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Safety Measures for Handlers/Workers against Herbicide Intoxication Risk

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Additional information is available at the end of the chapter

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Abstract

With the use of herbicides, there is a certain risk of intoxication to directly exposed workers, which depends on several factors. Risk factors can be grouped in the toxicity of herbicides and exposure provided by the specific working conditions. From the assessment of the risk of intoxication, working conditions can be classified as safe or unsafe. The safety of working conditions is based on the chronic toxicity of the pesticide and the absorbable amount of dermal and respiratory exposure. Safety can be determined by calculation of the margin of safety calculation (MOS). If the value of $MOS \geq 1$, the working condition is classified as safe, but if the $MOS < 1$, the condition and work is classified as unsafe. For working conditions classified as unsafe, workers should adopt safety measures to become safe. Safety measures at work are grouped into preventive and protection. The preventive safety measures are grouped into the selection of workers/personnel: psychological measures; administrative: legislation, standards, and procedures; and hygiene, cleaning, maintenance, and safety of the environment. The protection safety measures are grouped into collectives and individual. The Brazilian labor law mandates the use of preventive measures and protection, according to the pesticide manufacturers' recommendations on the labels.

Keywords: Pesticides, herbicides, occupational exposure, risk of intoxication, safety measure

1. Introduction

The convention 012 (C012) of the International Labour Organization (ILO) on the Compensation for Work Accidents (Agriculture), 1921, became internationally effective on 02.26.1923. Convention 012 extends the benefit of the laws to agricultural workers and regulates mandatory indemnification of victims of work accidents [4].

Work accidents occur due to the existence of risks in the working environment. Work risk is any possibility that some element or condition in a given process can cause damage or be destructive to the physical and/or psychological health of the worker. The risk outcome can be an accident, illness or suffering, or exposition to environmental pollution.

The ILO Convention 184 on safety and health in agriculture, 2001, states that member states should define, implement, and revise a coherent national policy on agriculture safety and health periodically. The purpose is to prevent accidents and health injury related to or as a consequence of work and to eliminate, mitigate, or control the risks in the agricultural working environment [9].

In Brazil, the NR 31 approved in 2005, and amended in 2011 and 2013, is still in force [6]. It is related to safety and health in agriculture, livestock, forestry, and aquaculture, meeting the obligations of signatory member countries of the ILO Convention 184.

Pesticides are chemical compounds used to control organisms harmful to crops. Pesticides are carefully selected to intoxicate the target organisms. Toxicity is the ability to cause harm and death of the target organisms [21]. However, nontarget organisms that come into direct contact with pesticides can be intoxicated, especially if they have the points of the toxic action. Therefore, working with pesticides poses a chemical poisoning risk to exposed workers [1].

The overall Brazilian legislation on health safety (NR 9) in the workplace provides that companies must implement the environmental risk prevention program (ERPP). The ERPP consists of the following steps: anticipation, recognition, quantitative assessment, and control of risks according to specific action levels [7].

This chapter informs the reader about the safety procedures required while working with pesticides. It aims at motivating the worker to make a habit of preventing herbicide poisoning. Moreover, it also serves to motivate the businessmen to implement safety measures in the working environment, to keep the risks at acceptable levels, while increasing business productivity and competitiveness.

2. Risk of intoxication with herbicides

The risk of worker intoxication with pesticides, especially herbicides, depends on several elements that can be grouped into two major factors: the toxicity of the handled herbicides and the exposure under the specific working conditions [1]. Therefore, the safety and health management during work with herbicides should be addressed using the steps set out by the industrial hygiene and the ERPP [7]. The steps are the ability to anticipate, identify, recognize, evaluate, and control the risks in the workplace.

2.1. Anticipation and identification of the intoxication risks associated with herbicides

A safety and health management plan for workers exposed to herbicides must anticipate and identify potential risks and health hazards before a given production process is implemented or modified, or new risk agents are introduced in the workplace.

The risks can be anticipated during the planning phase of the productive activity such as acquiring new equipment and/or materials (including pesticides), determining the work process, and preventive maintenance plans.

