide is present in the sample, but the amount is too small to be measured in quantity.

Until 1 September 2008, rather complex rules were applied in the area of pesticide residues. For some of the pesticide/product group combinations, the European Commission has established the MRL values through Directives 76/895/EEC, 86/362/EEC, 86/363/EEC and 90/642/EEC, covering mainly more important products and approved active substances. If for certain pesticide/product combinations the MRL was not determined at the EU level, the Member States determined the national MRL values, which often failed to be accepted in other Member States or provisional national MRLs in accordance with the common principles, which were often accepted in other Member States. The Member State informed the Commission on provisional MRLs, which could accept the provisional MRLs for active substances which were in the evaluation procedure or new active substances. Member States were allowed to prescribe MRL values higher than the provisional MRL values, especially for new uses. For certain pesticide/product combinations, especially for small cultures (eg, gooseberry, medlar, Jerusalem artichokes, okra, garden humps...) or somewhat exotic products (e.g. some spices), MRL values were often not established, both at the European Union level and by the Member States.

Importers and sellers faced a lot of problems because they had to take into consideration different regulations of Member States, which sometimes contained different national MRL values for the same pesticide/product combination and they were very often in doubt regarding which regulation on MRL values they shall follow, since the national MRL values in one state may not have been accepted in another Member State. Such situation was particularly confusing for the consumers and caused great concern among the consumers, especially in cases where residues discovered in food in one or several states were above the MRL values, while in other countries they were below the prescribed MRL values. Before the entry into force of Regulation (EC) No. 396/2005, the MRL values were mainly trading limits and posed a trade barrier, but with the entry into force of the aforementioned Regulation, the greatest emphasis when determining the MRL value is placed on consumer safety.

Regulation (EC) No. 396/2005 establishes a higher level of consumer protection against the exposure to pesticide residues through food. Although this Regulation was adopted in 2005, due to the transitional periods established by the Regulation, its full implementation was started only on 1 September 2008. The provisions of the aforementioned Regulation were transfered into the Ordinance on Maximum Residue Levels of Pesticides in or on Food and Feed of Plant and Animal Origin, which ceased to be valid upon the entry into force of the Act on the Implementation of Regulation (EC) No. 396/2005.
The Regulation contains the following appendices:

- Appendix I List of products of plant and animal origin,
- Appendix II EU final determined MRL values (Figure 1.10),
- Appendix III EU provisional MRL values for pesticides which are still evaluated, import tolerances and MRL values for new products (Figure 1.10)
- Appendix IV Substances for which MRL values are not determined since they are naturally present (plant hormones, pheromones, etc.),
- Appendix V Specific default LOD/LOQ MRL values or, for certain substances which are different from the common LOD value of 0.01 mg/kg, and are determined in accordance with the routine analytical methods available,
- Appendix VI Specific concentration factors/dilution factors/factors of transmission or processing for certain procedures of processing/mixing/processed products/composite food or feed,
- Appendix VII Active substance/product combinations for stored products intended for fumigation for which exceeding the MRL value is permitted.

![Figure 1.10: Schematic representation of the establishment of Appendix II and III of Regulation No. 396/2005 (prepared by: A. Bokulić)](image)

Regulation (EC) No. 396/2005 covers agricultural products intended for food and feed. The MRL values are currently established for 357 basic products in Part A of the Regulation, however, if their different sub-types and varieties from Part B of the Regulation are included in the number of basic products, the total number of products amounts to approximately 905. The number of products in Part B is constantly increasing. The MRL values for the aforementioned products in their raw state also apply to these products after treatment and/or processing, taking into account the dilution and concentration during treatment and/or processing procedures. This Regulation covers pesticides, which are currently used in agriculture, as well as pesticides, which were once used in agriculture and pesticides that are used outside the European Union. The Regulation includes approximately 532
different pesticides and their metabolites. For most of the products, the MRL value is established for at least 452 pesticides. In cases when the MRL value is not stated for some pesticides and products, the default MRL value of 0.01 mg/kg is applied.

When establishing the MRL values included in Regulation (EC) No. 396/2005, the risk to all consumer groups has been taken into account, including babies, children and vegetarians, and other vulnerable population. The risk assessment for consumers is performed by EFSA on the basis of the data on pesticide toxicity, expected MRL values in food and different eating habits of consumers in the European Union. The Regulation clearly defines the role of the Member States, EFSA and the European Commission in the procedure of determining MRL values. The Regulation also contains a large number of newly determined MRL values from former directives listed in Appendix II, provisional MRL values referred to in Appendix III, including MRL values transfered from national regulations, import tolerances and the list of substances for which it is not necessary to determine the MRL referred to in Appendix IV.

In order to ensure the proper determination of MRL values, the applicant requesting the approval for placing a plant protection product on the market shall submit scientific studies and data on controlled tests with visible data on good agricultural practice, the amount of plant protection products (dose) necessary to protect crops or plantations, the number of treatments, the stage of culture development and the waiting period, as well as data on pesticide residues, which remain in the product after the treatment, after a certain number of days. It is essential that these residues do not pose an unacceptable risk to humans. Following the submission of the studies, the Rapporteur State prepares the documentation evaluation and the evaluation report, which is submitted to EFSA and the Member States. On the basis of this report and all available data, EFSA performs the risk assessment and decides on the eligibility of documentation and issues their reasonable opinion, and the risk assessment includes all consumer groups, including vulnerable groups such as babies, children and vegetarians. On the basis of all available data, as well as the EFSA opinion and the evaluation report, the Commission prepares a draft of the regulation on determining/modifying the MRL value, and the final decision on the acceptance of the proposed MRL values is adopted at the Standing Committee on the Food Chain and Animal Health - Section for pesticide residues in which all Member States vote on the acceptance or rejection of the proposed MRL. When a risk for any consumer group is determined, the application for determining MRL values is rejected, or MRLs are established at the LOD level and the plant protection product shall not be granted the approval for use in the products for which the risk has been determined. Food safety is significantly more important than the protection of plants against harmful organisms.

However, since toxicological limits are far beyond the established MRL values, i.e. The MRL value is several times lower than the level, which may harm human health, and the mere exceedance of the MRL value does not immediately present a hazard for human health. Whether the MRL exceedance indeed presents a risk to a consumer group in a state is determined by a risk assessment. If the risk assessment shows an exceedance of the acute reference dose\(^1\) for a group of consumers, it is considered that there is a risk to consumers, however, if it is not exceeded, this is a case of exceeding legally tolerable limits, but human health is not endangered.

\(^1\) The acute reference dose (ARfD) is the assessment of the quantity of the substance in food, expressed on the basis of body weight, which can be introduced during a short period of time, usually during one day, without significant risk to consumers, based on the data from appropriate studies and taking into account sensitive groups within the population (e.g. children and unborn children)
Every exceedance of the MRL value indicates the need for:

- a risk assessment for consumers of this product,
- a warning to the product manufacturer to apply the pesticide in accordance with good agricultural practice, i.e. the instructions for the use of pesticides,
- the recommendation for inspection services to increase the control of samples of the product for which the analysis indicated the MRL value exceedance and of manufacturers that supply the market with those products.

The application of pesticides and types of pesticides used in the European Union varies and depends on numerous factors. For example, in the southern European Union Member States there is a significantly higher amount of insects and more insecticides are used. In other parts of the European Union where the climate is more humid (there is more moisture), better conditions for the development of plant diseases caused by fungi prevail and therefore, there is higher consumption of fungicides. These differences are taken into account when determining the MRL values. Due to the aforementioned differences, the European Union Member States are divided into the above mentioned zones with regard to pesticide residues: Northern and Southern.

The European Commission determines the MRL values for food and feed. In order to find out which MRL value refers to which products and which pesticide, the quickest way to obtain information is by using the EU pesticide database on the European Commission website. The access to the pesticide database established by the European Commission is possible via the following link http://ec.europa.eu/sanco_pesticides/public/?event=homepage. The database is easy to search and can be searched by product, crop group, product code or pesticide in all European Union languages, including Croatian. The search results can be exported into the MS Excel document format.

Agricultural producers, sellers and importers are responsible for food safety, including compliance with the prescribed MRL values. The competent authorities of the European Union Member States are responsible for the control of pesticide residues in food. In order to ensure official control of food for pesticide residues in a satisfactory and simple manner, the European Commission has three instruments: coordinated multiannual control programme of pesticide residues in food, inspections of the Food and Veterinary Office of the European Commission and the Rapid Alert System for Food and Feed.

A coordinated multiannual control programme of pesticide residues is a programme, which determines, for each Member State, the products of plant and animal origin to be sampled and analysed for pesticide residues, pesticides to be analysed in products of plant and animal origin and the minimum number of samples to be taken. For the purpose of implementing the coordinated multiannual control programme of pesticide residues in food, the European Commission annually adopts and passes the Implementing Regulation on the basis of which the Member States prepare their programmes for monitoring pesticide residues in food. Member States shall submit the results of the monitoring programs to EFSA, which publishes an annual report on the implementation of a coordinated multiannual control programs of pesticide residues in food.

European Union reference laboratories train the employees of analytical laboratories, develop the analysis methods and organise tests to evaluate the capabilities of national control laboratories.

The Food and Veterinary Office of the European Commission (FVO) performs inspections in the Member States with the aim of reviewing and evaluating their official controls of pesticide residues in food.
If pesticide residues in a product are at a level higher than the prescribed MRL value and the risk assessment indicates that they pose a risk to consumers, the Rapid Alert System for Food and Feed (RASFF) circulates the information and measures are taken to protect consumers.

Sampling of food for the purposes of official food controls for pesticide residues shall be performed in accordance with the Ordinance on the methods of sampling for the official control of pesticide residues in and on products of plant and animal origin. This Ordinance transposes the provisions of Directive 2002/63/EC.

The National programme for the monitoring of pesticide residues in food in Croatia (Figure 1.11) is implemented in accordance with the implementing regulations of the European Commission, which prescribe the types of products of plant and animal origin which are sampled and analysed for pesticide residues, the number of samples and the pesticides that need to be included in the analysis. This programme also includes additional products, such as products that are more represented in the diet of consumers in Croatia in accordance with eating habits, as well as products in which pesticide residues above the MRL value have been found in previous years.

If MRL exceedance is established in the Republic of Croatia within the National programme for the monitoring of pesticide residues in food or official controls, the following activities shall be implemented:

- warning measures are determined if the MRL exceedance is within the measurement uncertainty,
• the sale of products of plant and animal origin is prohibited if the MRL exceedance is beyond the measurement uncertainty,
• if the risk assessment indicates there is a risk to consumers, the withdrawal or recall of products of plant or animal origin which pose a risk to consumers is ordered,
• further/more frequent sampling of food from manufacturers/distributors for which the MRL exceedance was determined through analysis.
1.4 Chemicals

1.4.1 Labeling, former regulations

The label is the most important means of notifying the users and consumers of the harmful properties of chemicals, including plant protection products. Every plant protection product shall have a label, regardless of whether it is a single substance, a mixture of substances or a product, and regardless of whether it is intended for professional use or for general consumption. In the EU directives on classification, labeling and packaging of dangerous goods, a system of hazard pictograms, risk phrases (R phrase) and safety phrases (S phrases) has been developed, which indicate the hazardous properties of substances based on the criteria for classification according to physical and chemical, toxicological and ecotoxicological properties obtained through testing in accordance with the prescribed methodology. These directives have been transposed into Croatian legislation through the Regulation on classification, labeling and packaging of dangerous chemicals, which also applies to plant protection products. In the procedure of registration and re-registration of plant protection products, labeling of plant protection products is regularly checked and harmonised with the latest regulations on chemical safety.

Plant protection products shall be labelled with hazard pictograms and risk phrases (R phrases) and safety phrases (S phrases) (Figure 1.13), which shall be clearly displayed on the plant protection product package label. Graphic pictograms (symbols) and inscriptions which warn about the hazard in accordance with currently still valid Regulation on classification, labeling and packaging of dangerous chemicals are shown in Figure 1.12.

<table>
<thead>
<tr>
<th>Very toxic</th>
<th>Toxic</th>
<th>Harmful</th>
<th>Irritant</th>
</tr>
</thead>
<tbody>
<tr>
<td>letter T+</td>
<td>letter T</td>
<td>letter Xn</td>
<td>letter Xi</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Corrosive</th>
<th>Dangerous for the environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>letter C</td>
<td>letter N</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Oxidising</th>
<th>Explosive</th>
</tr>
</thead>
<tbody>
<tr>
<td>letter C</td>
<td>letter E</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Highly flammable</th>
<th>Extremely flammable</th>
</tr>
</thead>
<tbody>
<tr>
<td>letter F</td>
<td>letter F+</td>
</tr>
</tbody>
</table>

Figure 1.12: Graphic pictograms (symbols) and signs that warn of danger (source: [http://www.hzt.hr](http://www.hzt.hr); prepared by: R. Turk)
1.4.2 Labeling, new regulations (CLP)

Changes in chemical legislation of the European Union also affect the changes of the criteria and the method of classification, labeling and packaging of hazardous chemicals through Regulation (EC) No. 1271/2008 or the so called CLP Regulation (Classification, Labelling, Packaging), which has been in force in the European Union since 20 January 2009. The purpose is that each chemical placed on the European Union market is unequivocally classified and labelled and that one Safety Data Sheet (SDS) is prepared for it, which shall be translated into the languages of the Member States, but its content shall not vary from state to state.

The provisions of Regulation (EC) No. 1271/2008 were transposed into the Regulation on classification, labeling and packaging of hazardous chemicals, and from 1 July 2013. This Regulation and its amendments are directly applied in Croatia. New Labelling is introduced gradually, therefore it is already mandatory for all active substances in plant protection products, while it shall be introduced on the label of plant protection products, as well as other of products which contain mixtures of chemicals by the end of May 2015. As a result, on the Croatian market and the European Market market during the transitional period no later than 1 June 2017, the labels of plant protection products shall contain former or new labeling, i.e. it is possible that the same plant protection product shall be labelled in different manners.

The classification and Labelling of chemicals in accordance with the CLP Regulation is primarily the responsibility of the manufacturer or the company which places the chemical on the market. However, for certain chemicals such as active substances in plant protection products, biocidal products and for carcinogenic, mutagenic and reprotoxic chemicals, a so-called harmonised classification and Labelling is implemented, which is mandatory at the European Union level and implemented by ECHA.

The biggest novelty, which shall immediately be visible on the labels and SDSs of plant protection products labelled in accordance with the Regulation on classification, labeling and packaging of hazardous chemicals, is that instead of pictograms and risk phrases (e.g. Xn, T, T+), which have been used until now, now appear pictograms (Figure 1.14) which shall, depending on the hazard category, be accompanied only with Risk or Safety phrases, and no longer with more descriptive phrases Harmful, Toxic, Hazard for environment, etc. In addition to differences in colour, pictograms are mostly similar to the former symbols. Nevertheless, two completely new signs appear:

Figure 1.13: Example of risk (R) and safety phrases (S) (prepared by: R. Turk)
1. GHS06, which is, together with the term Warning, used for indication of the chemicals classified into the lower (lowest) category within each class of health hazard and it may be said that it actually replaces the symbol of St. Andrew’s Cross and signs Xn and Xi,

2. GHS08, which is, together with the term Hazard, used for indication of chemicals classified as carcinogenic, mutagenic and reprotoxic, as well as for the newly introduced category of chemicals which indicate specific toxicity for target organs following single or repeated exposure.

Figure 1.14: The meaning of hazard pictograms (source: http://www.hzt.hr; prepared by: R. Turk)
Instead of risk phrases (R), new H hazard phrases are introduced (after the English word hazard) for certain hazard categories: physical and chemical hazards, health hazards and environmental hazards (Figure 1.15).

For plant protection products, the phrase EUH 401 is also mandatory "in order to avoid risks to human health and the environment, comply with the instructions for use," which has until now also been stated on the label of the plant protection product instructions in Croatia.

![Warning phrases (H phrases)](image1)

**Figure 1.15:** Example of hazard phrases (H) (prepared by: R. Turk)

Instead of the safety phrase (S) new precautionary phrases P are introduced (after the English word precaution), which recommend the procedures for preventing harmful effects, actions in case of hazard or occurrence of harmful effects of chemicals, as well as the procedures of proper storage and disposal (Figure 1.16).

![Precautionary phrases (P phrases)](image2)

**Figure 1.16:** Example of precautionary phrases (P) (prepared by: R. Turk)
1.4.3 REACH

Together with the adaptation and adoption of the acquis communautaire, it is also necessary to implement new regulations in the field of chemical safety in the Republic of Croatia. These regulations came into force in the European Union on 1 June 2007 with the start of the application of Regulation (EC) No. 1907/2006 known as REACH (Registration, Evaluation and Authorization of Chemicals). The purpose of adopting this Regulation is the protection of human health and the environment through complete and rapid identification of harmful properties and potential risks from exposure to chemicals in all areas of their life cycle: from the production and use until disposal and recovery, both in industrial processes and in everyday life. The objective is optimal production and use of chemicals with as least as possible harmful effects on human health and the environment throughout the European Union by 2020.

Regularly renewed directives which regulate the placing of dangerous chemicals on the market, as well as directives which further regulate the field of chemicals intended for use, for example, in plant protection products and biocidal products, were introduced gradually and regularly in the European Union as early as 1967. European directives of the highest level on classification, packaging and Labelling of hazardous substances and the directives on classification, packaging and Labelling of hazardous products have also been transposed into the Croatian legislation, first through the Toxic Substances Act, and then in the form of the Chemicals Act and its accompanying ordinances. Therefore, the placing on the market and the use of chemicals were regulated in the European Union and the Republic of Croatia even before the adoption of the REACH Regulation.

However, it became evident that the existing legislation does not guarantee adequate safety and health protection of the employees, consumers and the environment, since for almost 99% of the total volume of chemicals on the market, a detailed assessment of potential risks has not been conducted. With the implementation of the REACH regulation, this situation shall gradually change in favour of better health and environment protection against the effects of chemicals.

Until now, the implementation of the risk assessment, the recommendation and implementation of measures to reduce the risk from chemicals have mainly been the responsibility of national authorities. Due to the limited capabilities of state authorities, even the most hazardous chemicals have been included very slowly into the list of banned chemicals, i.e. into the list of chemicals that are withdrawn from the market or whose use is limited. Until 2006, the aforementioned list included only approximately 40 chemicals, despite the fact that the European regulations on restricting the marketing and use of certain hazardous substances and preparations dates back to 1976. According to REACH, the responsibility for the safe use of chemicals and the costs of testing the harmful effects and the risk assessment for health and the environment is transferred to the economic operators who place chemicals on the market and gain profit based on it.

The REACH Regulation entered into force in the Republic of Croatia on the date of accession to the European Union, 1 July 2013 on the basis of the Act on the Implementation of Regulation (EC) No. 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals. However, certain parts of the REACH and CLP Regulations were transposed into the Croatian legislation before the accession of the Republic of Croatia to the European Union, such as, for example, the List of dangerous chemicals whose trade is prohibited or restricted, in order to prevent the sales of chemicals and plant protection products which have been prohibited in the European Union on the Croatian market.
1.4.4 Safety Data Sheet (SDS)

Since 1 July 2013, the REACH Regulation has been applied in the Republic of Croatia, including Appendix II of the REACH Regulation and its amendment pursuant to Regulation (EU) No. 453/2010 on the contents of the Safety Data Sheet, which has so far been regulated by the Ordinance on the Completion of Safety Data Sheets. Although the basic format of the SDS remained unchanged compared to the previous one, a number of changes were anticipated, most of which shall be applicable only after the implementation of the chemical registration process at the European Union level. The SDS is primarily intended for professional users. The producers of plant protection products shall also prepare a Safety Data Sheet for each plant protection product they place on the Croatian market. The Safety Data Sheet shall be in the Croatian language. At the request of the users of plant protection products, the producers of plant protection products shall make the SDS available to every user of a plant protection product. For the users of plant protection products, most of the required information shall be listed on the label of the plant protection product, however, additional safety information may be found in the SDS, in particular that regarding the selection of personal protective equipment as specified in Section 8 of each SDS.

1.5 Official controls

In order to ensure the implementation of acts and other regulations, the relevant inspection services perform official controls (Figure 1.17). The inspection authorities in the area of plant protection products, pesticide residues in food and the sustainable use of pesticides are regulated by a series of legal regulations, such as:

- Act on the Implementation of Regulation (EC) No. 1107/2009 concerning the placing of plant protection products on the market,
- Act on the Implementation of Regulation (EC) 396/2005 on Maximum Residue Levels of Pesticides in or on Food and Feed of Plant and Animal Origin,
- Act on the Sustainable Use of Pesticides,
- Food Act,
- Act on Official Controls Performed in Accordance with Food, Animal Feed, Health and Welfare Regulations,
- Act on Agricultural Inspections.

The Agricultural Inspection of the Ministry of Agriculture controls the placing of the plant protection products on the market and controls the proper application of plant protection products. This inspection controls the systems of sustainable pesticide use, such as the system of training professional pesticide users, distributors and advisors, the system of pesticide distribution and sales (wholesale and retail), the system of mandatory regular inspections of pesticide application equipment, the application of basic principles of integrated pest management and other controls in the field of sustainable use of pesticides. Agricultural inspection controls pesticide residues in products of plant origin in primary plant production.

The Veterinary inspection of the Ministry of Agriculture controls pesticide residues in products of animal origin in the primary animal production, at the level of producing and processing food of animal origin and during the import of food of animal origin.

The Sanitary Inspection of the Ministry of Health controls pesticide residues in products of plant origin at the level of processing, retail sales and during the import of food of plant origin at border crossings. The Sanitary Inspection also performs supervision over chemical production, including the production of plant protection products.
The Environmental Inspection of the Ministry of Environmental and Nature Protection controls the producers and distributors of plant protection products with the purpose of determining the manner of hazardous waste management pursuant to the regulations governing hazardous waste.

As an integral part of official controls in the field of plant protection products and pesticide residues in food, the Ministry of Agriculture prepares and coordinates the following monitoring programmes:

- The programme for post-registration control of plant protection products (formulation monitoring) which is aimed at controlling the validity of the registered plant protection products available on the Croatian market and controlling whether their physical and chemical properties comply with the decisions on registration. The Programme is prepared and coordinated by the Ministry of Agriculture, and the HCPHS <Croatian Centre for Agriculture, Food and Rural Affairs> - Institute for Plant Protection performs laboratory analyses of plant protection products, and the agricultural inspection takes samples and implements inspection measures.

- The national programme for the monitoring of pesticide residues in food aims to establish the amount of pesticide residues in food and to verify compliance with the prescribed MRL values. In this manner, the information on proper pesticide application shall be obtained, and the risk assessment shall provide insight into the extent to which pesticide residues exceeding MRL values pose a risk to humans who consume food containing such levels of pesticide residues. Monitoring is prepared and coordinated by the Ministry of Agriculture. The laboratory of the Croatian Institute for Public Health performs laboratory analysis of the samples of plant origin, and the laboratory of the Croatian Veterinary Institute performs the analysis of the samples of animal origin. The sanitary, agricultural and veterinary inspectors take samples in accordance with the division of authorities and implement inspection measures. The HCPHS – Institute for Plant Protection performs the risk assessment for the consumers in the event when pesticide residues above the prescribed MRL value are determined. Ministry of Agriculture funds the Programme and prepares the final report on Programme implementation and publishes the results on the website of the Ministry of Agriculture (www.mps.hr). The results of this Programme shall be submitted to the European Commission and the European Food Safety Authority since the monitoring is mutually coordinated at the level of all European Union Member States.

In addition to the aforementioned monitoring systems, supervision over the status of surface waters is performed, including coastal waters and groundwater, through systematic monitoring of the water status. The aforementioned monitoring is performed pursuant to the Water Act. Pursuant to the aforementioned Act, Hrvatske vode <Croatian Waters> are responsible for monitoring the state of the surface water, including the coastal waters and groundwater, on which they shall adopt an annual Monitoring Plan, with prior endorsement from the Ministry of Agriculture. The monitoring of the water status includes environmental and chemical indicators for surface waters, as well as chemical and quantitative indicators for groundwater. Water quality testing is performed by the Central Water Management Laboratory of Hrvatske vode and the laboratories authorised by the Ministry of Agriculture. Hrvatske vode are responsible for interpreting the results of the monitoring, on which they shall prepare an annual report, which they submit to the Ministry of Agriculture and the Environmental Protection Agency.

Monitoring of pesticides in drinking water shall be performed pursuant to the Act on Water Intended for Human Consumption. The aforementioned monitoring is prepared and coordinated by the Ministry of Health, and the laboratories of the Croatian Institute of Public Health perform
laboratory analyses of drinking water. The monitoring results are processed by the aforementioned laboratory and submitted to the Ministry of Health.

Figure 1.17: Schematic representation of the main legal areas and the main regulations governing the subject areas and of the inspection services competent for the implementation of official controls on the basis of regulations governing these areas (prepared by: V. Novaković)

2 SUSTAINABLE AGRICULTURE

Sustainable agriculture enables continuous production of primary agricultural products with the use of permitted chemicals which have the least possible impact on the environment and human health. It is based on the principles of sustainable development since it provides food, fuel and fibers, taking into account the economic and social constraints which ensure the sustainability of production in which ecological efficiency is more important than economic efficiency. Through all of the agrotechnical measures of sustainable agriculture, contamination of soil, water and air is reduced or avoided, which makes it an alternative to intensive agriculture which presents more risk to the environment and which is being abandoned in the European Union.

The principles of sustainable agriculture primarily include the use local resources, such as biological nitrogen fixation, soil restoration, use of natural enemies in plant protection, as well as the application of by-products of agriculture and other activities (e.g. the application of waste from the cities). In sustainable agriculture, the application of agrochemicals (plant protection products and fertilizers) is limited in all processing operations which degrade the soil and contaminate the environment, thus protecting the biodiversity and integrity of humans and other organisms which live there.

Sustainable agriculture is acceptable for both producers and consumers. It is the basis of economic and social development, and since it evenly distributes natural resources, taking into account the environment, it improves the durability of the system by using the resources in a prudent manner. In such system, a family agricultural holding or a farm is organised according to the sub-system principle which functions as a closed system open to all. Therefore, the main principles of sustainable agriculture are the following:

- **integrated pest management** which reduces the economic and health risk, as well as the environmental risk. Through the use of all available pest management measures, it reduces the application of plant protection products, and thus their possible harmful effect on consumer health and the environment;
- **grassfield crop rotation**, which provides high quality livestock feed by reducing the cost price and the application of recycled food in animal husbandry. Protects anthropogenic soil against negative abiotic factors, and protective crops and intercrops included in the crop rotation, as well as crop residues, have a special role because they stifle weeds, control erosion, increase nutrient content and improve soil structure;
- **conservation tillage**, which preserves the humus and soil humidity, reduces wind and water erosion, production costs, energy and time spent for tillage;
- **preservation of water and soil humidity** shall become the most important part of supervision in agriculture because agriculture is located among the forests, hills and water;
- **protective crops, intercrops and crop residues** protect the soil against adverse abiotic factors, control the erosion and stifle weeds, as well as improve the structure and increase the nutrient content in soil;
- **biodiversity** reduces the risk of the impact of adverse weather conditions and damage from disease and pest attacks, while trees and shrubs increase the population of beneficial insects and other fauna;
- **fertilisation** is based on the use of domestic fertilisers, manure, slurry and animal manure, as well as legume green manure in order to reduce the application of manufactured nitrogen fertilisers;
- **trees and shrubs** on the holding are the most reliable protection against strong winds;
the market changes because the sale of goods in cities is the key to profitability and direct sales to the customer on the property brings many benefits.

For integrated production, technological instructions are prepared, defining mandatory rules/prohibitions which the manufacturers in integrated production shall follow. The instructions are based on the principles of good agricultural practice and the minimum requirements to be met. Within the technological requirements, there is a separate part comprised of integrated pest management, where the requirements and methods of plant protection are specified according to cultures and harmful organisms. Technological instructions for integrated production are published each year on the website of the Ministry of Agriculture.

2.1 Integrated pest management

Integrated pest management entails careful use of all available protective measures against harmful organisms with gradual introduction of those measures, which prevent the growth of pest populations and keep the use of plant production products and other measures at the level of economic feasibility and reduce the risks to human health and the environment. Integrated pest management emphasises the cultivation of healthy crops with the least interference with the agroecosystem as possible and encourages the development of natural pest control mechanisms (FAO, 2002). It can also be added that integrated pest management uses all positive factors of agroecosystems. If agrotechnical measures are not sufficient to maintain pests below the critical number, biological, biotechnical and, only as a last resort, chemical protection are initiated. Agrotechnical measures shall ensure healthy development of the plant, keep pest population below the critical number, conserve natural enemies, reduce the risk of resistance occurrence, reduce the pesticides application and reduce hazard for the persons who work with pesticides, as well as for the environment. Integrated pest management, therefore, entails the application of chemical control methods only when all other possibilities of preventing the increase in the number of pests over the decision threshold have been used. The essence of integrated pest management is for it to achieve high yield of top quality products with a lower use of plant protection products.

This reduces the number of pesticide applications, consumption of non-renewable natural resources and harmful effects of agrochemicals on the environment. Integrated pest management is a system which has to be accepted and implemented by the majority of agricultural producers in a short period.

2.1.1 Principles of integrated pest management

The basic principle of integrated pest management is the reduction of plant protection product consumption. Monitoring the development of pests and preventive measures to reduce their population shall be taken into account prior to the application of direct protection measures, i.e. before the application of chemical measures.

The general principles of integrated pest management (Figure 2.1) according to the International Organisation for Biological Control (IOBC) are the following:

1. preventive protection measures,
2. monitoring, forecasting,
3. threshold values – basis for adoptong the decisions on direct protection measures are threshold values,
4. priority is given to non-chemical protection methods,
5. targeted protection - reducing the side effects (minimum impact on human health, non-targeted organisms and the environment),
6. reducing the use of chemicals to the required level,
Integrated pest management is a system of plant protection which applies specific methods and measures of pests, pathogens and weeds suppression, and which applies all available measures of plant protection justified from an economic, ecological and toxicological point of view. Integrated pest management strives to use all the advantages of a specific agroecosystem, and threshold values are used when assessing the situation. The applied measures shall:

- ensure full development of the crop,
- keep the population of harmful organisms below the critical level,
- conserve natural enemies,
- reduce the risk of occurrence of resistance/immunity to a plant protection product,
- reduce the amount of plant production products,
- reduce the risk for the employees working with plant protection products,
- reduce the risk to humans, animals and the environment.

Integrated pest management stipulates the measures, manner and time of suppression only for economically important pests, pathogens and weeds, based exclusively on the forecast of occurrence and spread through the plantation or crops. Today, such an approach is called sustainable, and the production system is called sustainable production or, even better, sustainable management. Such an integrated approach to plant protection is spreading constantly because it enables the application of the economically and environmentally most acceptable plant protection products, and today it is used in Croatia mostly in the production of apples, where it was introduced the earliest.
As part of the integrated pest management, in forecasting the occurrence and spread of pests, pathogens and weeds, the following shall be implemented:

- determining the threshold for the decision on harmful organism suppression, including the determination of the critical period of weed competition (CPWC)
- damage assessment,
- identification of the occurrence and spread of harmful organisms,
- implementation of methods for monitoring the occurrence and development of harmful organisms, as well as of forecasting models,
- monitoring the environmental conditions (rainfall amountl, leaf wetting length, temperature).

2.1.2 Preventive plant protection measures

Preventive plant protection measures are all agro-technical measures that indirectly affect the reduction in the occurrence of pests, pathogens and weeds (Table 2.1). The most important preventive plant protection measures are the following:

- the use of certified seeds and seedlings,
- cultivation of resistant or tolerant varieties adapted to local agroecological conditions,
- mandatory four-field crop rotation for crop farming and vegetable growing, introduction of green manure crops and intercrops into the crop rotation,
- fertilisation based on the soil chemical analysis data and the needs of the culture,
- tillage systems adapted to the demands of the culture,
- sowing within the optimal sowing period and the recommended framework.

Table 2.1: Preventive suppression measures in integrated pest management (prepared by: Ž. Budinšćak)

<table>
<thead>
<tr>
<th>measures</th>
<th>harmful organism</th>
</tr>
</thead>
<tbody>
<tr>
<td>certified seed and planting material hygiene</td>
<td>insects/mites</td>
</tr>
<tr>
<td></td>
<td>nematodes</td>
</tr>
<tr>
<td></td>
<td>diseases</td>
</tr>
<tr>
<td></td>
<td>weeds</td>
</tr>
<tr>
<td>selection of species, varietycrop rotation</td>
<td>+</td>
</tr>
<tr>
<td>fertilisation (n)</td>
<td>+</td>
</tr>
<tr>
<td>optimal time for field work (sowing, harrowing)</td>
<td>+</td>
</tr>
<tr>
<td>pruning (fruit trees, vines)</td>
<td>+</td>
</tr>
<tr>
<td>proportion of grass, processing</td>
<td>+</td>
</tr>
<tr>
<td>increase in the population of natural enemies</td>
<td>(+)</td>
</tr>
</tbody>
</table>

+ has an effect; (+) partial effect; - no effect

2.1.3 Hazard assessment and monitoring the occurrence of harmful organism

In order to properly determine plant protection measures, the occurrence of harmful organisms shall be monitored by appropriate methods. For suppression forecasting and early detection of possible damage, it is desirable to use reliable methods and systems, such as computer diagnostics system in agriculture (CDA - devices) which reliably determine the deadlines for pest control (Metos, Agra). Furthermore, official forecasts for pest and/or pathogen risks shall also be used. Optimal suppression deadlines based on the CDA device are determined on the basis of weather conditions during the
growing season (humidity and air temperature, rain, dew, etc.), which most affect the development of diseases and pests and phenophases of crop plants.

2.1.4 Direct protection measures

Direct plant protection measures are applied when forecasting and threshold values indicate the need for suppression, and they are divided into mechanical, physical, biological, biotechnical and chemical measures. Mechanical, physical, biological and biotechnological measures always have priority over chemical measures, and when these measures are no longer sufficiently effective, chemical protection measures are taken, out of which the local application and a combination of plant protection products with attractants have priority.

Mechanical measures prevent the spread of harmful organisms in a mechanical manner, which is achieved by deep plowing of crop residues, cultivation, dusting of stubble, hoeing, pruning of branches with overwintering forms of pests or pathogens, gathering in smaller areas or plowing of rotten fruits, removing the infected leaves, destroying the infected plants or a possible hosts, digging of catching channels, placing of sticky bands on tree trunks, cleaning of seed, setting traps for voles and nets for protection against birds and insects etc.

Physical measures include the use of low and high temperatures, radiation, high-frequency sounds, sticky coloured plates, etc. The most commonly applied are the following:

- High temperature thermal disinfection of the soil. Destruction of harmful microorganisms, pest and weed seeds is achieved by heating the soil at 95°C up to a depth of 30 cm for 5 minutes;
- Solarisation or the use of solar energy is a very effective measure for soil disinfection, and it is performed by covering the soil during the summer with a thin, transparent, polyethylene foil for 1 - 2 months;
- Differently coloured sticky boards attract pests with their colour, which get stuck to their adhesive surface. In this manner, the attack may be reduced and the number of pest population determined, as well as the initiation of suppression. In the protected area, yellow sticky boards are usually used for attracting aphids, whiteflies, and blue sticky boards for attracting California thrips. In fruit growing, yellow boards are used for attracting cherry and olive flies, and white boards attract wasps, blue attract thrips and red attract bark beetle;
- Collecting lights for determining the presence, and hence for the reduction in the population of insects on agricultural land and in warehouses;
- Lowering the humidity and temperature of stored agricultural products in silos;
- Controlled (modified) atmosphere in the cold storage for fruit.

Biological measures suppress harmful organisms by using their natural enemies, predators and parasitoids, as well as viruses, bacteria or fungi. All species of living organisms have antagonists or their natural enemies in the nature, among which the most notable ones are predatory ladybirds, predatory heteroptera, predatory mites of the genus Typhlodromus, parasitic wasps and others. (Figures 2.2. - 2.5). For their development and survival it is important to:

- Plant and maintain the trees and bushes on the farm (5% of the lot area shall be left uncultivated for the habitat of beneficial organisms),
- Maintain biodiversity,
- Arrange rocky ground and other shelters for useful animals,
- Set up houses for beneficial birds,
- Grow tall trees to attract birds of prey,
• monitor, administer and control useful fauna (ladybirds, predatory heteroptera, predatory mites, parasitic wasps, wasp flies, lacewings, etc.).

![Figure 2.2: Adult predatory ladybird](image1.jpg)  
(Coccinellidae), a natural enemy of aphids  
(Photo: M. Šimala)

![Figure 2.3: Adult predatory heteroptera](image2.jpg)  
of *Orius majusculus* species  
(Photo: M. Šimala)

![Figure 2.4: Predatory mite](image3.jpg)  
*Amblyseius degenerans* species  
(photo: M. Šimala)

![Figure 2.5: The parasitic wasp](image4.jpg)  
*Encarsia formosa* species  
(photo: M. Šimala)

**Biotechnical measures** include the use of attractants, means for attracting insects and insect growth regulators. Attractants are used to monitor pest occurrence in order to determine the optimal suppression deadline, and the most used ones are food and sex attractants. Food attractants attract both sexes, and they are used for monitoring and evaluation of pest populations. In fruit growing, apple juice is most commonly used to capture red-belted clearwings (*Synanthedon myopaeformis*), and in crop farming, sugar water is used for capturing owlet moths (*Noctuidae*). Sexual attractants are actually synthesized female hormones which attract males of the same species which, guided by the smell, get stuck to the adhesive board. In addition to monitoring the pest occurrence and reducing the number of males in the population, they can be used for suppression by the method of confusion, i.e., due to disorientation, males are prevented in finding the females.

Insect growth regulators interfere with normal growth and development of the larvae or insect caterpillars, they are prevented from making damage and die fast. Chitin synthesis inhibitors prevent larval molting, ecdysone agonists cause premature molting, and juvenile hormone regulate morphogenetic and reproductive development of the insect. Growth regulators may have larvicidal effect i.e. they effect the larvae and caterpillars, or ovicidal effect, i.e. they effect the eggs and thus do not harm the natural enemies and are very selective.

**Chemical measures** are still important for harmful organism suppression. Integrated pest management implies that the plant protection products are applied when satisfactory efficiency has not been achieved by any of the aforementioned measures, i.e. the risk of economic damage that may be caused by harmful organisms has not been completely reduced.
Integrated production allows the use of plant protection products which are not prohibited in integrated production according to the Technological instructions. The plant protection product which is used shall be of appropriate purpose, and the application time shall meet the requirements of the culture to which the plant protection product is applied. The maximum allowed dosage, number of treatments, spraying intervals and duration of the last application shall comply as indicated on the product label.

Plant production products in integrated pest management shall be:

- of a narrower scope of effect,
- harmless to beneficial organisms,
- not classified as dangerous for the environment,
- of a non-stimulative effect on harmful organisms.

Based on the monitoring results, the professional user shall decide if, when and which plant protection measures to apply, whereby the use of pesticides shall be limited to a minimum (Table 2.2).

**Table 2.2:** Direct non-chemical protection measures in integrated pest management (prepared by: Ž. Budinšćak)

<table>
<thead>
<tr>
<th>methods</th>
<th>harmful organism</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>insects/mites</td>
</tr>
<tr>
<td>biological suppression</td>
<td>+/+</td>
</tr>
<tr>
<td>confusion method</td>
<td>+/-</td>
</tr>
<tr>
<td>attract and kill method</td>
<td>+/-</td>
</tr>
<tr>
<td>sit - technique</td>
<td>+/-</td>
</tr>
<tr>
<td>protective nets</td>
<td>+/-</td>
</tr>
<tr>
<td>physical methods (mechanical, heat)</td>
<td>(+)</td>
</tr>
</tbody>
</table>

* has an effect; (+) partial effect; - no effect

**Authors:** Božena Dežđek, M. Eng. Zeljko Budinšćak, Ph.D., Darka Hamel, Ph.D.
3 ORGANIC PRODUCTION

The main goal of organic agriculture is to produce food of high nutritional value, relying on the protection and preservation of the environment. Adapting to the existing environmental conditions, organic farming places under control the application of substances originating from industry, such as all manufactured fertilisers and pesticides, heavy metals and potentially toxic substances, bio-stimulators and drugs. In addition to not applying hazardous substances, organic agriculture reduces environmental pollution which might result from agriculture and maintains biodiversity of both agroecosystems and other ecosystems. In the long term, through agro-technical measures, organic agriculture maintains or increases the existing soil fertility, and uses renewable raw materials and energy sources within a closed circle, on the mixed family agricultural holding where all the food is produced for the needs of domestic animals, and domestic animals, in addition to milk and meat, also produce fertiliser of the highest quality, manure. The emergence and development of organic agriculture was driven by the negative consequences of intensive agriculture such as reduced soil fertility, loss of natural habitats, environment contamination and human exposure to chemicals harmful to health, as well as the impoverishment of rural areas. The basic regulation stipulating the terms of organic agriculture is the Act on the Implementation of Council Regulation (EC) No. 834/2007 on organic production and Labelling of organic products.

Organic agriculture is most commonly mentioned as the production without the use of mineral fertilisers, pesticides, hormones, etc. Natural processes in the ecosystem are exploited and channeled into the production of raw materials, foodstuffs and processed products, and the intake of energy and dependence of production on industry is sought to be reduced or completely avoided. This definitely does not mean the return to extensive agriculture since organic agriculture requires an educated producer with a different outlook on life.

In organic production, higher losses due to harmful organisms attacks are tolerated. Fruits, food or processed products produced according to the principles of organic agriculture are not governed by market standards imposed by retailers since crops do not have to be flawless in appearance, regular, without any spots or stains and of strictly defined dimensions. Consumer confidence in organic products does not depend on the aesthetic appearance of fruit and vegetables. Organic production is under the supervision of authorised control authorities.

3.1 The future of organic agriculture

The development and the future of organic agriculture shall largely depend on the market and standards and values which shall prevail in the society. The demand for organic products is growing, accompanied by the growth in the number of organic agricultural holdings in Croatia. The market now inevitably imposes standards regarding the price, quality and quantity of agricultural products, thereby resulting in a highly productive agricultural production, as cheap and “resistant” to risks as possible, and many agricultural producers decide on continuing with conventional production. However, the public and society in general are becoming more aware of certain negative consequences of conventional agriculture and the legal frameworks governing agricultural production are changing. Stricter standards in environmental and human health protection are also imposed.

Organic agriculture shall be considered advanced, it shall be recognised, but it is unrealistic to expect that the area under organic farming shall drastically increase. The action plan for the development of organic agriculture in the Republic of Croatia for the period 2011 - 2016 envisages an increase in the share of area under organic agriculture in the total agricultural area in Croatia to 8% by 2016.
3.2 Plant protection in organic agricultural production

The environmental approach to plant protection entails the application of environmentally-friendly plant protection measures which, if applied professionally, are not dangerous to humans and beneficial organisms, do not contaminate or only temporary contaminate the environment, disrupt the established balance and biodiversity to a minimum extent possible.

The selection of plant protection products and plant protection measures in organic production is limited, therefore, the risk of damage caused by pests, pathogens and weeds is more pronounced in organic production than the risk in conventional or sustainable agriculture. Regardless of all preventive measures aiming to prevent the occurrence, harmful organisms originating from natural ecosystems regularly appear in every agricultural production, including the organic one. Therefore, the objective of the agroecosystem is to preserve and utilise the balance of natural ecosystems with the purpose of controlling the propagation of harmful organisms and preserving the natural enemies of different pests regardless of whether these are parasitic wasps, which attack only one type of aphids, or birds of prey, which regulate the populations of field rodents. Encouraging and preserving antagonistic microorganisms (bacteria and fungi) can be effective in preventing the propagation of pathogenic microorganisms, especially those that live in the soil. The balance, which is present in natural ecosystems, does not exist in any kind of agriculture since the relations between living organisms are established and maintained by man, and the occurrence of harmful organisms is undesirable.

Preventive measures in environmental plant protection include all available measures and methods, which have a greater or smaller effect on reducing the population of harmful organism, and are beneficial to the development of the population of beneficial organisms, and are also important for integrated pest management. For that purpose, airy, sunny and isolated positions optimal for the development of plants and unfavourable for the occurrence and propagation of harmful organisms are selected. Great attention is paid to crop rotation, selection of resistant, tolerant or less susceptible varieties, balanced fertilisation with manure, green fertilization, etc.

Mechanical and physical plant protection measures are also sought to be used to the greatest extent possible in organic production. Weed control in organic agriculture is performed exclusively through mechanical, and sometimes a combination of mechanical and physical measures. Among mechanical protection measures, manual collection of, for example, Colorado potato beetle in potatoes is usual, and among mechanical protection measures against diseases, pruning and manual removal of infected fruits or shoots shall be mentioned. In some cultures, it is possible to achieve high efficiency in protection against some pests by using coloured sticky boards.

Alternative measures for the suppression of harmful organisms include the use of live antagonistic microorganisms or their products, the use of environmentally friendly plant protection products and the use of plant defence activators, which induce plant defence mechanisms. The implementation of alternative measures requires significantly more knowledge and experience, and other than harmful organisms, their hosts and agro-ecological conditions, the knowledge on the organisms we use, is also required.
3.3 Plant protection products in organic agricultural production

Regulation (EC) No. 889/2008 and Implementing Regulation (EU) No. 354/2014 on detailed regulations for the implementation of Regulation (EC) No. 834/2007 on organic production and Labelling of organic products with regard to organic production, Labelling and professional control, cover the procedures and specific standards of plant cultivation and organic production management, as well as the measures and plant protection products for the suppression of harmful organisms.

Permitted biological and biotechnological measures for harmful organism suppression include the use of the following:

- natural enemies of agricultural plants pests (predators, parasitoids)
- pheromones (pheromone traps), when not applied directly to the plants,
- repellents (non-chemical synthetic repellents),
- traps for insects, coloured, sticky boards, ribbons, containers,
- mechanical means: fences for snails, illuminated night traps, nets, veils and traps and
- sterile males, if other treatments are not successful, but only with the permission of the controlling authority.

The use of plant protection products is also allowed when all other measures for activating own plant defences have been utilised. In organic production of plants and plant products, the use of plant protection products is permitted in accordance with Appendix II of the Regulation (EC) No. 889/2008 and Implementing Regulation (EU) No. 354/2014 on detailed regulations for the implementation of Regulation (EC) No. 834/2007 on organic production and Labelling of organic products (Tables 3.1 - 3.7). Plant protection products shall possess a decision on registration or a decision on the permit pursuant to Article 16, paragraph 1 of Regulation (EC) No. 834/2007.