The identification of pesticide poisoning risks starts with the specific agricultural production system. The production systems can be organic, when the use of synthetic toxic products is not allowed, or conventional, when the use of new agricultural technologies is allowed, including the use of pesticides. Therefore, the risk of occupational intoxication with pesticides exists only in conventional farming systems.

The use of pesticides in conventional crops depends on a wide variety of interrelated factors that can be grouped according to the direct relation to the crop, crop environment, and target organisms.

During the planning of an agricultural crop, the professional must be able to predict the occurrence of harmful organisms and control methods. The pesticides recommended for chemical control are legally required to inform the formulation registered in the Ministry of Agriculture, Livestock and Supply, MAPA, in the package leaflet [10].

2.2. Recognizing the intoxication risks of pesticides

In this step, the work environment is observed and carefully analyzed to identify the agents and their potential risks. The priority assessment and control of the risk involved must be established. Risk analysis should answer the following questions: What? Where? and How? A deep knowledge of the products involved in the process, working methods, process flow, and facilities layout is necessary to answer these questions [27].

It is necessary to analyze the information contained in the package leaflet regarding the product, the environment and protection of human health to recognize the poisoning risks of pesticides [10]. The leaflet also contains information about application methods and calibration settings of the application equipment. The handler is exposed to the product by drift, that is, the portion of the product that does not reach the target and drifts away. The extent of drift and exposure depends on several factors, predominantly the type of application and the equipment used. Therefore, the type of formulation is an important information contained in the leaflet regarding the handler's safety since it determines the type of application equipment to be used. The leaflet must also contain mandatory information on poisoning, acute and chronic toxicity of pesticides, the first aid procedures should an intoxication occur, and preventive measures to protect handlers.

The identification of the working conditions and the job are critical to determining the risk of poisoning with pesticides. Handler exposure is determined by the working conditions while working conditions are identified by the activities performed. The legislation on pesticide working safety (NR 31) defines workers in direct exposure as those handling pesticides, additives, and related products in any of the stages of storage, transportation, packaging opening, pesticides preparation and application, disposal and decontamination of equipment, and clothing [6].

Thus, it is necessary to identify homogeneous work groups (HWG). The HWG consists of workers performing the same activity and exposed to the same risks. Therefore, safety measures will be similar for all workers of the same HWG since the working conditions are the same [14]. The exposure assessment for any worker of the HWG is representative of the exposure of all workers of the group [29].

2.3. Quantitative assessment of pesticide poisoning risks

The procedure to perform risk assessment of intoxication with pesticides has been established in a document of the American National Academy of Sciences (USA) in 1983 as a four-step process [33]. The four steps are outlined in the diagram shown in Figure 1 [18].

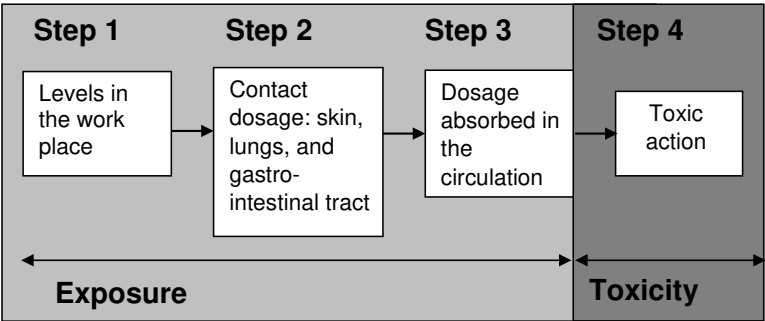


Figure 1. The steps of the intoxication risk assessment when working with pesticides [18].

Occupational exposure to pesticides is influenced by the type of work or activity performed, the way it is conducted, and the product formulation [20]. Toxicity is an intrinsic property of pesticides that is determined following national regulations, even before they are placed on the market.

2.3.1. Occupational exposure to pesticides

The worker’s exposure to pesticides can be real or potential. The actual exposure refers to the absolute amount of pesticide that comes into contact with the body during a determined working period and is readily available to be absorbed via dermal, respiratory, or oral routes [1].

Potential exposure refers to the amount of the pesticide that could be absorbed via dermal, respiratory, and oral routes if the worker had not worn personal protective equipment during the operation [32].