Table 3.1: List of substances of plant and animal origin permitted for use in organic production (prepared by: M. Ševar)

<table>
<thead>
<tr>
<th>Name</th>
<th>Description, requirements regarding the composition, terms of use</th>
</tr>
</thead>
<tbody>
<tr>
<td>azadiractin extracted from <em>Azadirachta indica</em> (Neem)</td>
<td>Insecticide</td>
</tr>
<tr>
<td>beeswax</td>
<td>Use during tree pruning</td>
</tr>
<tr>
<td>gelatine</td>
<td>Insecticide</td>
</tr>
<tr>
<td>hydrolysed proteins other than gelatine</td>
<td>Attractant, only for approved use in combination with other appropriate products from this list.</td>
</tr>
<tr>
<td>lecithin</td>
<td>Fungicide</td>
</tr>
<tr>
<td>vegetable oils</td>
<td>Insecticide, acaricide, fungicide, bactericide and sprout inhibitor Plant protection products based on active substances listed in the Appendix to Implementing Regulation (EU) No. 540/2011</td>
</tr>
<tr>
<td>pyrethrins secreted from <em>Chrysanthemum cinerariaefolium</em></td>
<td>Insecticide</td>
</tr>
<tr>
<td>quassia extracted from <em>Quassia amara</em></td>
<td>Insecticide, repellent</td>
</tr>
</tbody>
</table>

Azadirachtin, pyrethrin and quassia are substances which possess different mechanisms of affecting the insects (neurotoxic, respiratory obstruction, feeding and growth inhibitors), however, what they have in common is the fact that they affect a whole range of insect species, their effect is short-term, they are rapidly degradable and are very slightly toxic for humans.
The use of microorganisms for biological suppression of harmful organisms is permitted (Table 3.2).

**Table 3.2: Microorganisms used for pests and diseases suppression, which are allowed in organic production (prepared by: M. Ševar)**

<table>
<thead>
<tr>
<th>Name</th>
<th>Description, requirements regarding the composition, terms of use</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>microorganisms</strong></td>
<td>Plant protection products based on active substances listed in the Appendix to Implementing Regulation (EU) No. 540/2011 and not originating from GMO</td>
</tr>
</tbody>
</table>

Microbial insecticides are specially formulated and selected living organisms, which cause diseases to harmful insects and thus suppress them. They are pathogenic and aggressive for a particular type of insect, with the aim of achieving high mortality within the pest population. These products are only effective for one type or a smaller number of harmful insect species. Insects generally do not develop resistance to them, and they are highly selective and do not affect beneficial insects. The efficiency largely depends on external factors, the products are less effective compared to chemical insecticides, but microbial insecticides still offer the possibility of high-quality and safe protection against certain pests, which are difficult to suppress in organic production.

**Table 3.3: Substances produced by microorganisms, which are allowed in organic production (prepared by: M. Ševar)**

<table>
<thead>
<tr>
<th>Name</th>
<th>Description, requirements regarding the composition, terms of use</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Spinosad</strong></td>
<td>Insecticide Only if measures are taken to reduce the risk of key parasitoids as much as possible and to minimise the risk of the development of resistance as much as possible</td>
</tr>
</tbody>
</table>

Traps and/or dispensers, which are used, shall prevent the substances reaching the environment and their contact with the planted crops (Table 3.4). The traps shall be collected after use and removed safely.

**Table 3.4: Substances used in traps/dispensers, which are allowed in organic production (prepared by: M. Ševar)**

<table>
<thead>
<tr>
<th>Name</th>
<th>Description, requirements regarding the composition, terms of use</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>pheromones</strong></td>
<td>Attractants/baits, plant protection products which cause disruptions in sexual behaviour, only in traps and dispensers Plant protection products based on active substances listed in the Appendix to Implementing Regulation (EU) no. 540/2011 (numbers 255, 258 and 259)</td>
</tr>
<tr>
<td><strong>pyrethroids (only deltamethrin and lambda-cyhalothrin)</strong></td>
<td>Insecticide, only in traps with specific attractants/baits; only against <em>Bactrocera oleae</em> and <em>Ceratitis capitata</em> Wied.</td>
</tr>
</tbody>
</table>

**Table 3.5: Microorganisms spread on the surface among plants, which are allowed in organic production (prepared by: M. Ševar)**

<table>
<thead>
<tr>
<th>Name</th>
<th>Description, requirements regarding the composition, terms of use</th>
</tr>
</thead>
<tbody>
<tr>
<td>ferric phosphate (iron(III) orthophosphate)</td>
<td>Limacide (molluscicide)</td>
</tr>
</tbody>
</table>
There are other substances as well which are traditionally used in organic farming (Table 3.6)

Table 3.6: List of other substances from traditional use, which are allowed in organic production (prepared by: M. Ševar)

<table>
<thead>
<tr>
<th>Name</th>
<th>Description, requirements regarding the composition, terms of use</th>
</tr>
</thead>
<tbody>
<tr>
<td>copper compounds in the form of copper hydroxide, copper oxychloride, Bordeaux mixture, and trivalent copper sulphate</td>
<td>Only permitted for use as fungicides and bactericides in the amount of up to 6 kg copper per hectare per year. For perennial crops, the Member States may, by way of derogation from the first paragraph, prescribe that the limit of 6 kg copper in a given year may be exceeded, provided that the average quantity actually used over a five-year period, including the aforementioned year and the four previous years, does not exceed 6 kg. For the purpose of protecting water and non-targeted organisms, the measures shall be taken to reduce the risk, such as, for example, buffer zones. Plant protection products based on active substances listed in the Appendix to Implementing Regulation (EU) No. 540/2011 (number 277).</td>
</tr>
<tr>
<td>ethylene</td>
<td>Ripening of bananas, kiwis and persimmons; ripening of citrus fruits only as part of a strategy for the prevention of fruit fly damage in citrus fruits; encouraging pineapple flowering; prevention of sprouting in potatoes and onions. Only permitted for indoor use as a growth regulator. Only permitted for professional use.</td>
</tr>
<tr>
<td>potassium salt of fatty acids (lubricating soap)</td>
<td>Insecticide</td>
</tr>
<tr>
<td>lime sulphur (calcium polysulfide)</td>
<td>Fungicide</td>
</tr>
<tr>
<td>paraffin oil</td>
<td>Insecticide, acaricide Plant protection products based on active substances listed in the Appendix to Implementing Regulation (EU) No. 540/2011 (numbers 294 and 259)</td>
</tr>
<tr>
<td>quartz sand</td>
<td>Repellent</td>
</tr>
<tr>
<td>sulphur</td>
<td>Fungicide, acaricide</td>
</tr>
<tr>
<td>repellents of animal or vegetable origin which repel by scent/sheep fat</td>
<td>Repellent Only on the inedible parts of plants and if the plant material is not intended as sheep or goat feed Plant protection products based on active substances listed in the Appendix to Implementing Regulation (EU) No. 540/2011 (number 249).</td>
</tr>
</tbody>
</table>

Table 3.7: Other substances, which are allowed in organic production (prepared by: M. Ševar)

<table>
<thead>
<tr>
<th>Name</th>
<th>Description, requirements regarding the composition, terms of use</th>
</tr>
</thead>
<tbody>
<tr>
<td>aluminium silicate (kaolin)</td>
<td>Repellent</td>
</tr>
<tr>
<td>calcium hydroxide</td>
<td>Fungicide only for fruit trees, including nurseries, for the suppression of Nectria galligena.</td>
</tr>
</tbody>
</table>
| Plant defense mechanism activator | Laminarin  
Kelp shall be cultivated organically pursuant to Article 6d or harvested in a sustainable manner pursuant to Article 6c of Regulation (EC) No. 889/2008 |
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Fungicide and insecticide</td>
<td>Potassium hydrogen carbonate (also known as potassium bicarbonate)</td>
</tr>
</tbody>
</table>

Plant protection products based on copper are inorganic compounds, which are equally used in conventional, integrated and organic production of grapes, fruits and various vegetables. Plant protection products based on copper are broad spectrum contact fungicides, effective for some metabolic processes in fungi and bacteria, therefore, their implementation does not result in resistance.

In organic production, the use of up to six kilograms of copper per hectare per year is permitted in order to avoid the accumulation of copper in the soil. The withdrawal period for copper products is relatively long, and may have a phytotoxic effect during the application.

In organic production, repellents such as quartz sand and pheromones for attracting insects, their massive catch and “confusing” may be used.

Microbiological fungicides, often called biofungicides, are living organisms, which may be used to suppress plant parasites, pathogens. Different types of fungi and bacteria are currently used, all of which are permitted in organic production, however, only a small number of commercial preparations are available on the market. The most notable biofungicides are those in which the fungus *Trichoderma harzianum* is used. This fungus is an aggressive coloniser, which quickly takes up space, creates compounds, which indiscriminately kill other fungi, parasitizes and feeds on them, as well as encourages the development of induced plant resistance to diseases. *T. harzianum* fungi and other *Trichoderma* species are also an ingredient of many "microbiological fertilisers", which have proven to be highly efficient in protecting against pathogens that live in the soil.

Organic agriculture and sustainable agriculture fit into the concept of sustainable development, with their aim of environment preservation, as well as achieving the greatest economic impact through the use of available resources. Integrated and environmental approach are sustainable in plant protection, and these measures are divided into "green", "yellow" and "red" ones. "Green measures" include agrotechnical, biological, biotechnological, mechanical and physical measures (permitted in organic production). "Yellow measures" are implemented through plant protection products only when "green measures" cannot prevent economic damage (permitted in integrated, only some are allowed in organic). "Red measures" include plant protection measures that are prohibited in both integrated and organic agriculture.

**Authors:** Marija Ševar, M.Sc., Vlado Novaković, M. Eng., Dario Ivić, Ph.D.

**Expert consultant:** Darius Musulin, M. Eng.
4 ORGANISMS HARMFUL TO PLANTS AND PLANT PRODUCTS

Agricultural crops are attacked and damaged by harmful organisms - pests, pathogens and weeds. Harmful organisms damage agricultural crops from their sowing or planting until their harvest. Some pests and pathogens also occur during storage of agricultural products and reduce their quality.

4.1 Pests

The pests include insects, mites, nematodes, snails, rodents, game and birds.

4.1.1 Insects

Insects are the largest and most important group of agricultural crop pests. In our country, there are more than a thousand known insect species, which cause economically significant damage to agricultural crops.

Their body is composed of joints or rings covered by cuticle, and is divided into several parts: head (cephalon), chest (thorax) and back part (abdomen). They have three pairs of legs. They reproduce asexually and sexually. Insect females lay live young or lay eggs. The eggs may be placed on the plant or in the plant, in the soil, individually or in groups (egg masses) (Figures 4.3 - 4.5).

After a certain incubation period, larvae of different names, depending on the insect species, emerge from the eggs, for example caterpillars (butterfly), white grubs (cockchafers), turnip sawfly larvae etc. The larvae grow and feed intensively immediately after emerging from the eggs (Figures 4.2, 4.6 - 4.9).

Larvae growth occurs with the rejection of the cocoon (changing). The development or metamorphosis of insects can be complete and incomplete. In complete metamorphosis, there are stages: egg, larva, pupa (Figure 4.3) and the adult form (imago). In incomplete metamorphosis, there are stages of the egg, larva, which is similar to the adult form, and the adult form. Therefore, there is no pupa stage, but the larvae are directly changed into the adult form. Given the mouthpart structure, harmful stages of insects are divided into piercing (e.g. caterpillars of butterflies, larvae and adult Colorado potato beetle, Cereal leaf beetle) and sucking (e.g., aphids, thrips, psyllids, greenhouse whiteflies, San Jose scale).
Figure 4.3: Pear Leaf Blister Moth egg - left and Pear Leaf Blister Moth pupae (*Leucoptera malifoliella*) on an apple tree - right (photo: Ž. Budinščak)

Figure 4.4: European Grapevine Moth egg (*Lobesia botrana*) disposed on a grape (photo: Z. Pavunić Miljanović)

Figure 4.5: Egg - left and the adult form of codling moth (*Cydia pomonella*) - right (photo: Ž. Budinščak)

Figure 4.6: Larva - left and the adult form of the Cerial Leaf Beetle (*Oulemamelanopus*) - right (Photo: Z. Pavunić Miljanovic)

Figure 4.7: Cabbage butterfly caterpillars (*Pieris brassicae*) (photo: M. Šimala)

Figure 4.8: Turnip sawfly larvae (*Athalia rosae*) (photo: M. Šimala)
Biting insect species bite off edges of plants, cause damage in the form of holes or bite into the underground plant organs (Figures 4.1, 4.6, 4.10 and 4.11). Some of them may cause defoliation.

Sucking insects have a mouthpart structure that allows stabbing into the plant (stem, leaf, fruit) and suction of plant juices (Figures 4.12 to 4.16), thereby causing deformation, different changes in colour, yellowing and drying of plant parts.
The number and harmfulness of insects depends on heat, moisture, available food and the presence of natural enemies. Insect body temperature depends on the temperature, therefore, they feed and move more intensively in warm weather, thereby causing greater damage. On surfaces with the same cultures, where there is a lot of food, pests of those plant species propagate quickly, while their propagation is much slower on the meadows or in mixed crops or plantations. Natural enemies of insects are predators, which feed on them, or parasitoids, which live in the victim or on the victim and feed on it. Predatory insects are ladybirds, ground beetles, lacewings, some species of heteroptera, predatory mites etc. Parasitoids tachina flies, parasitic wasps etc.

Plant pests, which occur regularly every year, are permanent pests, and those, which occur occasionally are periodic pests.

Harmful insects which cause major economic damage to agricultural crops are beetles, caterpillars of butterflies (Figure 4.19), thunderflies or thrips, aphids, San José scales, greenhouse whiteflies, psylla, flies (Figures 4.17 and 4.18), hymenoptera and heteroptera. Larvae are usually more harmful than adult forms.

Preparations for harmful insect suppression are known as insecticides.
4.1.2 Mites

Mites are very tiny organisms, usually smaller than 1 mm. According to the systematic affiliation they belong to the Arachnida class - arachnids, order Acarina. Their body is divided into two segments, the front end or prosoma, and the back end or opisthosoma, and their body joints are not clearly separated, as in insects. They reproduce sexually. Mites have four pairs of legs, except for blackcurrant gall mites, which have only two pairs of legs. They do not have developed tentacles, but nuchal organs, and their mouthparts structure is adapted for piercing and sucking. Low relative humidity and high temperatures are favourable for their development, and they develop a greater number of generations per year. They reproduce sexually, and the females are usually oviparous. In mites, we differ between the winter eggs, which overwinter, and summer eggs, which appear during the growing season. Mite larvae change several times, and during the last change, they transfer into the stationary stage - nymph stage, from which the adult form is then developed.

They cause the most significant damage to fruit trees, grapevines, some field crops (soybean), vegetables and flowers.

The most common symptoms of mite attack are: bright spots, the appearance of fine cobweb on the underside of the leaf and twisting of plant organs. The most important mite families that cause the aforementioned damage are spider mites (Tetranichidae) (Figure 4.20) and blackcurrant gall mites (Eriophidae). In addition to harmful mites, it is also necessary to mention the useful predatory mites from the Phytoseiidae family, which are natural enemies of some harmful insects and effectively limit their propagation and may affect the reduction in population size. Preparations used to suppress harmful mites are called acaricides.

![Figure 4.20: Adult form of the European red mite (Panonychus ulmi) (photo: Ž. Budinščak)](image)
4.1.3 Nematodes

Nematodes are tiny animal organisms, in nature they are widespread in soil, salt or fresh water. Among many nematode species described until now, hundreds of species attack and feed on living plants. Such species are called phytophagous or plant-parasitic nematodes, and are among agricultural crop and other plant pests. Their body is microscopic in size, from 0.3 to several millimetres in length. Most plant-parasitic nematodes are of warm-like, needle-like, thread-like or string-like form. In the group of cyst-shaped nematode species, females assume the roundly shaped body in sexual maturity. According to the shape of the body, we differentiate between the round, pear-shaped and lemony form. Plant-parasitic nematodes feed by sucking plant juices using stylets, chitinous spikes placed in their oral cavity. Some species live and feed inside the host plants and are among endoparasites, while other feed in the soil outside the plant and are among ectoparasites. Similar to insects, nematodes also go through several stages during their life cycle - from eggs to the four stages of larvae (“juveniles stages”), after which they are transformed into adult forms through final metamorphosis.

Nematodes move through the soil relatively slowly, and they spread over a long-distance through infected plant material, soil or substrates. Symptoms caused by plant-parasitic nematodes on plants may be different, depending on the species. Feeding on the root of a lot of species leads to a general weakening of the plants, and often their complete decay after a shorter or longer period. Numerous species cause deformation of infested plant organs, while others may also cause symptoms on the leaves. Damage caused by plant parasitic nematodes are mostly not noticed at first glance, but can often be drastic. As the majority of plant-parasitic nematodes live in the soil, the symptoms are usually noticed in an advanced stage of attack or infection. Because of the special features in the lifecycle of these parasites, the suppression of nematodes is very complex and includes the use of all available protective measures, sometimes also including chemical measures.

Many species of plant parasitic nematodes have a very wide range of host plants. Among a significant number of species, the most harmful ones are root-knot nematodes (*Meloidogyne* species) on vegetables, fruit and ornamental plants, cyst-like nematodes on potatoes (*Globodera* species) (Figure 4.21), sugar beet (Figure 4.22.) or soybeans (*Heterodera* species), virus-vectors nematodes (*Xiphinema* species), stem (*Ditylenchus* species) or foliar nematodes (*Aphelenchoides* species). Preparations, which suppress nematodes, are called nematocides.

**Figure 4.21:** Potato cyst-like nematodes on the potato tuber (photo: I. Poje)

**Figure 4.22:** Beet cyst nematode on the sugar beet root (photo: I. Poje)
4.1.4 Snails

According to their systematic affiliation, snails belong to the Gastropoda class, and the members of the Pulmonata subclass are an important species in plant protection. Snails are hermaphrodites, and their bodies are soft, covered with mucus. We distinguish snails with shells (Figure 4.23) and those without it, slugs (Figure 4.24). Slugs are more mobile than snails with shells and they can therefore be more easily suppressed since it is easier for them to find bait. During the day, in sunny weather, they hide in shady places, and they feed at night. Previously, snails were mostly considered vegetable pests, however, recently they have been causing significant damage to agricultural crops, flowers, strawberries, as well as in orchards. They are voracious and can eat up to 50% of their mass in one day. They are polyphagous and they feed on many cultivated (Figure 4.25) and non-cultivated plant species. They cause direct damage by biting off the plant parts, making holes in the leaves, and they leave slime and excrement on the plants, i.e. they contaminate plants, making them lose their market value. They can also bite off plant stems, seeds and some fruits. They lay eggs in groups in the secret places at the beginning of the summer, and after 25-30 days, young snails hatch from the eggs. They reach sexual maturity after 60 days. Temperatures between 12 and 22°C and a relative humidity of the soil between 20 and 30% are favourable for their development. However, at soil humidity between 10 and 15%, and greater than 40%, mortality is high.

The indirect measures of snail suppression include all measures of processing and cultivation, which have an adverse effect on the population size, and the drainage of water from production areas. Some herbicides and fertilisers may also have an adverse effect on snails. They are directly suppressed by limacides, which are commercially available as finished baits. Baits are usually applied by spreading between the plants and they shall be spread in the evening and in dry weather. For the suppression on smaller areas, substances which cause dehydration of the body may be used, e.g. ashes, quicklime or slaked lime and some mineral fertilisers. Furthermore, mechanical measures, such as covering the crops with nets, fencing with impassable railing or collecting snails on smaller areas, can reduce their harmfulness.
4.1.5 Rodents

Harmful rodents include small mammals whose teeth are adjusted to gnawing. They are characterised by rapid propagation, often resulting in their overreproduction after which they may cause major economic damage. They are divided into field and indoor rodents.

Among field rodents, the most common are the field mouse (*Mus musculus*), common vole (*Microtus arvalis*), European water vole (*Arvicola terrestris*), striped field mouse (*Apodemus agrarius*) and yellow-necked mouse (*Apodemus flavicollis*). They are expressly periodical pests. In some years, when winter periods are relatively warm, their overproduction may occur, which often results in significant damage to agricultural crops.

Field rodents cause damage to arable crops (Figure 4.27), clover fields, lucerne fields and meadows (Figure 4.29), as well as to young orchards and vineyards, and this damage may result in yield loss of up to 50%. Voles prefer to feed on the young fruit trees roots. Significant damage in young orchards may occur in winter, and one vole can strip approximately hundred young trees during winter (Figure 4.26). The population of rodents in orchards shall be constantly monitored, particularly along the roads and canals that are overgrown with vegetation and in abandoned and uncultivated areas next to the orchards or within them. Damage is usually visible in spring, when the young fruit trees do not leaf out, are weakened, can be easily rooted out of the soil, and a stronger wind may topple them.

![Figure 4.26: Damage caused by voles on the young fruit trees in the nursery (Photo: Z. Budinščak)](image)

![Figure 4.27: Vole on the surface prepared for sowing arable crops (Photo: T. Rehak)](image)

In arable crops, field rodents cause damage by climbing on the ripe ears of grain, breaking them and carrying them back to their shelters. Damage can also be caused breaking the stems and ripping the ears.

In addition to direct damage to agricultural crops, they may also cause indirect damage by their activities under the soil surface. Through their activity, they dig holes in the soil surface whereby grooves shaped as channels are visible, (Figure 4.28) connecting the holes into burrows and corridors which pass beneath the soil surface. Openings and burrows are particularly dangerous on the mounds, which become porous and unsafe during defense against floods.

Rodents in warehouses damage and contaminate stored products with faeces, urine and hair. The result of their presence is smell, and due to their activity, damage to various objects and buildings occurs. The quality and market value of damaged and contaminated products is reduced, and at the same time they pose a risk for the consumers of contaminated products due to the possibility of various diseases occurrence. Since a large amount of food available to rodents is present in warehouses, problems often occur when implementing the protection and suppression. Large amount
of debris and various waste from grain cleaning can sometimes be found around the warehouses, which favours the gathering of rodents.

The decision on field rodent suppression is adopted as soon as their presence is established based on the active openings detections (Figure 4.28). It is important to suppress them regularly, and if their suppression is initiated when the population large, the success shall be insufficient, and the cost high. Suppression of field rodents shall be directed towards constant preventive suppression, and not towards occasional curative suppression, and the presence of more than 20 active vole holes per acre is considered hazardous.

They cause trichinosis and other diseases in humans and domestic animals.

Damage from field rodents can be prevented through organised monitoring and trained advisory service, which preforms the reporting and forecasting activities in the field, as well as through education of agricultural producers on the importance of this problem.

Greater success in suppressing the field rodents is achieved if the suppression is performed over a greater area. The suppression over a small area is not successful due to high mobility of the rodents and shall be organised so as to include all the surfaces at risk, regardless of the owner.

Preparations for rodent suppression are called rodenticides, and they are placed on the marked as finished poisoned bait. Rodenticides can also be authorised as biocidal products. Rodenticides as plant protection products are applied mainly in agricultural areas for the protection of plants and plant products from rodents. Biocidal products are applied for rodent suppression in the facilities where food is stored and prepared, as well as where people and animals live, with the purpose of protecting their health and objects, which are used, as well as on non-agricultural areas. The European Commission has prepared guidelines, which define the circumstances for plant protection products application, and the circumstances for biocidal products application.

It is important to note that some species of field rodents are protected and shall not be suppressed, which indicates the importance of knowledge on the population of field rodents. Protected species are European snow vole (Chionomys nivalis), Yellow-necked mouse (Apodemus flavicolis), European hamster (Cricetus cricetus), Alpine pine vole (Microtus multiplex), steppe mouse (Mus spicilegus), snow vole (Chionomys) and lesser mole rat (Nannospalax leucodon).

![Figure 4.28: Active holes and damage to the lawn caused by the activity of field rodents (Photo: D. Hamel)](image)

![Figure 4.29: Vole on the lawn (Photo: D. Hamel)](image)
4.1.6 Game

Different types of game can cause damage to agricultural crops. Harmful species of game include rabbits, wild boars and roe deer. They are most often harmful to crops near forests and they cause significant damage by gnawing the bark of fruit trees, sometimes vines, especially in winter when the snow is high. Damage caused by game is more significant during dry periods. The media often report on great damage caused by wild boars in agricultural crops. One manner to prevent damage from game is by applying plant protection products - game repellents. There are no registered repellents, which are plant protection products in Croatia. However, there are intense scent repellents for game repelling which are widely used and are not applied to the plants in the crops or plantation. These repellents are used in the manner that cloth or sponges are soaked and, using wooden stakes, arranged in regular distance around the crops. However, the safest manner to prevent damage to orchards is by placing a fence around the crops or placing a wire mesh around each individual seedling or young fruit tree. Crops and plantations can also be protected against some types of game by placing electric shepherds.

4.1.7 Birds

Harmful birds include starlings, sparrows, crows, magpies, pheasants, etc. Birds damage sown seeds, sprouts, newly grown corn, sunflower and other crops, as well as ripe fruit and grapes. They can damage sunflower heads and corncobs. They cause more significant damage on small areas near tall trees or power lines on which they gather than on larger lots. It is not permitted to kill birds, but only to repel them by using visual or sound repellents or to prevent their attack mechanically, using various frighteners and nets for covering crops and plantations. The occurrence of damage on the sown seeds is prevented by applying repellent preparations for seed treatment.

Some species of birds can also cause damage to the stored products, particularly grain. Mostly pigeons and sparrows feed on stored grain, and the most important measure for preventing such damage is by preventing access to such facilities by installing nets on the openings or placing metal spikes under roofs to prevent their nesting and gathering.
4.2 Pathogens

Plant diseases can be caused by various factors, which can be non-parasitic and parasitic.

Non-parasitic diseases or disorders occur due to low or high temperatures, low or high relative humidity, lack or excess of light, lack or excess of nutrients, toxicity of some elements in the soil, inadequate soil pH, phytotoxicity of plant protection products, etc. Non-parasitic diseases are mainly caused by unfavourable environmental conditions, which contribute to the sensitivity of plants to parasitic pathogens, most often in stressful situations. Non-parasitic diseases are not transmitted from plant to plant, i.e. they are not infectious.

Parasitic diseases in agricultural crops are caused by fungi and pseudofungi, bacteria, phytoplasmas, viruses and similar organisms. Parasitic pathogens are organisms, which parasitize in or on plant organs and thus provide food for their sustenance. Parasitic diseases are contagious and can be transmitted from the infected to a healthy plant.

4.2.1 Fungi and pseudofungi

The causes of most diseases in cultivated plants are phytopathogenic fungi and pseudofungi. The degree of damage caused by a fungal infection depends on the type of fungus or pseudofungus, weather conditions (temperature and relative humidity), sensitivity and condition of the infected plant. Diseases caused by fungi are called mycoses.

Fungi and pseudofungi can enter the host plant through various mechanically caused damages (e.g. wounds after pruning) or directly through the intact epidermis of plant organs.

The symptoms on plants, caused by fungal infections, usually manifest themselves as yellowing on the leaves, drying of the leaves (Figures 4.35 and 4.36) and/or fruit, leaf and/or fruits falling off, growth retardation and poor condition of the plant.

Figure 4.30: Dead arm of grape vine (*Phomopsis viticola*)
(photo: Z. Pavunić Miljanovic)
The body of the fungi and pseudofungi is composed of hyphae (filaments) that grow in all directions and form a combination that is called a mycelium. Mycelia of certain fungi species grows on the surface of affected organs and draws food from the host cells using pumps (haustoria). Such fungi are called ectoparasites. Ectoparasites include most powdery mildew pathogens. The mycelium of phytopathogenic fungi and pseudofungi also penetrates the attacked organs (endoparasites), spreading between cells (intracellular) or entering the cells (intracellular).

Fungi and pseudofungi reproduce using organs called spores. Most pseudofungi create zoospores in the zoosporangium, while true fungi spores are formed at various simple or branched carriers (conidiophores), which can be individual or in groups, for example, in a coremium (bundle) or sporodochium (cushion). The spores are released from spore-carrying organs and, carried by the wind, rain and insects, come to the plant organs. At favourable temperature and humidity conditions, they germinate and thus the process of the host plant infection begins. The time from the entry of the fungi or pseudofungi into the host plant to the occurrence of symptoms is called the incubation period. The incubation usually lasts 3 to 4 days, sometimes up to two weeks, after which fructification fungi organs appear (e.g. conidiophores with conidia in case of Botrytis) accompanied by the occurrence of symptoms (Figures 4.34 and 4.38). This creates a new generation of spores, which spread the infection (Figure 4.32). The fructification phase does not appear in all pathogens. In bacteria, viruses or tracheomycosis, there are no spore-carrying organs, however, the signs of the disease are still visible. After the end of the host plant life cycle, the fungus overwinters in plant residues or soil in form of fertile bodies characteristic for each individual species. One of the most important indirect protective measures are ploughing under or removal of infected plant residues or adherence to crop rotation due to a decrease in the possibility of infection in the next growing season.

Some of the well-known plant diseases caused by fungal infections are: potato blight (Phytophthora infestans) (Figure 4.37), grapevine downy mildew (Plasmopara viticola) (Figure 4.31), dead arm of grapevine (Phomopsis viticola) (Figure 4.30), apple and pear scab (Venturia inaequalis), peach leaf curl (Taphrina deformans), shot hole disease in stone fruits (Stigmina carpophilia) (Figure 4.33), powdery mildew of grape (Erysiphe necator = Uncinula necator), barley powdery mildew (Blumeria graminis = Erysiphe graminis), wheat leaf rust (Puccinia recondita), septoria leaf blotch (Zymoseptoria tritici = Septoria tritici), common bunt of wheat (Tilletia tritici) and cercospora leaf spot (Cercospora beticola). Preparations for the suppression of fungi, pathogens, are called fungicides.
4.2.2 Phytopathogenic bacteria

Plant pathogenic bacteria are single-celled organisms that cause diseases in plants. It is known that only 10% of the bacteria described until now belongs to phytopathogenic bacteria. Diseases caused by bacteria are called bacterioses. Phytopathogenic bacteria are usually mesophilic or thermophilic, rod-shaped and temperatures between 25 and 30 °C favour their development. They propagate very rapidly and are characterised by a high infective potential. They enter the plant through the stomata, lenticels, through flower nectar glands, through wounds or scars that occur after the leaves or fruits fall off or after mechanical damage. Phytopathogenic bacteria are endoparasite, which means they are located in the interior of the infested plant parts or the whole plant. They are mostly facultative parasites and remain in crop residues or soil, and as such represent a source of infection. They can also
be transmitted via seed. The most common carriers of phytopathogenic bacteria are: humans, insects and other animal organisms, water and air currents. Symptoms in form of necrosis, wilting of individual organs or entire plants, the presence of secretions – exudate, etc. appear on the affected plants. However, in order to determine the presence of a certain bacteria in the plant material, a bacteriological analysis in the laboratory is required.

Formulations based on copper show a certain effect on bacteria, but such formulations shall be applied carefully, in accordance with the accompanying instructions and good agricultural practice since they may cause phytotoxicity on some species.

The best-known bacterial diseases are fire blight of apple and pear (Figure 4.39), grapevine crown gall, common potato scab, potato brown rot, etc.

**Figure 4.39:** Fire blight (*Erwinia amylovora*) (photo: D. Ivić)

**Figure 4.40:** Grapevines infected with phytoplasma of Flavescence dorée (photo: Ž. Budinščak)

### 4.2.3 Phytoplasmas

Phytoplasmas are bacterial plant pathogens, which cause hundreds of plant diseases. Since they have no cell wall, they can change their shape (pleomorphism) and are generally of round shape. Diseases caused by phytoplasmas are called phytoplasmoses. They are transmitted via insects (phytoplasma vectors), grafting, cuttings, but not via seeds. Protection is based on the production of healthy planting material, vector suppression and the destruction of infected plants. Phytoplasmas known in Croatia are Apple proliferation phytoplasma and Pear decline phytoplasma present on pome fruit and European stone fruit yellows. In our vineyards, infection with phytoplasma causing Flavescence doré (Bois noir) has been confirmed (Figure 4.40).

### 4.2.4 Viruses and virus-like organisms

Viruses are plant pathogens causing diseases called viroses. They are smaller than bacteria and phytoplasmas. They are transmitted by touch or various vectors, such as insects, mites, nematodes, dodder or some lower fungi, by seed, cuttings, rootstocks as well as in anthropogenic manner. After the appearance of symptoms on plants (Figure 4.1), the infection cannot be suppressed, therefore the basis for protection against viruses is the sowing of healthy seeds, planting of healthy plants, vector suppression and the destruction of infected plants.

Some viruses causing diseases in agricultural crops are the barley yellow dwarf virus, cucumber mosaic virus, tobacco mosaic virus, tomato mosaic virus, plum pox virus, etc.
Viroids are, in contrast to viruses, the smallest group of pathogens. A viroid is a single-stranded circular RNA (ribonucleic acid) which is infectious and causes plant diseases. Some viroids, which are pathogens on agricultural crops, include Potato spindle tuber viroid (PSTVd), Citrus exocortis viroid (CEVd), etc. In order to determine with certainty the presence of a virus in the plant material, a virological analysis in the laboratory is required.

Figure 4:41: Symptoms on a leaf caused by the plum pox virus
(photo: Z. Pavunić Miljanović)
4.3 Weeds

4.3.1 Definition and damage

Although the definition of the term "weeds" seems simple, the situation is slightly different. Most people have a negative attitude towards weeds, and under such concept they consider a wild plant that grows in the crops (agricultural crop) and that needs to be suppressed. If the crops are covered in weeds, the yield shall be significantly reduced, and a complete lack of yield is also possible. However, is that kind of opinion of weeds correct?

Weed (thistles, brambles, grass, thorns, weeds) does not have to be a wild plant. Cultured plant species can also be weeds. For example, rye, if it sprouts, is weed in wheat, and sunflower in corn. There are many similar examples (Figures 4.42 and 4.43). In certain situations, (varietal tests, seed production) even one variety of the same type of crop is also considered weed if it grows within another variety.

Furthermore, weeds do not grow only in agricultural, but also in non-agricultural areas, such as roads, paths, routes, industrial buildings, parks, canals, sports facilities, airports, water surface, fairgrounds, cemeteries, infields, etc.

In addition to the aforementioned, the crop can be covered with weed without a significant impact on yield. Every culture goes through the development stage where weeds have the biggest impact on the yield (i.e. critical period of weed infestation). Outside of that phase, the crop can be covered with weed without a significant impact on the yield.

![Figure 4.42: Chamomile (Matricaria chamomilla) as a crop (photo: N. Novak)](image1)

![Figure 4.43: Chamomile (Matricaria chamomilla) as weed in oilseed rape (photo: N. Novak)](image2)

The general opinion that weeds shall be suppressed is also not always accurate. A part of wild plants on arable land is not harmful to the crop or the economic damage is minimal compared to the environmental benefits. The aforementioned depends on many factors, including, among other, the species and number (specifically biomass) of the weeds, culture development phase (as explained above), etc.

It is evident from the aforementioned that the term "weed" cannot be easily defined. In almost any definition, it is possible to find a mistake, that is, a case not covered by the definition. Somewhat broader definitions might be "an undesirable plant", "a plant in conflict with human interests" or "a plant which causes more harm than good". A more comprehensive definition is "any plant that grows in an undesirable location".

The aforementioned explanations and definitions refer to the weeds in the broad sense, i.e. they try to cover all situations in which a plant may be undesirable. Suppression of these weeds is generally easier than suppressing the plants growing along with the crop in cultivated areas - weeds in the narrow
sense. The latter can be defined as "the plants growing in the crop, which are not the objective of cultivation". These plants can harm the crop in different manners since they share, that is, they compete among each other for living space (above and below the ground surface), available water, nutrients and light. The lack of any of the listed resources for a culture can have a direct impact on yields, resulting in financial loss for the farmer. As it was mentioned above, the period in the development of culture when the weeds cause the greatest damage is called the critical period of weed competition (CPWC). In this period, it is desirable that weeds are eliminated or reduced to an acceptable level. Before and after the CPWC, weeds generally have no effect on the yield.

Every culture, i.e. crop has its own specific CPWC. For an environmentally friendly approach to weed control, knowledge of CPWC is essential, i.e. knowledge of the factors determining it, and these are competitive capabilities of a culture, species, number and weight of individual weeds, time of weed emergence in relation to culture, agrotechnical management practices in the cultivation technology, climate conditions, density, ground, etc.

Competitive capabilities of a culture are specific to individual species, even to cultivars within the same species. Thus, for example, sugar beet, in comparison to corn, sunflower or a high density culture, has significantly less competitive capabilities. Therefore, much more attention shall be paid to it with regard to weed control.

Framework CPCW for some cultures:
- corn: from development phase 4 to development phase of 10 (12) leaves,
- wheat: from mid-tilling to early stem extension,
- potato: 2-3 weeks after germination until the closing of the ranks,
- sugar beet: 3-9 weeks after germination,
- soybean: from first to third trifoliate leaves.

Regarding the types of weeds, not all weed species damage the crop equally. In terms of the number of weed plants per area unit, it is important to know that the cultures of high density at a lesser degree of weed competition can compete themselves with weeds if the agro-technical measures are implemented within optimal limits and in accordance with the requirements of the culture. The aforementioned does not apply to broad row, hoeing crops where even a small number of plants can cause equal or greater damage than a larger number of weed plants per area unit.

Regarding the time of emergence of weeds in the crop, the most damaging are the weeds emerging before and during the CPWC, while the weeds emerging in the crop after the CPWC do not affect the yield reduction significantly. However they may cause indirect damage, i.e. host economically important plant diseases and pests, make tillage and harvest difficult (Figures 4.44 and 4.45), increase moisture of grain, increase the cost of drying and processing, cause lodging of cultivated plants (e.g. field bindweed in wheat), increase the cost of seed cleaning, cause allergies and poisoning in humans and domestic animals, increase the bank of weed seeds in the soil, etc.

Preparations for weed suppression are known as herbicides.
4.3.2 Division of weeds

Weeds can be divided in several manners. Depending on the division criterion, we can differentiate between the following divisions, according to:

- botanical origin (family, genus, species)
- leaf shape (narrow leaved and broad leaved)
- life cycle (annual, biennial and perennial)
- seasonal dynamics of eruption (winter, spring, summer, autumn),
- crop they infect (weeds of high density cultures, hoeing crop weeds, perennial crops weeds, non-agricultural land weeds),
- location of infestation (land or terrestrial, water or aquatic weeds).

From an agronomic point of view, the most important weed division is according to the leaf shape and life cycle (method of propagation) since the herbicides activity is related to these groups, i.e. those groups describe the spectrum of herbicide activity. In fact, no single herbicide has an effect on all weed species. The label of each herbicide preparation refers to some of the aforementioned weed groups, i.e. the one on which the herbicidal preparation has the best effect (e.g. herbicidal composition intended for annual broadleaf weed suppression).

Botanically, broad leaved weeds belong to dicots (dicotyledon plants or dicotyledons), and narrow leaved to monocots (monocotyledon plants or monocotyledons). Most of economically harmful narrow leaved weeds belong to the family of grasses (Poaceae). The difference between these two large groups is not only in the leaf shape, but also in other properties, which are directly related to their sensitivity to herbicides.

**Annual or seed weeds** conclude the life cycle within one growing season, or a period shorter than one year. They propagate only by seed and hence the name seed weeds. The basis of the fight against annual weeds is the prevention of insemination. In addition to annual seeds, we also distinguish biennial weeds, which form vegetative organs during the first year, and produce fruit during the second year. They are generally not of major importance for agricultural production. The most well known biennial weed is wild carrot (*Daucus carota*).

**Multi-annual or perennial weeds** propagate by seed and vegetatively - through bulbs, tubers, rhizomes, root buds, twigs, etc. Once they become stable in some area, they are very difficult to eradicate due to the developed groundwater organs, which serve as a nutrient reserve. In their suppression, systemic (translocation) shall be used, and the target of suppression shall be the underground organs. Through fragmentation of underground organs (e.g. through milling), the farmer may unknowingly, thinking that they suppress them, help their propagation. It is also possible to suppress them mechanically (e.g. through cultivation, pulling or mowing), since a significant amount
of spare nutrients from groundwater organs are spent by removing the overhead part for the purpose of re-emergence. Through multiple repetition of this process, underground organs are worn out and they die off.

As stated before, good knowledge of weed species in accordance with the aforementioned divisions is of great importance when selecting a herbicidal preparation. Each plant protection product (including herbicidal preparations) has an attached label (Detailed instructions for use), which lists the species, i.e. group (groups) of harmful organisms on which this particular product has an effect. Thus, they may state that the herbicidal composition suppresses, for example, “annual broad leaved” or “perennial narrow leaved” weeds. The aforementioned statement is never entirely accurate since there is no herbicide, which suppresses all species within a particular group of weeds, but the largest number of species on which it has an effect belongs to the aforementioned group (groups). The group on which the preparation has a certain, but an insufficient effect is also often stated (e.g. herbicidal preparation intended for the suppression annual and perennial and annual grass weeds and the reduction of weed competition of annual broad-leaved weeds).

In addition to the aforementioned division, there is also an important division of weeds according to the crop they infect. Namely, according to one definition, weeds accompany cultures and are connected to humans and human activities. According to the culture they infect, weeds can be divided into high-density crops weeds (cereals, oilseed rape, etc.), hoeing crops weeds (corn, soy, sunflower, etc.), perennial crop weeds (orchards and vineyards) and non-agricultural area weeds.

The most common high density culture weeds from the annual broad leaved group are chickweed or chickenwort (Stellaria media), bideye speedwell (Veronica persica), ivy-leaved speedwell (Veronica hederifolia), red deadnettle (Lamium purpureum), henbit dead-nettle (Lamium amplexicaule), common poppy (Papaver rhoeas), cleavers or goosegrass (Galium aparine), chamomile (Matricaria chamomilla) (Figures 4.42 and 4.43), corn buttercup (Ranunculus arvensis), shepherd's-purse (Capsella bursa-pastoris), field mustard (Sinapis arvensis), wild radish or jointed charlock (Raphanus raphanistrum), field forget-me-not (Myosotis arvensis), wild radish or jointed charlock (Raphanus raphanistrum), drug fumitory (Fumaria officinalis), field pansy (Viola arvensis) etc. Most of the listed annual broad-leaved weeds are of a small habitus. Some species emerge in the fall, and some in the spring.

From perennial broad leaved weeds, the ones which occur most often in the spring are field bindweed (Convolvulus arvensis), larger bindweed (Calystegia sepium), various beans (Vicia spp.), creeping thistle (Cirsium arvense) (Figure 4.44) and somewhat less often comfrey (Symphytum officinale), corn sow thistle or dindle (Sonchus arvensis), curly dock or yellow dock (Rumex crispus) and other species. They can sprout from seeds or develop from underground organs.

The most important representatives of annual narrow leaved (grass) weeds in high-density crops are common windgrass (Apera spica-venti), slender meadow foxtail or black-grass (Alopecurus myosuroides), annual meadow grass (Poa annua), common wild oat (Avena fatua), etc.

Perennial narrow leaved (grass) weeds are represented by the lowest number of species. The most commonly occurring one is couch grass (Agropyron repens), while rough-stalked meadow-grass (Poa trivialis) and Bermuda grass (Cynodon dactylon) occur somewhat less often, along with some less common species.

From the group of annual broad-leaved hoeing crop weeds, the most important representatives are lamb’s quarters (Chenopodium album), many-seed goosefoot (Chenopodium polyspermum), velvetleaf (Abutilon theophrasti) (Figure 4.45), common ragweed or annual ragweed (Ambrosia artemisiifolia) (Figures 4:50 and 4:51), amaranth (Amaranthus), spotted lady's thumb (Polygonum persicaria), pale
persicaria (*Polygonum lapathifolium*), black-bindweed (*Polygonum convolvulus*), gallant soldier (*Galinsoga parviflora*), Jimson weed (*Datura stramonium*), common cocklebur (*Xanthium strumarium*), European black nightshade (*Solanum nigrum*), etc.

Perennial broad-leaved weeds are represented by a smaller number of species than perennial weeds. The most common are field bindweed (*Convolvulus arvensis*), larger bindweed (*Calystegia sepium*) and creeping thistle (*Cirsium arvense*), while comfrey (*Symphytum officinale*), curly dock or yellow dock (*Rumex crispus*), broad-leaved dock (*Rumex obtusifolius*) occur less often, along with some other less common species.

The most common narrow leaved (grass) species in broadcast (hoeing) cultures are cockspur (*Echinochloa crus-galli*), hairy crabgrass (*Digitaria sanguinalis*), green foxtail (*Setaria viridis*), bristly foxtail (*Setaria verticillata*), yellow foxtail (*Setaria pumila*), proso millet (*Panicum miliaceum*), witchgrass (*Panicum capillare*), fall panicgrass (*Panicum dichotomiflorum*). Other species are less represented.

The lowest number of economically important hoeing crop weed species belongs to the group of perennial narrow leaved (grass) weeds, among which the most common ones are Johnson grass (*Sorghum halepense*), couch grass (*Agropyron repens*) and Bermuda grass (*Cynodon dactylon*). Although they are underrepresented in their number of species, they pose a significant problem in farming.

**Weed flora of perennial crops** depends largely on the method of cultivation, agro-technical measures implemented in the plantation and the season. In perennial crops, the division of weeds by seasonal emergence dynamics is important.

With regard to damage, in perennial crops, indirect damage is more important than direct (with the exception of young plantations). Weeds of higher habitus hinder quality application of fungicides and insecticides, they host pathogens and pests, create a favourable microclimate for a stronger occurrence of diseases, interfere with harvesting, etc.

Differences from plantation to plantation regarding the manner of farming (cultivation form, row spacing, spacing in the row, etc.) and soil maintenance, which also includes weed control, are very significant, which is reflected on the weed fauna. Weeds may be controlled by tillage, cover cropping of soil surface, mowing and leaving mulch in the plantation, as well as by the application of herbicides. Each of the aforementioned measures can be implemented in different manners, and combinations of different measures are also very common (e.g. cover cropping and mowing between the rows, soil tillage within the row, etc.), which has a direct impact on the weed flora. Depending on the implemented measures, their level and intensity, the weed flora of perennial plantations is divided into the weed flora of intensive plantations and the weed flora of extensive plantations. In intensive plantations, most of the previously mentioned species can be noticed during the year, as well as some species atypical for the agricultural crops. In extensive plantations, the ratio changes in favour of species atypical for agricultural crops (ruderal weeds).

With regard to the seasonal dynamics of emergence and development, weeds can be classified in the winter-spring (winter), spring-summer and late summer (autumn) weeds.

If we talk about intensive plantations, winter-spring (winter) weeds include chickweed (*Stellaria media*), birdeye speedwell (*Veronica persica*), ivy-leaved speedwell (*Veronica hederifolia*), red deadnettle (*Lamium purpureum*), henbit dead-nettle (*Lamium amplexicaule*), shepherd’s purse (*Capsella bursa-pastoris*), annual meadow grass (*Poa annua*), field mustard (*Sinapis arvensis*), creeping
cinquefoil (*Potentilla reptans*), creeping yellowcress (*Rorippa sylvestris*) etc. Given that the aforementioned weed species develop from fall to spring, therefore, during the winter dormancy of plantations, they do not harm them. At the same time, they cover the soil, which prevents erosion. Therefore, it is not advisable to suppress them.

The group of **spring-summer weeds** of intensive plantations includes many economically important species, which are important competitors, therefore, it is necessary to suppress them in a timely manner. The same species also occur in late summer and early autumn. The most frequently occurring ones are lamb’s quarters (*Chenopodium album*), many-seed goosefoot (*Chenopodium polyspermum*), common ragweed (*Ambrosia artemisiifolia*), red-root amaranth (*Amaranthus retroflexus*), knotweed (*Polygonum* spp.), common purslane (*Portulaca oleracea*), annual nettle (*Urtica urens*), annual fleabane (*Erigeron annuus*), horseweed (*Conyza canadensis*), gallant soldier (*Galinsoga parviflora*), field bindweed (*Convolvulus arvensis*), common nettle (*Urtica dioica*), larger bindweed (*Calystegia sepium*), field horsetail (*Equisetum arvense*), common dandelion (*Taraxacum officinale*), creeping thistle (*Cirsium arvense*), common comfrey (*Symphytum officinale*), sorrels (*Rumex* spp.), cockspur (*Echinochloa crus-galli*), bristle grasses (*Setaria* spp.), hairy crabgrass (*Digitaria sanguinalis*), Johnson grass (*Sorghum halepense*), couch grass (*Agropyron repens*), Bermuda grass (*Cynodon dactylon*). Perennial weeds such as thistle, horsetail, field bindweed and larger bindweed, comfrey, large nettle, sorrels, Johnson grass, couch grass, bermuda grass are particularly harmful. All of the aforementioned weeds can be, as previously mentioned, suppressed mechanically, which is in compliance with the sustainable use of pesticides and the National Action Plan to achieve the sustainable use of pesticides. All non-chemical measures shall have priority in suppression. Frequent mowing shall suppress annual and exhaust perennial weeds, which shall result in a decline of underground organs, therefore, the weeds in perennial crops can be successfully suppressed without the use of chemicals means.

**Weeds of non-agricultural areas** or **weeds in the broad sense** are different from the typical agricultural weeds – crop companions. In non-agricultural areas, perennial, often woody weeds are of greater significance. The most hazardous are foreign (allochthonous) species that have become invasive after input (introduction), and which expand quickly and aggressively in the new habitat at the expense of the species whose presence is the result of natural processes only (indigenous or native species). Due to extreme aggressiveness, **invasive foreign weed species** cause significant damage. They change the environment, damage the ecosystem stability, damage agricultural, forest and aquatic plant stands, irreversibly affect the composition of natural habitats and cause social and economical damage to agriculture, forestry, tourism, animal husbandry, health care, etc. Invasive alien weed species have been globally designated as the **second greatest threat to biodiversity** and they have been the subject of intensive study worldwide.

**Figures 4.46 and 4.47:** Large areas covered with invasive foreign weed species - tree of heaven (*Ailanthus altissima*) and desert false indigo (*Amorpha fruticosa*) (photo: M. Novak and N. Novak)
The most widespread invasive foreign species in non-agricultural areas of Croatia are tree of heaven (*Ailanthus altissima*) (Figure 4.46), desert false indigo (*Amorpha fruticosa*) (Figure 4.47), tall goldenrod and Canada golden-rod (*Solidago gigantea* and *Solidago canadensis*) (Figure 4.48), Japanese knotweed (*Reynoutria japonica*) (Figure 4.49), black locust (*Robinia pseudoacacia*), annual fleabane (*Erigeron annuus*) and others.

**Figures 4.48 and 4.49:** Large areas covered with invasive foreign weed species - tall goldenrod (*Solidago gigantea*) and Japanese knotweed (*Reynoutria japonica*) (photo: M. Novak and N. Novak)

The invasive alien weed species the general public is most familiar with is common ragweed (*Ambrosia artemisiifolia*). It expands over agricultural areas, most often as a hoeing crops weed (Figure 4.51) both on stubbles (Figure 4.50) and on non-agricultural areas. The stubbles in Croatia are real "ragweed nurseries" because farmers fail to pay enough attention to the plots after harvest. The recommendation is to suppress the weed on stubbles mechanically before their insemination.

**Figures 4.50 and 4.51:** Common ragweed (*Ambrosia artemisiifolia*) on a stubble and among sunflowers (photo: N. Novak)

Ragweed is a global problem since every eighth inhabitant of the planet Earth is allergic to the pollen of this plant. In Croatia, one in four of the inhabitants in continental parts suffers from allergies to ragweed pollen, whose flowering starts in late July and reaches its peak in September. The cost of treating such a high number of people are enormous. In order to get a true picture of the costs incurred by this species, it is necessary to add the cost of suppression as well, which is often not sufficiently successful, as it is conducted in an unprofessional manner and at a wrong time. Many people suffering from allergies are temporarily incapable of working during ragweed flowering, despite taking medication, which presents an additional damage caused by this species.

Along with Hungary and certain other countries, Croatia has been designated as one of the most vulnerable countries in Europe, in which ragweed occupies vast areas. The problem would be solved much more efficiently if one part of the money spent on medication to relieve symptoms of allergy
would be directed towards monitoring and professional suppression of this species. Pursuant to the *Order on Measures for Compulsory Removal of Ragweed - Ambrosia artemisiifolia L.* in Croatia, similar as in many countries, the suppression of ragweed is the responsibility of the owners and users of gardens, arable land, meadows, forests, hunting grounds, etc.
4.3.3 Weed properties

Weeds are an excellent example of a successful fight for survival. They have developed a number of adjustments and features and it is impossible to enumerate them all. If we talk about the typical agricultural weeds (weeds in the narrow sense), all of them had to adapt to agro-technology and the lifecycle of cultivated plant species, which they accompany in order to be able to survive on arable land. Natural selection and survival of the fittest is a continuous process for uncultivated species. **Wide distribution** (ubiquists), which generates a **high genetic variability** is the main condition for successful adaptation to habitat conditions and other challenges of the environment (e.g. to the impact of farmers, i.e. to agro-technology). Weeds are able to sprout and grow in **different pedo-climatic conditions**, and the speed, timing and methods of growth take place in the manner, which is the most favourable for the species. Due to their biological strength (vigour), the weeds are **more tolerant of adverse abiotic factors** (drought, humidity, heat, cold...) than cultivated species. They are **more resistant to diseases and pests**. Many of them **possess special organs, which protect them** against destruction (sharp hairs, spines, etc.). Most weed species are **strong competitors**, and many species **secrete chemical compounds**, which prevent or delay the development of plants in their environment. Many weed species can shorten the vegetation period, i.e. they can complete development (**fast flowering and fruiting**) under unfavourable conditions in a very short period of time, therefore little plants of subsequently sprouted summer weeds (i.e. lamb’s quarters, ragweed, common amaranth...) can often be seen flowering and fruiting in the late summer and autumn, while being well below the average height of its population. Most of the weed species are capable of high seed **production (tens or even hundreds of thousands per plant)**. Some species (e.g. chickweed) are capable of **fruiting several times** during the year. The weed seeds possess the ability of **long-term germination retention** (usually several decades, even longer), which is the result of dormancy, i.e. natural feature of the seed that allows its dormancy until more favourable conditions for germination are achieved. Due to their structure and composition, the seeds of many weed species are **resistant to humidity and temperature fluctuations**. Soil tillage often improves germination conditions, but can also damage the weed seeds. Therefore, the number of viable seeds is reduced with the number of soil tillage. Thus, the longevity of weed seeds is generally higher in non-cultivated than in cultivated habitats.

It often happens with weeds that on the same (parent) plant, there are seeds of different standstill periods, one part germinates very quickly (the same growing season), the other within a few years, while others remain in the soil for a long time. This adjustment ensures the survival of the species in the event of an extremely unfavourable period, as well as benefits for one part of the population in the reverse case. In the event of favourable conditions for growth and development, the seeds of some weed species are **capable of germinating in the milk stage**. In addition to the aforementioned, they are **adjusted** in shape and weight to **different manners of spreading** which can take place with their own forces, but also via different agents (wind, water, animals, man...). Each species specializes in at least one manner of spreading.

In addition to seeds, many species **propagate vegetatively**, i.e. via bulbs, tubers, rhizomes, root buds, stems and similar. Some species may also propagate by means of aerial stems, which root up in contact with the ground and produce a new plant in the event of separation from the mother plant. Underground weed organs are rich in nutrient reserves and can resist stress more easily than surface weed organs. They penetrate deep into the soil and are breakable, therefore, perennial weeds are not easy to eradicate.

Many weed species are able to develop **resistance to herbicides**. A separate chapter in this manual is dedicated to the problem of harmful organism resistance, including weeds.

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5 ABOUT PLANT PROTECTION PRODUCTS

5.1 What are plant protection products?

Plant protection products are often identified with pesticides, but it shall be noted that the term "pesticides" includes a much larger number of substances, which are used not only in agriculture but also in other areas, such as public health, sanitation, veterinary medicine for combating pests on animals, etc.

Pursuant to the Act on Sustainable Use of Pesticides, the term is defined as:

a) a plant protection product as defined in Regulation (EC) No. 1107/2009 of the European Parliament and of the Council of 21 October 2009 concerning the placing of plant protection products on the market,


The definitions in the aforementioned Regulations read as follows:

**Plant protection products** are preparations in the form in which they are delivered to the user, consisting of or containing active substances and additional non-pesticide substances (protective substance (safener), synergist, carrier, stabiliser, an anticoagulant, athezit, disperzit, etc.) and which are intended for one of the following applications:

a. protecting plants or plant products against all harmful organisms or preventing the activity of such organisms, unless hygiene objectives are considered the main purpose of these products, rather than protecting plants or plant products;
b. affecting the plant life processes, such as substances which affect the growth, but in a different manner than nutrients;
c. preserving plant products if such substances or products are not subject to special Community provisions on preservatives;
d. destroying the undesirable plants or parts of plants, with the exception of algae if the products are not applied on soil or water with the purpose of plant protection;
e. preventing or suppressing undesirable plant growth, with the exception of algae if the products are not applied on soil or water with the purpose of plant protection;

**Biocidal products** are the following:

a. substances and mixtures, prepared in the form in which they are delivered to the user, consisting of one or more active substances, or containing or producing one or more active substances, and which are intended for destruction, diversion, rendering harmless, prevention of activities or control of any adverse organism by any means other than through physical or mechanical activity only,
b. substances and mixtures, generated from substances and mixtures which are not included in the first indent, and which are intended for destruction, diversion, rendering harmless, prevention of activities or control of any adverse organism by any means other than through physical or mechanical activity only.

The treated product that has a primary biocidal function is considered a biocidal product.

In accordance with the aforementioned, those can be plant protection products, preparations intended for agriculture and certain non-agricultural areas and biocides, products intended for the
control of organisms, which are harmful to human or animal health, and for the control of organisms, which cause damage to natural or manufactured materials.

Any plant protection product that is placed on the market in Croatia shall be registered or shall have the appropriate license from the Ministry of Agriculture. They shall be placed exclusively in the original packaging, marked and labelled with the prescribed information in the Croatian language. The trade name of the plant protection product is protected by law and recognisable for the user. Acronyms and numbers that follow the trade name usually indicate the type of formulation and the amount of active substance in the plant protection product. Two examples are listed below:

<table>
<thead>
<tr>
<th>Trade Name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>“FungicidSC 500”</td>
<td>The formulation is in the form of a concentrated suspension, and contains 500 g of the active substance per one litre of a plant protection product.</td>
</tr>
<tr>
<td>“Insecticide 10 G”</td>
<td>The formulation is in granular form, and contains 10% g of the active substance.</td>
</tr>
</tbody>
</table>

### 5.2 Purpose of using plant protection products

For the successful prevention or reduction of damage caused by harmful organisms, it is necessary to identify and determine the harmful organism species, and then, on the basis of knowledge of its biological, environmental and other characteristics, select the most appropriate plant protection measure.

Since the second half of the 20th century, the use of chemical plant protection products has become the most important plant protection measure against harmful organisms. Numerous toxicological, ecotoxicological, environmental and economic reasons indicate that it was necessary to rationalise the application of chemical plant protection measures. Many scientific studies have focused on finding their replacement by using non-chemical measures. By applying the principles of integrated pest management, the application of chemical plant protection products has been reduced to the strictly necessary level, thus reducing the risk to humans, beneficial organisms and the environment.

Plant protection products shall be used only when that is necessary and/or in accordance with thresholds, if there are any. The decision on the application of plant protection products shall be based on information collected in the field through the regular examination of crops and/or information from the forecasting service in accordance with the principles of good agricultural and environmental practice.

Each selection of plant protection products and their application shall be performed according to the instructions obtained during the purchase of a plant protection product, in accordance with the integrated pest management principles.

When using a plant protection product, it is necessary to:

- use a plant protection product in accordance with the label, respecting the amount, time and method of application as well as any restrictions specified on the label;
- apply integrated pest management measures against harmful organisms, in order to reduce the use of plant protection products;
• apply and handle the plant protection products in accordance with the regulations in the field of plant protection products;
• respect the principles of good agricultural practices and environmental protection;
• apply plant protection products in accordance with integrated protection in order to maintain the population of target pests below the economic threshold, along with the reduction of the negative impact on the species, which do not belong to the target group (e.g. local application of the product where the harmful organisms population exceeded the economic harmfulness threshold, and not over the entire surface);
• keep the plant protection products in the prescribed manner (in a special room, original packaging, away from food and feed...);
• dispose of the plant protection product residues and its packaging in an appropriate manner in accordance with the data stated on the product label;
• keep records of the use.

5.3 Composition of plant protection products

Plant protection products are a mixture of active and additional substances in certain concentrations, which form a formulated preparation.

The **active substance** is the basic ingredient of a plant protection product that has a general or specific effect on harmful organisms or on plants, plant parts or plant products. These are most often chemical compounds, micro-organisms and viruses, plant extracts and the like. The formulation of plant protection products may contain other additional substances whose purpose is to prevent or reduce phytotoxic effects at certain plants, e.g. a protective substance (safener) or to enhance the effect of active substance (so called synergists). Only plant protection products based on active substances listed in the Appendix to Implementing Regulation (EU) No. 540/2011 implementing Regulation (EC) No. 1107/2009 concerning the list of approved active substances may be placed on the market.

The active substance has a chemical name under the internationally agreed chemical nomenclature of the International Union of Pure and Applied Chemistry (IUPAC), which is generally very complex and not applicable for wider use. Due to the complexity of its chemical name, the active substance also receives a common (derived) name to be approved by the International Organisation for Standardisation (ISO), which has been accepted in scientific literature.

Examples of a common and chemical name:

| Common name: glyphosate       |
| IUPAC name: N- (phosphonomethyl) glycine |

| Common name: lambda cihalothrin |
| IUPAC name: *Isomer mixture in a ratio of 1:1: (S)-α-cyano-3-phenoxybenzyl (Z)-(1R,3R)-3-(2-chloro-3,3,3-trifluoropropenyl) 2,2-dimethylcyclopropanecarboxylate and (R)-α-cyano-3-phenoxybenzyl (Z)-(15,35)-3-(2-chloro-3,3,3-trifluoropropenyl) 2,2-dimethylcyclopropanecarboxylate* |

The label of each plant protection product states the chemical and common name of each active substance, which it contains. The amount of active substance in the plant protection product in the current formulations is expressed in grams of active substance per one litre of product (g/L), and for solid formulations, in grams of the active substance per one kilogram of a plant protection product (g/kg) or sometimes in percentages. Pure chemically active substances are generally not suitable for
direct use as a plant protection product. An exception are plant protection products in which the active substance without additives is used, such as those based on copper sulphate (blue vitriol) and certain formulations based on sulphur.

Additional substance in a plant protection product is any substance, other than the active substance, which the manufacturer has added to the formulation of a plant protection product. Additives in a plant protection product are also known under the name co-formulants. The type and amount of co-formulants in the formulation is a trade secret and it is generally not stated on the label or in the publicly available literature. The exceptions are those co-formulants, which possess certain toxicological properties due to which they shall be listed on the plant protection products label pursuant to regulations on chemicals. In this case, their exact concentration in the plant protection product is not stated, but the concentration is expressed with a value range pursuant to the regulations on chemicals. Some co-formulants are also available on the market as additional (auxiliary) plant protection products, which do not contain active substances. These are preparations, which are added during the preparation of a plant protection product as a spray in order to improve their effect (the so-called wetting agents or adjuvants).

5.4 Formulation (form) of plant protection products

Plant protection products are placed on the market as specially formulated preparations.

Formulated preparations shall provide the user with the following:

- **simple use and handling**, it is usually diluted before the application or it is used undiluted;
- **lesser exposure of the operator to the active substance during use**, which depends on the type of formulation, provided that the plant protection product is appropriately used and applied;
- **efficiency of the active substance**, since, for example, many of the active substances are not capable of passing the biological barriers (e.g. cuticle) sufficiently or remaining on the leaf without the additional substances;
- **even distribution of the active substance during the application**, which is important for those plant protection products which are used in very small amounts of active substances per hectare;
- **stability of a plant protection product** for a certain period (during storage).

The need for diverse methods of harmful organism suppression and safe use of plant protection products is an important factor for the development and use of different formulations. To this date, more than 90 types of formulations for plant protection products, which are used in plant protection, public health, municipal hygiene and other areas, have been the internationally recognised. In the Republic of Croatia, there are more than 30 different types of plant protection product formulations on the market, and the most common ones are emulsifiable concentrates (EC), suspension concentrates (SC), wettable powders (WP), soluble concentrates (SL) and water dispersible granules (WG). Approximately 80% of the registered plant protection products in Croatia (Figure 5.1) are among the five aforementioned formulations.
The plant protection product is called by its trade name given by the manufacturer and does not need to refer to the active substance. Different factories produce different plant protection products under different trade names, therefore the number of registered plant protection products is generally higher than the number of permitted active substances. That is because the plant protection products may be placed on the market:

- on the basis of the same concentration of the same active substance from the same manufacturer. due to commercial and other reasons, several plant protection products may be placed on the market on the basis of the same active substances of the same manufacturer with the same concentration of the active substance, under different trade names;
- on the basis of the same concentration of the same active substance from different manufacturers There may be several preparations from different manufacturers based on the same active substance on the market. More than 15 plant protection products from different manufacturers based on glyphosate with a concentration of 480 g/L of the active substance in the plant protection product are currently registered in Croatia;
- on the basis of the same active substance with different types of formulations. Active substances, one type of formulation is often not suitable for all required/expected applications. For example, some insecticides may be applied foliar as a soluble concentrate (SL) and in the form of a flow able concentrate for seed treatment (FS). Plant protection products intended for amateur users can often be preparations of lower concentration of active substances intended for application without dilution. The availability of different formulations based on the same active ingredient allows users the selection of a formulation with a higher and a lower risk level for the operator. For example, a plant protection product may be available on the market in the form of wettable powder (WP) and water dispersible granules (WG). When using a wettable powder (WP), there is a greater exposure of the operator due to dust inhalation. The selection of a plant protection product with a lower risk level, if available, is recommended;
- on the basis of the same active substance in a plant protection product. In this case, there are usually differences in the application method or the amount of application to a particular harmful organism between the products based on the same active substance but with different concentrations in a plant protection product. For example, products based on captan with a concentration of 110 g/kg, 500 g/kg, 600 g/kg and 800 g/kg of the active substance in the plant protection product are available on the market;
• in the form of combined plant protection products, comprised of two or more active substances with the aim of extending the spectrum of activity. For example, plant protection products based only on captan and those, which have another active substance in addition to captan, are available on the market: trifloxystrobin or penconazole.

Data on all registered plant protection products in the Republic of Croatia are publicly available and searchable via the search engine of the Phytosanitary Information System (http://fis.mps.hr/trazilicaszb/) on the home page of the Ministry of Agriculture (http://www.mps.hr/). The list of registered plant protection products is published several times per year on the website of the Ministry of Agriculture. In our professional literature on phytomedicine, a rule has been introduced that the names of active substances are written in lowercase letters, and that the names of plant protection products are capitalised.

5.5 Formulation types of plant protection products

The formulations of plant protection products are divided according to the state of matter and the method of application.

According to the physical state, we differentiate liquid and solid formulations of plant protection products. Examples of liquid formulations are emulsifiable concentrates (EC), suspension concentrates (SC), soluble concentrate (SL), and the examples of solid formulations are wettable powders (WP) and water dispersible granules (WG) (Figure 5.2).

![Figure 5.2: Different types of solid and liquid formulations: a) wettable powder (WP); b) water dispersible granules (WG); c) granules for direct application (G); d) emulsifiable concentrate (EC); e) suspension concentrates (SC); f) soluble concentrate (SL) (photo: M. Pelajić)
According to the method of application, there are different formulations of plant protection products, which are applied, in liquid form (spraying, dispersing, watering) and in solid form (spraying, dispensing the granules).

Most of the plant protection products need to be diluted with water before the application. Each plant protection product that is diluted with water and prepared for application is called a spray mixture. When mixing with water, and depending on the type of formulation, different forms of liquid are obtained (emulsion, solution or suspension). Various forms of liquid are obtained by mixing with water (Table 5.1)

Table 5.1: Names of liquids regarding the type of formulation mixed with water (prepared by: D. Hamel)

<table>
<thead>
<tr>
<th>FORMULATION</th>
<th>ABBREVIATION</th>
<th>WITH WATER IT RESULTS IN</th>
</tr>
</thead>
<tbody>
<tr>
<td>emulsifiable concentrate</td>
<td>EC</td>
<td>An emulsion</td>
</tr>
<tr>
<td>soluble concentrate</td>
<td>SL</td>
<td>A solution</td>
</tr>
<tr>
<td>suspension concentrate</td>
<td>SC FL or KS</td>
<td>A suspension</td>
</tr>
<tr>
<td>wettable powder</td>
<td>WP</td>
<td>A suspension</td>
</tr>
<tr>
<td>water dispersible granules</td>
<td>SG WG or DF</td>
<td>A suspension</td>
</tr>
<tr>
<td>Capsulated suspension</td>
<td>CS or MC</td>
<td>A suspension</td>
</tr>
</tbody>
</table>

However, there are also plant protection products, which are used without dilution. The Table 5.2 lists the various formulations of plant protection products, and the formulations used without dilution are separately stated. The formulations of pellets (P) or granules (G) which are dispersed over the soil surface or deposited in rows or along the plants are applied less frequently.

Table 5.2: Overview of labels and names of the most represented plant protection product formulations (prepared by: G. Peček)

<table>
<thead>
<tr>
<th>IDENTIFIER</th>
<th>FORMULATION NAME</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid formulations</td>
<td></td>
</tr>
<tr>
<td>EC</td>
<td>emulsifiable concentrate</td>
</tr>
<tr>
<td>SC</td>
<td>suspension concentrate</td>
</tr>
<tr>
<td>SL</td>
<td>water-soluble concentrate</td>
</tr>
<tr>
<td>EW</td>
<td>liquid concentrated emulsion in water</td>
</tr>
<tr>
<td>SE</td>
<td>suspo-emulsion</td>
</tr>
<tr>
<td>OD</td>
<td>oil-based suspension concentrate</td>
</tr>
<tr>
<td>Solid formulations</td>
<td></td>
</tr>
<tr>
<td>WP</td>
<td>wettable powder for suspension</td>
</tr>
<tr>
<td>WG-DF-WDG</td>
<td>dispersive granules or microgranules - suspension concentrate</td>
</tr>
<tr>
<td>SG</td>
<td>water-soluble granules</td>
</tr>
<tr>
<td>SP</td>
<td>water-soluble powder</td>
</tr>
<tr>
<td>CSR</td>
<td>Capsulated suspension</td>
</tr>
<tr>
<td>K</td>
<td>crystals</td>
</tr>
<tr>
<td>Formulations for seed treatment</td>
<td></td>
</tr>
<tr>
<td>FS</td>
<td>suspension concentrate for seed treatment</td>
</tr>
<tr>
<td>ES</td>
<td>emulsion for seed treatment</td>
</tr>
<tr>
<td>WS</td>
<td>wettable powder for a suspension for seed treatment</td>
</tr>
<tr>
<td>Code</td>
<td>Description</td>
</tr>
<tr>
<td>------</td>
<td>--------------------------------------</td>
</tr>
<tr>
<td>LS</td>
<td>solution for seed treatment</td>
</tr>
<tr>
<td>DS</td>
<td>powder for seed</td>
</tr>
<tr>
<td></td>
<td><strong>Formulations for administration without dilution</strong></td>
</tr>
<tr>
<td>G</td>
<td>Granules</td>
</tr>
<tr>
<td>P</td>
<td>pellets</td>
</tr>
<tr>
<td>ULV</td>
<td>homogeneous liquid for ULV application equipment</td>
</tr>
<tr>
<td></td>
<td><strong>Other types of formulations</strong></td>
</tr>
<tr>
<td>Pa</td>
<td>paste</td>
</tr>
<tr>
<td>Tpa</td>
<td>liquid pastes</td>
</tr>
<tr>
<td>M</td>
<td>baits</td>
</tr>
<tr>
<td>KM</td>
<td>concentrate for baits</td>
</tr>
<tr>
<td>Št</td>
<td>sticks</td>
</tr>
</tbody>
</table>
5.6 Plant protection products effect

According to their effect, plant protection products are divided according to their effect on biochemical natural processes in the target harmful organism or according to their behaviour on the treated plant. Active substances belonging to the same chemical group generally have the same biochemical activity (Table 5.3).

Table 5.3: Examples of the active substances division according to their biochemical effect of natural processes (prepared by: G. Peček)

<table>
<thead>
<tr>
<th>CHEMICAL GROUP</th>
<th>EFFECT</th>
<th>ACTIVE SUBSTANCES</th>
</tr>
</thead>
<tbody>
<tr>
<td>organophosphorus insecticides</td>
<td>Acetylcholinesterase inhibition</td>
<td>chlorpyrifos, dimethoate</td>
</tr>
<tr>
<td>sulfonilurea herbicides</td>
<td>inhibition of the amino acids synthesis</td>
<td>nicosulfuron, rimsulfuron</td>
</tr>
<tr>
<td>aryloxyphenoxypropionates</td>
<td>inhibition of lipid synthesis</td>
<td>quizalofop, fluazifop</td>
</tr>
<tr>
<td>triazole fungicides</td>
<td>inhibition of sterol synthesis</td>
<td>tebuconazole, propiconazole</td>
</tr>
</tbody>
</table>

After their application, plant protection products may behave nonsystematically or systematically on the treated plant.

**Non-systemic (contact) plant protection products remain in the form of a coating on the surface of the treated plant parts after the application and plant does not absorb them.**

**After its application, the plant absorbs the systemic plant protection products, conducts them through its conductive system to all plant organs, and stores them in these organs in the effective amounts over a certain period.**

According to their manner of movement in the plant, systemics are divided into several subgroups:

a) systemics with limited mobility (meso-systemics - locally systemic), after the application, the active substance enters the plant tissue and spreads only over the plant organ to which it has been applied, and does not transfer to the new growth. Such movement is also called translaminar movement;

b) xylem systemic (acropetal systemic); following the application, the active substance is translocated into the tissue to the xylem, and then it moves through the trachea (fast transport) or tracheid (slower transport) along the upward flows (acropetally);

c) phloem sytemic (basipetal systemic); following the application, the active substance is translocated into the tissue to the phloem (sieve tube cells and assistant cells), and then moves along the downward flows (basipetally);

d) real systemic (ambisystemic), after the application, the active substance moves in both directions along the xylem (upward flows) and phloem (downward flow) flows.

A plant protection product has a certain spectrum of effects on harmful organisms, which it suppresses effectively. In addition to the full effectiveness of the permitted target organism, many plant protection products can also have additional or side effects on other harmful organisms (e.g. some fungicides partially reduce the number of mites while others may enhance their occurrence...), but also on the useful organisms.
Any plant protection product shall not have a generalized effect, but selectively, that is, suppressed only by certain harmful organisms. It is essential for an insecticide to affect only on the target group of harmful insects, and not the beneficial insects as well. An example of selective insecticides, which, unlike the universal one, suppresses only one group of pests, is an active substance - pirimicarb - that affects only aphids, but not the natural enemies of insects. Herbicides shall only affect weeds and not the cultivated plants. Examples of selective herbicides are: dicamba, which shows a selective effect on corn in which it shall suppress annual and perennial broad-leaved weeds; fluazifop-p-butyl is a highly-selective herbicide in all broad-leaved crops (sugar beet, sunflower) in which it suppresses annual and perennial narrow leaved weeds.

5.7 Division of plant protection products

Plant protection products are divided in different ways. According to the origin of a plant protection product, they are divided into chemical and biological ones, while the most common division is according to the type of harmful organism, which is suppressed.

1. ZOOCIDES – products for suppressing or repelling the animals, they are divided into several groups:
   - insecticides – products for insects suppression,
   - acaricides – products for mites suppression,
   - nematocides – products for nematodes suppression,
   - limacides – products for snails suppression,
   - rodenticides – products for rodents suppression,
   - corvifuges – products for repelling the birds from seeds.

2. FUNGICIDES – products for suppression of fungi and pseudofungi and some bacteria pathogens

3. HERBICIDES – products for weed suppression

4. Other products - plant growth regulators and auxiliary products

5.7.1 Zoocides

5.7.1.1 Insecticides

insecticides are products for insects suppression. According to their effect, we distinguish between non-systemic and systemic insecticides.

Non-systemic insecticides affect insect when in contact with them, and some affect them gastrointestinally only after they have been introduced to the insect organism via food. Few insecticides affect deeply with their fumes - fumigative effect.

Systemic insecticides are intended primarily for the suppression of insects, which suck plant juices, but they also effectively suppress some insects, which feed by biting.

Systemics are applied foliarly and through soil treatment, therefore they can also protect the surface parts of plants from pests attack while entering the plant juices. Some systemic insecticides also have a contact effect, and thus suppress several species of pests.

According to the application method, insecticides are divided into:
1. plant treatment products,
2. soil and seed treatment products,
3. products for treatment of agricultural products in warehouses,
4. fumigation products,
5. wood protection products.

According to their origin we distinguish between the following insecticides:

1. chemical: organo-phosphorous, carbamate, synthetic pyrethroids, neonicotinoids, etc.,
2. biotechnical: insect growth regulators,
3. biological insecticides: microbial insecticides, naturalites and herbal insecticides.

According to their mechanism of action, most insecticides are divided into 4 groups:

1. nervous system insecticides (they affect one of the processes in the transmission of nerve impulses);
2. growth and development inhibitors (they affect the individual stages in the transformation);
3. microbial insecticides (they are composed of spores and toxins of bacteria and affect the membranes of the digestive system and cause various insects diseases. Acaricides with this mechanism of action are not known);
4. respiratory system insecticides (they are active during the cellular respiration process and disrupt the energy metabolism).

Action committee dealing with insects and mites resistance (Insecticide Resistance Action Committee - IRAC) (http://www.irac-online.org/) divides all insecticides and acaricides into 28 groups according to their mechanism of action (Table 5.4). Groups 26 and 27 are still available and free of active substances.

Knowledge of the mechanisms of action during the suppression of certain species of insects and mites by using and alternating between insecticides and acaricides which have effect through different mechanisms of action is extremely important for the prevention/slowing down of the resistance development.

<table>
<thead>
<tr>
<th>IRAC Group</th>
<th>mechanism of action</th>
<th>chemical subgroup or isolated active substance</th>
</tr>
</thead>
</table>
| 1          | inhibitors of acetylcholinesterase (AChE) | 1A carbamates  
1B organophosphorus insecticides |
| 2          | antagonists of chloride channels activated by gamma-aminobutyric acid (GABA) | 2A chlorinated hydrocarbons of cyclodiene synthesis  
2B phenylpyrazoles |
| 3          | sodium channel modulators | 3A pyrethroids and pyrethrins  
3B DDT and methoxychlor |
| 4          | antagonists of the nicotinic acetylcholine receptor (nAChR) | 4A neonicotinoids  
4B nicotine  
4C sulfoxaflor |
| 5          | allosteric activators of the nicotinic acetylcholine receptor (nAChR) | spinosyns |
| 6          | chloride channel activators | avermectins, milbemectins |
| 7          | juvenile hormone mimics | 7A juvenile hormone analogues  
7B phenoxy carb  
7C pyriproxyfen |
| 8 | mixed non-specific inhibition in multiple sites of action ("multi-site") | 8A alkylhalides  
8B chloropicrin  
8C sulfuryl fluoride  
8D borax  
8E antimony potassium tartrate |
|---|---|---|
| 9 | selective Homoptera feeding blockers | 9B pymetrozine  
9C flonicamid |
| 10 | mite growth inhibitors | 10A clofentezine, hexythiazox, diflouidazin  
10B etoxazol |
| 11 | Microbial disruptors of insect midgut membrane | 11A Bacillus thuringiensis and insecticidal proteins they produced  
11B Bacillus sphaericus |
| 12 | inhibitors of mitochondrial ATP synthase | 12A diafenthiuron  
12B organotin miticides  
12C propargite  
12D tetradifon |
| 13 | uncoupling of oxidative phosphorylation via protone gradient disruption | chlorfenapyr, DNOC, sulfluramid |
| 14 | Nicotinic acetylcholine receptor (nAChR) | Nereistoxin analogues |
| 15 | Inhibitors of chitin biosynthesis, type 0 | Benzoylureas |
| 16 | Inhibitors of chitin biosynthesis, type 1 | buprofenzin |
| 17 | Moulting disruptors in Diptera | cyromazine |
| 18 | Ecdysone receptor agonists | diacylhydrazines |
| 19 | Octopamine receptor agonists | amitraz |
| 20 | Mitochondrial complex III electron transport disruptors | 20A Hydramethylnon  
20B acequinocyl  
20C Fluacrypyrim |
| 21 | Mitochondrial complex I electron transport disruptors | 21A METI acaricides and insecticides  
21B rotenone |
| 22 | Voltage-dependent sodium channel blockers | 22A Indoxacarb  
22B metaflumizone |
| 23 | inhibitors of acetyl CoA carboxylase | cyclic ketoenols, Tetronic and Tetramic acid derivatives |
| 24 | Mitochondrial complex IV electron transport inhibitors | 24A Phosphine  
24B cyanide |
| 25 | Mitochondrial complex II electron transport inhibitors | Beta-ketocitrile derivatives |
| 26 | - | - |
| 27 | - | - |
| 28 | Ryanodine receptor modulators | Diamides |
| | Compounds of unknown or uncertain mechanism of action | Azadirachtin  
benzoximate  
bifenazate  
bromopropylate  
chimonethionat  
Cryolite |
5.7.1.2 Acaricides

Acaricides are mite suppression products, and they affect summer eggs, larva, mite nymphs, and some of them affect adult mites. Some insecticides also affect mites (some organo-phosphorus, pyrethroids, avermectins, and fumigants, as well as and mineral oils), as well as some fungicides based on sulphur.

5.7.1.3 Nematocides

Nematocides are nematode suppression products. They are applied by injection into the soil, pouring over the soil, incorporation into the soil or soil fumigation, however, regardless of their formulation, they all act as fumigants in the soil. Most of them have a prescribed period, which needs to pass from the application until sowing or planting.

5.7.1.4 Limacides

Limacides are snail suppression products, they are used in the form of poisoned baits, which are dispersed over the soil next to the plant when rain is not expected.

5.7.1.5 Rodenticides

Rodenticides are rodent suppression products. The three main purposes of rodenticide application are: suppression of field rodents, suppression of household rodents in agricultural facilities and suppression of household rodents in municipal hygiene. Many of them are permitted for all three purposes, and some just for rodents in agriculture and municipal hygiene (deratisation). All these rodenticides are included into plant protection products with the exception of those allowed in municipal hygiene only, which are biocidal products.

5.7.1.6 Corvifuges

Corvifuges are bird repellents. Only one corvifuge or a product for repelling bird attacks on the sown seed based on active substance methiocarb is registered in Croatia.

5.7.2 Fungicides

Fungicides are organic, inorganic substances or living organisms used for fungi and pseudofungi suppression, regardless of their location on the plants, on and in the seed and on wood (for impregnation).

According to their chemical composition, fungicides are divided into inorganic and organic fungicides.

Inorganic fungicides are classified into the group of fungicides with the surface (contact) effect because they remain on the surface of plant organs and prevent infections after their application. There are several groups of organic fungicides, which act in the same manner and they are classified as fungicides with surface effect. The most important two groups of inorganic fungicides are copper-based products and sulphur-based products.

Fungicides with surface (contact) effect shall be applied preventively, i.e. before the occurrence of infection.
Within the group of organic fungicides, we distinguish between two sub-groups:

a) organic fungicides with surface effect or non-systemics (e.g., dithiocarbamates, phthalimides, ...),
b) systemic and limited systemic organic fungicides (for example, ergosterol biosynthesis inhibitors, phenylamides, carbamates, ethyl phosphonates, strobilurins, ...).

After the application of systemic fungicides, a certain percentage of their active substance remains on the surface and acts as a fungicide with surface effect, while the other part of their active substance from surface cells enters the plant and expands through the stem, over the leaf or enters the new grown leaves, depending on the active substance properties, and thus has an adverse effect on the parasites inside the plant organs. Due to these properties, some systemic fungicides do not have only a preventative effect, but also a curative effect, and in some cases also an eradicating effect (they halt the development of the parasite completely), which greatly depends on the properties of the active substance, pathogenic fungus, host, the incubation period or the time of application.

Systemic fungicides move along upward flows towards the top of the plants (acropetally), towards the root (basipetally) or in both directions. In the true sense of the word, the systemic shall move in both directions (ambisystemic), but such fungicides are not numerous. Fungicides, which are less mobile and move only within the plant organs to which they have been applied are called translaminar fungicides or limited movement fungicides.

Systemic fungicides shall be applied rationally, only when they provide a distinct advantage (during high pathogen pressure, rainy season or the need for remedial action) in comparison with the surface effect fungicides.

A separate group of fungicides are biofungicides. These are the preparations of biological origin. In the broad sense, biofungicides include preparations based on microorganisms (fungi, pseudofungi, bacteria), infectious particles and natural compounds of plants (essential oils, plant extracts). The only biofungicide registered in Croatia is a preparation based on the Trichoderma harzianum fungus spores.

Fungicides have different effects on basic life processes in fungi. Fungicide Resistance Action Committee (FRAC) has divided fungicide active substances according to their biochemical effect on pathogenic fungi. Table 5.5 lists FRAC markings for particular chemical subgroups and their mechanism of action on fungi life processes (www.frac.info). Knowledge of the mechanisms of action during the suppression of pathogens by using and alternating between the fungicides which have effect through different mechanisms of action is extremely important for the prevention/slowing down of the resistance development.
### Table 5.5. Mechanisms of action according to FRAC-in (prepared by: T. Rehak)

<table>
<thead>
<tr>
<th>FRAC Group</th>
<th>mechanism of action</th>
<th>chemical subgroup</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>inhibit the function of RNA polymerase and nucleic acid synthesis</td>
<td>A1 phenylamides</td>
</tr>
<tr>
<td></td>
<td>inhibit the biosynthesis of adenosine deaminase and the synthesis of nucleic acids</td>
<td>2 hydroxy pyrimidines</td>
</tr>
<tr>
<td>B</td>
<td>effect on β tubulin, the cell division (mitosis)</td>
<td>B1 benzimidazoles</td>
</tr>
<tr>
<td></td>
<td>bind to β tubulin and interfere with the creation of the cytoskeleton and cell division</td>
<td>B3 toluamides</td>
</tr>
<tr>
<td></td>
<td>effect on cell division (mitosis)</td>
<td>B5 pyridine methyl benzamide</td>
</tr>
<tr>
<td>C</td>
<td>inhibit cellular respiration</td>
<td>C2 pyridine carboxamides</td>
</tr>
<tr>
<td></td>
<td>block the electron transfer to cytochrome bc1, interfere with the formation of ATP</td>
<td>C3 strobilurins</td>
</tr>
<tr>
<td></td>
<td>inhibit mitochondrial respiration by blocking the electron transfer to cytochrome bc1</td>
<td>C3 oxazolidines, imidazolinones</td>
</tr>
<tr>
<td></td>
<td>inhibit the activity of Ubiquinol—cytochrome-c reductase on the inner membrane of mitochondria, blocking the electron transfer to cytochrome bc1</td>
<td>B4 cyano-imidazoles</td>
</tr>
<tr>
<td></td>
<td>interfere with the oxidative phosphorylation by blocking the formation of ATP</td>
<td>C5 nitrophenol esters and fluazinam</td>
</tr>
<tr>
<td>d</td>
<td>inhibit the biosynthesis of amino acids (methionines) and some proteins</td>
<td>D1 anilino pyrimidines</td>
</tr>
<tr>
<td>E</td>
<td>affect the signaling molecules in fungi, the mechanism of action is unknown</td>
<td>E1 quinolines</td>
</tr>
<tr>
<td></td>
<td>affect the histidine kinase, leading to disruptions in osmosis</td>
<td>E2 hydroxy pyrimidines and fludioxonil</td>
</tr>
<tr>
<td></td>
<td>inhibit the signal transfer using the histidine kinase, leading to disruptions in osmosis</td>
<td>E3 dicarboximides</td>
</tr>
<tr>
<td>F</td>
<td>affect the synthesis of lipids and the permeability of the cell membrane</td>
<td>F4 carbamates</td>
</tr>
<tr>
<td>G</td>
<td>inhibit the biosynthesis of demethylase in sterol biosynthesis</td>
<td>G1 triazoles and imidazoles</td>
</tr>
<tr>
<td></td>
<td>inhibit the function of the reductase and isomerase enzyme in sterol biosynthesis</td>
<td>G2 morpholines, spiroxamines</td>
</tr>
<tr>
<td></td>
<td>inhibiting the keto-reductase enzyme and thus affect the biosynthesis of sterol</td>
<td>G3 fenhexamides</td>
</tr>
<tr>
<td>H</td>
<td>inhibit the biosynthesis of cellulose in cell walls of pseudofungi (Oomycota)</td>
<td>H5 cinnamic acid amides, mandelamides, amides-carbamates</td>
</tr>
</tbody>
</table>
5.7.3 Herbicides

Herbicides are chemical compounds intended for suppressing and/or halting the growth of undesirable plant species, i.e. weeds.

When the herbicide comes into contact with the plant, its activity is affected by several factors acting alone and in interaction. After applying the spray, a number of very complex physiological and biochemical processes takes place in the plant. These processes include absorption, moving (translocation), change in the chemical structure of herbicide molecules and the herbicide effect on the plant metabolism. Pedoclimatic factors before, during and after treatment (soil type, humidity and temperature of soil and air, etc.) have a major role in the effect of herbicides.

Herbicides can be divided in several manners:

- according to selectivity,
- according to their ability to move through the plant tissue,
- according to the manner (place) of absorption,
- according to their mechanism of action
- according to their chemical identity,
- according to the time of application.

**Division according to selectivity**

- **Total** – they destroy all the plants existing at the time of application. They are applied on agricultural land in the period between sowing/planting of two cultures or on non-agricultural land (industrial plants, railways, roads, paths, etc.).
- **Selective** - depending on the spectrum of their effect, they suppress certain types of weed plants, while at the same time being selective to the cultivated plant species. Herbicide selectivity depends on a range of factors (humidity, temperature, culture development stage, manner of application, etc.) which may increase herbicide phytotoxicity, and reduce selectivity to the crop.

In this division, it is important to emphasise that, depending on the amount, each herbicide may act as a total herbicide.

**Division according to their ability to move through the plant tissue**

- **Contact** – they are active in direct contact with the surface parts of the plant. Such herbicides destroy only those parts of the plant with which they have come into contact. They are not translocated through the conductive system.
- **Systemic (translocation)** - after the contact with the plant (leaf, stem, root system), they are absorbed and translocated through the conductive system throughout the plant, causing its deterioration. Systemic herbicides suppress perennial weeds, which, in addition to via seed, also propagate vegetatively, and the goal is to reduce the potential of underground vegetative organs.

**According to the manner (place) of absorption**

- **residual (soil)** – applied before the weed emergence by spraying over the soil or by entering into the soil. In order for them to be moved into the weed seed germination zone, i.e. into the liquid phase of the soil (where the plant absorbs them through the root), precipitation is necessary. They have the ability of developing a herbicidal effect over a longer period, which is why they are called residual herbicides. In addition to precipitation, the soil type also affects the selective herbicidal effect. Therefore, in
addition to the attached instructions, dosage for light (sandy) and heavy soils (rich in clay and/or organic matter) is also indicated for this group of herbicides.

- **foliar** - plant absorbs them through the leaf. After the absorption, depending on herbicide, i.e. on the method and mechanism of action, the herbicide moves in a limited manner through a vegetable tissue in (contact herbicides) or it moves to the place of (molecular) activity through the phloem and/or xylem (translocation or systemic herbicides) as described in Chapter 5.6.

Each herbicide effects certain weed species, i.e., has its own **spectrum of effect**. Due to the extension of the spectrum of effect, the herbicide may be combined with more herbicides of different modes of action, e.g. residual + contact + translocation. Already combined herbicidal compositions based on two or more active ingredients can be found on the market or the operator can mix two or more products (so-called tank mix) on their own during the preparation of the spray mix. Certain rules explained in Chapter 6.2.2. shall be followed in the process of mixing.

**Division according to the mechanism of action**

After the contact with the plant, herbicides interfere with the normal functioning of physiological processes in the plant. According to the Herbicide Resistance Action Committee (HRAC), from the viewpoint of the influence on the physiological processes of the plants, herbicides are divided into 21 groups.