The potential exposure results from the interaction of the dominant risk factors in specific working conditions. It has been determined that during the application of herbicides in field conditions, 99% or more of total exposure occurs via dermal and only 1% or less, via respiratory [35, 34, 26].

Therefore, knowledge about pesticide exposure and the relative importance of each pathway to the total exposure is essential to select the most effective, comfortable, economical, and applicable safety measures given the specific conditions.

2.3.1.1. Exposure routes

The potential routes of exposure to pesticides in the workplace are dermal and, to a lesser extent, respiratory. The relative importance of each exposure route is directly related to the specific working conditions or determinants of exposure. To tractor operators spraying eleven pesticides in a citrus orchard using a turbo type sprayer, 99.7–99.9% of the total exposure occurs via dermal, and only 0.1–0.3%, via respiratory route, on average [35]. This finding is greatly important for adopting safety procedures, especially regarding personal protective equipment (PPE).

The predominance of the dermal exposure under field conditions is explained by the spray droplets or mist, which drifts away towards the handler reaching the skin. The lower respiratory exposure is explained by the low contamination of the air that the handler breathes. The low contamination of breathable air is due to the fantastic dispersion of the spray droplets in the atmospheric air. Wolfe et al. reported that it is due to the distance between the tractor driver and the nozzles of the spray jet, the area with the greatest concentration of drops [35].

The potential reach of the bloodstream and the absorption of pesticides on the exposure routes should be also considered. After contact, the first entry stage of the toxic compound is absorption by the body. The absorption of a pesticide that reaches the lungs via respiratory route is fast and complete [16]. On the contrary, the absorption of herbicides via the dermal route is slower, partly because the skin is a natural, efficient barrier.

Respiratory exposure

Respiratory exposure consists of exposure to spray droplets containing the toxic compounds and possible toxic vapors present in the air that the worker breathes. The drops are particles suspended in the air, called liquid aerosols. Liquid aerosols are liquid particles produced by mechanical disruption of liquid, called mist [28]. The pesticide spraying is a mist of water droplets. The aerosols are classified by the diameter (\varnothing), as shown in Table 1 [27].

Type of particulate	Size (μm)
Sedimentable	$10 < \varnothing < 150$
Inhalable	$\varnothing < 10$
Breathable	$\varnothing < 5$
Visible	$\varnothing > 40$

Table 1. Classification of aerosols according to the type and size of particulates, for respiratory exposure [27].

The inhaled and breathable particles are the most harmful. Inhalable particles are usually deposited in the respiratory tract. However, the breathable particles enter the upper and lower respiratory tracts, reaching the lungs and the pulmonary alveoli. In the alveoli, the toxic compounds permeate the cellular membranes reaching the bloodstream and the toxic action site in the body.

The droplet size is one of the most important parameters of pesticide application technology. The spray droplets typically have a mean volume diameter (MVD) in the range of sedimentable and visible particulates (Table 1), or higher, from 100 to 300 μm . The droplet size can be one of the factors that explain lower respiratory exposure under certain field conditions [35, 34, 26].

Dermal exposure

The skin consists of the outermost and innermost layers, the epidermis and dermis, respectively. The dermis consists of connective tissue, blood vessels, nerves, hair follicles, sebaceous, and sweat glands. Direct contact with the external environment occurs through the follicles and the dermal glands. Thus, chemicals can be absorbed mainly by the epidermal cells and hair follicles.

The absorption speed of chemicals into the skin is mainly limited by the continuous stratum corneum. The fat-soluble substances penetrate through the lipids existing between the keratin filaments by passive diffusion. The rate of absorption of oily substances is indirectly proportional to their viscosity and volatility. For polar substances of low molecular weight, the absorption occurs through the outer surface of the keratin filament, the hydrated extract. The transepidermal absorption is the most frequent due to the high number of epidermal cells, although not very easy for toxicants.

The transfollicular absorption is less significant than the transepidermal. Some chemicals can penetrate the hair follicles and quickly reach the dermis. Penetration is easier for chemicals because they do not need to go through the stratum corneum. Fat-soluble or water-soluble, ionized or nonionized, gas or vapor, and acidic or basic substances can penetrate the follicles. The penetration of toxic compounds in the skin depends on its absorption pharmacokinetic model [25] and can vary from 0.8% to 6.0% [19] up to 80% [11].