**Table 5.6.** Mechanisms of action according to HRAC (prepared by: M. Novak)

<table>
<thead>
<tr>
<th>HRAC* Group</th>
<th>Mechanism of action</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>inhibitors of acetyl CoA carboxylase</td>
</tr>
<tr>
<td>B</td>
<td>inhibitors of acetolactate synthase (ALS)</td>
</tr>
<tr>
<td>C1, C2 and C3</td>
<td>inhibitors of photosynthesis at photosystem I</td>
</tr>
<tr>
<td>d</td>
<td>inhibitors of photosynthesis at photosystem II</td>
</tr>
<tr>
<td>E</td>
<td>inhibitors of protoporphyrinogen oxidase</td>
</tr>
<tr>
<td>C1, C2 and C3</td>
<td>inhibitors of carotenoid synthesis</td>
</tr>
<tr>
<td>G</td>
<td>inhibitors of EPSP synthase</td>
</tr>
<tr>
<td>H</td>
<td>inhibitors of glutamine synthetase and inhibitors of DHP (dihydropteroate) synthase</td>
</tr>
<tr>
<td>and</td>
<td>inhibitors of cell division</td>
</tr>
<tr>
<td>C1, C2 and C3</td>
<td>inhibitors of cell wall synthesis</td>
</tr>
<tr>
<td>L</td>
<td>inhibitors of cell wall synthesis</td>
</tr>
<tr>
<td>M</td>
<td>uncoupling (membrane disruption)</td>
</tr>
<tr>
<td>N</td>
<td>inhibitors of lipid synthesis</td>
</tr>
<tr>
<td>on</td>
<td>growth regulators (synthetic auxins)</td>
</tr>
<tr>
<td>Z</td>
<td>unknown</td>
</tr>
</tbody>
</table>

Knowledge of the herbicide mechanisms of action from the practical point of view is important since their proper selection prevents the problem of weed resistance to herbicides.

**Division according to chemical identity**
Herbicides are classified into more than 60 chemical groups (e.g. aminophosphonates, dipyridyls, triazines, sulfonylurea herbicides, chloroacetamides, amides, carbamates, etc.). A detailed division of herbicides according to chemical groups and active substances can be found on www.hracglobal.com.

Division according to the time of application

- Application before sowing or planting of cultivated plant species (pre-sowing, pre-planting)
- Application after sowing and before emergence of cultivated plant species (pre-emergence, pre-em)
- The application after the emergence of cultivated plant species (post-emergence, post-em)

Such a division of herbicides is related to a defined period of application depending on the herbicide mode of action and to the time of sowing, planting or the development stage of cultivated plant species (BBCH development stage) and/or weed (Germ. Biologische Bundesanstalt, Bundessortenamt und Chemische Industrie - BBCH). For a satisfactory herbicidal effect and an environmentally friendly approach to weed suppression, it is necessary to be familiar with the application conditions and factors affecting a particular period of herbicide application.

5.7.4 Other products

Plant growth regulators (phytoregulators, physiotrops, growth hormones) are complex organic compounds affect the physiological processes of a plant during their application. They are used in agricultural production as stimulators or inhibitors and their application can improve the productivity of cultivated species. According to their mode of action, they can cause a change in the appearance and shape of the whole plant or only a specific part of the plant. In both growth regulators and herbicides, the applied amount is a very important factor in the final performance.

Some of the effects, which are of agronomic importance, are the effects on yield and fruit quality (standardisation of tomato fruit ripening, facilitating the cherry harvest), durability during transport and storage (prevention of potatoes and onions sprouting), rooting of cuttings or growth inhibition, prevention of grain lodging, etc.

Auxiliary plant protection products (adjuvants) are approved products, which are added to a plant protection product or are used in conjunction with the plant protection product in the tank mix. The definition of adjuvants according to the mode of action is often not useful for practical reasons, as the same physical characteristics can cause different effects.

According to chemical division we distinguish between several groups of adjuvants, e.g., surfactants, mineral emulsifiers, vegetable oils, polymers, etc. Each of the aforementioned groups has a different role, activity or more of them, and they are important for the quality preparation and application and for achieving the required efficiency of a plant protection product. From an agronomic point of view, the important adjuvants are those, which affect the formation and transport of droplets (anti-drift and anti-evaporation), deposition of droplets (deposition and increased spread of droplets), penetrators, etc.

Authors: Vjekoslav Tadić, Ph.D., Tamara Rehak, M.Eng., Maja Novak, M.Eng.

6 APPLICATION OF PLANT PROTECTION PRODUCTS

Plant protection products shall be applied according to the instructions on the label and in accordance with good agricultural practice.

6.1 Label

For a plant protection product, label is its basic, important and binding document for the user. The label contains all the information necessary for the application of plant protection products: handling, storage, proper disposal of product residues and its packaging, information on the composition of the product, application, limitations, protection of health and the environment, and it is the obligation of every person using or handling the product to study the content of the label. The information to be stated on a label shall be clear and indelible on the packaging of each plant protection product as defined under the Regulation (EU) No. 547/2011 on the Implementation of Regulation (EC) No. 1107/2009 regarding the requirements for the plant protection products Labelling.

Table 6.1: Prescribed data and content of the plant protection product label (prepared by: D. Hamel)

<table>
<thead>
<tr>
<th></th>
<th>Trade name or designation of the plant protection product.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.</td>
<td>Name and address of the registration owner (approval user) and the approval number (class) of a plant protection product and, if different, the name and address of the person responsible for the final packaging and Labelling or for the final Labelling of the plant protection product on the market.</td>
</tr>
<tr>
<td>3.</td>
<td>The name of each active substance listed as provided for in Article 10, paragraph 2.3 of the Directive 1999/45/EC with a clearly stated chemical form. Name shall match the name given in the list contained within Appendix VI. of the Regulation (EC) No. 1272/2008 or, if not included in this list, its common ISO name. If the latter is not available, the active substance is referred to by its chemical name in accordance with the rules of the International Union of Pure and Applied Chemistry (IUPAC).</td>
</tr>
<tr>
<td>4.</td>
<td>The concentration of each active substance expressed as follows:</td>
</tr>
<tr>
<td>A</td>
<td>For solids, aerosols, volatile liquids (maximum boiling point of 50°C) or viscous liquids (lower limit of 1 Pas at 20°C), as % m/m and g/kg,</td>
</tr>
<tr>
<td>B</td>
<td>For other formulations of liquid/gel, as %m/mig/L,</td>
</tr>
<tr>
<td>C</td>
<td>For gases, as % v/v and % m/m,</td>
</tr>
<tr>
<td>d</td>
<td>If the active substance is a micro-organism, its content is expressed as the number of active units per volume or weight or any other unit that refers to a microorganism, for example, colony-forming units per gram (cfu/g) (cfu) or the number of propagules in grams.</td>
</tr>
<tr>
<td>5.</td>
<td>The net quantity of the plant protection product expressed in: g or kg for products in solid form, g, kg, ml or L for plant protection products in the gaseous state and mL or L for plant protection products in the liquid state.</td>
</tr>
<tr>
<td>6.</td>
<td>Serial number (batch) of the plant protection product and the date of manufacture.</td>
</tr>
<tr>
<td>7.</td>
<td>First aid information.</td>
</tr>
<tr>
<td>8.</td>
<td>Type of all special risks to human or animal health or to the environment, using the standard warning signs, which have been selected, depending on the case, by the competent authority among those listed in Appendix II.</td>
</tr>
<tr>
<td>9.</td>
<td>Precautionary measures for the protection of human or animal health or the environment, in the form of the standard warning signs, which have been selected, depending on the case, by the competent authority among those, listed in Appendix II.</td>
</tr>
<tr>
<td>10.</td>
<td>Type of action of the plant protection products (e.g. insecticide, growth regulator, herbicide, fungicide, etc.) and its mode of action.</td>
</tr>
<tr>
<td>11.</td>
<td>Type of preparation (formulation form) (e.g. wettable powder, emulsifiable concentrate, etc.).</td>
</tr>
</tbody>
</table>
12. Applications for which the plant protection product has been approved and all specific agricultural, phytosanitary and environmental requirements under which the plant protection product may or may not be applied.

Table 6.1: Prescribed data and content of the plant protection product label – continued (prepared by: D. Hamel)

| 13. | Instructions for use and conditions of use and dosage, including, where appropriate, the maximum dosage per hectare per application and the largest number of applications per year. The dosage is expressed by metric units for each use provided for under the terms of approval. |
| 14. | Where appropriate, the safety interval for each use between the last application and: |
| A | sowing or planting of the crop to be protected, |
| B | sowing or planting of the following crop, |
| C | access of people or animals, |
| d | harvest, |
| E | use or consumption. |

15. Information on possible phytotoxicity, varietal susceptibility and any direct or indirect harmful effects for plants or products of plant origin together with the time and spatial intervals to be observed between application and sowing or planting of:

| A | the subject crop or |
| B | following and adjacent crops. |

16. If the plant protection product is accompanied by a leaflet, as provided for in paragraph 2 of Regulation 547/2011, the sentence "Read the accompanying instructions before use":

17. Instructions for the appropriate storage conditions, safe disposal of the plant protection products and packaging.

18. Where necessary, the expiry date for normal storage conditions.

19. The prohibition concerning the re-use of packaging, except when reused by the registration owner (approval user), and provided that the packaging is specially designed to allow the re-use to the approval user.

20. All data required under the approval in accordance with Article 31, Article 36, paragraph 3, Article 51, paragraph 5 or Article 54 of the Regulation (EC) No. 1107/2009.

21. Groups of users who have been granted the use of the plant protection product in a case where the use is limited to certain categories.

The order of the prescribed data on the label attached to the plant protection product differs from the order of prescribed data in Table 6.1 for several reasons (e.g. different legislation under which the plant protection product is registered, different size and design of packaging and labels ...).

Information required under paragraphs 13, 14, 15, 17, 18 and 20 may be listed on a separate leaflet attached to the packaging if the space available on the package is too small. Such a leaflet is considered an integral part of the label.

Under no circumstances shall the label of the plant protection product package contain the signs "non-toxic", "harmless" or similar. However, the label may contain the information that the plant protection product may be used when bees or other species which are not targeted are active or when crops or weeds are in flower or other similar signs for bee protection, and may contain signs with similar data on the protection of bees or other species which are not targeted if the approval explicitly allows use under such conditions.

Labeling and packaging of plant protection products that are used for experiments or tests for purposes of research or development, as provided in Article 54 of Regulation (EC) No. 1107/2009 shall
be aligned only with items 2, 3, 4, 10 and 11. The label contains the information required by the permit for research purposes provided for in Article 54, paragraph 1 of Regulation (EC) No. 1107/2009 and the words “product intended for experimental use, not fully categorised, to be handled with extreme care”.

All data contained on the label shall be in the Croatian language and Latin script. They shall be true, clear, visible and legible, and in accordance with the decision on the registration of plant protection products. In the registration procedure, and before the placing on the market, the final appearance and content of the label, which shall be attached to a plant protection product, shall be submitted to the Ministry of Agriculture for each individual packaging size. For plant protection products that are registered under the Plant Protection Products Act (Directive 91/414/EEC) and the Regulation (EC) No. 1107/2009, all the information on the label shall be approved during the registration. For such plant protection products, the contents and the final appearance of the label can be found on the FIS website (http://fis.mps.hr/trasilicaszb/).

Exceptionally, a plant protection product may be labelled in another language only in the case of licensing for research and development and licensing of the plant protection product in emergencies when the plant protection product is not placed for sale but is applied by the end user who is issued a decision on the licence for an emergency or a decision on the licence for research and development. The decision shall contain all the necessary data for safe handling and application of plant protection products.

Providing all necessary information on the label of small packages is not possible due to limited space and in that case the plant protection product shall be equipped with a multi-part label (in the form of booklet, accordion-like...) or a leaflet (the accompanying sheet) which is attached to each plant protection product package and is considered an integral part of the label. In such cases, the packaging or label shall contain a warning Read the accompanying instructions before use.

6.2 Preparation of plant protection products for use

In plant protection there are many factors which affect the efficiency of plant protection products. Some factors, such as climatic conditions, are beyond our control and we cannot influence them. This is another reason why the procedures which we perform ourselves and which are under our control shall be carried out with maximum conscientiousness and accuracy, in order to achieve the greatest possible efficiency, regardless of the different factors before, during and after the application of a plant protection product.

After selecting a plant protection product for a particular purpose, preparation of the plant protection product for application is the following and one of the most sensitive steps to achieve optimum efficiency. The result of the of plant protection product preparation is a spray mixture. The spray mixture is a plant protection product diluted with water. The exception are plant protection products which are applied in solid state (by spraying or granules dispersion) or products which are finished, already prepared for application.

Liquid plant protection products are mixed with water in the tank of the application equipment, and rarely in a separate container before filling the application equipment. Wettable powders for suspension (WP) may not be immediately placed into the container of application equipment, but are mixed with some water in a separate container. A thick mixture is produced by mixing, taking care that the entire powder is moistened, after which, by successive additions of water and mixing, a suspension is produced which shall not be too thick, and which is as such poured into the tank of the application equipment which half-filled with the required amount of water. Granulated plant protection products
which are applied in liquid diluted form (WG) may be prepared directly in the tank unless otherwise stated in the instructions.

A measured amount of a plant protection product and water shall always be poured into the tank of the application equipment through the cleaner (filter, screen) in order to avoid clogging of the nozzle outlet (sucking-pipe, jets) with different impurities.

For the correct preparation of the product for application, it is necessary to follow the instructions listed on the label:

1. *The application equipment shall be clean and functional, and the spray flow equal.*
2. *Before opening the packaging of a plant protection product, the content needs to be well shaken.*
3. *Pour the required amount of product poured into the application equipment filled up to the half with the required amount of water in which the blender is turned on.*
4. *Add the remaining required amount of water to the tank while mixing constantly. Continue mixing during treatment and possible downtime in the field.*
5. *Use the prepared spray mixture in the same day.*

When preparing the spray mixture, caution and wearing of the prescribed personal protective equipment is required at any time.

6.2.1 Calculation of the dosage and concentration

The label of each plant protection product states the amount (dosage) or concentration in which the plant protection product shall be applied. In order to achieve optimum performance, with a minimum risk of negative impact of a plant protection product on the operator, various parts of the environment, beneficial and non-targeted organisms, it is necessary to prepare the prescribed dose or concentration accurately.

The **dosage** is the amount of a plant protection product which is applied per unit of area (ha, m²). For solid preparations, the dosage is expressed in kilograms (or smaller units) per hectare (1 kg/ha and 200 g/ha), while for the liquid preparations it is expressed in liters (or smaller units) per hectare (1 l/ha 200 mL/ha). The application of all herbicides, as well as of the majority of insecticides and fungicides that are used to protect field crops and in agricultural products storages, is expressed in dosage.

The term dosage is not determined by the volume of water in which the aforementioned amount shall be distributed per unit of area. The same amount of a plant protection product can be applied in a different volume of water which has no impact on its effect. By increasing the volume of water, the concentration of a plant protection product is decreased, which has no impact on its effect since the dosage remains the same. For example, a dosage of 1 l/ha or 1 kg/ha of a plant protection product can be applied in a spray mixture volume of 100, 200 or 400 L/ha. In doing so, the concentration of the plant protection product in that spray mixture shall amount to 1%, 0.5% or 0.25% (see Table 6.2, marked in gray), which is not of particular importance since the dosage remains the same - 1 L/ha or 1 kg/ha.

For a good effect and proper application, it is important that the required amount of a plant protection product is uniformly distributed over a particular surface. Due to the aforementioned, it is necessary to determine the water consumption per unit of area (ha, m²) prior to spray mixture preparation (it can be determined by a test trial). Otherwise, it may happen that we run out of the spray mixture or that the excess of it remains in the tank after spraying. In the first case, one part of the plot would
remain unsprayed, while a higher dosage than the prescribed one would be applied on the sprayed part of the plot.

In case of the spray mixture remaining in the tank, the dosage on the treated plot is too small. In such a case, it is necessary to dilute the remaining spray in water, according to the instructions on the label of the plant protection product, and spray it over the treated surface. It is easy to conclude that such a procedure results in uneven distribution of a plant protection product, which may, in both cases, result in various undesirable effects (reduced efficiency, occurrence of phytotoxicity and/or adverse impact on the environment, beneficial and non-targeted organisms). The data on the required water amount is stated on the label.
Trial test for determining water consumption per unit of area

Fill the application equipment with a known amount of water. In case of tractor equipment, 100 L, and in case of manual, 1 L. Determine the surface over which the application of water shall be performed. For tractor equipment, 1000 m², and for manual, 10 m². During the application, the tractor needs to move with a known speed. After passing the measured surface, it is necessary to measure the remaining amount of water in order to determine the amount spent. In this manner, water consumption per unit of area at a certain speed may be calculated, which is the basis for calculating the required amount of spray mix for the entire surface treatment. If a manual sprayer is used, it is necessary to monitor the number of times the entire surface is passed until the consumption of the entire water amount.

The concentration is the percentage of a plant protection product in water (spray mixture). The recommended concentration on the label of a plant protection product is an effective concentration verified through experiments intended for the suppression of certain pests or plant diseases pathogens (with the acceptable risk for the operator, environment, beneficial and non-targeted organisms).

The term concentration usually prescribes the application of a plant protection product, which suppresses pathogens and pests in vineyards, orchards, vegetables, floral and other cultures. In addition to the prescribed concentration, the required volume of water is also prescribed on the label. Typically, the aforementioned volume amounts to 1000 L/ha in orchards and vineyards, and smaller amounts for other crops. For example, in case of applications in orchards, greater mowing also requires a greater volume of water for better quality of covering with spray mixture, therefore in some registrations that consumption depends on its size (e.g. water consumption of 500 L/ha for a 1 m tall canopy). Moreover, for better quality control of some harmful organisms (e.g. wooly apple aphids or powdery mildew on grapevine) a greater volume of water is required. It is important to adhere to the prescribed volume of water stated on the label of the plant protection products. By increasing the volume of water, and in order to maintain the same concentration, the amount of the product in the spray mix shall be increased, thus increasing the total amount of the plant protection product per unit of area, which might result in a variety of adverse effects.

The risk assessment for each plant protection product is prepared exclusively for the approved amount or concentration of a plant protection product and the volume of water. It is therefore important, in addition to the approved amount or concentration stated on the label, to adhere to the prescribed volume of water.
The correlation between dosage and concentration is therefore evident from the above mentioned. In addition to a known dose and consumption of spray mixture, the operator often has to calculate the concentration as well. The concentration can be read from Table 6.2.

**Table 6.2: Reading of the concentration (source: Manual for Plant Protection; prepared by: N. Novak)**

<table>
<thead>
<tr>
<th>Consumptions of spray mixture in L/ha</th>
<th>50</th>
<th>100</th>
<th>200</th>
<th>300</th>
<th>400</th>
<th>600</th>
<th>800</th>
<th>1000</th>
<th>1500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Required product dosage (kg or L)</td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
<td>0.4</td>
<td>0.5</td>
<td>0.6</td>
<td>0.7</td>
<td>0.8</td>
<td>0.9</td>
</tr>
<tr>
<td>0.10</td>
<td>0.2</td>
<td>0.1</td>
<td>0.05</td>
<td>0.035</td>
<td>0.025</td>
<td>0.017</td>
<td>0.012</td>
<td>0.01</td>
<td>0.006</td>
</tr>
<tr>
<td>0.15</td>
<td>0.3</td>
<td>0.15</td>
<td>0.07</td>
<td>0.05</td>
<td>0.035</td>
<td>0.025</td>
<td>0.017</td>
<td>0.015</td>
<td>0.01</td>
</tr>
<tr>
<td>0.20</td>
<td>0.4</td>
<td>0.2</td>
<td>0.1</td>
<td>0.07</td>
<td>0.05</td>
<td>0.035</td>
<td>0.025</td>
<td>0.02</td>
<td>0.013</td>
</tr>
<tr>
<td>0.25</td>
<td>0.5</td>
<td>0.25</td>
<td>0.125</td>
<td>0.08</td>
<td>0.06</td>
<td>0.04</td>
<td>0.03</td>
<td>0.025</td>
<td>0.017</td>
</tr>
<tr>
<td>0.30</td>
<td>0.6</td>
<td>0.3</td>
<td>0.15</td>
<td>0.1</td>
<td>0.075</td>
<td>0.05</td>
<td>0.035</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>0.40</td>
<td>0.8</td>
<td>0.4</td>
<td>0.2</td>
<td>0.13</td>
<td>0.1</td>
<td>0.65</td>
<td>0.05</td>
<td>0.04</td>
<td>0.27</td>
</tr>
<tr>
<td>0.50</td>
<td>1.0</td>
<td>0.5</td>
<td>0.25</td>
<td>0.17</td>
<td>0.125</td>
<td>0.75</td>
<td>0.86</td>
<td>0.05</td>
<td>0.033</td>
</tr>
<tr>
<td>0.75</td>
<td>1.5</td>
<td>0.75</td>
<td>0.35</td>
<td>0.25</td>
<td>0.18</td>
<td>0.125</td>
<td>0.08</td>
<td>0.05</td>
<td>0.050</td>
</tr>
<tr>
<td>1.00</td>
<td>2.0</td>
<td>1.0</td>
<td>0.5</td>
<td>0.33</td>
<td>0.25</td>
<td>0.165</td>
<td>0.125</td>
<td>0.1</td>
<td>0.065</td>
</tr>
<tr>
<td>1.50</td>
<td>3.0</td>
<td>1.5</td>
<td>0.75</td>
<td>0.5</td>
<td>0.35</td>
<td>0.25</td>
<td>0.18</td>
<td>0.15</td>
<td>0.1</td>
</tr>
<tr>
<td>2.00</td>
<td>4.0</td>
<td>2.0</td>
<td>1.0</td>
<td>0.65</td>
<td>0.5</td>
<td>0.33</td>
<td>0.25</td>
<td>0.2</td>
<td>0.13</td>
</tr>
<tr>
<td>3.00</td>
<td>6.0</td>
<td>3.0</td>
<td>1.5</td>
<td>1.0</td>
<td>0.75</td>
<td>0.5</td>
<td>0.35</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>4.00</td>
<td>8.0</td>
<td>4.0</td>
<td>2.0</td>
<td>1.33</td>
<td>1.0</td>
<td>0.65</td>
<td>0.5</td>
<td>0.4</td>
<td>0.27</td>
</tr>
<tr>
<td>5.00</td>
<td>10.0</td>
<td>5.0</td>
<td>2.5</td>
<td>1.67</td>
<td>1.25</td>
<td>0.83</td>
<td>0.6</td>
<td>0.5</td>
<td>0.33</td>
</tr>
</tbody>
</table>

1 ha = 10000 m²
1 kg = 1000 g
0,1 kg = 100 g
1 L = 1000 mL
0,1 L = 100 mL

A certain dosage may be applied in a greater or lesser volume of water, thus changing the concentration of the spray spray mixture as well. If the amount of 2 kg or 2 L is applied in in 200 L of spray mixture, the concentration shall amount to 1% (marked in yellow). By reducing the volume of water at the same dosage, the concentration increases proportionally and vice versa, by increasing the volume of water at the same product dosage, the concentration decreases proportionally. Thus the amount of 2 kg or 2 L applied in twice lower spray amount (100 L) shall result in a twofold increase in concentration which shall then amount to 2% (marked in green). If that same amount is applied in in 400 L of spray mixture, the concentration shall amount to 0.5 % (marked in red).

Plant protection product operators often have problems with calculating the concentration with regard to the volume of water consumed or application equipment tank capacity. In order to avoid calculation, the Table 6.3 provides an overview of the product amount required for achieving a certain concentration in tanks of different sizes.
Table 6.3: The amount of a plant protection product requires to be placed into the container of a certain capacity in order to achieve the desired concentration (source: Manual for Plant Protection; prepared by: N. Novak)

<table>
<thead>
<tr>
<th>Required concentration</th>
<th>Spray mixture volume (in litres)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>grams or millilitres of a plant protection product in the spray mix</td>
<td></td>
</tr>
<tr>
<td>0.01 %</td>
<td>0.1</td>
</tr>
<tr>
<td>0.02 %</td>
<td>0.2</td>
</tr>
<tr>
<td>0.03 %</td>
<td>0.3</td>
</tr>
<tr>
<td>0.04 %</td>
<td>0.4</td>
</tr>
<tr>
<td>0.05 %</td>
<td>0.5</td>
</tr>
<tr>
<td>0.06 %</td>
<td>0.6</td>
</tr>
<tr>
<td>0.10 %</td>
<td>1.0</td>
</tr>
<tr>
<td>0.12 %</td>
<td>1.2</td>
</tr>
<tr>
<td>0.15 %</td>
<td>1.5</td>
</tr>
<tr>
<td>0.20 %</td>
<td>2.0</td>
</tr>
<tr>
<td>0.25 %</td>
<td>2.5</td>
</tr>
<tr>
<td>0.30 %</td>
<td>3.0</td>
</tr>
<tr>
<td>0.40 %</td>
<td>4.0</td>
</tr>
<tr>
<td>0.50 %</td>
<td>5.0</td>
</tr>
<tr>
<td>0.60 %</td>
<td>6.0</td>
</tr>
<tr>
<td>1.00 %</td>
<td>10.0</td>
</tr>
</tbody>
</table>

It is evident from the table that the concentration of 0.1% means 1 g or 1 ml of a plant protection product (marked in yellow) in 1 liter of spray mix. As many times we want to increase the concentration in the same volume of spray mixture, that many more times we have to add a plant protection product. Thus, for obtaining, for example, a 0.4% concentration in the same amount of the spray mixture, 4 times more, that is, 4 g or 4 ml of a plant protection product (marked in red) is required. If we want to maintain the same concentration, and increase the volume of the spray mix, the amount of the plant protection product shall be increased by the same amount by which we increased the volume of the spray mixture. Thus, for obtaining 10 litres of a spray mixture with the concentration of 0.12 %, 12 g (mL), that is, twice as much of the plant protection product (marked in green) is required. For obtaining the double amount of the spray mixture (20 L), while maintaining the same concentration, 24 g (mL), that is, twice as much of the plant protection product (marked in gray) is required.

By analogy, it is easy to calculate the required amount of a plant protection product for any spray mixture volume. The amount of a plant protection product required for 400 liters of spray mixture is multiplied by four with the amount of the product required for 100 liters of spray mixture. If we want a concentration of 0.20% of a plant protection product in a spray mixture of 400 litres volume, the number 200 (marked blue) is multiplied by 4, which amounts to 800 g (mL) of a plant protection product in the aforementioned volume.

When preparing the spray mixture, the volume of the plant protection product itself is often forgotten, resulting in the error in concentration which we want to achieve. Therefore, 1 liter of product in 99 (not 100) liters of water produces a 1% spray mixture. The above mentioned shall also be considered when preparing the spray mixture.
6.2.2 Mixing of plant protection products

Mixing of different plant protection products enables their simultaneous application with the aim of extending the spectrum of effect, saving the fuel and time and reducing the costs.

Mixing of plant protection products is a sensitive process limited by certain physical or chemical properties that may cause changes in the mixture and thus prevent the application, change the effect on organisms which are suppressed and on the beneficial and non-targeted organisms, as well as on the treated plant (phytotoxicity). Many plant protection products shall not be mixed together. When registering a particular plant protection product, manufacturers only investigate certain mixtures with other plant protection products (and/or active substances), which are expected to expand the spectrum of effect or other specific cost-effectiveness, which is why other possible combinations are often left unexplored.

The possibility of mixing two plant protection products depends on the compatibility (tolerance) of their formulations, but also on other factors that may affect the safety of such application. When mixing incompatible plant protection products, visible excretion or the formation of deposits in the spray mixture may occur. Figure 6.1.a shows the examples of mixing different combinations of plant protection products which show what is happening in the application equipment tank when the spray is prepared by mixing two or more plant protection products. It can be clearly seen from Figure 6.1.b that in some cases of mixing, visible excretions occurred in the spray mixture (e.g. deposition), while in certain mixtures there are no visible signs of plant protection products incompatibility in the spray mixture (Figure 6.1.c).

Figure 6.1.a: Different physical and chemical compatibility of different plant protection product mixtures (photo: M. Pelajić)
The label of the majority of plant protection products, in the part relating to mixing with other plant protection products, states that it is necessary to inquire the owner of the decision on registration or the representative on the possibilities of mixing a plant protection product with other plant protection products, adjuvants and mineral fertilisers.

An employee in the agricultural pharmacy may recommend mixing of plant protection products only when that is specified in the instructions on the label or when they are in possession of information on mixing options provided by the owner of the decision on registration, manufacturer of the plant protection product, representative or distributor. The same applies to mixing of plant protection products with fertilisers.

The basic principle of mixing the plant protection products of different formulations is that plant protection products of solid formulations are first added to the application equipment tank, and then the liquid formulations. For the proper preparation of spray mixtures, the adding order is following:

- water-soluble bags,
- wettable powders,
- dispersible granules,
- suspension concentrates,
- emulsifiable concentrates,
- soluble concentrates,
- auxiliary products for the improvement of the plant protection product effect (e.g. wetting agents).

In this process, foam may be created, therefore, attention shall be paid to the intensity of mixing. In some cases, deviations from these principles are possible.

When mixing a plant protection product, it is also necessary to pay attention to the dosage of each plant protection product in the combination, which may be different from the dosage during the application of each plant protection product separately. The same applies to the time of application. The best option during mixing is for the plant protection products to interact synergistically, i.e. to mutually strengthen their effect on the target organisms, without harmful effects on the culture (phytotoxicity), beneficial and non-targeted organisms. In this manner, the costs of protection and intake of plant protection products in the environment may be reduced, which shall be the aim.

There are already proven combinations on the market, i.e. the combined plant protection products, which are in their composition finished mixtures of two or more active substances and other necessary additions. These are usually combinations of herbicides or combinations of fungicides which present the greatest need for mixing and whose range of effect is thus significantly increased and the need for additional treatments is decreased.

### 6.3 Methods of applying plant protection products

Proper preparation of plant protection products for the application is followed by the application, which is also an important factor in the success of protective measures. In order to achieve the optimum efficiency, both preparation and application shall be performed flawlessly.

Methods of plant protection products application are sprinkling, spraying, application of liquid aerosols or fogging, aerial spraying, granules dispersion, chemical sterilization of the soil, seed treatment, injection into the soil, pouring over, pouring into the soil, coating. There are some other methods as well, and those most commonly used shall be described below.

Plant protection products are most commonly used diluted with water, that is, as a spray mixture. The main criterion by which methods of liquid plant protection products application are differed is the size of droplets.

**Sprinkling** is the most common application method of plant protection products diluted in water with droplets larger than 150 micrometres, i.e. in the form of a light drizzle.

In crop farming and vegetable growing, sprinkling is the most common plant protection product application method. The main disadvantages of sprinkling in the protection of orchards and vineyards are a small range of the spray and worse area coverage, although it can be sufficient in certain situations (individual fruit trees, low plantations, seedlings, young fruit trees). Sprinkling is also used for the application of herbicides.

The advantage of sprinkling over other methods is its lesser dependence on the wind, which negatively affects the quality of work. Spray mixture drift is lesser, due to larger droplets. This advantage is especially pronounced when applying herbicides, which shall be applied particularly carefully. Low pressure of the jet during the herbicide application creates a jet of larger droplets (using nozzles for this purpose), which reduces the drift. The disadvantage of sprinkling is in the large water consumption per unit of area, making the application difficult in areas with insufficient access to water or on plots away from water sources. In such cases, additional equipment is often required (tanks, pumps, etc.),
the costs of water supply increase, and due to the weight, the soil is more compressed during transport and operation.

**Spraying** is the application of spray mixtures with smaller droplets sized from 50 to 150 micrometres, and it is most commonly used for protection against diseases and pests in orchards and vineyards. The fragmentation of droplets, that is, jet dispersion, is enabled by the airflow produced by a fan. Dispersion equipment - dispersers usually have all the essential parts of a sprinkler with the addition of fans and pipes intended for directing the airflow. The spray mixture is also directed together with the airflow.

Dispersion, due to the small size of the droplets, enables a reduced consumption of spray mixture in comparison to sprinkling. The airflow increases the jet range, enables penetration into the canopy, causes flickering of leaves and thus a better adherence of the product over the reverse side of the leaves as well. This is especially important for contact plant protection products. The main disadvantage of spraying in comparison to sprinkling the increased drift hazard, due to small droplets, which represents a greater potential hazard for the operator, adjacent surfaces (crops), beneficial and non-targeted organisms, water surfaces, domestic animals etc. Therefore, additional caution is required during spraying.

For individual fruit trees and smaller plantations, backpack sprayers with which the operator directs the airflow, i.e. spray mixture, are sufficient. Sprayers carried or pulled by tractors intended for large plantations provide automatic treatment without direction.

The **application of liquid aerosols** or **thermal fogging** is the application of spray mixtures in droplets smaller than 50 micrometers. Due to their small dimensions, droplets are suspended in the air and remain part of the atmosphere for a longer period. The liquid consumption is very low. Drift hazard is extremely significant.

With this method, it is possible to use some insecticides, rarely fungicides, mainly in protected and enclosed spaces.

**Aerial spraying** is the application method for plant protection products in tiny solid particles in powder form. Due to large consumption of powder mixture per unit of area, the concentrations of active substances in powder mixtures are very low (except for sulphuric powder mixtures).

Water is not necessary for aerial spraying, therefore, that represents the advantage of aerial spraying in the areas with the significant issue of lack of water and/or of its supply to the plot. Drift hazard is greater than in spraying, during and after the application. Disadvantages of aerial spraying are: increased exposure of the operator, low quality of product distribution, uneven dosage, significant product losses, adverse effects on the environment and non-targeted organisms. When we add the possible removal of powder mixture by wind and rinsing with rain after the application, it is clear that aerial spraying is a very dangerous, and not a sufficiently effective method which is usually replaced by sprinkling or spraying.

**Granules dispersion**, i.e. the application of plant protection products in the form of granules is most often used for the suppression of pests in the soil and for chemical sterilisation of the soil. Herbicidal granules which can be mixed with fertilisers may sometimes be found on the market.

There are several types of granules deposits, which need to be calibrated before the application, i.e. adjusted according to the size of the granules intended for application. Depending on the purpose, the
granules may be dispersed over (maximum consumption), in strips, in rows (grooves) or only along seed, which reduces the dosage significantly.

**Chemical sterilisation of the soil** can be performed by granules dispersion and by injecting it into the soil. Liquid plant protection products are converted into gas, which sterilizes the soil by its permeation.

**Seed treatment** is an important and cost-effective protective measure. Fungicides destroy pathogens on or in the seed and prevent the attack of pathogens after sowing. Insecticides are used for seed protection against pests, which live in the soil. The companies, which process the seeds also treat them simultaneously. Seed treatment using plant protection products outside the seed treatment equipment is not recommended since proper distribution of plant protection products on the seed would not be ensured in this manner. During sowing, the badly treated seed may lose the product through dusting, which reduces the efficiency and is undesirable for the environment and non-targeted organisms. Seed distributors sell pre-treated seed, therefore, precautionary measures are required during handling.

When planting the treated seed, particular attention shall be paid to the protection of operators, bees, birds and mammals in terms of dusting prevention, seeding at the prescribed depth and special precautions aimed at preventing spills and leftovers of even the smallest amounts of such seed on the soil surface.

### 6.4 Application of plant protection products on non-agricultural surfaces

Non-agricultural areas are areas along different roads, paths, railroads, cemeteries, sports fields, canals, industrial facilities, airports etc. These areas are often not cultivated and maintained, therefore different kinds of weeds grow on them and various insects, rodents, snails and, in wet areas, mosquitoes gather there. In order to prevent the spread of harmful organisms to arable and cultivated surfaces, cultivation, mowing and mulching of non-agricultural areas, and sometimes also chemical suppression measures are required.

When implementing the measures for the suppression of harmful organism on non-agricultural surfaces, it is necessary to place a notice stating which harmful organism is being suppressed, the name of the plant protection product and active substance, work waiting period, an antidote (if any), operator’s name, address and telephone/mobile phone number, e-mail address, telephone number in case of an accident: National Protection and Rescue Directorate (112) or Poison Control Centre (01/2348342)

#### 6.4.1 Weed suppression

Weed suppression on non-agricultural surfaces is performed through the direct protection measures, mainly mechanical and/or chemical ones. Given the many adverse effects of plant protection products, priority shall be given to all non-chemical measures. Moreover, for the purpose of biodiversity conservation, the suppression shall be considered and implemented only when it is justified. This is usually the case when an invasive foreign weed species aggressively suppresses the autochthonous plants in their surroundings and forms a monoculture (Figure 6.2).
One of the wide spread invasive foreign weed species in Croatia is common ragweed or annual ragweed (Ambrosia artemisiifolia) (Figure 6.3), about which more was written in the chapter on weeds and whose suppression is the legal obligation of every citizen of the Republic of Croatia, both on agricultural and non-agricultural surfaces.
As a result of the application to undesirable plants, which can be found on public surfaces, cemeteries, sports fields, along roads (Figure 6.4), railways (Figure 6.5), airports, parks, channels (Figure 6.2), gardens, etc., the plant protection products can end up in the environment (through evaporation, washing into groundwater, etc.) and they cause (in)direct exposure of people, pets, beneficial and non-targeted organisms, as well as water surfaces. Therefore, in weed suppression on non-agricultural surfaces, wherever possible, priority shall be given to non-chemical protection measures.

Mechanical measures such as cutting, mowing, or, on smaller surfaces, covering the soil with mulch, manual hoeing and weeding of weeds, if performed regularly, can be very successful. The basic principle in the fight against annual weeds is the prevention of insemination. Perennial weeds, in addition to insemination prevention, should be "exhausted" using repeatable treatments. When suppressing larger wood species, the combination of mechanical and chemical methods is efficient when freshly cut stumps are coated with herbicide. Herbicide can also be injected under the bark of the plant. These manners are "slower" than conventional sprinkling, but are very effective and represent a minimal risk for the operator, environment, beneficial and non-targeted organisms.

6.4.2 Suppression of rodents, snails and mosquitoes

Non-agricultural surfaces are not cultivated and they become suitable locations for rodent burrows, and thus a source from which rodents go to the agricultural surfaces and cause damage. Since these are very large surfaces (e.g. approximately 10 m wide belt to the left and right side of the Macelj – Lipovac motorway in the length of approximately 300 km), chemical measures are not performed. An exception may occur if the rodents appear close to gas stations, rest stops, stops, industrial facilities and similar in order to prevent damage to the facilities and the possible infection of people. In order to reduce the population of rodents on non-agricultural surfaces, it is necessary to regularly perform mowing, shallow tillage (harrowing) where possible, and to leave the trees for the nests of birds which feed on rodents.

Humid and shaded surfaces are suitable for the development of snails. This means that on mowed surfaces, where hay is collected and mulch is not left, the conditions for their development are unfavorable.

Since mosquitoes develop in water, draining water from the surfaces on which they gather through amelioration projects, speeding up the water flow in the channels and cultivating the banks of channels, streams and rivers is necessary. For mosquito suppression, biocidal products, not plant protection products are used.
6.5 Plant protection products for special purposes

6.5.1 Protection of stored agricultural products

Agricultural products, cereals or oilseeds can be stored in silos or floor warehouses, and meal only in floor warehouses. During the storage of agricultural products, it is important to maintain the health safety and amount by maintaining order and cleanliness, measuring the temperature of the stored goods, and taking samples of the goods for analysis. This requires proper construction of the building and landscaped environment around the warehouse without the low bushes.

The greatest damage during storage nowadays occurs when the goods are kept in silos where transfer and blowing in cold air are not possible, when the floor warehouse is above the rooms that are heated or is open.

Damage in warehouses is caused by insects which damage the whole grain or continue damaging the damaged grains, mites, rodents and birds.

6.5.2 Suppression

Proper storage, at favourable low temperatures and low humidity, the spread or propagation of pests in and on the grain may be halted, and when they are multiplied, their suppression has to be initiated.

Some warehouse pests spend a part or whole of their life not only on stored cereal grains but also inside of them, and it is often difficult to perform effective suppression and select the appropriate method and the appropriate plant protection product.

Preventive treatment is performed prior to visible pest occurrence using the direct application of powder mixture, diatomaceous earth. In the event that there is a hidden infection, that is, the presence of insects inside grain, insecticide spraying shall not have an insecticidal effect on these insects. Direct application on the grain ensures that for some time after the treatment there shall be no spread of the insects because they shall die in contact with the treated grain.

The disadvantage of this procedure is that the treatment performed without knowing whether a harmful insect species shall appear or not.

Curative treatment is performed after the presence of insects, which cause damage is established. The application of insecticides which are applied directly to cereals shall have effect on the insects located outside the grains during treatment. At the same time, eggs, larvae or caterpillars, pupae and adult beetles, weevils (Sitophilus spp.) or angoumois grain moths (Sitotroga cerealella), which are located within the grain shall be able to continue their life or development. After leaving the grain, the insects shall encounter treated grain and die. As a consequence, offspring shall not develop and after a certain period, the present population of insects shall completely die. This enables dying of insects over a longer period, i.e. the effectiveness depends on the conditions for development. If there are optimum conditions for the development of insects, they shall develop sooner and the full efficiency shall be achieved sooner. This procedure is only acceptable when a longer storage after treatment is expected. It shall be noted that as long as there are living insects inside grains, damage occurs, that is, quality is reduced and there are losses in grain mass. Insects in grain are successfully suppressed by fumigants, which may be applied only by specially authorised persons (professional users for professional applications).
6.5.3 Fumigation

Fumigation is the process of suppressing warehouse pests in stored cereals or oilseed with the use of gas. Only formulations which release phosphine gas are currently present in Croatia. This is one of the fundamental procedures for suppressing pests on stored agricultural products in our silos/warehouses. The dosages and exposure time are determined by insect species and their development stage, and the quality of goods with regard to humidity, impurities and temperature is not a negligible factor. The applied dosage of fumigant shall be in accordance with the permit, whereby keeping in mind the important influence of temperature and the functionality of the equipment in the silo. It is not necessary to fumigate an empty warehouse/silo, but it is better to clean it and sprinkle the surfaces with an appropriate insecticide which is registered for such purpose.

Preparations for performing fumigation

For fumigation, it is necessary to determine the state of the stored goods. Before making a decision on treatment, it is necessary to be familiar with the period between the storage of goods in the warehouse and the moment of placing it on the market. Various insect species or developmental forms are suppressed using different dosages/concentrations at different time of exposure. For example, lesser grain borer is more resistant than other insects, and eggs or cocoons than larvae. The goods to be treated shall be placed in a clean space.

The staff responsible for the organisation of fumigation shall be familiar with the amount of fumigant required for the treatment of room (g/m³) or goods (g/ton). The goods shall be prepared for the treatment, the devices for transferring goods (transporters) shall be functional, and the person responsible for the silo/warehouse shall be familiarised with the method of use and the amount of plant protection product to be applied, as well as with the precautionary measures. In accordance with the situation, it is necessary to use appropriate personal protective equipment (clothing, masks, etc.). Contractors are required to familiarise the employees in the silo/warehouse with the procedure which performed, i.e. with the plant protection products with which the treatment shall be performed, with precautionary measures which shall be taken in order to prevent poisoning of the employees and perform the fumigation properly. During the treatment in the silo, a dispenser shall be used, and a probe for probing in the warehouse.

Improper application often appears as a problem, especially as contractors often think the omissions that have been made during the treatment, when a dose less than the prescribed is applied, shall not be identified. This happens when fumigation operators do not use dispensers for pellets/tablets/beads and occasionally add a certain amount, which is usually not sufficient. Re-treatment of everything cannot be justified, even of those amounts which do not show visible infection or possibly have a small population of secondary pests present.

It is not good when silo/warehouse employees allow operators to perform treatment alone, which enables improper application.

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7 HAZARDS AND RISK DURING THE USE OF PLANT PROTECTION PRODUCTS

7.1 Introduction

Hazards and risks of plant protection products use shall be known before placing each plant protection product on the market. An integral part of the registration process is the performance of the risk assessment, which defines the hazards and risks during the use and handling of plant protection products. The risk assessment takes into account all the proposed actual conditions of the plant protection products use, as well as the possible consequences of its use on human health, animals and the environment. Some of the key factors considered within this framework are the range of effects, dosage, method, frequency and timing of applications, properties and composition of plant protection products, residues, behaviour in the environment, effects on non-targeted organisms and many other.

A hazard is a possible harmful effect or impact of a plant protection product during the conventional application, i.e. harm relating to the use and properties of the plant protection product itself. Examples of hazards are toxicity, tendency to wash into water bodies (rivers, lakes) or tendency to accumulate in fat in humans and animals.

A risk is the probability that a particular hazard shall be realised, such as, for example, the exposure to a certain amount of plant protection products, dietary exposure due to excessive residues or exposure to certain concentration during the application due to failure to use the prescribed personal protective equipment. The risk can be expressed through numerical values, and there are prescribed methodologies for its calculation in different cases. Using the appropriate methodology, the risk of plant protection product harmful effects can be reduced.

Risk mitigation measures are a set of information, procedures and limitations by which the risk in the use of plant protection products is reduced to an acceptable level.

Examples of measures:

- prohibition of application on light soils,
- crop rotation limitation,
- prescribed personal protection,
- prohibition of application during the activities of bees and other pollinators,
- adherence to the buffer zone to the water body or non-agricultural areas and similar.

In the process of registration and risk assessment, the hazards and risks in the use of plant protection products are determined:

- in case of human exposure,
- with respect to pesticide residues,
- against possible environmental impact,
- against the potential impact on non-targeted organisms and
- the possibility of influence over the efficiency.

If risk reduction measures are stated on the label, each user is obliged to adhere to the risk mitigation measures or the prescribed limits. Hazards and risks to be considered in the risk assessment arise from the actual conditions of use provided for an individual plant protection product, and they are different for different plant protection products.
7.2 Human exposure

7.2.1 Types of hazards and risks of use of plant protection products

During production, use and application of plant protection products, there is always the possibility of exposure of humans and animals, as well as of side effects in the environment, and much later through the treated plants, food and the environment, human exposure and potential adverse effects on human health and the environment may occur. A plant protection product may have harmful effects on human health or cause poisoning, which means that a disturbance or damage to the organs and organ systems in the body occurred after the exposure. **Acute poisonings** occur after a single short-term exposure to a plant protection product during its use, and the signs and symptoms of poisoning develop rapidly, i.e. after several minutes or hours, depending on the manner of exposure to the active substance in the plant protection product. **Chronic poisonings**, signs and symptoms appear after the long-term (several weeks, months, years) or repeated exposure and it is therefore difficult to detect the relation between the exposure and possible damage to health.

It is important to know that each exposure does not necessarily mean poisoning as well, but that there is a risk of exposure to the plant protection product and its impact on human health. The health risk is dependent on the plant protection product itself or on its hazardous properties and the exposure, the amount, manner and time in which a person is in contact with the plant protection product. Long-term exposure to a plant protection product which has no hazardous properties does not represent a major risk to health. Short-term exposure to a hazardous plant protection product may result in damage to health, which of course means that the risk during its use is significant and that appropriate risk mitigation measures shall be taken. The effects of chronic exposure are very difficult to detect, therefore, regardless of the toxicity of a particular plant protection product, unnecessary exposure to humans and the environment shall always be avoided. The risk of poisoning depends on the health status and previous diseases, especially of skin and internal organs (liver, kidney and nervous system) which causes different sensitivity in individuals. As a rule, children and elderly persons are more sensitive. Particular care shall be taken to avoid unnecessary exposure of pregnant women and nursing mothers, since some plant protection products may have harmful effects on the fetus, and some also pass into the breast milk.
7.2.2 Hazardous properties of plant protection products

Plant protection products are labelled and classified in the same manner as all other chemicals on the basis of characteristics that can cause adverse health effects.

Plant protection products can be classified and labelled as:

a) very toxic, toxic or harmful: can cause death, acute or chronic damage to health, if ingested, inhaled or in contact with skin;
b) caustic (corrosive): may cause burns in contact with skin and mucous membranes;
c) irritant: may cause irritation and inflammation in contact with skin or mucous membrane;
d) allergenic (sensitising): may cause hypersensitivity reactions upon inhalation or skin contact;
e) carcinogenic: may cause cancer or increase its incidence if swallowed, inhaled or in contact with the skin;
f) mutagenic: may cause heritable genetic damage or increase its incidence if swallowed, inhaled or in contact with the skin;
g) reproductively toxic: may cause or increase the potential for non-heritable adverse effects on offspring, disrupt male or female reproductive functions or have harmful effects on fertility, the fetus or offspring if swallowed, inhaled or in contact with the skin.

Chemicals labelled as flammable, oxidising and explosive also pose a hazard to health, however, plant protection products rarely have such properties.

In addition to the type and quantity of the active substance, toxicity of a plant protection product also depends on the type and amount of additives in the formulation, as well as on the formulation.

All symbols and signs warning users on the hazards of a particular plant protection product use shall be stated on its label. Detailed information on safety measures at work, personal protective equipment, symptoms and first aid measures in case of poisoning are listed on the label or in an accompanying sheet which is an integral part of the label for each package of the plant protection product. For professional users, comprehensive safety information can be found in the Safety Data Sheet, which can be requested from the manufacturers, seller, and is also available on the website of the Croatian Institute for Toxicology and Antidoping (www.hzt.hr).
The harmful effect of a plant protection product on human health also depends on the method and duration of the exposure, the amount (dosage) that came into contact with the skin or mucous membrane and was then reabsorbed into the bloodstream and enters the tissues and organs. A plant protection product dosage which does not lead to harmful effects is determined via the experiments on animals, and based on that value, the permissible exposure level for humans during the application is determined.

In the process of plant protection product registration, the exposure assessment shall be performed separately for the following categories:

- for the operator,
- for the employee entering the treated area after the application,
- for other persons present (accidentally exposed passers-by, officials etc.) and
- for residents living near the area where the plant protection product is applied.

The exposure assessment is performed using mathematical models of exposure for each application method (e.g. for a tractor and backpack sprinkler, outdoors and in the protected areas, on crop farming areas and in orchards, etc.) or, if that is not possible, through a direct measurement of exposure during the application using experiments in the field. The exposure level assessed in this manner shall not exceed the previously determined permissible level of exposure because placing of the plant protection product on the market shall not be allowed in such case. This procedure of comparison between the permitted and estimated exposure level is an integral part of the risk assessment and ensures that during the proper application of plant protection products in accordance with the instructions for use, excessive, possible harmful exposure does not occur. If the application is not in accordance with the instructions on the label, there is a risk of excessive exposure and even of the occurrence of poisoning and adverse effects on human and animal health.

In addition to the risk and safety phrases (R and S, recently H and P phrase), the label may state special phrases as well (so-called SPo phrases) relating to protection measures at various stages of handling and application of a plant protection product, as well as the required personal protective equipment (clothing, gloves, masks, etc.). These signs shall be observed already during the selection of a suitable plant protection product so as to, if possible, select the one which is less harmful and easier to use.

For certain plant protection products, the label may specify an operation prohibition, i.e. a period during which entrance into the treated area without personal protective equipment is not permitted due to the danger of excessive exposure, as well as the period in which the entrance is prohibited to domestic animals. The operation prohibition is usually expressed in hours.

If the label of a plant protection product states the warning that it is intended for "professional users for professional application", this means that only certain categories of professional users can buy and handle it.

During handling and application, the biggest exposure is through the skin, especially of the hands. Handling a plant protection product during the preparation of spray mixture (opening the packaging, mixing and filling the sprinkler tank) represents the greatest risk of excessive exposure although the exposure time that is relatively short. During the application itself, the exposure is generally much lower since most of plant protection products are used heavily diluted with water (as spray mixtures). Since the function of the skin is to protect the body from external influences, only a small portion of a plant protection product which comes into contact with the skin shall penetrate into the deeper layers and enter the body. This means that the general signs of intoxication rarely occur after the contact
with skin, however, localised damage may appear on the skin at the point of contact with the plant protection product if it has dangerous properties of irritation or causes allergic reactions. Some plant protection products containing organophosphorus insecticides may also enter the body through the skin in an amount sufficient to cause poisoning, especially if they are formulated in the form of an emulsifiable concentrate (EC) since the solvent content enhances the penetration of organophosphorus compound through the skin.

During handling and application of plant protection products, the respiratory system is an important point of entry into the body, as well as a possible target for their harmful effects. During the preparation and application, gases, vapours, dusts and aerosols containing one or all of the formulation components - from the active ingredient to the solvent and other substances present in the formulation, and finally in the spray mixture, may be inhaled. Gases and vapours, depending on the particle size, as well as aerosols and dust, can also penetrate to the lungs and thus enter the bloodstream and cause poisoning symptoms. Only localised reactions at the respiratory system itself are also possible. Due to duration, the highest level of exposure occurs through inhalation during the application of a plant protection product, which due to high dilution rarely leads to excessive exposure or poisoning symptoms. However, certain plant protection products may be readily volatile or contain volatile solvents which mostly evaporate during plant protection product handling. Therefore, attention shall be paid to signs R 20 (H 332) or R 23 (H 331) or even R 26 (H 330) which indicate that a plant protection product is harmful or toxic if inhaled and apply the prescribed respiratory protection measures.

**Ingestion** is a less important manner of entry into the body during handling and application, although one shall refrain from smoking and eating and drinking during operation or from poor hygiene after the operation since in that case the risk of contamination and the unwanted entry of a plant protection product into the body exists. In a single exposure even such negligent behavior shall rarely cause severe poisoning symptoms, but chronic adverse effects can not be excluded after months or even years of exposure. Poisoning through the ingestion of plant protection products usually happens by accident, as a result of improper storage (together with food and drink, easily accessible to children, in poorly labelled non-original packaging), and in such case the victims are mostly children. Due to relatively low toxicity of plant protection products which are currently on the market and very small amounts of the ingested plant protection product in most cases, such unintentional poisonings often do not have severe consequences even though they require medical supervision. In addition to accidental poisonings, suicide attempts by ingestion of plant protection products are also possible, when the amount of the ingested plant protection product is significant (from few sips to several deciliters), therefore the likelihood of serious poisoning is significant and fatal outcome is also possible.

Speaking of exposure by ingestion, it is important to point out the **dietary exposure**, i.e. through residues of plant protection products which enter the food chain of animals and humans through treated plants and to which all of us are exposed through the consumption of food of plant and animal origin. The plant protection products users have a great responsibility in protecting the health of consumers since the level of residues in food depends directly on their adherence to the instructions for use of plant protection products.
7.2.4 Symptoms and signs of poisoning and first aid measures

7.2.4.1 Symptoms and signs of poisoning with plant protection products

Excessive exposure of humans to plant protection products can cause localised damage or reaction at the very point of contact with the skin or mucous membranes, and also entrance to the body and distribution to tissues and organs through the bloodstream, causing the so-called systemic poisoning.

**During skin contact,** a plant protection product may cause damage to the skin, which usually occurs after a prolonged or repeated exposure. Such localised skin reactions range from redness, itching, swelling and various rashes to drying and cracking of skin and occurrence of wounds, and scars and dark coloration or discoloration of the skin may remain as permanent consequences. The cause may be skin irritation, decreasing and removal of its protective horny layer followed by inflammation that can also be turned into a chronic dermatitis which shall continue even after the cessation of exposure. Another type of reactions are allergic reactions, which are relatively rare on plant protection, and they are also visible as rash, redness, itching and blisters on the skin which retreat during several days after the cessation of exposure, but may reoccur in repeated contact with the same or similar plant protection product, sometimes in a more severe form. Plant protection products containing pyrethroids can irritate the skin in a manner that a burning sensation and tingling can be felt, especially on the face skin, but with no visible changes to the skin. This is a local effect on the nerve endings in the skin which spontaneously retreats several hours after the end of exposure, without permanent consequences.

In case of direct contact (for example, accidental splashing during the spraying of the mixture preparation), plant protection products may have a very irritative effect to the eyes and cause burning, tearing, redness, pain and swelling of the eyelid. Certain plant protection products may widen the iris and cause blurred vision, but such reactions are generally short-termed and are not a sign of systemic poisoning. The resorbed amount of a plant protection product after the contact with eye is generally too small to cause other symptoms besides the localised short-term eye damage.

**Inhalation** of plant protection products can also cause localised reactions, most often due to irritation of the nose, throat and bronchi accompanied by burning, coughing, sneezing and even serious reactions with difficulty in breathing and suffocation, which are fortunately quite rare in the plant protection products application. Allergic reactions in the form of bronchoconstriction, asthma and even anaphylaxis are also possible, but are extremely rare. The active substances and plant protection products which have been proven to cause oversensitivity of the respiratory system cannot be granted a licence for placing on the market or are withdrawn from the market, if such a threat has been confirmed subsequently. Certain active substances such as organophosphorus insecticides may be absorbed through the lungs into the bloodstream in sufficient quantities to cause systemic poisoning symptoms. Fumigants which act as gas and vapours can also cause severe systemic poisonings in which the symptoms of irritation, warning the exposed person to danger, can be very mild or completely absent.

After **ingestion,** depending on the amount and type of a plant protection product, symptoms of poisoning, which can range from only digestive problems (nausea, vomiting, diarrhea) to serious organ damage and even death may develop within a few minutes or hours. The absence of poisoning symptoms immediately after ingestion does not mean that the poisoning symptoms shall not occur later, therefore a physician shall be consulted in each such. Ingestion of the spray mixture can lead to poisoning only exceptionally, due to the high dilution.
Chronic poisoning with plant protection products generally occurs only with the people employed in the active substances and formulation production, if they are exposed to excessive concentrations of active substances and/or additives on daily basis. With proper application of plant protection products, there is no danger of excessive exposure, thus the risk of chronic damage to health is reduced to a minimum.

With the advancement of science, the requirements regarding the safety of plant protection products for humans and the environment are becoming increasingly more strict and are constantly improved. Due to strict legislation, plant protection products suspected to cause cancer or genetic damage, to have adverse effects on fertility or accumulate in the body and cause damage to health after a long-term exposure are no longer permitted and may not be placed on the market in Croatia and European Union states.

It is also important to know that the symptoms of poisoning with plant protection products are not specific for each individual plant protection product or group of plant protection products and are difficult to identify if there are no reliable information on the type of the plant protection product a person was exposed to, the time and manner of exposure. Moreover, if health problems arise during or after the application, this does not necessarily mean that there is a harmful effect of the plant protection product, but it may be caused by some other health disorder.

7.2.4.2 First aid measures

The first and most important first aid measure is the termination of exposure. This means that the victim shall immediately be taken out from the treated area or into the fresh air if the poisoning occurred in a protected area. The protection of the rescuer, who shall use protective gloves and a mask or half-mask for respiratory protection, shall thereby be taken into consideration. Rest shall be provided, the respiratory tract shall be freed (unbutton tight clothing) and, if necessary, the injured person shall be warmed up. The unconscious person shall be laid in the left lateral position, respiratory tract shall be freed (remove dentures, clean the mouth of food remains or vomit), breathing checked and, if needed, CPR shall be initiated. If the accident occurred during fumigation or through the ingestion of a plant protection product, when CPR could endanger the rescuer, CPR shall be limited only to the external continuous chest compression. Never administer anything by mouth to the unconscious person. With poisoning by ingestion, if the person is conscious and willing to cooperate, rinse their mouth with water or give no more than one glass of water to drink. Do not give any milk or alcohol. Do not cause vomiting neither by the irritation of the palate or through giving salt water or any other substance. Immediately contact the National Protection and Rescue Directorate (112) or a physician and listen to their advice until the arrival of emergency medical assistance or transportation to a medical institution. If a severe poisoning or only suspected poisoning occurred, it is also advisable to consult the Poison Control Centre (phone 01/2348 342) which can provide useful advice on the procedure in case of possible poisoning or excessive exposure to plant protection products.

After the vital functions have been secured or if only contact with skin and eyes occurred, decontamination shall be initiated. All contaminated clothes and shoes shall be removed immediately, liquid plant protection product or residues of powder or granules of solid plant protection products shall be wiped off, and skin shall be thoroughly washed with warm water and, if possible, mild soap, also taking into account the skin folds, nails, and hair if needed. Do not rub or otherwise mechanically damage the exposed skin. Do not use any means other than water for rinsing. If redness and other signs of skin damage are visible, do not apply any wraps or ointments, only cover with gauze and seek medical advice. If a plant protection product or spray mixture splattered into the eyes, the eyes shall be rinsed immediately with a gentle stream of clean and, if possible, warm water, so as to first remove the possible contact lenses by water, then part the eyelids gently using the thumb and index finger and
then initiate rinsing. The water stream from the tap or the container is directed into the inner corner of the eye, and the head is tilted to the side so that the stream flows over the cheek, thus preventing the contamination of the other eye. If both eyes require rinsing, the stream shall be directed towards the base of the nose. If the plant protection product which came into contact with the eyes is marked by the symbol C (corrosive), continue rinsing for 15 minutes. Do not use any means other than water for neutralization or rinsing. After completing the rinsing, seek advice from a physician or Poison Control Centre. It is thereby necessary to convey as accurately as possible the medical information on the type of the plant protection product or more of them, and in case of a transport to a medical institution, bring the packaging or the label of the plant protection product if possible, or provide the physician with the information on the name of the plant protection product so that the doctor can find the label in the web search engine of the registered plant protection products in Croatia (http://fis.mps.hr/trazilicaszb/)

7.3 Hazards and risks during the special conditions of use

Sprinkling outdoors using tractor sprinklers is the usual method of plant protection products application, which also includes the preparation of the spray mixture. The greatest risk of exposure is present when handling a plant protection product during the preparation of the spray mixture, and if strong foaming occurs, the operator may be exposed to the spray mixture when filling the sprinkler container as well. In orchards and vineyards, dispensers (atomisers) are also used, with which the greater exposure of the head and the upper body occurs due to spray mixture drift, which shall be taken into consideration when selecting personal protective equipment (head cover, protective clothing, goggles, mask...). Maintaining the outer and inner parts of the application equipment and personal protective equipment clean shall prevent secondary contamination of the skin. The backpack sprinkler is often used for low crops, whereby a greater exposure of the lower body and legs occurs, and it shall be particularly taken careful so as to ensure that the spray mixture does not soak the clothes on the operator’s back due to improper closing of the spray mixture container, since possible skin damage or even the appearance of general symptoms of poisoning may occure due to the long contact period and increased absorption under the layers of clothing. Certain application methods, such as fogging or the use of the high pressure application equipment, create smaller droplets which therefore penetrate deeper into the respiratory system, thus such application method requires adequate respiratory protection. In addition to acting in the form of vapour or gas which can be easily inhaled, the fumigation agents also contain highly toxic compounds (phosphine or even hydrogen cyanide), therefor the unauthorised and incompetent application may endanger the life not only of the operators, but also of other exposed persons. During the application of plant protection products in a protected area (hothouses, greenhouses) with poorer ventilation and at elevated temperatures, there is a possibility of excessive exposure through skin and inhalation. Such exposure is possible during the application and the entry of other employees, as well as activities on the treated plants before the spray mixture has dread and if the premises have not been properly ventilated. In all of the aforementioned cases, the label shall clearly indicate the risks of exposure and recommended appropriate personal protective equipment (protective clothing, masks, gloves...) for both the operator and the employee. The plant protection products used to treat soil shall also be taken in consideration, therefore, the operation prohibition and the necessity to perform the activities wearing the protective suit and gloves shall be checked during processing or, for example, during florist production when planting the flower pots.
7.4 Emergency protective measures in case of accidents

7.4.1 Emergency measures to protect human health and the environment

In case of leakage or spillage of a plant protection product or spray mixture, including water resources in case of accidental spillage or leakage and contamination, and in extreme conditions where washing of a plant protection product may occur, emergency measures to prevent harmful effects on humans, animals and the environment shall be taken. Instructions on the procedure in case of accidents are listed on the label or the accompanying sheet of the safety data sheet.

In case of an accident in a closed and protected area, all persons entered the contaminated area shall be protected first. Before entering, personal protective equipment (rubber boots, protective suit, protective gloves) and a filter half mask or a mask for protection against particles in the case of powder mixture or granules shall be put on, and in case of plant protection products containing solvents, a mask with the appropriate filter.

In case of larger amounts from the damaged container, transfuse a plant protection product into the functional container using a pump in a safety mode. Sprinkle an absorbing material (e.g. sand, dry earth, sawdust) over the spilled plant protection product and collect it thoroughly into the container designed and labelled for that purpose. After that, wash the contaminated surfaces with water and detergent or 5% water solution of sodium hydroxide, which shall also be disposed in the container with the collected plant protection product residues after use.

In case of spilling the spray mixture or a large amount of plant protection product, the spilled liquid shall be enclosed by dams and then collected into a suitable container. The collected spray mixture or a plant protection product shall be collected separately into the suitable, labelled containers, which may be tightly closed. Contaminated items and floor shall be thoroughly washed with water with detergent or 5% water solution of sodium hydroxide and rinsed with clean water, while observing the environmental protection regulations.

The collected material is delivered to the person authorised for the collection or disposal of hazardous waste. After cleaning, remove contaminated clothing and other personal protective equipment, and wash skin with soap and water.

In case of an accident in the outdoor area other than the aforementioned, the plant protection product shall be prevented from entering deeper layers of soil by placing sand dams, barriers or by digging canals. If the plant protection product is easily soluble in water and tends to wash, the use of water in firefighting and cleaning of contaminated surfaces shall be avoided. In such conditions, water becomes a medium by which a plant protection product is washed into the deeper layers of the soil and ultimately into groundwater. Plant protection products shall not be discharged into sewage, surface water and groundwater.

If the area has been affected by a fire, extinguishing with a water spray, foam, powder or CO2, shall be initiated immediately, and exceptionally by water jet, according to the instructions on the label or safety data sheet, with mandatory use of personal protective equipment for respiratory organs (self contained breathing apparatus with open or closed loop).

In case of an accident during transport, the vehicle engine shall be turned off, the event location secured and other traffic participants warned. In addition to the mandatory use of personal protective equipment, the damaged packaging shall be separated from the undamaged one. Collect the spilled plant protection product and place it in a special package, and sprinkle the absorbing material over the
spilled liquid plant protection product and collect it into a suitable container as well. In case of fire, immediately initiate extinguishing and request assistance from the fire brigade. Report to the nearest police station on the accident. In case of poisoning, provide first aid and contact a doctor. In the case of contamination of rivers, lakes or drainage, inform the National Protection and Rescue Directorate (112).

7.4.2 Medical supervision and the possibility of emergency alarm in case of an accident

The employer shall enable the agricultural employees applying the plant protection products and working in the treated areas with adequate medical supervision, i.e. provide periodical medical examinations, depending on the risk assessment for specific jobs. Agricultural workers shall inform the family physician on the use of plant protection products, who shall decide on prospective regular or special medical examinations. Useful information in case of suspicion of damage to health due to exposure to plant protection products can be also obtained from the 24-hour information service of the Poison Control Centre at the phone number (01)/23 48 342. In case of an accident and suspicious events, the National Protection and Rescue Directorate (112) shall be contacted immediately, which shall continue to coordinate other necessary services, including emergency medical assistance.

7.5 Risk mitigation measures

7.5.1 Personal protective equipment

The use of personal protective equipment is one of the main risk mitigating measures when handling the plant protection products which enables safe work to the operators and agricultural workers.

When handling the plant protection products, the following personal protective equipment can be used: protective clothing, protective apron, protective hat or hood, protective footwear, face shields, safety goggles which adhere tightly, protective filter mask or half mask and during the special operating conditions, self-contained breathing apparatus as well. The need for the use of personal protective equipment and their selection primarily depends on the instructions on the label and/or the accompanying sheet of a particular plant protection product. If the instructions do not specifically state the material of which the personal protective equipment is made, the safety data sheet for the plant protection product shall be requested and the instructions provided in Section 8 (Exposure controls and personal protection) shall be followed or the information from the plant protection product or personal protective equipment manufacturer, representative of the manufacturer or distributor shall be requested. Resistance of the material the personal protective equipment is made of can also be verified by spilling a plant protection product over a piece of equipment and leave it to the product effect for the approximately same period as we intend to use that part of personal protective equipment. If there is a change in the material colour, softening, solidification, porosity, appearance of bubbles or the material begins to melt or becomes gelatinous, stiff or brittle, such personal protective equipment is not suitable for the operation with the plant protection product for which it was tested.

Basic safety requirements to be met by personal protective equipment are prescribed by the Ordinance on Placing of Personal Protective Equipment on the Market, which divides them into three categories:

- Category I (for minimal risk): personal protective equipment of simple design for which the manufacturer or their authorised representative predicts that the user can assess on their own the level of provided protection against minimal risks, and whose effects, if they are gradual, can be safely determined in a timely manner. This type of protective equipment is not suitable for work with plant protection products.
- Category II (for medium risk): This type of equipment is suitable for work with the majority of plant protection products other than those designated as toxic or very toxic.
- Category III (for high risk): personal protective equipment of complex design intended for the protection against mortal danger and dangers that may seriously and irreversibly harm the health and whose immediate effects, provided for by the manufacturer or their authorised representative, cannot be identified by the user in a timely manner. It is suitable for protection when handling toxic and highly toxic plant protection products.

Each part of protective equipment shall be marked by the category number and the CE mark, with which the manufacturer guarantees that the equipment has been manufactured in accordance with the provisions of the Ordinance.

7.5.1.1 Protective clothing and head covers

Protective clothing covers or replaces personal clothing and provides protection against one or more risks that may pose danger to the safety and health at work. It shall be marked in such a manner so as to indicate the name (e.g. protective suit) and the name of the clothing manufacturer, trade name and number, the number of the specific norm according to which it was manufactured (e.g. HRN EN 340), a pictogram that indicates a specific hazard and the level of protective action, as well as the manner of maintaining the clothes. Protective clothing can be a one-piece, in the form of coveralls, or two-piece and of appropriate size so as to be comfortable enough and not to adhere to the body excessively (Figures 7.1 and 7.2). Long trousers and a shirt with long sleeves shall be worn beneath it. When handling toxic or corrosive plant protection products, impervious protective clothing resistant to chemicals and water shall be worn. If such protective clothing is not available, an apron resistant to chemical which extends from the neck to the knees shall be worn while preparing the spray mixture. Some protective clothing and coveralls also have a hood which serves as the head and neck protection. If the hood is not used, it shall be bent along the neck in order to prevent the accumulation of a plant protection product. Other head covers resistant to chemicals may be used for the head and neck protection, such as plasticised hat with a wide brim. Caps or hats made of cotton or similar fibers are not a suitable protection since they absorb substances and cannot be thoroughly washed after the use.

Figures 7.1 and 7.2: Protective clothing, footwear, gloves and masks (source: https://www.fluegel-gmbh.de)
Due to its impermeability, clothes resistant to chemicals can be very warm, therefore work shall be adapted so as to avoid heat stress (work during the cooler part of the day, more rest, taking enough fluids). After completing the work, before removing the protective clothing, it shall be briefly rinsed with water on the outside, especially in the areas contaminated with the agent or spray due to spilling or direct contact. The protective clothing shall then be taken off and stored in a sealed plastic bag until washing. While taking it off, care shall be taken so as to prevent contact of the contaminated parts of the protective clothing with the skin. Protective clothing shall be maintained and regularly washed after each use, separately from other laundry, using a pre-wash cycle of a washing machine and intensive washing with a strong detergent. If the protective clothing was heavily contaminated with plant protection products, the washing process shall be repeated. After washing, the washing machine shall be flushed by initiating a washing cycle with detergent, but with no laundry. Protective clothing shall be stored in a dry and well-ventilated room, separately from other clothing. If the contamination of clothing worn underneath protective clothing occurs, it shall also be taken off after work and stored in a sealed plastic bag until washing.

7.5.1.2 Protective footwear

When working with plant protection products, footwear which completely covers the foot and has a rubber sole shall be used. Shoes or boots shall be chemical resistant (HRN EN 13832) when handling the plant protection products. When performing sprinkling, the trouser legs shall cover shoes in order to prevent seeping of spray mixture into shoes. Before taking the shoes off, the outer part of the shoe shall be cleaned with water.

7.5.1.3 Protective gloves

Appropriate hand protection is achieved by wearing gloves resistant to chemicals that do not leak water, mineral oils and organic solvents (HRNEN 374). Most often, these are gloves made of nitrile rubber, beneath which another pair of thin nitrile gloves may be worn when handling plant protection products containing organic solvents (EC formulations). It is also recommended the use of gloves marked with CE certificate from Category II or III of personal protective equipment. All gloves shall have appropriate labels, on the gloves themselves, on the packaging and in the operating instructions (7.3, 7.4, 7.5 and 7.6). Mandatory Labelling for the gloves of Category II shall include the name of the product and the manufacturer, size, operating instructions, CE label and pictograms indicating the scope of application with the resistance marks and the relevant standard. For Category III gloves, the number of the certifying body, which performed the product quality control, shall also be indicated.

Figure 7.3: Example of gloves labelling (source: http://www.hzzzsr.hr/index.php/sigurnost-na-radu/osobna-zastitna-sredstva/138-zaštita-ruku)
The recommended length of the gloves is up to the middle part of the forearm, whereby the sleeves of the protective clothing shall be pulled over the glove and buckled. When working above the head, the gloves are worn over the sleeves of the clothing and folded outwardly at the ends in order to prevent the seeping of the plant protection product down the arm. Procedures for handling plant protection products in which wearing gloves and other personal protective equipment is mandatory are listed on the label in the form of special safety precautions for operators (SPo label). The most important thing is to wear the gloves when handling an undiluted plant protection product, during the preparation of the spray mixture, pouring of a plant protection product into the container of the application equipment and adding water into the application equipment container since in those cases the greatest possibility of contamination exists. Irritative and allergenic properties of plant protection products are most significant before dilution. Gloves shall not be placed on wet hands, nor can the gloves which are damaged or which have their inner surface contaminated with a plant protection product be used. Before their removal, the gloves shall be washed with water and removed without touching the outer surface. Before and after using the gloves, hands shall be washed with soap and water, and it is also useful to apply a protective hand cream after completing the work. During the application of plant protection products with a tractor sprinkler, it is important not to enter the cabin wearing the gloves contaminated with a plant protection product, since in that case it would contaminate the entire interior of the cabin and thus increase exposure.

1. Indicates water resistance and low chemical resistance;
2. Indicates high chemical resistance (drawn by: R. Turk)
7.5.1.4 Respiratory protection

Personal protective equipment for respiratory protection shall be used in accordance with the warning signs and notifications on the label and the accompanying sheet of each plant protection product. The use of a mask or half mask is mandatory if the label of a plant protection product indicates the warning signs R 20 (H 332) or R 23 (H 331) (hazardous/toxic by inhalation) or R 37 (H 335) (irritates the respiratory tract) or appropriate information signs (for example S 39 or SPo) which require respiratory protection. It is also recommended when working in or entering the protected areas (hothouses, greenhouses) after treatment, as well as when handling the treated seed. The label of a plant protection product most usually indicates the use of a disposable filter half mask (or a so-called respirator) for the protection against particles (Figures 7.7 and 7.8) covering the nose and mouth and it is indicated by the acronym FF (HRN EN 149), and the most commonly recommended filter is a filter for the protection against particles. Depending on the efficiency, the filters with low (P1), medium (P2) and a high ability to capture particles (P3) are used.

![Figure 7.7: Disposable half mask with a filter for coarse dust FF P1](https://www.fluegel-gmbh.de)

![Figure 7.8: Filter half mask for fine dust FF P2](https://www.fluegel-gmbh.de)

When applying the plant protection products which contain solvents or are readily volatile, a protective half mask (HRN EN 140) or mask (HRN EN 136) shall be used with the appropriate filter for the protection against gases and vapours, or with a combination filters for the protection against gases, vapours and aerosols (Figure 7.9 and 7.10). For the proper use and maintenance of the mask, the operating instructions shall be followed and the expiry date of the filter shall be checked. When the filters are saturated, they shall be replaced, as well as if breathing difficulties occur or the scent of the plant protection product can be noticed while wearing the mask. The filters shall be regularly replaced at least once a year. After use, the mask shall be cleaned according to the manufacturer’s instructions and kept in a cool, dry place, packed in a plastic bag.
7.5.1.5 Protective goggles and face shields

When handling certain plant protection products, eye protection equipment (Figure 7.11) is prescribed, of which the best protection are goggles with good adherence, and goggles with protective sides and face shields are also used. A full face mask also provides equally good eye protection. While mixing during the preparation spray mixture, there is a greater possibility of splashing, therefore shield, which covers the entire face, provides better protection. During the application of plant protection products when the exposure to the spray mixture mist is increased, googles with good adherence provide better eye protection. After use, wash the googles and face shield in warm soapy water.

Authors: Nenad Novak, M.Sc., Gorana Peček, Ph.D.
After the application of pesticides (plant protection products, veterinary medicinal products and biocidal products) on the treated plants, products of plant and/or animal origin, the residues remain which may have a harmful effect to human and animal health. Residues may include active substances that are currently used or were used before, their metabolites and/or degradation products, reaction products and impurities. In case of the opinion that the residues in food are toxicologically significant, the assessment of exposure and risk of people ingesting the pesticide residues through food shall be performed.

Following the proper dosages for application, number and timing of treatment, adherence to the waiting period and applications only to those cultures for which the plant protection product has been approved shall influence whether the residues shall be in accordance with the maximum residue levels for pesticides (MRLs) or they shall be found in food in inadmissible concentrations that could potentially threaten the health of consumers, especially of vulnerable groups such as children, pregnant women, the sick and the elderly persons.

The pesticide residue level depends on the amount of the applied plant protection product, the agricultural crop, the shortest period that has passed since the last treatment of the culture, i.e. the waiting period, the number of applications and the physical and chemical properties of a plant protection product.

The waiting period is a period counted in days, which shall pass after the last application of a plant protection product until the harvest or picking. The safety interval is required in order for the applied plant protection product to decompose, for the purpose of not exceeding the prescribed MRL at the time of harvest/picking. The waiting period is prescribed for each plant crop separately and is determined according to the properties of a plant protection product, method of use, the amount of product applied and the metabolism of the active substance in plants. The waiting period of the same plant protection product thus differs for different cultures.

Operating prohibition is the time that shall pass after the application of a plant protection product before the workers may enter the treated area again. It is determined on the basis of a risk assessment regarding the exposure of workers, and depending on the hazardous properties of a plant protection product, the manner of use and the amount of application for certain plant protection products.

It is also possible to impose the operation prohibition for animals, which time limits the entry/grazing of domestic animals in the treated area. Operating prohibition is usually expressed in hours for humans or days for animals.

In order to protect the consumers from the exposure to unacceptable levels of pesticide residues in food and feed, the MRLs are determined. These values are prescribed in the Regulation (EC) No. 396/2005 and the related amendments, and they apply equally to all member states. The MRL value is the safe, legally permissible concentration of pesticide residues, expressed in mg/kg of food, which shall not be exceeded if a crop protection product is applied in accordance with the directions on the label. Increasing the plant protection product amount of application in relation to the approved amount stated on the label and/or increasing the number of applications causes elevated residues in or on treated plants and products. Failure to comply with the waiting period enables the occurrence of residues exceeding the permissible ones at the time of harvest or picking on the treated plants. In case of application on the plants for which the application of a plant protection product has not been approved, pesticide residues in food for which it is not known how they shall affect the health of humans and animals may occur.
The MRL values are determined during the approval of active substances at the European Union level or in the process of a plant protection product registration according to the results of residues research for the proposed application, and they are later amended in regulations as required. The MRL values are determined according to the intended application of a plant protection product, on the basis of outdoor experiments or experiments in a protected area, in where the highest residue values are expected, i.e. during critical applications. Critical application takes into account the maximum proposed amount of a plant protection product, the maximum number of applications, the minimum time interval between two applications and the shortest waiting period. Maximum expected residues are also verified with respect to the safety of consumers as well as a range of toxicological values and data. On the basis of certain maximum expected residues, an assessment of the theoretical maximum daily intake (TMDI) is performed, taking into account the dietary habits of a certain population as well. By comparing the theoretical maximum daily intake with toxicological parameters, it is estimated whether there is a risk of a plant protection product having a harmful effect on human and animal health.

In addition to pesticide residues occurring as a result of the direct application of a plant protection product in/on certain crops (in production, storage and transport), the residues can also be found on the adjacent, untreated crops. The pesticide residues on adjacent crops may occur if the plant protection product is used in windy weather, which causes the drift of spray mixture to nearby cultures.

Failure to comply with restrictions in crop rotation can cause pesticide residues occurrence in following crops due to residues transmission through the soil. The term “residues arising from unauthorised application” means the residues of those pesticides whose application for a particular agricultural crop has not been approved. For example, in case of the herbicide which has been approved for use in corn only, meaning that it is not permitted in other crops, if after application the residues of that herbicide occur on the following culture in the crop rotation (wheat, barley, rye), those are the residues arising from an unauthorised application.

8.1 Types of hazards and risks

Human exposure to pesticide residues is mostly caused by the consummation of food that has been treated with plant protection products or which was in close contact with the treated area. In addition to fruits and vegetables which were directly treated with plant protection products, pesticide residues may be located in industrially or domestically processed food and in food of animal origin. In order to minimise the harmful effect on the health of consumers, the restrictions and prohibitions are prescribed, as well as measures of good agricultural practice.

Pesticide residues are not considered relevant if they may be found at the time of harvest/picking on the treated plants in concentrations below the limits of analytical determination (LOD/LOQ). This is a usual case with the application of herbicides, the application of contact insecticides and fungicides applied before flowering in orchards or in seed treatment. In such applications, the undetected residues are the consequence of the active substance properties, the method and time of application, quantity of the applied plant protection product and the active substance metabolism. Due to early implementation, the period from the application of plant protection product until the harvest/picking is long enough and the active substance has time to be metabolised into its degradation products (which are not of toxicological concern). In such applications, the waiting period is often ensured through the application time (OVP) and it is not necessary to define it in days. However, in such cases, the residues are not hazardous to humans but can pose a risk during animal nutrition.
In contrast to the early application of a plant protection product, the application before the harvest/picking may lead to a higher concentration of residues (higher than the limit of determination, or even MRL values) in/on treated crops or parts thereof intended for consumption. In such applications, it is especially important to follow the instructions for the application, i.e. to apply a certain number of days before the harvest/harvest, so as not to increase the intake of pesticide residues through food consumption, which increases the risk for human health due to exposure to pesticide residues.

In assessing the risk to humans due to exposure to pesticide residues through food consumption, the data on plant protection product residues are compared with the toxicological reference values of the acceptable daily intake (ADI) and acute reference dose (ARfD). The acceptable daily intake is the substance amount that can be introduced into the body every day over a lifetime without adverse effects. The acute reference dose is the substance amount that can be introduced into the body through one meal or during one day without adverse effects.

With respect to the safety of food consumption, a certain type of food is considered safe for the consumers if the estimated intake of a harmful substance does not exceed the ADI or ARfD value. The simplified comparison is shown in Figure 8.1.

![Figure 8.1: Risk assessment through the comparison of the exposure to pesticide residues with toxicological reference values (prepared by: D. Čelig)](image)

When assessing the exposure, in addition to the data on the residues concentration, the data on the consumption of certain food type are also taken into consideration, knowing the nutritional habits of a certain population.

It shall be noted that the risk of exposure to pesticides is currently estimated for an individual active substance/product combination (of plant/animal origin, before and after industrial processing). The cumulative risk of exposure to a mixture of several active substances has not been possible to assess yet.

**8.2 Impact on humans and animals**

Pesticide residues in food have no nutritional value and can potentially pose a risk to human and animal health. Humans can also enter the pesticide residues into the body through food of animal origin. Domestic animals can be exposed to pesticide residues in three manners:
- through direct application to animals (veterinary medicinal products and biocidal products),
- through feed and
- by using treated crop residues for litter.

If the animals feed on the treated crops, there is a possibility for the pesticide residues to be entered into the animal body. Residues can be transferred into meat, milk, eggs and edible offal through animal nutrition. MRLs for pesticide residues are also determined for food of animal origin.

The physiological processes in the animal body can store the active substance and/or metabolites, distribute them throughout the body, decompose and/or eliminate them. Metabolism of active substances in the domestic animals organism changes their structure and toxicological properties. In some cases, a plant protection product may show toxic effects on the animals only after it has been converted into a more reactive form by the animal metabolism.

Effects on animals are determined by the chemical composition of a plant protection product, activity metabolism and manner of decomposition in animals. All animals do not respond to all the pesticides in the same manner since a reaction may be specific to the species or individual. One animal species may metabolize the pesticide to non-toxic metabolites while the other species may not.

Intake of pesticide residues in the human body through nutrition depends on the level of present residues in/on food and on the amount of consumed food, which contains pesticides residues. The risk of exposure to pesticide residues is thus higher in children, as opposed to the exposure of most adults. In relation to their body mass, children generally eat more than adults do, therefore they may be more exposed to certain pesticide residues due to their different nutrition. For example, children consume larger quantities of milk, apple puree or orange juice. If the amount of entered residues is counted per kilogram of body mass, the amount of residues entered through food shall be higher in children than in adults.

8.3 Food preparation and processing

Residues in/on plants and plant products are in many cases unavoidable despite of the plant protection product being applied in accordance with the instructions for use and in accordance with good agricultural practice. Industrial processing and/or domestic preparation of food may lead to changes in the level and type of residues. In some cases, the active substance can be transferred into toxic decomposition products during processing.

During food preparation, the residue levels may be increased, as is the case with the production of oil from the oilseeds and olives, during the fruit drying process or the production of tomato concentrate due to the loss of water during the process.

The residue level usually decreases in the preparatory procedures for processing, such as washing, peeling, blanching, boiling, squeezing, as well as in the process of conservation.

Most insecticides and fungicides are applied directly to the culture, which means that most of the pesticide residues can be found on the outer parts of plants/fruits/leaves, depending on the type and properties of a plant protection product. For example, citrus peel, husks of grain and outer leaves of lettuce, kale or cabbage contain most of the pesticide residues amount. Although pesticide residues may be present in concentrations below MRL values, removing the outer leaves, stripping the fruit skin and washing before processing can reduce the levels of residues in the prepared food.
During processing, toxicologically important decomposition products or residues reaction may occur, for which separate risk assessment is performed. As a research result, it is possible to:

a) determine whether this is the case of reduction or concentration (increase) of the residues in the individual phases of processing and final products and
b) assess the transmission factors.

Since the majority of plants and plant products are processed before consumption, collected real data on pesticide residues are collected through the studies investigating the effects of processing/preparation on the type and level of residues. Through the knowledge on any possible created metabolites, reduction or increase in the residue levels, a realistic risk assessment is enabled, i.e. an estimate of residue intake through nutrition, especially for those products that are consumed after processing (e.g. wine after grapes processing). Figure 8.2 shows schematically the preparation of industrial apple juice. Pesticide residues may be determined at each step, whereby an insight is gained into the actual concentration of residues in the final product.

![Figure 8.2: Schematic representation of the industrial apple juice preparation (prepared by: D. Čelig)](image)

In addition to the possibility of pesticide residues decomposition through processing, the part of the plant containing pesticide residues may be removed during the very process. When the residues concentration is determined in the particular the steps of the industrial process, distribution of residues between edible and non-edible parts of food can be noticed. In this case, higher MRLs may be acceptable if it is clear that the residues in the whole product are destroyed or reduced through food processing (e.g., washing and peeling the apples).
An example of the residue distribution between the edible and non-edible part of food is shown in Figure 8.3. It has been concluded in the implemented risk assessment that the consummation of oranges treated with imazalil poses a risk to human health. Considering that the remains of imazalil can mostly be found on the orange peel, transmission factor was used for the realistic risk assessment. If the orange peel is not used in nutrition, risk to human health is considered to be acceptable. Data on the residues in the industrial processing/preparation provide better, more realistic assessment of exposure to pesticide residues.

Despite the safety standards for pesticide residues, which are allowed in or on food, additional precautionary measures may be taken which can, reduce pesticide residues in food to be bought and consumed. These are some of the suggestions:

- removing the fat from the meat (residues of some pesticides accumulate in the fatty tissue);
- removing the skin from the fish;
- separating the fat from the soups and the fat or oil from roasting;
- thorough washing of fruits and vegetables with water and cleaning with a sponge/brush and peeling, if possible. These safety steps shall eliminate most of the existing surface residues, together with the remaining impurities. Surface cleaning (rinsing and scrubbing) shall not remove pesticide residues from fruit or vegetables that have been absorbed during the growing season;
- cooking or roasting of food can further reduce the residues of some pesticides.

The scope of the assessment of exposure and risk to human health through the intake of pesticide residues via food is summarised in Figure 8.4. After the application of plant protection products, in accordance with good agricultural practice, pesticide residues in/on raw crops used for human consumption and animal feed are assessed. Crops can be consumed raw and/or they can be processed into products such as flour, oil, juice and wine, or can be used as animal feed. What is estimated are the intake of residues through animal nutrition and the distribution of residues in the products of animal origins (eggs, milk and other products). Data on residues in/on plants and plant products, processed products and products of animal origin shall be taken into account in the risk assessment. Depending on the dietary habits of a certain population, the estimated intake of residues is compared
with toxicological parameters and a decision is made on whether the risk arising from the aforementioned products consumption is acceptable for human health or not.

If a plant protection product is applied in larger amounts than the prescribed ones, the risk for human or animal health is increased through the consumption of fruits and vegetables which are raw, prepared by cooking or roasting or processed, as well as through the food of animal origin containing pesticide residues in concentrations higher than the allowable MRLs, due to exposure to pesticide residues.

**8.4 Hazards and risks in special conditions of use**

Certain pesticide residues in food generated as a result of the plant protection product application are used for determining the MRLs and for assessing the risks for people due to the intake of pesticide residues via food.

The use of plant protection products outdoors (in the field) is not comparable to other areas of application. Climate conditions in the protected areas (hothouses, greenhouses, climate chambers), which are different from those in the open, can most often lead to higher concentrations of residues on treated plants.

Since the plant protection products can be used both outdoors and indoors, risk assessment is performed with the highest residue concentration regardless of the area of application. Most usually, the plant protection product application in a protected area shall generate higher levels of pesticide residues. If it can be concluded through risk assessment that such application shall not have a harmful effect on human health, it is assumed that the application of the same plant protection product on the
same culture, outdoors, is also safe for human health. However, such conclusions are made only if the
data on pesticide residues are available in both cases.

Example 1: The plant protection product has been approved for application to/on tomatoes
outdoors. Failure to comply with the label and the instructions for use by applying the product
to/on tomatoes in the protected area may cause the concentration of pesticide residues to
exceed the prescribed MRLs. Such application may increase human exposure to pesticide
residues through the consumption of treated tomatoes and lead to increased risk to human
health.

Example 2: The plant protection product has been approved for application on tomatoes
outdoors and in the protected area. The label specifies the waiting period of 3 days for tomatoes
outdoors and of 5 days for tomatoes in a protected area. It has been concluded based on the
studies that the waiting period for tomatoes in the protected area is longer since more days are
required from the application of a plant protection product until the harvest for the same
concentration of residue to be reduced to a safe limit. Failure to comply with the waiting period
shall cause the residues to exceed the prescribed level and possibly pose a risk to human health.

After the application of the seed treatment product, pesticide residues shall most commonly not be
found in the edible parts of plants at the time of harvest/picking. Although such application is
considered irrelevant from the viewpoint of pesticide residues, experiments are conducted to confirm
that the remains are below the limit of determination. After it has been demonstrated through the
experiments that there would be no pesticide residues, such application may be approved and listed
on the label.

Plant protection products can be applied on agricultural products during their storage (e.g. cereals,
potatoes) and MRLs are determined for them as well. If a plant protection product is used for the
surface treatment, the time that shall elapse from the treatment until the entry of goods into the
warehouse shall also be determined.

For the special conditions of application in forestry and non-agricultural areas, as well as elsewhere
where plants are not used to feed people and animals, MRLs are not determined.

The exceptions are applications in pastures and grassland, which can be used for grazing by the
domestic animals. In this case, the risk for animals due to the intake of pesticide residues through feed
(fresh grass, silage, hay, straw, etc.) is assessed. If the label of a plant protection product indicates the
operating prohibition for animals, in the form of safety period or limitation, this means that the entry
into the treated area is prohibited. Otherwise, harmful effects on the health of animals, as well as the
people who consume meat and meat products from such animals, may occur.

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9 WATER PROTECTION

9.1 Soil and groundwater protection

The Water Act is a fundamental provision governing water protection in the Republic of Croatia. Water supplies are not inexhaustible and can be easily contaminated, therefore the preservation and protection of water also depends on the level of environmental awareness of every individual. The plant protection products application in accordance with good agricultural practice and default restrictions, adhering to the regulations on water, ensures that the plant protection products application does not cause pesticides emergence in surface and groundwater above the prescribed limit values. Prior to the plant protection products application, it is necessary to read the label and instructions for use in order to be familiarised with possible additional restrictions relating to the protection of water and the environment (for example, prohibition of application in the karst area for the purpose of groundwater protection) (Figure 9.1).

9.2 Sanitary water protection zones

Sanitary water protection zones are protected areas intended for collecting the drinking water, where additional protective measures are implemented for the purpose of water and water environment protection. Ordinance on the Conditions for Identifying Sanitary Water Source Protection stipulates the requirements for determining the zones of sanitary source protection, which are used for public water supply, as well as the measures and restrictions contained implemented therein. Hrvatske vode have established the Register of Protected Areas in electronic form, in which the data and information on formally and legally declared protected areas are entered.