2.3.2. Quantification of dermal and respiratory exposures

The whole-body method is the most suitable for assessing dermal exposure. In this method, the worker dresses in a cotton coverall, according to the protocol VBC 82.1 [36]. This method evaluates the potential and actual dermal exposures directly on the coverall used by the worker over the safety equipment, under normal working conditions for a certain evaluation period (Figure 2A and B).

The coveralls are long-sleeved with a hood made of white denim material. They are used to quantify the dermal exposures of the head + neck, trunk (back and front), arms, and legs (back and front). Cotton gloves are used to quantify the dermal exposure of the hands. The face and feet exposure is evaluated using Carefree™ female sanitary napkins that are attached to the semidisposable facial masks and rubber boots [22, 23].

Respiratory exposure is evaluated using personal continuous air flow pumps (Figure 2A and B) with specific respirator filters, cartridges, or cassettes for collecting particulates, gasses, and vapors [27].



Figure 2. Workers applying pesticide in the field during assessment of potential dermal exposure: A—quantified in coverall and unprotected, exposure real: B—quantified in coverall worn under the personal protective equipment during the evaluation period, according VBC 82.1 [36].

2.4. Controlling the risk of intoxication with pesticides

Safety, health, and environment management is regulated by a specific labor legislation for pesticides, the regulatory standard no. 31, known as NR 31 [6]. The NR 31 prioritizes implementation of safety measures to eliminate the risks by replacing or adjusting the production processes, machines, and equipment; by adopting collective protective measures to control the risk at the source; and by introducing personal protection. Safety procedures should be implemented based on risk assessment and risk acceptability criteria. Working conditions can be classified as safe or unsafe according to the adopted risk acceptability criterion. The acceptability criterion of poisoning risk with pesticides is based on toxicity and handler exposure determined by working conditions.

Safety evaluation is fundamental to classify working conditions and select the appropriate safety procedures needed to reduce the risk of poisoning to acceptable levels.

2.4.1. Acceptability criterion of intoxication risk with pesticides

The acceptability criterion of pesticide risk is based on the no observable effect level (NOEL) in mg/day/kg body weight. The NOEL is determined by assessment tests of the chronic toxicity of pesticides using mice in laboratory conditions. The studies follow international standard procedures.

The acceptability criterion of poisoning risk with pesticides can be quantified by calculating the margin of safety (MOS) proposed by Severn [30] and adapted by Machado-Neto [23]. MOS is determined dividing the safe dose (calculated by multiplying the NOEL value and the worker body weight) by the absorbable quantity of exposure (AQE) via the dermal and respiratory tract, under working conditions:

$$\text{MOS} = \frac{\text{NOEL} \times W}{\text{AQE} \times \text{SF}}$$

where NOEL is the no observed effect level (mg/kg/day); W is the mean body weight of the worker, considered to be 70 kg; AQE is the absorbable quantity of exposure (mg/day); and SF is the safety factor.

AQE via the dermal route is determined for each molecule in the dermal exposure studies with laboratory animals or human skin tissue grown in the laboratory. For molecules wherein dermal absorption has been determined, it is considered to be 10% of the evaluated dermal exposure for each working condition, according to Byers et al. [13].

The AQE in the respiratory tract can be considered as 100% of respiratory exposure evaluated for each working condition [23].

The SF, which multiplies AQE, is used to compensate for the extrapolation of the NOEL results obtained in laboratory animals, to humans [12]. The used safety factor may be 10 [12], to compensate for interspecies extrapolation, or 100; 10 for interspecies times 10 for intraspecies extrapolation.

The MOS is calculated for the activities and daily exposure times according to working conditions. For formulations with two or more active ingredients, the commercial product safety rating is based on the smallest value among the MOS calculated for the active ingredients.

The risk acceptability criterion depends on the toxicity of the pesticide, while the intensity of risk depends directly on the intensity of worker exposure to pesticides.