Figure 9.1: Overview map of sanitary water source protection zones (source: Water Management Plan, as of September 2012, Hrvatske vode, 2013)
Sanitary water protection zones (Figure 9.2) are determined by the type of aquifer for:

1) springs with capturing groundwater, including:
   a) from aquifers with intergranular porosity
      - restriction and supervision zone – Zone III,
      - strict restriction and supervision zone – Zone II and
      - strict protection regime and supervision zone – Zone I.
   b) from aquifers with fracture and fracture-cavernous porosity
      - restriction zone – Zone IV,
      - restriction and supervision zone – Zone III,
      - strict restriction and supervision zone – Zone II and
      - strict protection regime and supervision zone – Zone I.

   In Zone I of sanitary protection, all activities are prohibited, except those regarding the capturing, conditioning and transportation of water into the water supply system.

   In Zone II of sanitary protection agricultural production is prohibited, among other, in addition to organic production with the use of permitted fertilizers and plant protection products under Regulation (EC) No. 889/2008 and Implementing Regulation (EU) No. 354/2014.

   In Zone III of sanitary protection, agricultural production is permitted, but agricultural holdings shall ensure the conditions and implement the measures stipulated by the corresponding programme of water protection against pollution caused by nitrates of agricultural origin and to follow the principles of good agricultural practice.

*Figure 9.2: Overall representation of the sanitary protection zone structures in the Republic of Croatia (source: Water Region Management Plan, Hrvatske vode, 2013)*
2) springs with capturing of surface water, including:

a) from reservoirs and lakes,

- restriction and supervision zone – Zone III,
- strict restriction and supervision zone – Zone II and
- strict protection regime and supervision zone – Zone I and

In Zone I of sanitary protection of water with capturing surface water from reservoirs and lakes, it is prohibited, among other, to use fertilizers and plant protection products.

In Zone II of sanitary protection of water with capturing surface water from reservoirs and lakes, it is prohibited, among other, to perform agricultural production, in addition to organic production, with the use of permitted fertilizers and plant protection products under Regulation (EC) No. 889/2008 and Implementing Regulation (EU) No.

In Zone III of sanitary production of water, agricultural production is permitted, but agricultural holdings shall ensure conditions and implement measures prescribed by the relevant programme of water protection against pollution caused by nitrates of agricultural origin and to follow the principles of good agricultural practice.

b) from open watercourses.

Only Zone I of sanitary protection of water shall be determined for capturing surface water from open water courses, in which it is prohibited to use fertilizers and plant protection products.
9.3 Monitoring of pesticide residues in water

Pursuant to the Water Act, Hrvatske vode are responsible for monitoring the state of the surface water, including the coastal waters and groundwater, on which they shall adopt an annual Monitoring Plan, with prior endorsement from the Ministry of Agriculture. The monitoring of the water status includes environmental and chemical indicators for surface waters, as well as chemical and quantitative indicators for groundwater.

The chemical status of watercourses and lakes refers to their burdening with priority substances, regarding which environmental quality standards have been stipulated at the European Union level, in particular in Directive 2008/105/EC. 33 priority substances have been identified, from which thirteen substances have been separated, which are, due to toxicity, decomposition and bioaccumulation, identified as priority hazardous substances (such as hexachlorobenzene, endosulfane).

Pesticides covered by the monitoring of surface water and groundwater are mainly pesticides, which are priority substances under Directive 2008/105/EC and which the EU Member States are required to follow. Since plant protection products containing priority substances have long since been prohibited, it is also necessary to include into the monitoring the pesticides that are not priority substances, and that are used in Croatia and according to their properties can be hazardous to water and the organisms that live in water. This particularly applies to groundwater because they are largely (90%) the source of drinking water.

The monitoring of drinking water is under the competence of the Ministry of Health. Two monitoring procedures of pesticide residues in drinking water are conducted:

1. monitoring of drinking water sources and
2. monitoring of drinking water from the distribution network.

These monitoring procedures are implemented by the Croatian Institute for Public Health in cooperation with county institutes. The results of the monitoring procedures are processed by the Croatian Institute for Public Health and the annual results of the monitoring are submitted to the Ministry of Health.

Pursuant to the new Act on Water for Human Consumption, which is fully harmonised with Directive 1998/83/EC, it is necessary to analyse a much higher number of water samples from the distribution network in relation to the existing number of samples, which are analysed, as well as a significantly higher number of pesticides in drinking water.
9.4 Environment

9.4.1 Types of hazards and risks

Negligent behaviour towards the environment over a long period, the expansion of agricultural areas due to the growing demand for food production, the intensification of production, increase of the pesticides amounts and many other factors contributed to the pollution of natural resources which have a direct impact on human health, quality of life, flora and fauna. The impact of agriculture on the environment is reflected in the pollution of air, soil and water.

![Possible paths of environmental pollution via the plant protection products](image)

Paths of environmental pollution via the plant protection products are numerous. Soil, air and water environment may be exposed to direct and indirect pollution by applying the plant protection products. Indirect pollution of the environment through the plant protection products is caused by the drift during the application in windy weather, washing through the soil profile, removal of surface precipitation from slanted and erosive surfaces, drainage (runoff), evaporation, adsorption, sedimentation, hydrolysis, photolysis, biological decomposition, etc. (Figure 9.3). Application of the herbicide directly to the soil leads to pollution of soil, and washing on light and sandy soils leads to groundwater contamination. Contamination may also occur if a plant protection product is applied near the surface water, without adhering to the distance restrictions indicated on the label and instructions for use.

Physical and chemical properties, decomposition rate or mobility in the soil greatly affects the distribution of plant protection products in the environment. Active substances that are readily soluble in water pose a greater risk to the water (the risk is even greater if they are prone to washing or if they do not bind well to soil particles), and the active substances that bind strongly to the soil pose a risk for the organisms in the soil and cultures in the crop rotation.

9.4.2 Water

Water is the basic prerequisite of life, creation and development of civilisation and it represents a value unmeasurable by material goods. It is the most represented substance in the structure of all living organisms, therefore it may be rightfully claimed that water is the source of life. The water cycle in
nature is a continuous process that enables life on Earth. Through evaporation, water enters the atmosphere, where it condenses and falls to the ground in different forms. A part of the water is used for life as a fundamental natural resource, a part goes back to the surface and groundwater, and the process is continuously repeated.

The protection of water against pollution is implemented in order to preserve human life and health, as well as to protect other components of the environment by enabling safe and unimpeded use of water for various purposes.

9.4.2.1 Surface water

Drift of plant protection products during treatment poses the greatest risk of pollution for the surface water environment. The wind affects the strength of the drift, and an inappropriate method of applying a plant protection product carries the product to an unwanted surface. Surface waters can be, to a smaller degree, contaminated by plant protection products through runoff from the soil surface during rain (especially after treatment on slopes) and through drainage via the drainage systems and after the application of plant protection products.

In order to assess the pollution of surface waters, the Regulation on water quality standards has been adopted, stipulating the substances and amounts, which are considered hazardous in surface waters.

According to the overall assessment of the quality elements, the condition of the surface water body is shown on maps, which contain a review of the surface water body condition in corresponding colours (Figure 9.4), as follows:

- very good condition, blue,
- good condition, green,
- moderate condition, yellow,
- poor condition, orange,
- very poor condition, red.
Buffer zones (safety distances) are stipulated between the treated surfaces and water bodies in order to further protect surface water. Due to a different impact of each individual plant protection product on aquatic organisms, buffer zones of different widths shall also be prescribed and indicated on the label, and they shall be observed when treating the crops with plant protection products. The method of determining a buffer zone is indicated in Figure 9.5.
9.4.2.2 Groundwater

Groundwater is of extreme importance for the Republic of Croatia since they are mainly used for drinking water supply (approximately 90%). There are two types of aquifers in Croatia: aquifers of the Pannonian basin and aquifers of karst areas. Permeability and geological composition of the layer separating the groundwater from the surface affect the quality of groundwater.

The main issue in the preservation of groundwater quality in Northern Croatia is the pollution of major watercourses (rivers Sava and Drava and their tributaries) due to urbanisation and the application of plant protection products and mineral fertilisers on agricultural land and unintentional contamination. Croatian territory south of Karlovac is mostly mountainous karst area, containing high quality groundwater. This is primarily caused by a weaker economic development and the present water quality can be preserved in the future through careful protection. The sources of the rivers or sources of high karst fields are the least contaminated, and water quality gradually decreases in the downstream parts of the karst basins.

The manner in which an active substance shall reach groundwater and in what concentration depends on many factors, of which the most important ones are: the physical and chemical properties of the active substance, dosage and method of application, the time of year when the plant protection product is applied, weather conditions before, during and after the application and soil properties. Groundwater is most vulnerable in karst areas, light and sandy soils and on soils with low organic matter content (Figure 9.6). Improper use of plant protection products may be one of the manners of groundwater contamination.
Active substances, which are commonly found in groundwater, belong to the group of herbicides. The main reason for their higher tendency to wash into the groundwater are the physical and chemical properties of the herbicide, as well as the fact that out of all of plant protection products, they are the ones most commonly applied on the bare soil.

Groundwater in Croatia is of better quality than groundwater in highly developed countries, although it is necessary to emphasise that its quality is in constant decline. Such a trend can be halted only by raising awareness and active involvement of all citizens.

9.4.3 Soil

Soil is one of the basic resources for life on Earth. The creation and development of the soil is a complex spatial and temporal phenomenon, and the most important factors that influence the formation of soil are climate, vegetation, parent material (rock), living organisms, time and human activity. The soil is an extremely complex medium, with a number of important functions for sustaining life: it provides nourishment, biomass, raw material, habitats and gene reserves, stores, filters and transforms...
nutrients, water, carbon, etc. At the same time, soil is subject to degradation processes and threats, which may seriously threaten and disable its functions in a short period. The consequences can be revealed through desertification (deterioration of soil quality), loss of soil fertility, biodiversity, air and water quality, and an impact on climate change is also possible.

The solid phase of the soil generally consists of particles of sand, silt and clay. These particles vary in size, which affects the ability to bind water to its surface. Soils containing more clay and organic matter retain more water. The structure of the soil and the proportion of pores depends on the size of the particles and their ability to link into the structural units. The most important factors that affect the porosity (permeability) of soil are texture (mechanical soil composition), soil structure, organic matter content in the soil, tillage, vegetation and organisms in the soil. Porosity is a very important property of soil since it affects the air-water and thermal regime of the soil, as well as soil fertility. Soil fertility is its ability to provide nutrients, water, air and heat to the plant. Soil is an effective natural purifier of water, which enters the underground through the soil. The soil is also a universal buffer, which inactivates substances entering its mass through deposition, or being released by mineralisation of organic matter (prevents sudden changes in pH). The organic matter content is an important factor in determining the buffer capacity of the soil. Microorganisms in the soil (bacteria, actinomycetes, fungi and algae), together with other soil organisms (flora and fauna) participate in various transformation processes of organic and mineral substances.

Behaviour of the plant protection products in soil mostly depends on the soil type, property of the plant protection product soil, microbial activity and climatic conditions. As soon as an active substance of a plant protection product comes into contact with the soil components, a number of different physical and chemical and biological processes follow, directly affecting its efficiency and behaviour in the environment. In the soil, each plant protection product is subject to the processes that affect its loss (adsorption, washing, evaporation, absorption caused by living organisms and plants) and the processes that affect its decomposition (photochemical, chemical and microbiological processes) (Figure 9.7). Each of the aforementioned processes directly affects the stability (persistence) of a particular plant protection product and the period over which it remains in the soil in active form, and as such represents a potential hazard to the environment. It shall be noted that the less stable (persistent) plant protection product poses a lesser hazard to the environment and this needs to be considered when selecting a plant protection product. In addition to stability, the degree of adsorption of a plant protection product to soil particles also has an important role. The more a plant protection product is prone to adsorption, the less it is subject to washing into groundwater. The restrictions indicated on the label and instructions for use regarding environmental protection, in particular the prohibition of application to certain types of soils, mean a prohibition of a plant protection product application in the karst areas, light and sandy soils due to its indication of either persistence or low adsorption of the active substance in soil particles, and the prohibition of application on slanted and erosive surfaces indicates strong adsorption of the active substance in the soil particles.
Figure 9.7: Overview of the behaviour of plant protection product in the soil (prepared by: N. Nikl)
9.4.4 Air

Air is a mixture of gases forming the Earth's atmosphere. The most represented gases in the Earth’s atmosphere are nitrogen and 78% and oxygen 21%, and noble gases (0.94%), carbon dioxide (0.03%), water vapour, ozone, hydrogen are present to a lesser extent. In addition to the elements constantly present in the air, the presence of other substances is also possible in smaller concentrations, which can have a negative impact on human health and the environment. The presence of pollutant particles is mainly caused by human activity. In the Republic of Croatia, the risk assessment and anticipated plant protection product concentrations in the atmosphere are mainly assessed on the basis of their physical and chemical properties. Given that the majority of registered plant protection products in Croatia are poorly volatile, their application does not present a significant threat to the atmosphere if performed in accordance with good agricultural practice and instructions on the label.

As in many European countries, **aerial treatment with plant protection products is prohibited** in the Republic of Croatia. It is exceptionally permitted in some cases at the request of a legal or natural person and the prior approval of the Ministry of Agriculture.

9.5 Hazards and risks during special conditions of plant protection products applications

Hazards and risks of environmental pollution are also present during special conditions for the application of plant protection products. These are, for example, application in warehouses, production and business premises, which may result in the contamination of the environment if not performed in accordance with the instructions on the plant protection products label. It is important to adhere to environmental protection measures, with proper sealing of the facility within which the application is performed (especially during the application of a plant protection product in gaseous form), conscientious handling of the remaining amount of a plant protection product and packaging after use. What is important is the quality of wastewater discharged into surface water or public sewage system. In case of wastewater containing plant protection product residues, they shall be treated (purified) prior to discharge pursuant to the Ordinance on Emission Limit Values for Wastewater Discharges.

9.6 Measures for reducing the risk associated with the behaviour of pesticides in the environment

The condition of the environment depends on the level of environmental awareness of every individual and rational use of natural resources, application of systematic technology, wastewater processing and treatment, controlled application of plant protection products, controlled and safe disposal of all categories of waste, planning of activities and behaviour in accordance with the objective of environmental preservation and protection.

In order to reduce the risk of environmental contamination, the plant protection product users shall:

- work in accordance with the instructions of good agricultural practice;
- apply non-chemical methods wherever possible;
- give preference to plant protection products, which have not been classified and labelled as hazardous for the environment (symbol "N") or, if possible, select a plant protection product which has a less hazardous impact on the environment;
- adhere to the accurately prescribed buffer zones (security distances) between the surfaces on which the treatment shall be performed and surface water, as well as the sanitary water protection zones in order to protect water resources;
- use "nozzles (sucking-pipes, jets) for reducing drift";
- reduce or completely exclude the application of plant protection products in cemeteries, parks, along roads, railways and other ruderal surfaces (give priority to the mechanical method of weed removal), on very permeable surfaces, as well as near the surface (or high ground) water;
- reduce or completely exclude the application of plant protection products on impermeable surfaces where a high risk of run-off into surface water or sewage exists;
- strive to reduce the use of plant protection products on public surfaces (parks, gardens, sports and recreational grounds, school and children playgrounds);
- prepare the plant protection product, clean the application equipment and handle the remaining amount of the plant protection product together with its packaging in accordance with its label;
- follow the instructions and comply with all restrictions indicated on the label and instructions for use of a plant protection products, reduce or completely exclude the application of plant protection products in protected areas;
- reduce or completely exclude the application of plant protection products in protected areas.

Author: Nataša Nikl, M. Eng.
10 NON-TARGETED ORGANISMS AND BIODIVERSITY

10.1 Types of hazards and risks

Biodiversity of Croatia is considered one of the richest in Europe. The great diversity of habitats has resulted in a great wealth of species. Direct destruction of habitats by converting land into construction land or agricultural land, construction of roads and other things leading to the division of habitats poses a threat to all species in the area.

During outdoor application of plant protection products, the non-target organisms may be exposed to the plant protection product and its residues through the entry of contaminated food and drinking water, as well as direct exposure during application. Birds and mammals can be additionally exposed through eating fish and earthworms, which have been in contact with the plant protection product. Certain active substances are extremely harmful for some non-targeted organisms, therefore risk mitigation measures shall be implemented during the application of plant protection products. If the active substance contained in the product poses hazard for a particular group of organisms that is indicated in the implementing regulations of the Commission on the conditions for the approval of active substances.

When the application of a plant protection product is performed in protected areas (hothouses, greenhouses) or indoors (warehouses, silos), the risk of non-targeted organisms exposure in the environment is lower.

10.2 Birds and mammals

101 species of mammals and 375 species of birds are recorded in the fauna of the Republic of Croatia. The application of plant protection products in compliance with the prescribed risk mitigation measures shall preserve the richness of our fauna.

During plant protection product registration, the exposure of birds and mammals to the active substance, product and its metabolites is assessed and, if necessary, risk mitigation measures are prescribed. Birds and mammals may be exposed to a plant protection product and its residues through the consumption of insects, fish, earthworms and plant parts containing plant protection product residues and by drinking water containing plant protection product residues.

Plant protection products in the form of granules, pellets, baits and treated seed present a major hazard to birds and mammals. During the application of such products or sowing the treated seeds, special attention shall be paid to the following:

- plant protection product and treated seed shall be fully entered (incorporated) into the soil, including the end of rows,
- a scattered plant protection product and treated seed shall be immediately collected and removed,
- the plant protection product and treated seed shall not be left outside the storage area.

Compliance with the aforementioned restrictions reduces the potential for exposure of birds and mammals to a plant protection product and its residues. Treated seed shall not be used for the nutrition of domestic animals or game.

In the event that the application of a plant protection product poses a risk to birds and mammals, its label shall indicate the following signs prescribed in Article 49 of the Regulation (EC) No. 1107/2009:
**SPe 5** *For the purpose of protecting birds/wild mammals, the product shall be fully entered (incorporated) into the soil, including the end of rows.*

The sign is used for plant protection products in the form of granules or pellets, which shall be entered into the soil in order to protect birds or wild mammals.

**SPe 6** *For the purpose of protecting birds/wild mammals, the scattered product shall be removed.*

The sign is used for plant protection products in the form of granules or pellets in order to avoid consummation by birds or wild mammals. It is recommended for all plant protection products in solid state, which are used undiluted.

**SPe 7** *Do not apply during bird mating period.*

The sign is used if the assessment performed for one or more applications indicated on the label shows that it is necessary to take risk mitigation measures.

Based on the implemented risk assessment, some additional restrictions relating to the protection of birds and mammals may be included on the label of a plant protection product. In the event that the product is applied for seed treatment, the label shall indicate the following warning: **For the purpose of protecting birds and wild mammals, treated seed shall be fully entered (incorporated) into the soil, including the end of rows. Do not leave treated seeds on the soil surface. Scattered seeds shall be immediately collected and removed.**

### 10.3 Aquatic organisms

Plant protection products may have harmful effects on all groups of aquatic organisms, fish, aquatic invertebrates, algae and aquatic plants (hydrophytes). In the event that a plant protection product, active substance or its metabolites have an adverse effect on any group of aquatic organisms, it is necessary to implement risk mitigating measures in the form of buffer zones to the water surface, use of nozzles for reducing drift or planting a green belt.

Aquatic organisms can be exposed to plant protection products during the application. The most common source of aquatic organism exposure is drift, however, there are also other possibilities, such as washing from the soil surface or drainage.

The size of the buffer zone is determined by calculation, and it depends on the culture, development level and phase of the culture to which the plant protection product is applied, physical and chemical properties and toxicity of the active substance in a plant protection product and the number of applications.

For highly toxic active substances, the prescribed buffer zones for aquatic organism protection are large and difficult to implement in practice. Therefore, in some cases buffer zones are prescribed only together with the use nozzles for reducing drift. An additional measure for drift reduction can be the use of green belts that are planted near the crops.

In case the implementation of risk mitigation measures is required, the label shall include the following signs:

**SPe 2** *For the purpose of protecting groundwater/aquatic organisms, do not apply to the soil (soil type or other special conditions are indicated).*
The sign can be used as a measure for mitigating the risk of potential groundwater or surface water contamination under vulnerable conditions (e.g. due to soil type, topography or drained soil) if the assessment performed for one or more applications specified on the label shows that it is necessary to take measures to reduce the risk of unacceptable effects.

**SPe 3 For the purpose of protecting aquatic organisms, buffer zones of (the distance in metres is indicated) to the water surface shall be observed.**

This sign is used in order to protect non-targeted plants, non-targeted arthropods and/or aquatic organisms if the assessment performed for one or more applications specified on the label shows that it is necessary to take measures to reduce the risk of unacceptable effects.

**SPe 4 For the purpose of protecting aquatic organisms, do not use on impermeable surfaces such as asphalt, concrete, cobblestones, railway tracks and other surfaces where there is a high possibility of surface washing.**

Depending on the method of applying plant protection products, the sign can be used to mitigate the risk of surface washing in order to protect aquatic organisms or non-targeted plants.

If case the product is toxic to aquatic organisms, it shall be marked by risk phrases (R or H phrases) and safety phrase N or a pictogram - Hazardous for the environment according to the Ordinance on classification, labelling and packaging of hazardous chemicals.

10.4 Bees and other pollinators

During application, bees and other non-targeted arthropods may be exposed to the plant protection product and its residues. The use of plant protection products from the group of insecticides, as well as sowing the seeds treated with active substances from the group of neonicotinoids, represents a major hazard for bees and non-targeted arthropods.

When a plant protection product is applied, it poses hazard to bees and non-targeted arthropods, therefore the risk mitigating measures shall be implemented. The application of plant protection products during the activity of bees and other pollinators is therefore prohibited, especially if the culture to which it is applied is flowering. The application of plant protection products during the flowering of weeds located in these cultures is prohibited or the removal of weeds is prescribed. If the plant protection products, which are applied, are very contact toxic, the hive closing measures are prescribed for a certain period depending on the duration of the toxicity of the plant protection product.

In case when a plant protection product is toxic to non-targeted arthropods, buffer zones for non-agricultural areas are prescribed, which shall ensure the recovery of populations on the treated surface.

If the implementation of measures for mitigating the risk for non-targeted arthropods and bees is required, the following signs shall be included on the label of a plant protection product:

**SPe 3 For the purpose of protecting non-targeted arthropods/insects, buffer zones of (indicate the distances) to non-agricultural areas shall be observed.**

This sign is applied in order to protect non-targeted arthropods if the assessment performed for one or more applications specified on the label shows that it is necessary to take measures to reduce the risk of unacceptable effects.
**SPe 8 Hazardous to bees/For the purpose of protecting bees and other pollinators, do not treat the crop during flowering/Do not apply at the time of bee grazing/Remove or cover the hive during the application for a specific time (indicate) after the application as well/Do not apply at the time of weeds flowering/Remove weeds before flowering/Do not apply the product before (time is indicated).**

The sign is used for plant protection products for which the assessment performed for one or more applications specified on the label shows that it is necessary to take risk mitigation measures in order to protect bees or other pollinating insects. Depending on the product application method, the appropriate sign aimed at minimising the risk to bees and other pollinating insects and their brood may be selected.

**For the purpose of protecting bees, the plant protection product user shall inform the nearest beekeepers’ organisation and the Croatian Beekeeping Association at least 72 hours prior to the treatment with a plant protection product harmful to bees.** Beekeepers associations shall notify the beekeepers immediately, but no later than 24 hours after the receipt of the information on the announcement of treatment. During the application of plant protection products, any other measures in compliance with the sustainable use of pesticides shall also be followed.

### 10.5 Organisms in the soil

Organisms in the soil can be exposed to plant protection product residues and their metabolites, which end up on soil during application. The worst-case scenario of the exposure of organisms in the soil to the plant protection product and its metabolites is during the application of herbicides, because the entire amount of the applied plant protection product ends up on the soil. For other applications, depending on the development stage, a part of a plant protection product is retained on the plant parts of the culture to which the product is applied. In the event that there is a risk for organisms in the soil, risk mitigation measures shall be prescribed and the following sign is placed on the proposed label:

**SPe 1 For the purpose of protecting organisms in soil, do not use this or any other product containing (the active substance or group of active substances are indicated, where relevant) for more than (time period or number of applications is indicated).**

The sign is used for plant protection products for which it has been determined that for one or more applications indicated on the label, risk mitigating measures shall be taken in order to reduce the risk of product accumulation in the ground, due to the effects on earthworms or other animal organisms that live in the soil or soil microorganisms.

### 10.6 Non-targeted plants

Non-targeted plants can be exposed and vulnerable during the application of plant protection products, which are primarily aimed at suppressing the plants of weed species (herbicides). During the application of plant protection products, in case of a drift, non-targeted plants located in non-agricultural areas near the site of application may be affected. In the event that there is a risk for non-targeted plants, the use of buffer zones to non-agricultural areas is proposed, thus reducing the risk. The buffer zone size shall be determined in the process of plant protection product registration through the preparation of a risk assessment and it shall be indicated on the label. As an additional risk mitigation measure, the application of plant protection products in windy weather is prohibited. The use of a certain plant protection product on impermeable surfaces may have an adverse effect on the non-targeted plants. In the event that there is a risk for non-targeted plants, risk mitigation measures shall be prescribed and the following sign is placed on the proposed label:
SPe 3 For the purpose of protecting non-targeted plants, buffer zones of (the distance in meters is indicated) to non-agricultural areas shall be observed.

This sign is applied in order to protect non-targeted plants if the assessment performed for one or more applications specified on the label shows that it is necessary to take measures to reduce the risk of unacceptable effects.

SPe 4 For the purpose of protecting non-targeted plants, do not use on impermeable surfaces such as asphalt, concrete, cobblestones, railway tracks and other surfaces where there is a high possibility of surface washing.

Depending on the method of plant protection product application, the sign can be used to mitigate the risk of surface washing in order to protect the non-targeted plants.

10.7 Natura 2000 sites

Natura 2000 is an ecological network comprised of sites, which are important for the conservation of endangered species and habitat types in the European Union. The ecological network of the Republic of Croatia was declared by the Regulation on the Ecological Network, and represents the ecological network sites of the European Union Natura 2000. It is aimed at conserving or re-establishing the favourable state for more than one thousand of endangered and rare species, as well as for approximately 230 natural and semi-natural habitat types. Approximately 30,000 sites over almost 20% of the European Union surface have been included in the subject ecological network so far, making it the largest system of conserved areas in the world. NATURA 2000 is based on EU directives, the sites are selected according to scientific criteria, and in the management of these sites, the interest and welfare of the people who live therein are also taken into account.

The Birds Directive and the Habitats Directive represent the basis of European Union legislation concerning nature protection. Their implementation takes place through the establishment of the ecological network Natura 2000.

The establishment of the ecological network in the Republic of Croatia is regulated by the Nature Protection Act. Ecological network sites in Croatia have been declared by the Regulation of the Croatian Government. Ecological network sites in Croatia are divided into internationally important sites for birds and sites important for other wild types (species) and habitat types. The ecological network of the Republic of Croatia includes 36.67% of land area and 16.39% of coastal sea (Table 10.1), and consists of 571 polygon Conservation sites important for species and habitat types (SAC), 171 point Conservation sites important for species and habitat types (mostly cave structures) (SAC) and 38 polygon Important Bird and Biodiversity Areas (IBA), as well as two corridors: the corridor for sea turtles and the corridor Palagruža-Lastovo-Pelješac (important bird migration area) (Figure 10.1).

Many sites covered by NATURA 2000 are located in agricultural areas. High biodiversity is associated with extensive agricultural production and most of the agricultural areas in NATURA network are in marginal agricultural areas rather than in agricultural areas that are intensively cultivated. Examples of low-intensity agricultural production are mountain meadows and pastures, alluvial plains and wetlands, where species whose survival depends on low-intensity agriculture may be found.
Figure 10.1: Areas covered by the ecological network Natura 2000 (source: State Institute for Nature Protection)

<table>
<thead>
<tr>
<th></th>
<th>Mainland surface RC (km²)</th>
<th>% of RC mainland</th>
<th>Coastal sea surface RC (km²)</th>
<th>% of coastal sea surface RC</th>
<th>Total surface area of the RC (km²)</th>
<th>% of total surface area RC</th>
<th>Number of Natura 2000 sites</th>
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</thead>
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<td>4.903,12</td>
<td>15,44</td>
<td>20.962,69</td>
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<td>1.040,13</td>
<td>3,28</td>
<td>18.147,68</td>
<td>20,54</td>
<td>38</td>
</tr>
<tr>
<td>Natura 2000</td>
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<td>36,67</td>
<td>5.204,63</td>
<td>16,39</td>
<td>25.959,60</td>
<td>29,38</td>
<td>780</td>
</tr>
</tbody>
</table>
10.8 Hazards and risks in special conditions of applying plant protection products

The application of plant protection products has an adverse effect on biodiversity. Plant protection products can have a short-term toxic effect in direct application or long-term adverse effects as a result of changes in habitat and food chain.

Some plant protection products lead to direct poisoning of species and can cause a reduction or disappearance of natural populations, and some may gradually accumulate in the food chain, which is especially harmful to the species that are at the top of the food chain, usually predators. Predators often suffer from secondary poisoning through the consummation of animals, which have been poisoned, or plants exposed to plant protection products. Plant protection products can reduce the density of weed species and insects, which are an important food source for many species.

In the application of plant protection products, there is a possibility of an adverse effect on any group of non-targeted organisms, therefore the risk mitigation measures that shall be observed shall be prescribed.

Author: Ana Mrnjavčić Vojvoda, M. Eng.
11. RESISTANCE

11.1 What is resistance?

Resistance is the occurrence of a decrease in the sensitivity of pests, pathogens or weed population specimens to the plant protection products effects. If a decreased sensitivity is considerably expressed, the pest, pathogen or weed plant are considered to be resistant to a certain insecticide, fungicide or herbicide. **Frequent use of a plant protection product with the same mechanism of action is the most important cause of resistance occurrence, which is hereditary and is transmitted to the offspring. The consequence of the resistance occurrence is a gradual decrease in the efficiency of a plant protection product, which had an effect over the population at the beginning of application.**

Plant protection products are highly toxic to pests, pathogens or weeds. Examples of sensitivity/resistance of organisms:

- 99% of a harmful butterfly caterpillar specimens in an area die after consuming 0.01 micrograms of an insecticide per gram of body weight, while 1% of the same species caterpillars die only if they intake 10 micrograms of the same insecticides into their body. These 1% of caterpillar specimens in a population can endure a 1000 times higher amount of the same toxic substance and can therefore be considered resistant;
- a certain fungicide may completely prevent germination of certain fungus spores if the spores are exposed to a concentration of 0.1 micrograms of that fungicide in a litre of water. However, if the spores of the same fungus species after multiple exposure to this fungicide can germinate even at a concentration of 10 micrograms of the same fungicide in a litre of water, it can certainly be said for that fungus (more precisely for its isolates) that it has become less sensitive, i.e. resistant;
- regarding weed resistance to herbicides, the terms "tolerance" and "resistance" shall be distinguished. In the example showing the spectrum of action of a herbicidal product, weed species have been classified into the sensitive, medium-sensitive, medium-tolerant and tolerant group. The herbicidal product suppresses the first group well, the second one partially, the third one insufficiently, while it does not suppress the tolerant species. Thus, the tolerant species are resistant to the herbicidal product effect from the beginning. In contrast, resistance, as in the previous examples, occurs as a result of a long-term application of herbicidal products with the same mechanism of action, which slowly lose effectiveness, and is a result of selection pressure, i.e. suppression of sensitive and multiplication of resistant biotypes of the same species.

11.2 Resistance and sensitivity limit

The occurrence of resistance to plant protection products is the result of selection pressure on living organisms when they are exposed to the effects of substances, which are toxic to them. It is known that all living organisms adapt to the environment in which they live, whereby those who may adapt to the new situation survive in nature. Adapting to the environment is the essence of evolution, and such adaptations in nature within a species are developed through hundreds of thousands of years. In case of the application of plant protection products, a distinct "accelerated evolution" under human influence occurs. The specimens within some species population (strains, biotypes) that have a particular advantage to survive and resist the negative impacts in the environment more successfully shall adapt and transmit their characteristics to offspring, while the weaker ones shall gradually become less represented in the population. Within each population of pests, pathogens and weeds, there are very few of those that are less sensitive to some of the toxic substances used as insecticides, fungicides or herbicides. If the application of the same product in the same area continues, through a
longer or shorter period, within a population, the number of less sensitive ones shall decrease and the number of resistant ones shall increase, and they shall continuously reproduce. After a certain period, those that are more resistant to the effect of a certain plant protection product shall become dominant. Further application of the same plant protection product shall not be effective and it can be said that the emergence of resistance occurred.

Examples of reduced efficiency:

A fungicide can have an efficiency of nearly 100% in the first season when it was used to suppress a pathogen in a certain area. If the same preparation is used each year, and it shows the efficiency to the same disease of 50% in the fifth year, 30% in the sixth, and is completely ineffective during the seventh and eighth year, there is reasonable doubt that a development pathogen resistance of to the fungicide occurred. This decrease in efficiency is the result of resistant specimens becoming dominant and possibly the only ones present within the pathogens population in this area, and being able to further develop (and thus cause disease) during the application of the recommended fungicide amount.

It shall be noted that the resistance of certain types of pests, pathogens or weeds can be demonstrated through laboratory tests as evidence of a decrease in effectiveness due to the appearance of field resistance. The observed decrease in product efficiency in practice may be the result of certain other factors, therefore the conclusions on the occurrence of resistance shall be made with certain caution. In practical conditions, it is almost certain that the emergence of resistance occurred if it is noticed that one or all products based on the same or chemically similar active substance gradually lose their efficiency in a particular area at similar application methods. Conversely, if it has been noticed that the same product is effective in the area of one agricultural producer and has a poorer effect at the neighbouring producer during two seasons, it shall not be immediately concluded that the emergence of resistance occurred. Moreover, if the efficiency of the same product is variable over several years with the same producer that does not mean that resistance has occurred. To this date in Croatia, scientific research confirmed the resistance of Colorado potato beetle (Leptinotarsa decemlineata) to organophosphate insecticides, of fungus Botrytis cinerea to fungicides from the group of dicarboximides and of lamb’s quarters (Chenopodium album), red-root amaranth (Amaranthus retroflexus) and common ragweed (Ambrosia artemisiifolia) to triazine herbicides. It is realistic to assume that the cases of resistance to plant protection products in our country are much more numerous and that the resistance of certain pests, pathogens or weeds to some preparations represents a problem in some areas of Croatia. Unfortunately, due to a lack of funds and a small number of institutions involved in research work in agriculture in Croatia, it is not possible to systematically monitor the occurrence of resistance in the manner it is done in some countries in Europe and worldwide.

It is interesting to note that some species of harmful organisms are "more prone" to becoming resistant. For example, Colorado potato beetle resistance to 54 insecticide active substances from almost all chemical groups has been established to this date!
11.3 Types of resistance

The mechanism and method of action of plant protection product resistance are important factors in understanding the concepts of cross and multiple resistance, as well as for explaining the fact why with some plant protection products resistance develops relatively quickly, while it has never been recorded with the others. Some active substances of plant protection products affect a larger number of different life processes in target organisms. Such an effect may be called a **multiple effect**. It is very difficult for a living organism to resist the interference with the functioning of a large number of life processes, incomparably more difficult than to develop the ability to "resist" the toxic substance at only one molecular location. Many insecticides, fungicides and herbicides that are currently on the market affect only and exclusively one life process in harmful organisms, which can be called a "**single effect**". As a rule, resistance occurs with single effect plant protection products, while it has mostly not been recorded for those having multiple effect. For example, a large number of pathogens has developed resistance to fungicides from the group of strobilurin when they appeared on the market in the 1990s. Strobilurins are single effect fungicides, and they have been in use of approximately twenty years. On the other hand, resistance cases have generally not been recorded at all for copper fungicides, despite them being used in agriculture for almost 130 years. Copper fungicides are fungicides with multiple effect.

Plant protection products are generally classified into groups according to their chemical composition, whereby those belonging to the same group usually have the same mode of action, thus affecting the same life process in the target organism.

Examples of resistance:

**Cross-resistance** is a phenomenon when a specific organism, after developing resistance to one active substance, also becomes resistant to all other active substances of the same mechanism of action.

For example, imidacloprid, thiamethoxam, thiacloprid and acetamiprid affect the same process in harmful insects. They are chemically similar and are classified into the group of neonicotinoids. If an insect develops resistance to imidacloprid, thus managing to "create" the ability to resist the toxic effect of that insecticide, it shall automatically become resistant to other insecticides from the group of neonicotinoids.

**Multiple resistance** is a phenomenon where a specific pest, pathogen or weed develops a resistance to more active substances with different modes of action. These are cases when certain harmful organisms succeed in developing a way to resist the effect of two or more toxic substances affecting different life processes. Such cases are common in agricultural practice. Multiple resistance usually occurs when a plant protection product is used frequently resulting in the occurrence of certain harmful organism resistance, whose population in a particular area becomes generally resistant. If after that another plant protection product of a different mechanism of action starts to be used frequently, resistant harmful organism may also eventually develop resistance to another plant protection product.
11.4 Strategy to prevent the occurrence of resistance

The resistance of pests, pathogens and weeds to plant protection products is a major problem in practice. If a certain harmful organism develops resistance to a plant protection product, that product shall no longer have an effect or shall have a weaker effect. Damage (losses) shall occur for agricultural producers, and, more importantly, they shall lose one of the solutions (a product) for a certain harmful organism. Of course, pests, pathogens or weeds spread, and there is always the possibility of resistant types spreading across a larger area and becoming predominant there. The plant protection product shall no longer be sold since it is not effective and the manufacturers and distributors shall lose part of their income. This represents a great loss for manufacturers of plant protection products if we know what the price of developing one active substance and its positioning in the market amounts to. Thus, the development of resistance causes losses to agricultural producers, the chemical industry and traders, as well as unnecessary losses in agricultural production that could have been prevented.

In order to prevent the aforementioned losses, all participants shall be included in the resistance prevention strategy. Producers of plant protection products themselves restrict the use, trying to prevent the irrational and the mass use of the same plant protection product. The users of plant protection products shall apply plant protection products carefully in accordance with the instructions on the label. Indication of the resistance prevention strategy is nowadays mandatory during the registration of plant protection products and it is regularly indicated and declared on the label.

The most important point to notice is that almost all the measures taken as part of integrated pest management are in a manner also the measures to prevent the occurrence of resistance. The basic measure aimed at preventing the occurrence of resistance is avoiding excessive, irrational or unjustified use of a plant protection product. Frequent use of a plant protection product leads to a higher, permanent selection pressure on harmful organisms in which the resistant specimen soon becomes dominant.

Effective agro-technical, mechanical, physical or biological measures can lead to reduced use of plant protection products, which automatically contributes to the reduction of the risk of resistance. Both susceptible and resistant harmful organisms can be adequately suppressed by the implementation of these measures. Tillage tools shall plough lamb’s quarters (*Chenopodium album*) specimens resistant to a herbicide and the sensitive ones equally well, and it is definitely all the same for a predatory mite *Phytoseiulus persimilis* whether it eats a red spider mite, which is resistant or sensitive to an acaricide.

When using plant protection products, the occurrence of resistance can be prevented, delayed or mitigated by following several key principles. The first principle is that the user shall adhere to the recommended amount of a plant protection product and the intervals between the treatments. Larger amounts shall create a bigger pressure on the population of harmful organisms, and smaller ones lead to a rapid selection of specimens that are a somewhat less sensitive to a particular active substance. Shortened intervals between the treatments may accelerate the selection of resistant specimens since the pest population becomes exposed to a toxic substance in short intervals. If it is noticed that a plant protection product gradually loses efficiency over a certain period, it is advisable to stop with its use and try to replace it with a plant protection product of a different mechanism of action, if such is available. The users of plant protection products in such situations often make the mistake of trying to increase the dosage, shorten the intervals between treatments or treat several times, which actually only enhances the resistance within a pest population.

If there are data showing that a certain pest, pathogen or weed in a particular area has become resistant to some active substance, it is certainly advisable to avoid the use of a plant protection product based on the same active ingredient and all active substances with the same mode of action.
Finally, the most important and most effective manner to avoid the occurrence of resistance is the **alternating use of plant protection products with different modes of action**. If a certain harmful organism has developed resistance to a plant protection product or group, the plant protection product with a different mode of action shall have an effect on it.

For example, if the fungus causing powdery mildew (*Erysiphe necator*) developed resistance to tebuconazole, resistant specimens shall remain sensitive to, for example, quinoxyfen. The fungus causing mildew, which is resistant to tebuconazole has developed a way to resist its toxicity, to survive and continue its development, but has not developed a way to simultaneously resist a completely different toxic effect of quinoxyfen. By modifying the plant protection products with different modes of action on the one hand the excessive use of one plant protection product is avoided, and possible resistant specimens are suppressed by the use of another product. In this manner, the selection pressure is decreased, and the destruction of resistant specimens prevents their further propagation and the increase of their numbers.

Since the occurrence of resistance in pests, pathogens and weeds is an important issue at the global level, the development of resistance is systematically monitored as much as possible. The most important international organisations monitoring the occurrence of resistance to plant protection products in insects, plant pathogens and plants are the Insecticide Resistance Action Committee (IRAC), Fungicide Resistance Action Committee (FRAC), Herbicide Resistance Action Committee (HRAC). Many information and data are available on their web sites, and they are certainly recommended to anyone interested in founding out more on the resistance to pesticides.

Since the repeated use of plant protection products based on the same active substance or those which have the same mode of action in the same areas over many years can cause the development of resistance, the label recommendation on the resistance prevention strategy indicates the following: **In order to prevent the occurrence of resistance, do not apply (name of the plant protection product) or other product which contains (name of the active substance) for more than (enter the number of applications) times per year on the same surface in accordance with the instructions for use on the label and/or in the accompanying sheet.**

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12 PLACING ON THE MARKET AND STORAGE OF PLANT PROTECTION PRODUCTS

12.1 Placing on the market, procurement, sales, distribution, transportation

Placing on the market means keeping for the purpose of sale, including offering for sale or any other form of ceding, with payment or free of charge, as well as the sale, distribution and other forms of ceding, but not including the return to the previous dealer. The release for free circulation represents the placement on the market.

Any plant protection product can be placed on the market as a preparation if it has been registered with the Ministry of Agriculture, and if it has been classified, packaged, labelled and equipped with a label containing the prescribed data (declaration) and instructions for use in accordance with special regulations on hazardous substances and preparations. The owner of the decision on registration or license is any legal or natural person holding a decision on registration of a plant protection product.

The representative is a legal or natural person authorised and legally representing the owner of the decision on registration or license.

The distributor is a natural or legal person who places pesticides on the market, including wholesalers, retailers, vendors and suppliers. Distributors of plant protection products shall have their seat in Croatia and be entered into the electronic records of the Phytosanitary Information System (FIS).

12.2 Sale

The distributor shall have a full time employee acting as a responsible person with completed at least the following: graduate university study or undergraduate university study or professional study in agronomy or forestry with completed at least 90 hours of modules in plant protection or 9 ECTS credits.

In case the distributor has several sales points, they shall have one full time employee acting as a responsible person at each sales point, which includes the pesticide sales to the end professional user, except for that sales point where advice is provided by the responsible person.

In addition, legal and natural persons engaged in the distribution of plant protection products shall meet the following:

- general, special and additional requirements regarding the facilities and space

The distributors performing storage, keeping and issuance of plant protection products within the framework of their activities shall have at their disposal the adequate facilities for storage, keeping and issuing of plant protection products which meet the technical and sanitary-hygienic requirements with regard to location, method of construction, quality of the walls and floors, lighting, ventilation, temperature and humidity.

Premises in which plant protection products are stored or sold shall have ventilation, which ensures that the concentration of harmful gases, vapours, dust and aerosols in the work environment does not exceed the exposure limit values laid down in the relevant regulations on occupational health and safety.

Cabinets, shelves and the premises in which plant protection products are stored and kept shall be clearly labelled and marked with the prescribed hazard signs and risk phrases.

- conditions for the sale of plant protection products
The distributors for the sale of plant protection products shall have a sufficient number of employees with the appropriate identification card.

Plant protection products **intended for professional users** may be sold only by the employees (persons) who have completed the exam in the corresponding module (advisor or advisor seller) and a valid identification card only to the professional users who have completed the exam in the appropriate module (professional user, advisor, distributor) and possess a valid identification card. Plant protection products may also be sold to the authorised lecturer if the authorised lecturer is a professional user.

Plant protection products **intended for non-professional users** may also be sold only to the persons who have not completed the exam in the appropriate module and who do not possess the valid identification card provided that they are only sold by the employee who has completed the exam in the appropriate module (distributor and advisor) and who possesses a valid identification card.

At each sales point, access shall be enabled to a web search engine of registered plant protection products (http://fis.mps.hr/trazilicaszb/) containing the information on all registered plant protection products approved for placing on the market and use in the Republic of Croatia

- regarding the responsible person and the employee

The person responsible takes care and is responsible for the import, procurement, takeover, storage, keeping and issuing of plant protection products, takeover and proper temporary storage of plant protection products, their remaining amounts and empty packaging, record keeping and data delivery, supervision of employees training and work. The responsible person also takes care of the waste generated from plant protection products, unused plant protection products, empty packaging in accordance with the regulations governing hazardous waste and regulations governing hazardous packaging.

The responsible person and the advisor provide the end user with the advice and instructions for proper use of plant protection products, as well as with the instructions for safe operation of the plant protection products and other relevant information, they verify whether the customer possesses the appropriate identification card if they are purchasing a plant protection product intended for professional users or professional users for professional applications.

- keeping records on plant protection products

Manufacturers, suppliers, distributors, importers and exporters of plant protection products maintain and keep for at least five years the records on plant protection products produced, imported, exported, stored or placed on the market. The registration owners are required to submit the data on the total annual volumes of plant protection products sold in accordance with the Regulation (EC) No. 1185/2009. The decision owners may deliver the data via their legal representative or distributor in Croatia. The data are submitted electronically in Excel tables prepared by the Ministry. The Ministry of Agriculture plans to develop a Phytosanitary information system module, which shall support the data delivery (Figure 1.12).

Regardless of the requirement regarding the submission of data on the annual plant protection product amount sold, the registration owners and distributors are required to submit the data
on the total annual volumes of plant protection products sold to end users. The data on the amounts of plant protection products sold obtained in this manner are much closer to the actual use of plant protection products since the data on the total amount of plant protection products sold differ significantly from the actually consumed amount. In both cases of data submission, it is necessary to avoid the duplication of data.

Professional users keep and maintain the records on the used plant protection products for at least 3 years. Records shall be kept in electronic or paper form, and the records kept by professional users shall contain the following data: trade name of the plant protection product, the date and time of initiation and completion of treatment, the amount of the applied plant protection product (dosage, concentration), surface size and treated crop or plant product, object, surface, some other use. The professional user may keep the records on the plant protection products in a format, which suits them best (record sheet, book, electronically, in a database ...), however, the records shall contain the prescribed information.

At the request of the competent authority, the relevant information from the records shall be submitted to the competent authority for a review.

Highly toxic plant protection products (T*) may be sold only to the person who has completed the exam for the professional users for professional applications category.

12.3 Import of plant protection products

Import of plant protection products implies only imports from third countries. Procurement of a plant protection product from a European Union Member State is not considered import. In the Republic of Croatia, plant protection products may be placed on the market only by legal and physical persons (distributors) with a seat and address in the Republic of Croatia and with registration in the central registry of the Phytosanitary Information System, which is maintained electronically. Only registered plant protection products or plant protection products, which have been issued an appropriate license, may be placed on the market since the right of free movement of goods within the European Union market is not applied to the plant protection products.
12.4 Existence and risks of illegal (counterfeit) plant protection products

In the Republic of Croatia, placing on the market, supply, sale and use of unregistered plant protection products are not permitted. However, sales of such products may occur occasionally and it is important to prevent it as soon as possible. It is necessary to distinguish between two possible situations of plant protection products illegal sales:

- sales of a plant protection product, which has not been registered in Croatia, but which is an original plant protection product placed in its original packaging of a known manufacturer and registered in another, often neighbouring country. The use of such a plant protection product is not illegal, nor is its import and placing on the market without a proper registration or license; and
- the sale of a counterfeit plant protection product, usually of an unknown manufacturer and composition since it is declared and packaged as an original, registered plant protection product of a specific manufacturer.

Several cases of unregistered or counterfeit plant protection products have been recorded in the Republic of Croatia, whereby one of the larger amounts seized did not contain active substances at all, and which fortunately did not reach the market. The proportion of counterfeit pesticides on the market is unknown, there are only estimates, but it is important to note that such products exist, and the purchase of products of dubious origin shall be avoided. Counterfeit plant protection products are not limited only to the territory of the Republic of Croatia, their occurrence has become a global problem. In the international trade, this is defined as organised crime with the aim of a quick profit with minimal investment, with no regard to the protection of consumers and end users.

The examples of risks arising from the use of unregistered and counterfeit plant protection products are the following:

- economical for the plant protection product user, due to possible insufficient efficiency or occurrence of phytotoxicity,
- negative effect on the humans and animal health and the environment, due to insufficient information or incorrect information on the label,
- risk due to unauthorised substances in the product,
- use of a plant protection product whose quality is below the prescribed standards, and can have an adverse effect on human and animal health and the environment.

Counterfeit plant protection products generally contain active substances of questionable purity, and may include toxicologically and ecotoxicologically relevant impurities above the prescribed limit values, as well as the substances and/or additives (co-formulants), which are prohibited in the plant protection products formulations due to their extreme toxicity or carcinogenicity. They can also contain completely different active substances from those indicated on the label, as well as the ingredients phytotoxic to the culture, thus causing unwanted damage.

There is no easy manner to identify counterfeit plant protection products, since there are cases in which they are very difficult to identify. Counterfeits may appear on the market for which is immediately obvious that they are not a genuine product, only by the appearance of the label or packaging, however, those whose labels and packaging are difficult to distinguish from the original plant protection product can also be found. Frequent quality of counterfeit plant protection products is a label, which does not contain all the required data or which lacks the plant protection product registration number or which indicates the wrong number and on which the data on the date of manufacture or production batch is missing. Such counterfeits can also be identified by inadequate packaging (e.g. the lack of a protective cap, packaging which is not used for plant protection products, packaging for food products, etc.) or the packaging is visually different from that of the original
registered plant protection product. It is also possible to notice the differences in the quality of label printing between the counterfeit and genuine registered plant protection product, and the cases without the labels on the packaging have also been recorded.

Counterfeit plant protection products often bypass retail chains, which are subject to regular inspection control. The sale is usually focused directly to the user, and they are sold at substantially lower prices than those of registered plant protection products. The sale of counterfeits is often performed without the possibility of issuing an invoice and is done via unusual or non-official channels.

Regular inspection and analysis of plant protection product samples is a very important method of combating counterfeit and unregistered plant protection products. The official control of the plant protection products (i.e. the post-registration control or formulation monitoring) is implemented in the Republic of Croatia, within which the competent inspection takes samples from the market and sends them to the physical and chemical laboratory analysis. In case of a doubt that a plant protection product has been counterfeit or not registered, that shall be reported to the competent agricultural inspector.

12.5 Storage of plant protection products

Storage is an integral part of placing the plant protection products on the market, aimed at ensuring the functionality of plant protection products until its issuance to the customer and/or user. The appropriate conditions for keeping and storage are the basis of preserving the formulation quality of the plant protection product on the market, as well as for the protection of health and the environment. Plant protection products shall be stored under the following general conditions:

- at a safe location where no damage to the packaging can occur,
- protected against humidity, rainfall, extreme temperature oscillations and freezing,
- in a room with proper air circulation,
- in the original packaging,
- in a manner, which prevents the interaction of two or more plant protection products,
- separately from food, beverages, feed and other products and
- out of the reach of children and non-professionals or other persons shall not be able to come in contact with the plant protection product.

For storage in the marketing chain, minimum requirements have been prescribed regarding the facilities and rooms in which storage, keeping and issuing of plant protection products is performed. In the premises where plant protection products are stored and sold, the conditions corresponding to the conditions indicated on the label of each plant protection product shall be ensured. In case of plant protection products intended for fumigation, additional storage conditions shall also be met.

In addition to providing protection against adverse climatic conditions (direct sunrays, atmospheric residue, gases, vapours, heat and freezing), facilities shall also be made of materials, which do not absorb plant protection products. Cloakrooms and adequate sanitary facilities shall also be anticipated and made functional in the facility. In warehouse and sales areas, access to unauthorised persons shall be prevented. All premises shall have natural or artificial ventilation, which ensures that the concentration of harmful gases, vapours, dust and aerosols in the work environment does not exceed the limit values laid down in the regulations on the occupational health and safety. All employees handling the plant protection products in the premises shall be provided with adequate personal protective equipment, as well as with a cabinet (auxiliary pharmacy) with the means for providing first aid. Artificial lighting and, where necessary, heating and cooling of rooms shall be provided in these areas.
The possibility of storing other types of products in the warehouse for plant protection products is limited to those products, which cannot be affected by plant protection products in any manner. The storage of plant protection products and seeds, seedlings, mineral and organic fertilisers, substrate for the cultivation of plants, animal feed and other products, which may be affected by the plant protection products in the same warehouse is not permitted (Figures 12.6 and 12.7). Plant protection products application equipment and other products, which cannot be affected, by plant protection products may be placed in the same premises with the plant protection products, however, free access to plant protection products shall be ensured.

Facilities intended for wholesale distribution of plant protection products are constructed at the locations with the most favourable climatic conditions (with respect to the wind rose, soil configuration, temperature changes and other relevant climatic conditions), at an appropriate distance from the facilities in which people live and work, schools, kindergartens, health, rehabilitation and other public institutions, in the areas not prone to flooding and in which there is no possibility of water pollution. Facilities are distributed so as to allow free access to fire-fighting units in case of fire. They shall have adequate facilities for the storage of plant protection products, temporary waste storage (empty packaging, unused plant protection products or plant protection products with the expired shelf life or which are improper), and a physically separated room for the responsible person. The premises shall not be located in the office and residential buildings or facilities for the animals. The doors of the facilities intended for wholesale distribution of plant protection products shall be constructed of non-flammable material and designed so as to close automatically. An exception are only the plant protection products labelled as harmful, corrosive, irritant, leading to hypersensitivity or classified as category 3 carcinogenic chemicals, category 3 mutagenic chemicals, chemicals toxic to reproduction of category 3 chemicals and chemicals that are harmful to the environment are stored in the facilities.

Facilities intended for retail distribution of plant protection products shall have an adequate room for the storage of plant protection products (Figures 12.2 and 12.3), the room and/or space for temporary waste storage (empty packaging, unused plant protection products or plant protection products with the expired shelf life or which are improper), retail space and the working premises for the responsible person in those sales locations where the responsible person is employed. The working premises for the responsible person and the sales area shall be separated from the storage premises.

Users maintaining the warehouse for the plant protection products until their application:

- shall ensure the storage conditions as prescribed on the label of each plant protection product,
- shall keep a plant protection product out of the reach of children, preferably in a locked room or cabinet,
- are prohibited from streaming/transferring a plant protection product from the original packaging into other types of packaging,
- shall not accumulate stocks of plant protection products, but plan their procurement,
- in case the entire amount of a plant protection product is not used, the remaining amount shall be tightly closed in the original packaging until its reuse,
- shall dispose of the plant protection product residues and its packaging as described on the label,
- shall keep own records on the procured plant protection products they have in the inventory, preferably in the form of the following recommended table.

It is recommended for the professional users to keep records on the procured plant protection products they have in the inventory in the form of the following recommended table.


**Table 12.1: Recommended method of keeping records on the plant protection products (prepared by: G. Peček)**

<table>
<thead>
<tr>
<th>Name of the plant protection product</th>
<th>Purpose (herbicide, insecticide, fungicide...)</th>
<th>Active substance</th>
<th>Amount kg/L</th>
<th>Production date</th>
<th>Batch number</th>
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12.5.1 Interior of the premises for the storage of plant protection products

Floor on the premises shall be smooth, easily washable, impermeable and resistant to plant protection products. There shall not be a direct drain into the sewage in the floor. When storing the plant protection products labelled as explosive, oxidising, highly flammable, easily flammable or combustible, the floor shall be electrically conductive or grounded. At the entrance into the premises where plant protection products are kept/held/stored, the threshold shall be constructed to the appropriate height so as to contain the spilled of scattered plant protection products. Shelves, cabinets, showcases, work surfaces and other equipment shall be made of resistant and inert materials which do not absorb the plant protection products and which can be easily and quickly cleaned and which guarantee safety at work (Figures 12.4 and 12.5).

When storing the plant protection products, sufficient space between particular shelves and/or deposits shall be ensured for the purpose of safe and undisturbed transfer of containers, provision of free air circulation and enabling the access in case of fire or other accident (Figures 12.2 and 12.3). Shelves and/or deposits height shall be such so as to guarantee their safety and prevent mechanical or other damage to individual packages (Figures 12.4 and 12.5).

12.5.2 Walls of the premises for the storage of plant protection products

The walls shall be constructed of materials, which are easily washable and resistant to hazardous chemicals. In the event that the plant protection products are classified and labelled as explosive, oxidising, highly flammable, easily flammable or combustible, the walls shall be constructed of non-combustible materials in order to prevent the spread of fire.
Figures 12.2 and 12.3: Retail warehouse which meets the requirements for the storage of plant protection products in terms of interior space design (source: www.grupoan.com; selected: V. Novaković)

Figures 12.4 and 12.5: Shelves in the retail warehouse which do not absorb the plant protection product and are easy to clean and maintain (source: agricultural Inspection)

Figure 12.6: Improper storage of plant protection products. Storage of seedlings together with plant protection products and difficult access to plant protection products (source: agricultural Inspection)

Figure 12.7: Improper storage of plant protection products. Storage of animal feed together with plant protection products and difficult access to plant protection products (photo: M. Kladarić)
12.5.3 Installations in the premises for the storage of plant protection products

Water and sewage pipes, as well as electrical and other lines that pass through the walls of the facility and premises and their openings shall be tightly closed.

12.5.4 Warehouse organisation

Plant protection products shall be stored in their original packaging in accordance with the conditions indicated on the label of a particular plant protection product. Plant protection products shall be packed in their original packaging, safely and clearly arranged according to purposes (insecticides, fungicides, herbicides, etc.). The schematic layout of plant protection products shall be placed at a visible location and easy access to it shall be enabled at any time (Figures 12.2, 12.3, 12.4 and 12.5). Access to plant protection products may not be hindered (Figures 12.6 and 12.7). Regular controls of the plant protection products condition and their packaging shall be performed in the warehouse.

Cabinets, shelves and the premises and in which plant protection products are stored and kept shall be clearly labelled and marked with the prescribed hazard signs and risk phrases.

Plant protection products, which may mutually react, shall be kept separately from each other in separate premises or in separated the same area, so as to prevent their direct contact in case of simultaneous leakage or spillage.

Plant protection products labelled as highly toxic (T+) shall be kept in different premises, separated from the rest of plant protection products and locked, and they may be sold only to the entity that has been authorised to operate these hazardous chemicals by the Ministry of Health or that possesses the identity card of a professional user of plant protection products intended for professional users for professional application.

In the space and/or premises for temporary waste storage, there shall be six appropriate containers with a lid or appropriate covering: a container with a suitable absorbent material (sand, perlite, clay, etc.), an empty tank for temporary collecting of scattered plant protection products, an empty tank for temporary collecting of spilled plant protection products, a container for collecting empty packaging, a container for collecting the packaging containing the residues of the unused plant protection products and a container for plant protection products with the expired shelf life or the decision on registration or the permitted period for sale and similar. Containers shall be labelled according to their purpose. Appropriate personal protective equipment (protective clothing and footwear, gloves, protective masks or half-masks), tools for collecting spilled or scattered plant protection products shall be provided in that room.

12.5.5 Storage of plant protection products on the agricultural holding

Plant protection products shall be kept in special premises or a special cabinet in its original packaging, separate from the food and feed, seed and seedlings, and other objects of general use, out of reach of children, according to certain requirements regarding the temperature, humidity and light and in accordance with other conditions stated on the label.

A professional and amateur user shall not possess, keep or apply the products, which have not been registered in the Republic of Croatia, that is, which do not have a valid decision on the registration or decision on the licence. In case of revoking or the expiry of the registration validity, the user may not own a plant protection product if the permitted period for the sales of the existing stocks defined by the Act in case of revoking the registration or the deadline for the sale of the existing stocks permitted
by the individual decision have expired. The user can verify these data using a Web search engine of FIS (http://fis.mps.hr/trazilicaszb/).

The professional user is required to collect separately the empty packaging of plant protection products, packaging with plant protection product residues and spray mixture residues and store them temporary until its submission to the authorised person in accordance with a special regulation governing the waste management.

The method of storage and the size of storage room is directly related to the amount of plant protection products used by professional users. For the professional users using small amounts of plant protection products, it is recommended to store the plant protection products in the closets of appropriate size (Figures 12.8, 12.9 and 12.10) or in separate premises in one of the existing facilities on the holding (Figures 12.11 and 12.12).

Figures 12.8, 12.9 and 12.10: Cabinets for storage of plant protection products (source: www.numak.eu/ecological-line/cabinets-plant-protection-product; selected by: V. Novaković)

Figures 12.11 and 12.12: Separate room for storage of plant protection products (source: www.topps-life.org; selected by: V. Novaković)
Professional users who use larger amounts of plant protection products may also store the plant protection products in a specially constructed facility, which ensures proper protection from rainfall and significant temperature oscillations, natural ventilation and which is protected from the ingress of surface water into the interior of the premises during major rainfall (Figure 13.12). Professional users who use larger amounts of plant protection products may also store the products in a warehouse constructed separately as a solid and enduring facility (Figure 12.14).

**Figures 12:13 and 12:14:** Separate premises for the storage of plant protection products, source: www.coleacp.org/pip; selected by: V. Novaković

Shelves in cabinets or facilities, where plant protection products are kept on the agricultural holding, shall be made of smooth and easily washable materials (e.g. metal shelves with protective coating), which cannot adsorb the plant protection product in case of spillage or leakage. In case of storing larger amounts of plant protection products on the holding, it is necessary to keep sandbags for absorbing the liquid near the cabinet or in the facility in case of accidental spills of liquid plant protection products. When storing larger quantities of different plant protection products, it is also necessary to pay attention to the internal organization of the warehouse and group the plant protection products according to their application (fungicides, herbicides, insecticides) and the state of matter (liquid, solid).

In the event that a certain amount of unused plant protection products remains in the warehouse in open packaging, they may be stored until reuse exclusively in the tightly closed original packaging together with the accompanying label.

Empty packaging of the plant protection products is kept in plastic bags or containers in the room where plant protection products are kept or stored.
12.6 Disposal of empty packaging, spray mixture and plant protection products residues

Disposal of empty packaging, spray mixture and plant protection products residues is governed by the regulations on waste and falls into the hazardous waste disposal category. The manufacturer of a plant protection product, as well as the holder of waste, are obliged to dispose of empty packaging, spray mixture and plant protection products residues in a manner which is safe for health and the environment.

According to the regulations on waste, the following are defined:

- the **manufacturer of the product** from which the waste originates is responsible for selecting the waste disposal solution, which is the most acceptable for the environment according to the product properties and production technology, including the product duration and the use of best available technology.
- the **waste holder** bears the costs of preventive measures and measures for waste disposal, waste management costs not covered by revenue generated from waste processing, and is financially accountable for the implementation of preventive and remedial measures in relation to environmental damage, which is caused or could be caused by waste.
- **recovery and/or disposal of waste** shall be performed in the nearest appropriate facility or device, taking into account economic efficiency and acceptability for the environment.

Empty packaging of plant protection products shall not be used for other purposes. Decanting of a plant protection product into another type of packaging, which is not intended for that purpose, is not permitted since it would also become a hazardous waste in that case. Unused plant protection product or spray mixture and packaging waste shall be delivered to the authorised company for hazardous waste disposal.

Croatian Crop Protection Association - CROCPA, performs the activities of collection and disposal of plant protection products packaging waste. Only the packagings of CROCPA EKO MODEL project member companies are collected through these activities. More information on the manner and place of the plant protection products packaging collection can be found on the website of the Association ([www.crocpa.hr](http://www.crocpa.hr)). There is a need for temporary storage with the user on the locations where waste packaging is occasionally collected. In this case, it is the obligation of the user to temporarily store the waste packaging until the delivery to authorised company for hazardous waste out of the reach of children, domestic and wild animals, protected from rain and direct sunlight, and other conditions in which a release of plant protection product residues in the environment might occur. Waste packaging shall not be stored in the same room with the food, drink, feed and similar products.

Systematic approach to the procurement of plant protection products is also closely related to the disposal of the remaining amount of a plant protection product and its packaging. After the application, the packaging of plant protection products remains, which is considered hazardous waste according to current regulations, and therefore it shall be kept in mind that it shall be disposed of properly. The hazardous waste also includes the spray mixture residues and unused products with the expired period of use, as well as improper plant protection products. Systematic approach to the procurement of plant protection products reduces the need for disposal of spray mixture residues and unused plant protection products to a minimum or removes it completely. Such approach is directed towards the protection of human health and the environment preservation, and ultimately also affects the financial expenses for disposal.
After the application of liquid plant protection products formulations, the remaining product in the packaging shall be rinsed with water at least three times in order to utilise the entire contents of the package and reduce the risk to human health and the environment arising from the insufficiently washed packaging. The effectiveness of the packaging triple rinsing shall be documented by the manufacturer of a plant protection product in the form of a study, which is assessed in the registration process and is the basis for the decision on the best method of packaging disposal for a particular plant protection product. The liquid generated by packaging rinsing is transferred into the application equipment container and used for the treatment. This process shall be conducted on the surface where the treatment is performed, in a manner to prevent contamination of water bodies or negative effects to the health of humans and animals or the environment. For certain plant protection products, especially certain herbicides (e.g. sulfonylurea herbicides), triple rinsing with water is not sufficient but it is necessary to use the approved products for cleaning the application equipment, which are listed on the label of the plant protection product.

Packaging of solid plant protection products is generally not rinsed with water.

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13 PLANT PROTECTION PRODUCTS APPLICATION EQUIPMENT

The efficiency of plant protection products also depends on the method of application and the quality of the application equipment. This would mean that the plant protection product, despite being applied in the optimal period, shall not be efficient and can cause a number of negative toxicological and environmental consequences with faulty application equipment. Therefore, we recognise the claim that the plant protection product is as efficient as its application is proper. There are different methods used for the application of plant protection products. Plant protection products are diluted with water are most often applied with sprinklers and sprayers. The basic difference is that sprinklers form larger droplets than sprayers. Sprinklers are used for the protection of agricultural crops, vegetables and for the application of the herbicides, and sprayers are for used for the application in fruit growing and viticulture.

13.1 Sprinklers

Sprinklers can be divided into: sprinklers with own engine, tractor sprinklers, manual sprinkler and battery sprinklers. Spraying is a method of plant protection products application through droplets with a diameter greater than 150 µm. There are different types of sprinklers on the market: backpack (manual), backpack (battery), backpack (motor), tractor (trailed and mounted), self-propelled and portable sprinklers with own engine (on the cart). The difference is in the operation mode, the volume of the tank, the number of nozzles and the operative reach.

In contrast to the small backpack tanks, bigger tanks have blenders, which shall be constantly in operation in order to maintain the spray mixture homogeneous. The treatment machine on backpack sprinklers carries one to three, and in the larger ones ten or more nozzles, which can spray downwardly (field machine) or horizontally on both sides of the (vineyard machine). Increasing the pressure can increase the range of vineyard machines, but still insufficiently for the treatment of wide rows plantations.

The main parts of the sprinklers are: pump, valves, tank, fittings (pipe system) and nozzle.

Pump

The pump creates a pressure required for the transport of spray mixture to the tank until the release from the nozzle. In manual sprinklers, the pressure of 3-6 bars is used, and in the engine ones of up to 40 bars. In addition to the pressure, the flow-rate or pump capacity is also important. The flow-rate of the pump is the maximum amount of water in litres which the pump releases per minute. The most important types of pumps in sprinklers are piston and piston-diaphragm ones. According to the release of liquid, they are divided into the pumps with continuous or pulsing liquid release. The manometer is a pressure regulator, which regulates the pressure within the limits of the pump operation.

Valves

The main valve stops the release of the spray mixture flexible lines with nozzles are connected to spare valves.

Nozzles

Nozzles (sucking-pipes, jets) are parts of the sprinkler on which a larger or smaller opening is located, which is smaller in diameter than the pipe leading the spray mixture to the nozzle.
Nozzles are among the most important parts of the sprinkler since the form of the range, angle and throw distance of the jet, droplet size, as well as the capacity of the entire sprinkler depend on them. Each type of nozzle, with a certain pressure, produces a jet of specific properties. The ultimate effect of a plant protection product depends on the choice of the most suitable type of a nozzle for a certain measure and its functionality and proper use. The operators of plant protection products shall pay attention to the application of appropriate nozzles for a particular protection measure, their proper use, as well as the regular replacement of worn nozzles with new ones.

**Fittings**

The fittings represent a metal structure, which carries the flexible lines with nozzles. It can be set into operative (unfolded) and transport (folded) position.

**Tank**

The tank contains the spray mixture for the treatment. There are various volumes of tanks according to the sprinkler type. Tractor sprinklers (trailed or mounted) have tanks of a larger volume containing a blender. The homogeneity of the spray mixture is maintained by mixing, so-called. The swirling (return) or hydraulically, using the nozzles placed inside the tank. The blender is an important part of the tank, which maintains spray homogeneous, meaning that the amount of a plant protection product is equal in all parts of the spray mixture. In addition to the main tank, new tractor sprinklers also have one tank of a smaller volume of approximately 50 litres of clean water intended for hand washing and rinsing of the spray mixture tank interior.

**Purifiers**

Purifiers are used to prevent clogging of nozzles. Clogging causes a waste of time, an increased risk of negative effects of plant protection products (in case of need for cleaning during the operation) and an irregular distribution of the spray mixture if the clogging is not detected. Factors such as the water quality, spray mixture properties and the possibility of active mixing of spray mixture in the tank define the cleaning system in the sprinkler/sprayer. The number of purifiers is defined as the number of openings per length of 1 inch (25.4 mm.). Several purification levels are usual in the application equipment:

- tank purifier (50 mesh),
- purifier at the suction (40 - 80 mesh),
- pressure purifier (40 - 80 mesh)
- nozzle purifier (50 - 100 mesh).
### 13.2 Sprayers

The application of plant protection products in fruit growing and viticulture is based on the application of tiny droplets over the plant surface using a sprayer (assisted sprayer, atomiser). The main task of spraying is that the air flow intakes and sprays the liquid in fine droplets sized from 50 to 150 µm. Spraying enables lower consumption of spray mixture in comparison to sprinkling. Sprayers are divided into backpack, tractor trailer and tractor mounted ones.

**Backpack sprayers** - intended exclusively for small surfaces inaccessible by tractor. The tank capacity amounts to up to 15 L, engine power up to 3 kW, fan capacity up to 1200 m³/h of air and nozzles up to 5 l/min of spray mixture (capacity).

**Tractor mounted sprayers** - used in smaller crops and crops at an angle. The tank capacity amounts up to 200-600 L, fan capacity up to 50,000 m³/h of air and flow-rate (capacity of all nozzles up to 20 l/min of spray mixture.

**Tractor trailed sprayers** - used in larger crops on flat to slightly sloping surfaces. The tank capacity amounts up to 600-3000 L, fan capacity up to 70,000 m³/h of air and flow-rate (capacity) of all nozzles up to 40 l/min of spray mixture.

Basic parts of the sprayers are divided into two groups. One group consists of parts, which are required for the handling of spray mixture: tank, pump, control circuit and the nozzle, and the second group consists of the parts used for creating the air currents: fan with drive and routers.

**Tank**

Basic characteristics of the tank are smooth interior walls, rounded edges, lid with a good seal, which is large enough, and a spray mixture level indicator. In addition to the main tank, new sprayers also have one tank of a smaller volume of approximately 50 litres of clean water intended for hand washing and rinsing of the sprayer interior after completing the operation. The reservoir contains a hydraulic blender, which is used for maintaining an even distribution of a plant protection product and prevention of its deposition in the spray mixture.

**Pump**

The required flow-rate (capacity) of the pump depends on the atomiser model and is correlated with the diffuser size and the number of nozzles on the diffuser since this directly affects the required selection of the pump.

**Control circuit**

It contains a pressure regulator, nanometre of at least 6cm with glycerine filling, sector valves and valves for fast closing and opening.

**Nozzles**

In recent years, they are made of stainless material resistant to wear. All nozzles on the sprayer, which are placed in the operating position, shall be the same, their capacity may not deviate by more than 10%, and they shall be flexible with the ability of individual closure.
Airflow

In most crops, airflows shall have the shape of two fan-shaped segments, which shall be symmetrical in form, speed, direction and altitude.

Fan

Each sprayer has an installed fan for the purpose of creating airflow. Axial, radial or tangential fans are most usually installed on the sprayers. In the axial fan, the air enters in the direction of its axis and is released in the same direction, while in the radial fan, the air enters in the direction of its axis, and is released at a certain angle in relation to that direction.

Most sprayers have an axial fan, since it produces a larger amount of air at lower output speed and consumes less operating power in comparison to the radial one. Tangential fan is a newer type of the fan. Unlike the previous two fans, it is of a cylindrical shape with a vertical axis. It is equipped with high routers so that the airflow is emitted perpendicularly to the crop, the path to the crop is shortened, and the penetration of spray mixture into the crop is better.

13.3 Preparation of the plant protection products application equipment

The application equipment shall be technically correct and aligned in order to be able to properly and uniformly distribute the required quantity of a plant protection product over the desired surface. In the spring, after the release of liquid antifreeze from all parts of the application equipment, it is necessary to perform a visual inspection of the equipment and reset the pieces, such as electronics, nanometre, etc. which were removed and stored during the winter.

The preparation of the application equipment can be performed in several steps:

- connect the sprayer/atomiser to the tractor, making sure that all protective equipment on the tractor and the application equipment is functional and properly installed,
- control manometer functionality (Figure 13.1)
- the purifier shall be checked, cleaned if necessary, and returned to its place (Figure 13.2)
- inspect the oil level in the pump,
- measure the air pressure in the pressure chamber (as recommended by the manufacturer),
- fill the tank with clean water to check the impermeability,
- when filling the tank with water, be careful to avoid spilling (always be in the proximity of the application equipment)
- spread the supporting fittings of the nozzles,
- initiate equipment operation,
- check nozzle operation.

When initiating the operation of the application equipment, 540 r/min of the connecting tractor valve shall be ensured in order to provide the full operative capacity of the pump (L/min). Set the pressure regulator to a minimum and gradually increase the operating pressure, depending on the type of the nozzle. During the visual inspection, attention shall be paid to the angle and shape of the jet and possible leakage of fluid at joints, flexible lines (so-called hoses), the regulator and the pump.
Flexible lines shall not be folded, since the operating pressure is reduced in this manner, and thus the flow-rate of liquid as well (Figure 13.3).

Clogged or partially clogged nozzles shall be cleaned with a soft brush or the compressor blowing procedure shall be applied. Nozzles shall never be blown by mouth. Cleaning the nozzle opening with metallic objects (steel brushes, needles, nails, etc.) or other hard objects is prohibited, since their use damages the nozzle opening, and thus changes the flow-rates and normal distribution of fluid in the jet. When conducting the inspection on older sprayers, which have nozzle holders without the in-built angle for preventing the jet collision, it is necessary to set the array of jets at an angle ranging from 5° to 10° (Figure 13.4).
The nozzle flow-rate measurement can be performed using a measuring vessel (graduated cylinder) or an electronic device for the flow-rate measuring (Figure 13.5). The flow-rate of all nozzles is measured and the average value is calculated. All nozzles in which flow-rate deviation of +/- 10% from the set one (the tables) is established shall be cleaned or replaced with new ones.

**Figure 13.5:** Electronic flow-rate metre of the company 'AAMS'
(Source: Improving the pesticide application techniques, D. Banaj)

### 13.4 Calibration of pesticide application equipment

The aim of each application of a plant protection product is to distribute the prescribed amount of the active substance evenly over the target surface/volume. In order to achieve the aforementioned, it is not sufficient to be familiar only with the dosage or concentration, but also with the sprinkling/spraying speed, operative pressure and nozzle selection, movement speed, etc. In order to ensure proper application of plant protection products, reduce the risk to human and animal health and the environment as well as the risk of phytotoxic effect on the crop, the application equipment shall be calibrated periodically, several times a year. Technical functionality of the application equipment, i.e. the accuracy of nozzles, flow-rate and pressure, uniform tractor speed, etc. are thus checked.

For the implementation of calibration, it is important to:

- have a functional and clean application equipment,
- install the functional nozzles,
- pour clean water into the application equipment tank,
- determine the area on which the coverage shall be measured,
- prepare the paper indicator, measuring vessels and the machines.

It is best to perform the calibration in the conditions prevailing on the land on which a plant protection product is applied (wheel slip, slope of the terrain, ...), but it is also possible on a flat concrete or earth surface where the mark of discharged liquid is easily noticeable.
13.4.1 Sprinkler calibration

The consumption of spray mixture and operating speed is usually first determined. In this case the selection of nozzles is limited to a choice of the accepted work pressure (the preferred operating pressure for standard nozzles is 2-2.5 bar). This can be found in the calibration circuit (calibration disk) (Figure 13.7) or a desired nozzle flow-rate can be calculated and the flow-rate value found in Table 13.4.

Example 1

If we want to apply the spray mixture amount of 150 L/ha at 8 km/h, it is necessary to do the following:

a) Check the operating speed

The work unit speed measurement (tractor + application equipment) (Figure 13.6) begins with the selection of the section, i.e. path on the surface to be sprayed or on the surface or similar appearance with respect to the micro-depressions (meadows, arable land). The recommended path length is approximately 50 m for determining the speed of up to 8 km/h or 100 m at a speed of 8 to 14 km/h. The measurements shall be performed with half-filled tanks. The speed measurement shall be performed three times in order to get a reliable measurement mean value. The following equation is used for determining the driving speed:

\[ v = \frac{s}{t} \times 3.6 \]

where:

- \( v \) - spray velocity (km/h),
- \( s \) - path length (m),
- \( t \) - time (s) spent for section passing,
- 3.6 - coefficient for converting m/s to km/h.

![Figure 13.6: Representation of the of work unit speed measurement (Source: Improving the pesticide application techniques, Đ. Banaj)](image)

The table for operating speed determination may also be used (Table 13.1).

**Table 13.1:** Elements to determine the operating speed (source: Improving the pesticide application techniques, Đ. Banaj)

<table>
<thead>
<tr>
<th>Movement speed [Km/h]</th>
<th>Time required to cross the path for the experiment [s]</th>
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<tbody>
<tr>
<td></td>
<td>25 m</td>
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<td>11</td>
<td>8.2</td>
</tr>
<tr>
<td>12</td>
<td>7.5</td>
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</table>
b) Calculate the necessary flow-rate and select the nozzles

The standard nozzle spacing is 50 cm.

\[
\text{nozzle flow (L/min)} = \frac{\text{controlled speed (km/h)} \times \text{spraying standard (L/ha)}}{1200}
\]

Rotation of the connecting valve shall not exceed 540 r/min\(^{-1}\), or be below 400 r/min\(^{-1}\) (if mixing is satisfactory).

c) Check the operation of the application equipment

For checking the operation of the application equipment, it is necessary to:

- always use clean water,
- set the selected nozzles on nozzle holders (fittings)
- during the control of system for leakage, turn on the sprinkler and sprinkle with an operating pressure of at least 7 bar and
- control the mixing of liquids.

d) Check the nozzle flow-rate

When checking the nozzle flow-rate it is necessary to:

- set the operating pressure,
- adjust the valves for equalizing the operating pressure,
- measure the nozzle flow-rate (L/min) and
- calculate the average nozzle flow-rate.

If the nozzle flow rate is not as required (nozzles have not been spent for more than 10%), a new operating pressure shall be defined.

\[
\text{new operating pressure (bar)} = \left( \frac{\text{new flow (L/min)}}{\text{measured flow (L/min)}} \right)^2 \times \text{measured operating pressure (bar)}
\]

Example 2

- the measured operating pressure is 2 (bar)
- the average flow-rate is 1.06 (L/min),
- the measured flow-rate (L/min).

The aim is to get the nozzle flow-rate of 1.0 L/min, therefore we need to measure the new operating pressure.

\[
\left( \frac{1.00 \text{ L/min}}{1.06 \text{ L/min}} \right)^2 \times 2 \text{ bar} = 1.77 \text{ bar}
\]

When adjusting the operating pressure at 1.77 (bar), we shall achieve the desired flow-rate of 1.01 L/min. It is necessary to measure the flow-rate one more time, to check.
Determining the liquid consumption in l/ha while knowing the flow-rate in L/min, the speed of the power unit (tractor + application equipment) in km/h and the nozzle distance of 50 cm can be determined by using the data in Table 13.2.

Table 13.2: Consumption of liquid in l/ha at a flow-rate in L/min at a speed in km/h (source: Improving the pesticide application techniques, D. Banaj)

<table>
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<tr>
<th>L/min</th>
<th>4 km/h</th>
<th>5 km/h</th>
<th>6 km/h</th>
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<td>345.00</td>
<td>306.67</td>
<td>276.00</td>
</tr>
<tr>
<td>2.40</td>
<td>720.00</td>
<td>576.00</td>
<td>480.00</td>
<td>411.43</td>
<td>360.00</td>
<td>320.00</td>
<td>288.00</td>
</tr>
<tr>
<td>2.50</td>
<td>750.00</td>
<td>600.00</td>
<td>500.00</td>
<td>428.57</td>
<td>375.00</td>
<td>333.33</td>
<td>300.00</td>
</tr>
<tr>
<td>2.60</td>
<td>780.00</td>
<td>624.00</td>
<td>520.00</td>
<td>445.71</td>
<td>390.00</td>
<td>346.67</td>
<td>312.00</td>
</tr>
<tr>
<td>2.70</td>
<td>810.00</td>
<td>648.00</td>
<td>540.00</td>
<td>462.86</td>
<td>405.00</td>
<td>360.00</td>
<td>324.00</td>
</tr>
</tbody>
</table>
**Calibration circuit (calibration disc)**

Calibration is performed with a calibration circuit (Figure 13.7) in which the data for the nozzles are presented. Example 3 shows the calibrating circuit of the company "Hardi" with data for the ISO 4110 series nozzles. The calibration disc is designed for the standard nozzle spacing of 50 cm.

If the volume (L/ha) and the spray rate (km/h) are selected, then the data can be traced on the calibration circuit, and the appropriate flow-rate can be selected. A calibration circuit can be used in several ways depending on the known parameters (Figure 13.7).

**Example 3**

If the work unit speed (tractor + application equipment) is checked, and amounts to 5.0 km/h (a), and our aim is to apply 200 L/ha (consumption of spray mixture), we turn the circuit and overlap 5 km/h and 200 L/ha (b). In the window on the upper half of the circuit, it can be read that each nozzle shall have a flow-rate of 0.83 L/min (c). On the lower half of the circuit, it can be read that this can be achieved with a nozzle 02 at an operating pressure of 3.3 bar (d) or nozzle 025 at a pressure of 2.1 bar (e).

---

*Figure 13.7: Calibration disk (source: [www.hardi-international.com](http://www.hardi-international.com))*
13.4.2 Sprayer calibration

For the sprayer calibration, it is necessary to know the operating speed, the selection of nozzles and operating pressure.

If the operating speed and the spray mixture consumption amount per ha are known, the flow-rate of all nozzles can be calculated based on the following equation:

\[
\text{total nozzle flow (L/min)} = \frac{\text{row width (m)} \times \text{spray consumption per hectare (L/ha)} \times \text{speed (km/h)}}{600}
\]

Example 4

- Row spacing: 5 m
- Standard spraying: 600 L/ha
- Movement speed: 4 km/h

\[
\text{total nozzle flow (L/min)} = \frac{5 \text{ (m)} \times 600 \text{ (L/ha)} \times 4 \text{ (km/h)}}{600} = 20 \text{ L/min}
\]

The total flow-rate through all the nozzles is 20 L/min. The aforementioned flow-rate is divided by the number of nozzles on a sprayer.

\[
\text{single nozzle flow (L/min)} = \frac{\text{total nozzle flow (L/min)}}{\text{nozzle number}} = \frac{20 \text{ L/min}}{10} = 2 \text{ L/min}
\]

The appropriate nozzle for the operating pressure at which spraying is to be performed can be found in nozzle table (Table 13.3 and 13.4).
Checking the spraying technique with water sensitive papers (paper indicator)

Papers sensitive to water (yellow paper turns blue in areas where water droplets fall) are a very useful tool in helping with the spraying technique optimisation (Figure 13.8).

This is especially important if a very dense assembly of plants is treated, and it is necessary that the plant protection product penetrates well into the assembly, therefore it is recommended to check the penetration of water prior to spraying with a plant protection products in the following manner:

1. place the sensitive paper at the spraying location - plant (use paper clips or staple gun, but avoid changing the position of the leaf,
2. mark the plant with a label so as to make it easier to find later,
3. spray the plant and then check on the paper if the drops have been deposited where it was wanted. If not, try to improve that by changing the spraying conditions (nozzle, operating pressure, spraying speed).

Figure 13.8: Water sensitive paper (photo: V. Tadić)
**13.5 Nozzles**

Nozzles (sucking-pipes, jets) are the output elements of almost all types of plant protection products application equipment and the entire technical value of the equipment is realized through them, i.e. their jet. Since the nozzles determine the precision of each operation of the application equipment, we consider them the most important parts of the sprinklers or sprayers. The ultimate effect of the applied plant protection product depends on the choice of the most suitable type of a nozzle for the implementation of a certain suppression measure and its functionality and proper use. It is extremely important that all who apply plant protection products be well acquainted with the nozzle properties.

The main task of the nozzles is to release spray mixture through small openings under pressure and at a certain speed, forming the required jet shape by breaking the liquid up into small drops. Each nozzle type, even the same type of different manufacturers, produces a jet of specific properties at a certain pressure. Each application of plant protection products requires certain jet properties, therefore the nozzle selection also depends on these requirements. There are no universal nozzles. Some nozzles are suitable for single application or only next to each other or for a low or high pressure. Nozzles can produce smaller or larger droplets. The stream they produce can be homogeneous or heterogeneous.

The nozzles shall ensure:

- uniform transversal distribution of spray mixture,
- work with minimal losses due to drift,
- creation of droplets of a certain medium volume diameter,
- technical functionality for as long as possible.

The nozzle capacity, nozzle disintegration and spray form depend on the nozzle kind and type.

**13.5.1 Labelling of nozzles**

Each nozzle bears a printed label that provides the most important information on the nozzle:

- nozzle type,
- jet angle,
- nozzle flow-rate.
Figure 13.9 shows a nozzle labelled as TEEJET 11004VS. The labels mean:

- TEEJET - company name,
- 110 - operating angle of 110°,
- 04 - fluid flow-rate in gallons per minute (in this example 0.4 US gallons, that is, 0.4 x 3.785 L/min = 1.514 L/min at 2756 bar or for easy calculation 0.4x 4.00 L/min at 3.00 bar = 1.60 L/min),
- VS - stainless steel.

Figure 13.9 Nozzle Teejet 110 04 VS.
(Source: www.teejet.com)

Figure 10.13: Marks on the crop sprayer nozzle
(Source: Improving the pesticide application techniques, Đ. Banaj)

Figure 13.10 shows a nozzle labelled as HARDI-ISO-F-03-110. The labels mean:

- HARDI - company name,
- ISO - ISO standard 10625
- F - nozzle type (nozzle with a fan-like jet)
- 03 - fluid flow-rate in gallons per minute
- 110 - operating angle of 110°,
Table 13.4: Labelling of fan-shaped nozzles and the use of nozzles colours from 01 to 05 (source: Improving the pesticide application techniques, Đ. Banaj)

<table>
<thead>
<tr>
<th>Nozzle colour</th>
<th>Sieve colour</th>
<th>Pressure bar</th>
<th>Flow-rate L/min</th>
<th>Standard spraying (L/ha) at the spraying speed (km/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>110-01 80-01 orange</td>
<td>Sieve 100M Red</td>
<td>1.5</td>
<td>0.283</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.0</td>
<td>0.327</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5</td>
<td>0.365</td>
<td>110</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.0</td>
<td>0.400</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.0</td>
<td>0.462</td>
<td>139</td>
</tr>
<tr>
<td>110-015 80-015 green</td>
<td>Sieve 100M Red</td>
<td>1.5</td>
<td>0.424</td>
<td>127</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.0</td>
<td>0.490</td>
<td>147</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5</td>
<td>0.548</td>
<td>164</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.0</td>
<td>0.600</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.0</td>
<td>0.693</td>
<td>208</td>
</tr>
<tr>
<td>110-02 80-02 yellow</td>
<td>Sieve 50 M Blue</td>
<td>1.5</td>
<td>0.566</td>
<td>170</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.0</td>
<td>0.653</td>
<td>196</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5</td>
<td>0.730</td>
<td>219</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.0</td>
<td>0.800</td>
<td>240</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.0</td>
<td>0.924</td>
<td>277</td>
</tr>
<tr>
<td>110-03 80-03 blue</td>
<td>Sieve 50 M Blue</td>
<td>1.5</td>
<td>0.849</td>
<td>255</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.0</td>
<td>0.980</td>
<td>294</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5</td>
<td>1.095</td>
<td>329</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.0</td>
<td>1.200</td>
<td>360</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.0</td>
<td>1.386</td>
<td>416</td>
</tr>
</tbody>
</table>
Table 13.5: Labelling of fan-shaped nozzles and the use of nozzles colours from 06 to 20
(source: Improving the pesticide application technique, Đ. Banaj)

<table>
<thead>
<tr>
<th>Nozzle colour</th>
<th>Sieve colour</th>
<th>Pressure bar</th>
<th>Flow-rate L/min</th>
<th>Standard spraying (L/ha) at the spraying speed (km/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>110-06</td>
<td>Sieve</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80-06 gray</td>
<td>24 M gray</td>
<td>1.697</td>
<td>407</td>
<td>339</td>
</tr>
<tr>
<td></td>
<td>white</td>
<td>2.0</td>
<td>1.960</td>
<td>470</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5</td>
<td>2.191</td>
<td>526</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.0</td>
<td>2.400</td>
<td>576</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.0</td>
<td>2.771</td>
<td>665</td>
</tr>
<tr>
<td>110-08</td>
<td>Sieve</td>
<td>1.5</td>
<td>2.263</td>
<td>543</td>
</tr>
<tr>
<td>80-08 white</td>
<td>24 M white</td>
<td>2.0</td>
<td>2.613</td>
<td>627</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5</td>
<td>2.921</td>
<td>701</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.0</td>
<td>3.200</td>
<td>768</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.0</td>
<td>3.695</td>
<td>887</td>
</tr>
<tr>
<td>110-10</td>
<td>Sieve</td>
<td>1.5</td>
<td>2.828</td>
<td>679</td>
</tr>
<tr>
<td>80-10 black</td>
<td>24 M white</td>
<td>2.0</td>
<td>3.266</td>
<td>784</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5</td>
<td>3.651</td>
<td>876</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.0</td>
<td>4.000</td>
<td>960</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.0</td>
<td>4.619</td>
<td>1109</td>
</tr>
<tr>
<td>110-15</td>
<td>No sieve</td>
<td>1.5</td>
<td>4.243</td>
<td>1018</td>
</tr>
<tr>
<td>80-15 pink</td>
<td></td>
<td>2.0</td>
<td>4.899</td>
<td>1176</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5</td>
<td>5.477</td>
<td>1314</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.0</td>
<td>6.000</td>
<td>1440</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.0</td>
<td>6.928</td>
<td>1663</td>
</tr>
<tr>
<td>110-20</td>
<td>No sieve</td>
<td>1.5</td>
<td>5.657</td>
<td>1358</td>
</tr>
<tr>
<td>80-20 light</td>
<td></td>
<td>2.0</td>
<td>6.532</td>
<td>1568</td>
</tr>
<tr>
<td>blue</td>
<td></td>
<td>2.5</td>
<td>7.303</td>
<td>1753</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.0</td>
<td>8.000</td>
<td>1920</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.0</td>
<td>9.238</td>
<td>2217</td>
</tr>
</tbody>
</table>

CONDITIONS: nozzle distance of 50 cm, the data for water at 20°C, the pressure is measured near the nozzle.
13.5.2 Selection of nozzles using diagrams

Many nozzle manufacturers in their catalogues and instructions present diagrams on the proper selection and use of nozzles, with which it is possible to select properly the appropriate type of the nozzle while taking into account the desired operating speed, use of spray mixture (L/ha) and properties of sprinkling/spraying. From the diagram in Figure 11.13, the appropriate type of the nozzle selected properly in a few simple steps.