The working condition is classified as safe if $\text{MOS} \geq 1$; exposure as tolerable and intoxication risk as acceptable.

The working condition is classified as unsafe if $\text{MOS} < 1$; exposure as intolerable and intoxication risk as unacceptable.

2.4.2. Control action level of intoxication risk

According to NR 9, the action level is a value above which preventive measures should be initiated to minimize the likelihood that exposures to environmental agents exceed the exposure limits [7].

For pesticides, the action level to implement the risk control measures is when the working condition is classified as unsafe ($\text{MOS} < 1$). For unsafe conditions, preventive and protective

measures should be intensified enough to make the working conditions safe ($MOS \geq 1$). The preventive safety and protection measures should control toxicity and/or exposure to make unsafe working conditions safe.

3. Safety measures while working with pesticides

Controlling the intoxication risk with safety measures is a key step to planning health and safety management while working with pesticides. The specific labor legislation for pesticides, the NR 31 [6], states that the rural employer or similar should conduct risk assessments to ensure the safety and health of workers. Based on the results, the employer must adopt preventive and protection procedures to ensure that all activities, workplaces, machinery, equipment, tools, and processes are safe and in compliance with health and safety standards. The legislation also determines the prioritization of measures to prevent accidents and occupational diseases [6].

3.1. Preventive safety measures

The preventive safety measures may be applied early in the planning of agricultural activities, during the previously described steps of anticipation, identification, and recognition of the risks. Preventive safety measures target the risk factors and can be divided into two groups, to eliminate and to reduce poisoning risk. Preventive measures aim to ensure a safe work environment and maintain workers skilled and motivated and in good health conditions.

Most safety measures determined in the specific legislation to work with pesticides, NR 31, are preventive [6]. The administrative measures are highlighted among the preventive safety measures determined in the legislation on safety and health at work. Administrative preventive measures are adequate policies and procedures to the specific working conditions.

In the planning of agricultural activities with the use of pesticides, prevention measures will act on risk factors, to reduce the toxicity of the pesticide and/or exposure caused to the workers by the working conditions.

3.1.1. Selection of workers/personnel

The personnel selection process is critical to prevent the occurrence of accidents. To work with risky activities, employees must have a physical and psychological profile suitable to the working conditions.

Every worker acquires personal characteristics that form the personality resulting from physical and mental growth over the years in the work environment in which he/she lived. The personality traits can be strong and striking, positive and negative, displaying strengths and weaknesses as irresponsibility, stubbornness, irritability, etc. [3].

The worker's personality, whether positive or not, is carried into the working environment and can cause unsafe acts or unsafe working conditions. Due to negative traits, the worker can

act unsafely ignoring safety rules and make mistakes when performing his or her work that may result in work accidents. Unsafe acts are the way workers expose themselves, consciously or unconsciously, to accident risks (e.g., using machines without a license or permission, not using the required PPE, etc. [3]).

Therefore, the selection process should take into account the physical and psychological profile of the employee required to work in risky activities. Thus, the occurrence of accidents can be prevented. Once selected properly, the worker must be trained to perform especially risky activities.

3.1.2. *Psychological measures*

When the worker interacts in the workplace as a whole (physical or abstract space), he/she is influenced positively or negatively, thus changing his or her physical, mental, and social state. On the other hand, it is natural that the worker brings his or her personal problems to the workplace [2]. Therefore, it is impossible to pretend that all is well when, in fact, the worker is experiencing personal problems. The only one able to understand and evaluate the anguish of losing a loved one, the disappointment of a treacherous love, among others is the person itself. These factors are, for the most part, largely responsible for the increase in the indices that measure delays, work absences, illnesses, and accidents [2].

In working activities, there is a personal unsafety factor when the employee works grudgingly, under abnormal physical conditions (illness, physical, or mental disability), without experience, knowledge, and proper training. Due to personal unsafety factors, the worker may cause accidents and/or occupational illnesses that result from negligence, recklessness, or malpractice [2].

Companies must implement measures that value the worker, by enabling professional growth and personal development to control the human factor effects on the risk of poisoning with pesticides. Such actions elevate the workers' self-esteem and improve performance and commitment, thus making the working environment more pleasant. There are other positive actions such as dynamics between employees, awards campaigns, and the willingness to hear suggestions to improve the workplace.