Example:

1. Determine the consumption of spray mixture (L/ha) – we have determined 300 L/ha.
2. Determine the operating speed of the tractor - the determined speed is 8 km/h. Operating speed depends mostly on the humidity and relief of the soil, the type of crop and the growth stage.
3. Determine the desired category of droplet size - Very coarse droplets have been determined according to BCPC Classification (British Crop Protection Council). It is important to define the aforementioned depending on the purpose of treatment (fungus, insect, weed...), and on external conditions (wind speed, temperature, relative humidity).
4. Based on three predetermined parameters, read the recommended nozzle type, flow-rate and the required operating pressure from the diagram (Figure 11.13). In this case, it would be optimal to choose the air or injector nozzle under label ID 120-03. The required operating pressure is 4.5 bar.
5. The last step has a control function. The nozzle flow-rate shall be checked using a graduated cylinder or instrument.

![Figure 11.13: Diagram of nozzle selection according to the size of the droplets (source: www.lechler.de; modified by: V. Tadić)](image)
13.5.3 Droplet size and coverage area

Data on the droplets size are related to the size of each individual droplet in the jet released from the nozzle. That jet contains droplets of different sizes. The droplet size is expressed in micrometres (µm) (1 micrometre = 1 micron = 0.001 mm). Median volumetric diameter is used for defining the droplets size as a function of the dispersed volume of the solution, therefore, that droplet diameter often serves as a factor for comparing the nozzles properties.

In the last several years the classification of droplet size has been used in Europe, determined by the nozzle type and pressure advised by BCPC and is accepted as the international classification. Median volumetric diameter is used as the most important indicator of the droplets size in the jet (Table 13.6). Droplets smaller than 80 µm cannot be seen by the bare eye without a magnifier.

**Table 13.6:** Size and categorisation of droplets according to the British standard
(source: Improving the pesticide application techniques, Đ. Banaj)

<table>
<thead>
<tr>
<th>droplets category</th>
<th>droplet size (µm)</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>very small droplets</td>
<td>&lt;125</td>
<td>Insecticides and fungicides</td>
</tr>
<tr>
<td>small drops</td>
<td>125-250</td>
<td>Insecticides and contact herbicides</td>
</tr>
<tr>
<td>medium sized droplets</td>
<td>250-350</td>
<td>Translocation herbicides</td>
</tr>
<tr>
<td>large droplets</td>
<td>350-450</td>
<td>Translocation herbicides and foliar fertilisers</td>
</tr>
<tr>
<td>very large droplets</td>
<td>450-575</td>
<td>Foliar fertilisers</td>
</tr>
<tr>
<td>extremely very large droplets</td>
<td>&gt;575</td>
<td>Foliar fertilisers</td>
</tr>
</tbody>
</table>

Small and large drops have different properties, which can be compared and are shown in the following table (Table 13.7)

**Table 7.13:** Comparison of small and large droplet properties
(source: Improving the pesticide application techniques, Đ. Banaj)

<table>
<thead>
<tr>
<th>droplet property</th>
<th>small droplets</th>
<th>large droplets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evaporation</td>
<td>strong</td>
<td>weak</td>
</tr>
<tr>
<td>Sensitivity to wind</td>
<td>strong</td>
<td>weak</td>
</tr>
<tr>
<td>Surface coverage</td>
<td>good</td>
<td>poor</td>
</tr>
<tr>
<td>Penetration into the leaf mass</td>
<td>poor</td>
<td>good</td>
</tr>
</tbody>
</table>

13.5.4 Selection of nozzle type

According to the jet shape, there are two types.

**Nozzles with a fan-like jet**

Nozzles with fan-shaped (flat) jet are used today almost exclusively in farming and vegetable growing. The reason is that the fan-shaped jet achieves the best droplets distribution. The jet angle is usually 110° (and can also be 80°, 90° and 120°). If the nozzles have been installed on the sprinkler boom at a distance of 50 cm, a so-called double overlap between the nozzles is achieved (Figure 13.4). The optimum height from the nozzle tip to the surface, which is sprayed, is 50 cm, and still satisfactory
distribution is achieved if that height (due to uneven terrain) varies from 35 to 70 cm. In order to avoid jet collision, nozzles are rotated by 5° to 10° to the sprinkler boom.

There are three types of nozzles with a fan-shaped jet currently on the market (Figure 13.12):
- standard or conventional,
- low drift
- air induction, air inclusion, air injector.

**Standard nozzles** that generate a flat jet are also called universal nozzles. Depending on the pressure and size of the opening, the nozzles generate a jet with a wide range of droplets (small, medium and large droplets). If we use nozzles with a small opening (01, 015 and 02) we shall get a jet with the largest share of small and medium-sized droplets, which achieve a uniform distribution, better adherence and even coverage of the surface which is sprayed. Small droplets are very sensitive to wind, they evaporate quickly, therefore the losses due to drift are often significant. Therefore, these nozzles are applied in weather conditions, which are favourable for sprinkling. However, the drift can be somewhat reduced in the area of low pressure up to 2.5 bar and at a wind speed of 3 m/s. During operation at a higher pressure (> 3 bar), with larger nozzle openings and volume share of droplets smaller than 100 µm, the drift can then reach up to 30%, which is the main drawback of this type of the nozzle.

![Figure 13.12: Cross-section of nozzles with a fan-shaped jet](Source: Plant protection Newsletter, V. Duvnjak, M. Ćuljat)

**Anti-drift nozzles:** Unlike standard nozzles, this type of nozzle has an integrated pre-chamber of a prismatic shape. Decrease in fluid pressure in the pre-chamber, before opening of the exit opening, reduces the share of unwanted small droplets, which are generated through the spraying process. By using these nozzles, a narrower range of droplets in a jet, satisfactory distribution and low drift are achieved. The application can be performed up to a wind speed of 4 m/sec.
Injector or air nozzles are designed in such manner that by using the injector cartridge in the body of the nozzle, the air is sucked into the nozzle on the Venturi principle, which is mixed with spray mixture, thus creating large droplets that contain air bubbles. The amount of air in a droplet depends on several factors, and one of the most important is the formulation of a plant protection product for the preparation of the spray mixture that is sprayed. Both the liquid and the air medium in the spray mixture are in the ratio of approximately 1:1, and they are mixed in the nozzle chamber. Final dispersion occurs with the release of the liquid through the nozzle opening. The main goal of this type of a nozzle development was to achieve drift reduction, while retaining all the good properties, which the nozzles with a fan-shaped jet generally possess. Numerous tests of these nozzles under actual operating conditions have shown that the drift can be reduced by up to 90% in crop farming and up to 75% in the vineyards protection, compared to the conventional nozzles of the same size. Depending on the manufacturer, injector nozzles are designed in several manners:

- long design (ID) has higher values of mean volumetric diameter in a wider range of pressures (from 3 to 8 bar), and maintains the quality of the jet constantly,
- short design (IDK) has high values of mean volumetric diameter, but up to the working pressure of 2.5 bar. Increasing the pressure above 2.5 bar results in a decrease of mean volumetric diameter values, and the quality of the jet changes.

There are also double jet nozzles currently on the market, which have two fan-shaped jets at an angle. Injector nozzles have a large reduction in drift, they are accurate and resistant to wear. They are suitable for cereals, sugar beet and high-density crops. They have the improved effect in the application of fungicides. Injector nozzle AI3070, produced by the company “TeeJet” has two jets at an angle of 30° forward and 70° backwards. A large part of the droplets spectrum are large and medium-sized droplets, which reduces the wind drift and enhances the penetration of droplets into the crop (first jet), while the accompanying jet has a good coverage of the surface part of the crop (Figure 13:13).
Cone jet nozzles

Cone jet nozzles (conical jet) are usually installed on the sprayers and are traditionally used to protect crops of fruit, grapes and in field crops and vegetable growing for the fungicide application. According to their design, they can be:

- nozzles with hollow conical jet (Figure 13.14),
- nozzles with full conical jet.

Their main characteristic is that they create a jet with much smaller droplets (very fine/fine) and of relatively narrow spectrum at the same pressure and the size of the opening. Due to the aforementioned characteristics, these nozzles achieve good adhesion and high level of coverage of the surface, which is sprayed. For that reason they are almost exclusively used in orchards and vineyards, for the application of fungicides and insecticides, where it is important to apply a plant protection product on both sides of a leaf. Their main drawback is that their jet is subject to drift.

Table 13.8: Data for 1299 Hardi nozzle with a hollow cone (source: www.hardi-international.com)

Figure 13.14: Appearance of the ceramic nozzle "Hardi" 1299 with a conical jet (jet shape - hollow cone) (Source: www.hardi-international.com)
13.5.5. Nozzle wearing and their timely replacement

Nozzles on sprinklers and sprayers are worn during their use and shall be replaced with the new ones after a certain number of operating hours. Nozzle material wear is a result of the abrasive and corrosive action. Corrosion is the result of chemical, and abrasion is the result of the mechanical action of the liquid passing through the nozzle. Today, the nozzles are made mostly of stainless materials, which resolves the issue of wear due to corrosion. As a result of the nozzle opening wear, the jet shape is changed and the nozzle flow-rate nozzle L/min is increased in comparison to the proper declared amount.

Worn nozzles on sprinklers and sprayers are one of the most common causes of spending the unjustifiably large amounts of plant protection products, which increases the risk of use of inadequate plant protection products amounts, damages the plants, contaminates the environment, and significantly increases the cost of production. The nozzle shall be replaced when the flow-rate of liquid per unit time (L/min) is greater by 10% or more than the declared nozzle flow-rate, at a given pressure. In order to avoid the differences in the flow-rate of new and old nozzles, that is, for the purpose of even spray-mixture distribution, it is important replace all nozzles at the same time.

13.6. Consumption of spray mixture

Before the initiation of sprinkling or spraying, the optimum consumption of spray mixture shall be determined. The spray mixture consumption depends on the surface area, the volume of plants or parts of plants to be treated, the type of pests, pathogens and weeds to be suppressed, the property of the plant protection product and application equipment.

European and Mediterranean Plant Protection Organisation (EPPO) has classified the application into the grades shown in Table 13.9 according to the spray mixture consumption per unit area.

Table 13.9: Consumption of spray mixture in different types of crops (source: Improving the pesticide application techniques, D. Banaj)

<table>
<thead>
<tr>
<th>Croatian name</th>
<th>English name</th>
<th>in orchards and vineyards</th>
<th>in vegetable and crop farming</th>
</tr>
</thead>
<tbody>
<tr>
<td>High consumption of spray mixture</td>
<td>HV - high volume</td>
<td>&gt;1 000 L/ha</td>
<td>&gt;600 L/ha</td>
</tr>
<tr>
<td>medium consumption of spray mixture</td>
<td>MV - medium volume</td>
<td>500-1000 L/ha</td>
<td>200-600 L/ha</td>
</tr>
<tr>
<td>low consumption of spray mixture</td>
<td>LV - low volume</td>
<td>200-500 L/ha</td>
<td>50-200 L/ha</td>
</tr>
<tr>
<td>very low consumption of spray mixture</td>
<td>VLV - very low volume</td>
<td>50-200 L/ha</td>
<td>5-50 L/ha</td>
</tr>
<tr>
<td>ultra-low consumption of spray mixture</td>
<td>ULV - ultra low volume</td>
<td>5-50 L/ha</td>
<td>1-5 L/ha</td>
</tr>
<tr>
<td>ultra, ultra-low consumption of spray mixture</td>
<td>UULV - ultra, ultra-low volume</td>
<td>&lt;5 L/ha</td>
<td>&lt;1 L/ha</td>
</tr>
</tbody>
</table>

Technically speaking, in our types of crops, amounts from 150 to 400 L/ha (Figure 13.15) with droplet size of 100 to 300 µm can be normally distributed using the working units (tractor + sprayer). It has
been established that such a solution is also the most economically acceptable one, since it represents a compromise between the required investments in machinery and labour costs, and it is also environmentally acceptable.

![Figure 13.15: Sprayer operating in the orchard (photo: V. Tadić)](image)

Increasingly more strict environmental requirements relating to the plant protection shall in the near future probably also require the limitation of the spray mixture consumption per hectare, while the entire remaining surplus falls to the ground. According to some authors, that amount is only 600 L/ha of spray mixture. Since this retention volume is even smaller for smaller hectare volumes, it is logical that for achieving the environmentally acceptable plant protection, the consumption of water per hectare and the plant protection product have to be adjusted to some extent to the crop hectare volume. There are several methods for solving this issue in Europe. For example, in this sense Swiss experts recommend the spray mixture hectare consumption of 400 L/ha for the plants volume of 10 000 m³/ha early in the season, while for the crops of a stronger or weaker ages, they linearly increase or decrease it. Although it is still not clear when and how these new, somewhat revolutionary procedures in plant protection shall be introduced, it is certain that they shall be based on a better preparation of the equipment, precise procedure selection and a more careful operation in the crops.

**Filling the sprinkler/sprayer tank**

The amount of a plant protection product in a tank is (L or kg):

\[ \text{PPP quantity for the tank (kg) or (L)} = \frac{\text{tank volume} \times \text{PPP dosage (kg/ha) or (L/ha)}}{\text{spray consumption (L/ha)}} \]

*If a full tank is not used, then real volume of liquid that is intended for use is entered instead of the tank capacity.*
13.7 Maintenance of the plant protection products application equipment

Proper maintenance and proper use of the application equipment enables reliable use of a plant protection product, which means that in order for the plant protection products application equipment to operate properly, they need to be regularly maintained. This means a systematical inspection of the equipment, and if necessary, replacement of the worn and malfunctioning parts of the sprinkler/sprayer. This does not includes only the parts such as pumps, hoses and nozzles, but also nozzle holders, shafts, bearings, connecting shaft, tank etc.

During the regular inspection of the plant protection products application equipment, it is necessary to:

- check the oil level prior to use,
- after sprinkling/spraying, empty the tank and wash the remains of the plant protection product with clean water,
- check all hoses and joints sealing,
- remove and clean the main purifier after each use (while being careful not to damage it),
- regularly check the nozzles flow-rate and jet shape (if the deviation of the flow-rate exceeds 10%, replace the nozzles),
- nozzles made of different materials do not have the same life span (e.g. nozzles made of brass are worn much faster)
- all nozzles on the application equipment have to be made of the same material and be of the same degree of wear.

During the plant protection products application, it is necessary to be careful about:

- the permanence of the selected operating pressure and operating speed,
- the regular shape of the jet,
- the accuracy of the nozzle height on agricultural sprayers (from 35 to 70 cm)
- proximity to water courses, i.e. operate at a distance in accordance with the instructions on the label,
- wind speed, i.e. stop sprinkling/spraying at the wind speed higher of 3 to 4 km/h
- operation of the blender and mixing of the plant protection product in the tank (the blender shall be turned on from the beginning of spray mixture preparation until the end of the plant protection product application) and
- that the tractor is not stopped while the application equipment has a function of applying the plant protection product.
Tank

The application equipment tank shall be washed inside and outside after each use. If the calibration of the application equipment has been performed well, a small amount of spray mixture shall remain in the tank after sprinkling/spraying, and the cleaning process itself shall be shorter and simpler. The remaining amount of the spray mixture shall be diluted with clean water and sprayed over the already treated surface (this time with a significantly diluted solution, which shall not harm the crop). An extremely important part of the sprinkler is the tank with clean water, which is used for washing the application equipment (inside and outside). During any handling of the application equipment, the use of personal protective equipment is mandatory (primarily gloves because of the residues of plant protection products on all parts of the application equipment) (Figure 13.16). In addition to general instructions for cleaning (washing) of the tank, the instructions for cleaning the application equipment contained on the label of a particular plant protection product shall be followed.

![Figure 13.16: Filling the application equipment while using the personal protective equipment](Source: www.hardi-international.com)

Purifiers

Plant protection products and small impurities (which passed through the purifiers at the entrance to the tank) can accumulate on the purifiers, either on the suction or discharge side of the application equipment. This is particularly the case while using the plant protection products formulations in the form of powders (WP, SP, WS). It is therefore necessary to clear all the purifiers after the final spraying in order to prevent the drying of the plant protection product, thus obstructing the normal flow during the future spraying. In such case, the impurities would be much harder to clean, and the purifier could be damaged.

Pump

The vital parts of the pump are valves, which, can be damaged over time if impurities accidentally appear in the tank. In addition to the valves, the pump also has the membranes that are in contact with the spray mixture. In case of a damage to the membranes, mixing of the oil and spray mixture may occur. In that case, it is necessary to disassemble the pump and take it immediately it to be repaired in the authorized service centre.
Regulator

One of the reasons, which may prevent the achievement of the sprayer operating pressure, can also be a malfunctioning pressure regulator. Proper operation of the regulator can be check during the operation with clean water. The main valve as well as the valve for each section shall be well sealed and the dripping shall not occur after they are closed. In such case, the seals on the valves shall be replaced and finally all parts that can be opened or closed need to be lubricated.

Manometer

A functioning manometer is required for determining the correct amount of spray mixture per unit of area. The functionality of the manometer can be checked by using the new nozzles of a known flow-rate in such manner that a pressure of 3 bars is adjusted on the manometer and the quantity of water passing through the nozzle during one minute is measured in the measuring vessel measured and compared with the values of nozzle follow-rates in the table placed in the vicinity of the nozzles.

Nozzle holders and protection against corrosion

In order to maintain the application equipment functional for as long as possible and reduce the maintenance costs, it is also necessary to take care of the lubrication of the individual parts. Many plant protection products are aggressive and difficult to wash after they have dried. After the use of plant protection products, the application equipment shall, if possible, be washed in the field, if it is equipped with a machine for washing under pressure. After rinsing the entire system with water under pressure and drying, the metal parts shall be coated with an anticorrosion product (oil).

Connecting shaft

Protection on the connecting shaft shall always be set in order to avoid possible accidents at work.
13.8 Using the tractors

Since the tractor is a great investment for farmers, it is important to make a maximum use of it, which would mean that it is necessary to select a tractor in accordance with the characteristics of the agricultural land (area, crop, distance between crops, slope, etc.) in order to achieve the maximum performance with the lowest price.

13.8.1 Use of a tractor with a closed cabin

The plant protection product application using the sprinkler or sprayer aggregated with a tractor without a cabin can result in the exposure of skin and respiratory tract to harmful effects of plant protection products. The use of a tractor with a closed cabin, which reduces the potential exposure of operators, is recommended. Furthermore, the tractors and application equipment shall be harmonised, which means that the tractor shall have enough power (kW/hp) for the equipment to operate efficiently under all operating conditions. All systems (hydraulic, electric and pneumatic) shall be functional. It is therefore important for the protection of the driver during spraying or sprinkling that the tractor is equipped with a cabin (Figure 13:17), and that it has an efficient air purifying system. Closed cabin protects the user from external influences (atmospheric influences, mist etc.). It shall meet the minimum standards and be certified.

![Figure 13.17: Orchard-vineyard tractor with a cabin](source: www.antoniocarraro.it)

![Figure 13:8: Control of air in the cabin of Antonio Carraro](source: www.antoniocarraro.it)

Tractors with control of air (air control) in the cabin (Figure 13:18) can currently be found on the market, in which active ventilation the cabin creates the overpressure in the cabin, which is filled with clean air (by the passing of the polluted air through a carbon filter which is turned on). At the driver’s request, the tractor guarantees the maintenance of overpressure in the cabin, and constantly informs on the effectiveness of the system. It shows the operating hours of the carbon filter (including the information - how many operating hours are left until the replacement carbon filter) and the value of overpressure in the cabin, which guarantees the isolation of the interior of the cabin from the external harmful effects of plant protection products.
13.8.2 Precautionary measures during tractor use

The tractor shall be managed in accordance with the manufacturer's instructions and with the greatest caution. For safety reasons, it is necessary to comply with some general guidelines:

- get familiar with the tractor operation before use,
- avoid the use of tractors on steep surfaces or in narrow turns in order to avoid overturning,
- do not connect the equipment that is too strong for the tractor power.

During the sprinkling with tractor, it is necessary to:

- when using a tractor with a closed cabin, keep clean gloves in the cabin in case the application equipment shall be repaired (e.g. unclogging the nozzles, etc.),
- when turning the tractor at the end of the rows, close the sprayer or sprinkler nozzles,
- prevent spray mixture drift on the neighbouring crops/plantations/surfaces. Whenever possible, use the nozzles with a reduced spray mixture drift. In case of a spray mixture drift, it is necessary to determine the cause and correct the error.

13.9 Special application techniques - sprayers with lower spray mixture consumption (ULV)

Most of the plant protection products are applied in the form of a jet that is transformed into droplets and distributed over the target object (plant). Uneven coverage of the target plant is a waste, costs and results in unwanted and unnecessary environmental pollution. Droplet size is important for achieving the best biological results. For most plant protection products applications, there is a certain size of droplets spectrum that shall be the most effective. In standard sprayers, nozzle produces a wide spectrum of droplet sizes. Droplets of very large and very small size often represent a loss - large often end up on the ground, while the small droplets are subject to washing and environmental pollution. This inefficiency means that a higher amount of liquid from that necessary for successful treatment shall be used, which reflects negatively on the time spent, effort and the expenses. Controlled Droplet Application (CDA) provides solutions for certain aspects of application. This efficiency allows the use of small and very small amounts of spray mixture.

13.10 Possibilities of application quality improvements

In field conditions during the treatment, i.e. transport of droplets form the application equipment to the plants to be treated, the loss of spray mixture may occur due to drift, and significantly reduce the effectiveness of the application. During the application, it is important to prevent drift to non-targeted surfaces and objects. This is a negative phenomenon resulting in the contamination of the plants on adjacent plots, and can also lead to the poisoning of people, domestic animals, game, bees, environmental pollution and fish kill if product ends up in the nearby waterways. The most important causes of drift are: wind, air humidity and warm weather, therefore sprinkling or spraying shall be performed in favourable weather conditions, although it sometimes has to be performed and when the risk of drift is high.
A combination of factors that can contribute to drift (Figure 13.20):

- wind speed,
- nozzle height, equipment design and conditions on the ground,
- jet quality (depends on the choice of the nozzles and the operating pressure)
- tractor movement speed (sprinkler/sprayer)
- type of crops, vegetation or no vegetation,
- local weather conditions,
- functionality of the equipment used in the application,
- adjustment of the sprinkler/sprayer.

Figure 13.20: Factors affecting the drift of liquid and its impact on the environment
(Source: Improving the pesticide application techniques, Đ. Banaj)
For the plant protection products application, it is necessary to know the following:

- do not sprinkle/spray close to sensitive areas, streams, rivers, lakes, settlement if upon the arrival to the place of plant protection products application wind is noticed (e.g. the flickering of leaves, branches)
- hot and dry weather reduces the droplets size and increases the possibility of drift. The safest conditions are: cold and wet weather with constant wind of up to 7 km/h (light breeze) which blows from the direction of the sensitive areas.
- Avoid sprinkling/spraying during temperature inversions.

During clear nights, the soil can lose heat quickly in a dry atmosphere and cold layers of air are formed along the soil surface. Under these conditions, the air near the ground is cooler than the air in higher layer, which is known as a temperature inversion (Figure 13.21). This phenomenon tends to suppress the vertical movement of air and thus create a barrier to penetration of small spray mixture droplets into the crop canopy. The inversion often occurs during very quiet weather (no wind). It is therefore necessary to avoid spraying at such a weather, since small droplets can float in the air for a long time, between the layers, and can cause serious damage kilometres away from the place of treatment. It is also necessary to know that:

- lower air humidity causes greater droplets evaporation.
- higher air temperature causes greater droplets evaporation.
- small droplets are more susceptible to evaporation from the large ones.

**Figure 13.21:** Temperature inversion (Source: http://www.geograph.org.uk/photo/959775)
Procedures to prevent drift and contamination:

- Monitor the weather forecast and conditions on the land plot before initiating the plant protection product application. Do not treat if there is a possibility of droplets drift from the target surface.
- By reducing the spray mixture consumption, the amount of the plant protection product taken away by the wind shall be reduced.
- Use nozzles that produce larger droplets (injector or air nozzles that are more resistant to drift).
- Keep the branches agricultural sprayer in a position as low as possible, which enables good lateral distribution of the spray mixture. Proper height nozzle shall depend on the jet angle, nozzle spacing, plot arrangement and design of the sprinkler branches.
- Not treating the peripheral part of the plot that is the closest to the border downwind (buffer zone).
- Plant trees as a natural protection from the wind along the edge of the orchard.
- Use different sprinkling/spraying systems, that are available, in order to reduce drift. Acceptable systems for reduction may include the twin fluid nozzles, injector nozzles, sprayers with air support, recirculating tunnel sprayers (for orchards, vineyards and bushy plants).
- The use of anti-drift additives depends on the type of equipment used and the spray mixture.

The effect of the wind speed shall be expressed depending on how far the droplets shall travel horizontally. The forces of gravity are very small in this case, since the droplets mass is small. Very small droplets (less than 100 µm) fall very slowly and often remain floating in the air for up to twenty minutes, i.e. they behave as fog. According to scientific findings, a droplet with a diameter of 200 µm, with an increase in speed of 1 m/s (3.6 km/h), shall be carried by the wind for up to 21 m before it falls to the ground. A droplet of 100 µm size needs approximately 11 seconds to fall from a height of three meters. If we release that droplet into the wind current of a 2.2 m/s (8 km/h) speed, it shall be carried for approximately 23 m before it falls to the ground.

Newly developed air-injector nozzles generate larger droplets than standard fan-shaped and conical nozzles. Large droplets slide from the leaf surface, but the droplets of air-injector nozzles create air bubbles within the droplet. With the fall of such droplet to leaf, it is scattered across the surface. In this manner, a very small drift occurs because of the creation of larger droplets, and the effect of the surface coverage is approximate to that of smaller droplets. All types of injector field nozzles for plant protection products application have become necessary in modern agriculture for the successful application from the economic point of view and from the point of view of environmental protection in all standards. One of the great advantages of the injector nozzle technology is drift reduction without affecting the other sprinkling factors.
13.11 Special designs of sprinklers/sprayers

13.11.1 Sprinklers with air support

The trend is the development of sprinklers with low spray mixture consumption per unit of area with the least possible loss on the non-targeted site (harmful organisms). At the same time, a more significant loss through droplets drift (sensitivity to wind) may occur with smaller droplets. Through the innovations of technical systems in the plant protection, a sprinkler model with air support HARDI TWIN was developed (Figure 13:23). Twin system consists of conventional branches with flat nozzles and one or two fans, which blow the air through the airbag. The air is then transferred over the entire length of the branches by airbags.

The airflow directs, thrusts, pushes the spray mixture droplets towards the plants. In order to minimize the sensitivity to weather conditions (wind), there is a possibility of angle nozzles rotation depending
on the speed and direction of the wind (Twin: ± 18° and Twin force ± 30°, 40° forward and backwards), thus achieving the optimal spraying of the treated surface (Figure 13.24).

Figure 13.24: Demonstration of angle change in the "Twin" system (Source: www.hardi-interacional.com)

The sprinkling process takes place in small droplets. The reduction in losses using air support is so great that spraying can be successfully performed even at a wind speed of 8 m/s. The sprinkling limit for the conventional sprinkler is at a wind speed of 4 m/sec. This type of the sprinkler is more appropriate for the application of fungicides and insecticides in the later stages of the crop development (e.g. cereals). It is less or not at all appropriate for the application of herbicides.

System properties:

- Lower consumption of water and plant production products,
  Long experience from practice shows significant reduction in water consumption, as much as by 50%. The aforementioned savings are expressed in crops, which are the beginning of the vegetation, and regardless of the nozzle type, i.e. the droplets size. When sprinkling the plants in further vegetation development stage, the savings increase and amount to up to 80%. Practice has shown that water consumption is about 150 l/ha, which also means that the time for filling the tank is shorter and a larger surface can be sprinkled.
- Lesser contamination of adjacent land plots by drift
  The loss by the removal can be so great with conventional sprinklers that the sprinkling procedure shall be stopped when wind speed is greater than 3 to 4 m/s. Using the "Twin" system, this limit is moved to 8-9 m/s, whereby the loss due to drift is lesser than the loss at normal conditions when using conventional sprinklers. The use of such sprinkling techniques provides uniform distribution, a large deposit of droplets and better coverage of the target surface (Figure 13.25).
Figure 13.25: Display of test papers surface coverage and the droplet size with different nozzles at the same operating conditions (source: www.hardi-interacional.com)
13.11.2 Tunnel equipment for the treatment of vineyards and low crops in orchards

Using the technology to recycle spray mixture, which is not deposited on the plant, spray mixture is carefully filtered, pumped into the tank and re-used. This is a great benefit for vine grape and fruit growers, as well as for the environment. The innovative equipment applies spray on both sides of the crop and ensures optimal application (Figure 13.26).

**System properties:**

- requires up to 30% less spray mixture,
- reduces drift almost completely (up to 75%),
- possibility of application near protected areas (waterways, near the settlements...)
- increases the product deposit up to 60%
- safer work for the operator.

*Figure 13.26: Tunnel equipment for the treatment of vineyards and low crops in orchards (Source: www.interempresas.net/Agriculture)*
**13.12 Specific risks associated with the use of manual and backpack sprinklers**

Manual and backpack sprayers (Figure 13:27) are mostly used for the application on small surfaces and for amateur use. It takes great skill and attention during the treatment in order to cover the plant surface without overlapping, which would cause the loss through leakage, and may increase the risk of phytotoxicity. Enviable skill is necessary to ensure uniform application. The spray mixture amount, movement speed and coverage shall be conditional on temperature activity, terrain slope and surface configuration over which the operator moves. Manual and backpack sprinklers shall be equipped with a manometer in order to control spray mixture consumption (droplet size), and distributes it evenly over the target surface.

**Calibration of manual or backpack sprinkler:**

1. prepare the sprinkler for sprinkling,
2. measure and mark the terrain for the calibration of a 25 m² surface, and mark it with stakes,
3. fill the tank with clean water (up to the mark of for example 5 litres),
4. sprinkle the surface using the operating pressure and walking speed that shall be used during the operation,
5. when sprinkling of the marked plot is finished, (25 m²), measure the amount of consumed water - up to the mark of 5 litres.
6. the amount of water applied on 1000 m²; or on one hectare can be calculated from the following formulae:

The amount of liquid/1000 m² = litres consumed in the calibration area (25 m²) x 40
The amount of liquid/ha² = litres consumed in the calibration area (25 m²) x 400 or we may use the data listed in Table 13.10.

**Table 13.10: Consumption of spray mixture on the surface (litres/1000m², litres/ha) (source: www.hardisprayer.com)**

<table>
<thead>
<tr>
<th>Litres spent on the plot (25 m²)</th>
<th>Litres/1000m²</th>
<th>Litres/ha</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>10</td>
<td>100</td>
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<tr>
<td>0.30</td>
<td>12</td>
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<td>38</td>
<td>380</td>
</tr>
<tr>
<td>1.00</td>
<td>40</td>
<td>400</td>
</tr>
</tbody>
</table>
13.13 Risk management measures

Measures of controlling the exposure to plant protection products

For the purpose of controlling the exposure when preparing the plant protection product (e.g. when opening the packaging) and when moving, diluting, mixing and pouring a plant protection product in the application equipment tank, the following shall be done:

- procure a plant protection product in packages of the size appropriate for the treated surface, or the amount of spray mixture that is prepared. In such manner weighing or measuring of the exact dosage for each tank filling can be avoided;
- prepare the plant protection products in the open and airy place;
- use rubber gloves, rubber boots, protective clothing, head cover, protective goggles, respirator or nose filter;
- open the packaging carefully so as to prevent the plant protection product droplets coming into contact with eyes and skin;
- use closed systems (equipment that is designed and manufactured to dose and measure precisely from the original packaging the amount of a plant protection product for the equipment tank) with a compatible packaging;
- use the equipment for rinsing the packaging; avoid rinsing by hands,
- when operating a plant protection product – do not lift the vessels containing the plant protection product above the head level;
- reduce the dosage of a plant protection product whenever possible;
- select the best equipment for the job;
- if a plant protection product application method would increase the risk for the user, a different method of application shall be considered;
- use a tractor with a cabin whenever possible;
- check the functionality of the application equipment;
- new equipment shall meet the standards for reducing the risks of contamination during the use or maintenance (use of equipment with controls in the tractor cabin, self-cleaning filters, with a built-in internal washing of the tank);
- check the functionality of nozzles for dripping when the application equipment is turned off;
- keep the plant protection products application equipment clean (inside and outside). while cleaning dry or powdery deposits, do not use the air flow (compressor), since particles pollute the air when using this method;
- maintain equipment and never use it when it is malfunctioning;
- calibrate the equipment (check the hectare dosage) using clean water;
- while working with a plant protection product, it is forbidden to eat, drink or smoke;
- be prepared to terminate the application of a plant protection product at the time of adverse weather conditions (wind speed greater than 15 km/h, or the wind of a changing direction).

Spray mixture transportation

The risk of possible environmental pollution during the transport of plant protection products, spray mixtures and while working the application equipment shall be reduced to a minimum if the following instructions are followed:

- drivers of tractors and vehicles towing trailers and plant protection products application equipment shall check that all the devices and equipment on the application equipment and the tractor are in place and secured;
• everyone involved in the transportation of plant protection products shall be familiar with the procedures in emergencies;
• in the event of spray mixture and plant protection products spillage and the risk for other people, animals or the environment, quickly limit the potential negative impact (e.g. prevent further outflow of spray into the soil, surface water or groundwater);
• in order to protect the waters from the risk of contamination, always avoid passing through water (streams, rivers) - use bridges;
• check whether the valves that control the spray mixture flow are closed during transport, in order to reduce the risk of leakage or dripping;
• check whether the tank lids are tightly closed;
• check if the sprinkler/sprayer tank is overfilled - which can cause leakage during transportation, particularly on rough terrain, which can lead to environmental pollution;
• during the spray mixture transport, turn off the pump in the tank and close the valves, so that the equipment system is not under pressure, and therefore under an increased risk of spray mixture leakage;
• whenever possible, plant protection products shall be added to the tank in the vicinity to its application;
• do not perform the spray mixture transportation in the presence of children, animals or near food and feed.
13.14 Regular inspections of the pesticide application equipment

Pursuant to the regulations on the sustainable use of pesticides, the pesticide application equipment used by professional users is subject to regular inspection (Figures 13.28 to 13.31). The inspection verifies the compliance of the application equipment with certain technical requirements in order to achieve a high level of protection of human and animal health, and the environment. They shall be inspected at least once before 26 November 2016. After that date, professional users may use only the equipment, which has successfully passed the inspection, and have a sign of the performed inspection (Figure 13.32). Sprinklers and sprayers are subject to regular inspection at list once within the period of 3 years. The sign of the inspection shall be issued for a period of 3 years.

New application equipment is exempt from the inspection. The new sprinklers and sprayers are considered those, which have been sold after 1 January 2013. This equipment shall be given a sign of the performed inspection for a period of 5 years from date of purchase. Used application equipment which have been purchased in an European Union Member State and which have a sign of the performed inspection from the competent authority in that State are also exempt from the regular inspection, provided that the technical requirements for the inspection and frequency of regular inspections in that country are the same as in Croatia (3 years). All manual sprinklers, mechanical, battery-powered and motor-powered backpack sprinklers and motor-powered backpack sprayers are exempt from the inspection.

Regular inspections may be performed only by those inspection stations authorised by the Ministry of Agriculture. After a successful inspection, inspection stations issue to the application equipment owner a report on the performed inspection and mark the sprinkler or sprayer with a sign of the performed inspection. Inspections are conducted at the locations of the owners or users residence or the locations closest to them. The information on the place, date and time of the inspection are provided by inspection stations in advance through posters, announcements in professional journals, through the Advisory Service, and similar.

By September 2014, a total of 5 inspection stations have been authorised in Croatia. Two inspection stations operate within the Department for Mechanisation of the Faculty of Agriculture in Osijek, and three inspection stations within the company Agro Electronics d.o.o. based in Višnjevac.

Conditions for the inspection station authorisation are the same for public and private sectors. The authorization for performing the regular inspections can only be obtained by a legal or natural person who possesses the prescribed equipment, whose employees have the required qualifications and meet the prescribed requirements in terms of education for the performance of the application equipment regular inspections.

The Ministry of Agriculture has prescribed the maximum amounts, which may be charged for the inspection performance in order to protect the equipment owners and users from forming the too high and unrealistic costs of the inspection. The inspection prices depend on the operating engagement and number of nozzles, and range from HRK 400.00 to 800.00, VAT excluded. Fees from the charged inspections are the revenue of the inspection station, which performed the inspection.

The owners or users of pesticide application equipment shall thoroughly clean the sprinklers and sprayers inside and outside prior to the inspection. Spray mixture tank shall be filled with clean water up to at least half of its volume. The water used during the inspection shall be returned to the spray mixture tank after the inspection completion. Such water can be used at the first following preparation of spray mixture.
A valid personal identification document with a correct address of residence (identity card or passport) shall be brought to the inspection location. If PIN is not specified in the document, it is necessary to bring the PIN. Technical information on the sprinkler or sprayer (manufacturer, year of manufacture, model, serial number, if available, etc.) shall also be brought at the location of the inspection.

At least the following shall be brought to the inspection:

- for new equipment - provide evidence of purchase, documents containing the technical data and the declaration of conformity;
- for used equipment - provide evidence of purchase, technical data;
- for the recognition of inspection in an EU member state – submit the data on the European Union Member State in which the equipment was purchased, as well as the information on whether the equipment has a valid sign of the performed regular inspection, in which EU member state the sign has been issued and date of its validity.

More detailed information on the preparation of equipment before the official inspection by the authorised inspection station shall be stated in the notification on the inspection performance. If the notifications do not contain such information, we refer you to request such information from the authorised inspection station, which has issued the notification and announced the inspection.

Equipment owners/ users shall report the following to the inspection station:

- new equipment and request the sign before the first use of the equipment, and not later than within three months from the purchase,
- any change of ownership data within 30 days from the occurrence of changes in writing and provide evidence on changes,
- equipment, which, for technical or other reasons, is not in use or more than 30 days, has passed from the expiry of the sign for the purpose of signing off on such equipment.

Equipment owners/ users shall request the following from the inspection station:

- recognition of the inspection and issuance of a sign for the used equipment that has been inspected in an EU Member State,
- issuance of the new sign from that inspection station which issued the last sign in case of sign damage.
The inspection consists of several parts:

- entering the data on the equipment owner or user into an electronic application,
- entering the technical data on the equipment into an electronic application,
- preparing the equipment for the inspection,
- inspection of the equipment and transfer of data on the inspection results into the special application connected to the device for the inspection which enables the representation and preparation of the inspection results,
- issuing the report on the inspection (certificate),
- entering the data on the inspection into an electronic application,
- issuing the sign of the performed inspection.

In case of minor irregularities that can be removed by the technicians present at the inspection location, it is possible to repeat the inspection on the same day. In case of critical irregularities, the inspection shall be repeated. In this case, a report on the inspection is issued, but the sign of the performed inspection is not issued. The sign of the performed inspection is issued only in cases when the application equipment meets the prescribed requirements.

Figures 13.28 and 13.29: Regular sprinkler inspection (photo: I Grepo)

Figures 13.30 and 13.31: Regular sprayer inspection (photo: V. Tadić)
The equipment owner/user is also required to:

- keep the report on the inspection until the next regular inspection;
- submit the report on the last performed inspection to the inspection station if they bring for the inspection the equipment that has already been inspected, but the sign of the inspection has been lost or destroyed;
- check regularly the functionality of the equipment before the pesticides application, calibrate and replace the worn parts and check the functionality of the device before pesticides application in accordance with the appropriate training they have received as persons liable for training.

Figure 13.32: Appearance of the sign of the performed application equipment regular inspection (prepared by: V. Novaković)
Instructions for the preparation of sprinklers/sprayers for the winter period

The first important step in the preparation of sprinkler for conservation is its cleaning. During the external washing, it is also necessary to clean the tank from the inside, as well as a complete system of hoses. The cleaning begins by washing the tank from the inside and the complete recirculation of clean water to all hoses. The amount of water for washing is at least 10% of the total volume of the tank, therefore, for a sprinkler with a volume of 4400 litres, at least 440 litres of water is required. Washing is performed three times whereby 1/3 of the water at our disposal for washing is used each time. The means for tank washing can be added in water, which is sometimes supplied by the companies engaged in the sale of plant protection products or sprinklers/sprayers or which perform regular inspections of application equipment. In this case, this amounts to approximately 150 litres. After the first use of clean water for washing, contaminated water shall be sprinkled over already treated surface since the concentration of a plant protection product in that water is already small enough that further spraying does not harm the plants. The procedure is repeated two more times and then it can be said that the sprinkler is clean and ready for conservation.

Freezing of water in sprinkler/sprayer pipes may occur in winter if the application equipment is not stored in a room where the temperature is above 0°C throughout the winter. Since this the case in almost all agricultural holdings, the equipment shall be prepared for low temperatures. After washing the sprinkler, clear water remains in all hoses. Sprinklers/sprayers can have a wide network of hoses in which a certain amount of water may remain. It is therefore important to pour antifreeze into the sprinkler (the amount varies depending on the model and size of the sprinkler/sprayer), and let it pass through a closed equipment system (pump, filters, valves, hoses, blender...) and finally through the nozzles. The procedure is repeated for each section at the sprinkler branch. Freezing point (from -20 to -25°C) is measured using a hydrometer. Conservation protects the application equipment from freezing, and at the same time ensures that the seals are wet all the time. The problems that may occur next spring, when water leaking would occur on seals in which have been dry the whole winter are thus eliminated. In the end, it is necessary to dismantle the manometer from the sprinkler since a small amount of water that could freeze during in temperatures still remains in its thin Bourdon pipe.

In the spring, the antifreeze that is left in the application equipment is released through one of the end nozzles, and is used in the next process of conservation, with the prior quality control of the antifreeze. In case of storing the application equipment in external conditions, it is necessary to dismantle and store the equipment, which is not resistant to external influences (e.g. spray monitor).

13.16 Cleaning the application equipment

The process of application equipment cleaning shall be effective in order to ensure the removal of plant protection products residues, which could cause damage (phytotoxic effects) to agricultural crops during the next application.

The process of application equipment cleaning depends on the physical and chemical properties of the active substance, the type and properties of the formulation, as well as the sensitivity of agricultural crops to certain plant protection products.

The next step in the application equipment cleaning depends on the plant protection products properties. Herbicides require special attention and, depending on the plant protection product, various steps in the process of application equipment cleaning.

There are three main methods of application equipment cleaning:
• single water rinsing,
• triple water rinsing,
• rinsing together with the use of detergents for the application equipment cleaning or sodium hypochlorite.

If a plant protection product was used for which triple rinsing with water is not efficient, since the product is poorly soluble in water, the process of application equipment cleaning is performed with the detergent or sodium hypochlorite. Detergent or sodium hypochlorite also needs to be rinsed from the plant protection products application equipment.

When cleaning the application equipment, all parts need to be rinsed equally. All visible layers need to be removed, tank, pipes, nozzles, screens and filters need to be well rinsed with clean water. At the end, the entire equipment needs to be rinsed with clean water in accordance with the prescribed procedure in the instructions for use. Application equipment shall be thoroughly cleaned and washed to avoid phytotoxicity when applying on another crop.

For the purpose of people and environment protection, the application equipment and nozzles shall be washed in places where the plant protection product cannot reach the surface water and where there is no danger to humans and animals.

Figure 13.33: Washing the sprinkler from the outside on the surface where the treatment was performed
(Source: Improving the pesticide application techniques, Đ. Banaj)


Expert consultants: Vjekoslav Tadić, Ph.D., Anamaria Bokulić, M.Eng.
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## LIST OF REGULATIONS FOR THE PURPOSES OF THE MANUAL

### LIST MOST IMPORTANT CROATIAN REGULATIONS

1. Act on Sustainable Use of pesticides (Official Gazette of the Republic of Croatia No. 14/2014)

2. Ordinance on Establishing an Action Framework to Achieve the Sustainable Use of Pesticides (Official Gazette of the Republic of Croatia No. 142/2012)
   * Ordinance shall be replaced by the Ordinance on the Sustainable Use of Pesticides


### OTHER IMPORTANT CROATIAN REGULATIONS

5. Chemicals Act (Official Gazette of the Republic of Croatia No. 18/2013)


11. Ordinance on the conditions for the establishment of water source sanitary protection zones (Official Gazette of the Republic of Croatia No. 66/2011 and 47/2013)


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of active substances and licensing of plant protection products (Official Gazette of the Republic of Croatia No. 38/2013)

### IMPORTANT DOCUMENTS

1. National Action Plan to achieve sustainable use of pesticides
   ([http://www.mps.hr/UserDocsImages/BILJNO%20ZDRAVSTVO/HR-NAP.pdf](http://www.mps.hr/UserDocsImages/BILJNO%20ZDRAVSTVO/HR-NAP.pdf))

2. Code of Good Agricultural Practice
   ([http://www.mps.hr/UserDocsImages/publikacije/Na%C4%8Dela%20dobr%20poljoprivredne%20prakse.pdf](http://www.mps.hr/UserDocsImages/publikacije/Na%C4%8Dela%20dobr%20poljoprivredne%20prakse.pdf))

3. Technological instructions for integrated production
   ([http://www.mps.hr/default.aspx?id=8534](http://www.mps.hr/default.aspx?id=8534))

4. Water Management Plan,
   ([http://www.voda.hr/puvp/](http://www.voda.hr/puvp/))

   (Official Gazette of the Republic of Croatia No. 81/1999 and 143/2008)

6. Action plan for the development of organic agriculture
   ([http://www.mps.hr/UserDocsImages/strategije/AKCIJSKI%20PLAN%20RAZVOJA%20EKOLOŠKE%20POLJOPRIVREDE%20ZA%20RAZDOBLJE%202011-2016.pdf](http://www.mps.hr/UserDocsImages/strategije/AKCIJSKI%20PLAN%20RAZVOJA%20EKOLOŠKE%20POLJOPRIVREDE%20ZA%20RAZDOBLJE%202011-2016.pdf))

### CROATIAN REGULATIONS THAT WERE REPEALED (VOID REGULATIONS)


6. Ordinance on the labelling of plant protection products (Official Gazette of the Republic of Croatia No. 11/2007), with the exception of Article 9


8. Ordinance on the plant protection products registration procedure (Official Gazette of the Republic of Croatia No. 57/2007, 119/2009 and 142/2012), with the exception of 14a


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### LIST OF MOST IMPORTANT EUROPEAN UNION REGULATIONS


### OTHER IMPORTANT REGULATIONS OF THE EUROPEAN UNION


List of regulations prepared by: V. Novaković)