The work environment should be a harmonious and welcoming place for all to engage in their activities with satisfaction and enthusiasm. The standards and rules set by the company are also important to promote good communication. The basic behavioral rules that are desirable in the workplace are as follows: mutual respect, call people by name, be calm, participate actively in the activities that are delegated to you, be willing to help others, do not judge people, and do the best you can. Dialogue is always important to avoid conflicts, to respect people differences, and to avoid intrigues, gossip, and side conversations.

Companies, more than ever, are looking for professionals who can work in groups, be proactive, and capable of leading. The website of a Brazilian company recruiting employees states, "For all opportunities, Eldorado Brazil seeks professionals with good communication and interpersonal skills and 'owner' attitude" [17].

3.1.3. Administrative: Legislation, standards, and procedures

The companies should implement security measures to meet specific labor laws and local regulations to prevent workplace accidents. The preventive security administrative measures are mandatorily applied at all stages, starting at the registration of pesticides up to before labor legislation. The legal commercialization of pesticides in the country is regulated by the legislation on pesticide registration, Decree Law no. 4074 [10].

According to the Decree Law no. 4074 [10], pesticides can only be produced, handled, imported, exported, commercialized, and used in national territory after being registered with the appropriate federal agency. They are required to meet the guidelines and requirements of federal agencies responsible for the sectors of agriculture, health, and environment.

The Ministry of Agriculture, Livestock and Supply (MAPA) is the federal agency responsible for registering pesticides. The Ministry of Health (MS) is responsible for evaluating and classifying toxicologically the pesticides; performing preliminary toxicological evaluation of pesticides, technical products, premixes, and the like, used for research and experimentation; and establishing the reentry interval in a treated environment, among others, as set out in Decree Law no. 4074 [10].

The main administrative preventive measure prohibits the registration of pesticides that can cause harm. The Decree Law no. 4074 [10] prohibits pesticide registration for which there are no available methods for disabling its components in Brazil. There is no antidote or effective treatment.

The teratogenic and carcinogenic compounds present enough evidence as such from observations in humans or studies in experimental animals.

The mutagenic compounds might induce mutations observed in at least two tests, one for detecting genetic mutations, performed using even metabolic activation and the other to detect chromosomal mutations.

Some compounds cause hormonal disorders and harm the reproductive system. They are more dangerous to humans than animals based on tests, according to updated technical and scientific criteria, and some compounds harm the environment.

Tests, trials, and studies about mutagenesis, carcinogenesis, and teratogenesis, conducted in at least two animal species should be performed according to criteria accepted by national or international technical and scientific institutions.

The legislation on working with pesticides (NR 31) requires a management plan regarding health, environment, and safety for rural works [6]. The management plan must include preventive measures for the workers' health (medical examinations) and other actions catering to specific needs, SESTR—Specialized Service on Safety and Health for Rural Work and CIPATR—Internal Commission for Rural Work Accident Prevention.

According to the risks in the workplace, the risk management program should also contemplate the Hearing Conservation Program (HCP), the Respiratory Protection Program (RPP), the Dermatoses Occupational Program (DOP), and the Ergonomic Action Program (EAP) [14].

As internal and specific standard, each company must have in written form the operating procedure (OP) or operating instructions (OI), based on the manuals for machines and pesticide application equipment (NR 31), and the service order (SO), as set out in NR 1 [5] for each OP.

Companies should also have other internal rules to regulate the health and safety of workers, such as hygiene, cleaning, and maintenance of machine and equipment. To meet the requirements of NR 31, the preventive safety procedures also include training workers on prevention of accidents with pesticides, ergonomic measures, safety of machinery, and equipment. The workers should also be granted access roads to workplaces, transportation of workers and cargo, living areas for meals in the field and toilets, and collective and personal protection measures [6].

3.1.3.1. Pesticide packaging

The Decree Law no. 4074 [10] states that pesticide containers shall be designed and constructed to prevent leakage, evaporation, loss, or alteration of its content, and to facilitate the cleaning, sorting, reuse, recycling, and proper disposal. The packages should be resistant to the contents and not able to form harmful or dangerous compounds. Packages must be resistant everywhere and adequately meet the conservation requirements.

Packages must have sealing wax or another external device to ensure visually the package has not been violated. When stacking of rigid packaging is allowed, the maximum number of units that can be stacked should be stated.

The rigid packaging containing formulations miscible or dispersible in water must be submitted to triple washing operation, or equivalent technology, by the user according to the instructions on their labels, leaflets, or brochure supplement.

Users should return the empty containers of water miscible pesticides and their lids, triple washed, to the shop of purchase at the latest 1 year from the date of purchase. Users should make available to the supervisory authorities the empty containers return vouchers, provided by the shops, receiving stations or gathering centers for at least 1 year after the packaging has been returned.

Packaging containing products unfit for use or unused should be disposed of following the guidelines informed in the package leaflet. It is the responsibility of the company that registered, produced, and commercialized the product to collect and dispose of the products.

3.1.3.2. Pesticide labels and package leaflets

The pesticide registration legislation, Decree Law no. 4074 [10], requires that warnings regarding the danger of pesticides should be placed on the label and package leaflet. The pesticide labels should have on the bottom a distinctly colored band separated from the rest of the label, with a height equivalent to 15% of the label/package height. The colors of the bands correspond to different toxicological classes established by the Ministry of Health, in Ordi-

nance no. 03 [8], for pesticides: red, extremely toxic products (Class I); yellow, highly toxic (Class II); blue, moderately toxic (Class III); and green, slightly toxic (Class IV).

A white circle with a diameter equal to the band height containing the skull and crossbones in black on white background should be included on the front panel of the label, with the words "caution poison." Specific pictograms, internationally accepted, should be placed along the colored band from the center to the edge occupying 50% of the band height (Figure 3).

The label central column shall contain the manufacturing and expiration dates, indications whether the content is explosive, flammable, oxidizing, corrosive, irritant, or subject to applied sales. The following warnings should also be on the label: "The use of personal protective equipment is required. Protect yourself" and "The return of the empty package is required," along with the toxicological and potential environmental hazard classification.



Figure 3. Warning band required at the bottom of the label, colored according to the toxicological class and pictograms about environmental and worker safety.

The labor legislation NR 31 [6] prohibits the handling of any pesticide not registered and not authorized by the relevant government agencies, complementing the preventive safety measures established in the legislation for pesticide registration. It prohibits the handling by persons under 18 and over 60 years old and pregnant women. It prohibits the handling of any pesticides in the workplace at odds with the indications and the instructions on the label and package leaflet.

It prohibits working on newly treated areas before the end of the reentry interval set on the label, except with the use of recommended protective equipment. It also prohibits any person to enter and stay, during aerial spraying, in the area to be treated.

3.1.3.3. Mandatory precaution measures in the package leaflet of pesticides

Decree Law no. 4074 [10] requires that the precaution measures against the poisoning risk of workers should be on the labels and in the package leaflet. Sample data related to the protection

of human health are stated on the label and in the package leaflet of the herbicide Front™ follows [15].

The herbicide Front™ is registered by the company Du Pont of Brazil SA, in the Ministry of Agriculture, Livestock and Supply—MAPA, under number 10110, containing the following herbicides: diuron (603 g/kg), hexazinone (170 g/kg) and sulfometurom methyl (14.5 g/kg), and other inert ingredients (212.5 g/kg). To prevent spraying drift and reducing the occurrence of worker exposure, the herbicide package leaflet recommends the following:

Winds: Windspeed higher than 10 km/h or situations when the absence of winds causes a thermal inversion increases the potential for drift. The wind conditions and many factors, such as droplet diameter and type of equipment determine the potential spray drift. Do not apply if there are gusts of wind. Do not perform aerial application when there is no wind.

Reentry interval for people in the treated crops: People are not allowed to enter the area where the product was applied before it is completely dried (at least 24 hours after application). If it is necessary to enter during this period, the personal protective equipment (PPE) recommended for use during application should be used as well.

Instructions for product storage, conservation, and accident prevention: Keep the product always closed in its original packaging. The site should store exclusively toxic products, away from food, drink, feedstock, or other materials. The construction must be masonry or noncombustible material. The location must be ventilated, covered, and have waterproof floors. Warning signs such as “CAUTION: POISON” should be placed in the area. The place should be locked to prevent access of unauthorized persons, especially children. There must always be adequate packaging available to wrap broken packaging or to collect leaked product. In case of warehouses, the instructions of ISO 9843, ABNT—Brazilian Technical Standards Association should be followed. Observe the provisions of state and local legislation.

Data related to the protection of human health: Read the instructions carefully before use. Dangerous product. Use personal protective equipment as indicated.

General precautions: Product exclusively for agricultural use. Do not eat, drink, or smoke while handling and applying the product. Do not handle or apply the product without the recommended PPE. Recommended PPE must be worn in the following order: overalls, boots, apron, respirator, goggles, hood, and gloves. Do not use damaged PPE. Do not use equipment with leaks or defects. Do not unclog spray tips, nozzles, and valves with your mouth. Do not carry the product together with food, medicine, feed, animals and people.

Precautions when preparing the product for application: Product extremely irritating to the eyes. In the event of accidental contact with the product, follow the guidelines outlined in first aid procedures and quickly seek emergency medical service. Open the package carefully to avoid dispersion of dust. Use PPE: water-repellent cotton overalls with long sleeves going over the gloves and pants legs over the boots, rubber boots, waterproof apron, respirator with mechanical filter class P2, safety glasses with side shields, hood, and nitrile gloves. Handle the product in open and ventilated area.

Precautions during application: Avoid as much as possible contact with the treated area. Do not apply the product in the presence of strong winds and the hottest hours of the day. Do not

apply product against the wind, when using a backpack herbicide applicator. When using a tractor (or plane), apply product against the wind. Apply the product only at recommended doses and observe the safety interval (time interval between the last application and harvest). Use personal protective equipment (PPE): water-repellent cotton overalls with long sleeves going over the gloves and trouser legs over the boots, rubber boots, respirator with mechanical filter class P2, safety glasses with side shields, hood, and nitrile gloves.

Precautions after application: Flag the treated area with the words “Entry prohibited. Treated area.” Keep the warnings until the end of the reentry period. If you need to enter the area treated during this period, use the PPE recommended during application. Keep the remaining product properly closed in the original packaging and locked away from children and animals. Before removing PPE, wash the gloves while still dressed to avoid contamination. Recommended PPE must be removed in the following order: hood, goggles, aprons, boots, overalls, gloves, and respirator. Take a bath immediately after applying the product. Change and wash protective clothing separately from regular family laundry. When washing the clothes, use gloves and waterproof apron. Maintain and wash protective equipment after each product application. Follow correctly the manufacturer’s specifications regarding filter usage time. Do not reuse the empty package. Use the PPE during package disposal: water-repellent cotton overalls with long sleeves, nitrile gloves, and rubber boots.

First aid: Go to an emergency medical center and take the packaging, label, package leaflet and agronomic prescription for the product. *Ingestion:* If the product has been swallowed, do not induce vomiting. If vomiting occurs naturally, lay the person sideways. Do not give anything to drink or eat. *Eyes:* In case of contact, wash with plenty of running water longer than 15 minutes. Prevent the wash water from entering the other eye. *Skin:* In case of contact, remove contaminated clothing and wash the skin with running water and mild soap. *Inhalation:* If the product has been inhaled, take the person to an open and ventilated place.

3.1.3.4. Training of workers

Even with technical training, the worker can make mistakes that result from carelessness, inattention, overconfidence, lack of technical expertise, and mechanical and emotional factors [3]. The employee must be trained, in detail, about the correct storage, transportation, and use of pesticides as described on the label and in the package leaflet.

The employee must also be trained on proper equipment maintenance of both backpack and mechanized applicators. Workers must be able to apply the pesticide with the least possible contact. On the other hand, the employer must select the least toxic products and create conditions to mechanize and automate operations to minimize contact between worker and pesticide.

The training on pesticide handling and application in field conditions is essential to reduce risks and prevent poisoning. Labor legislation NR 31 [6] states that the machinery and implements must be used according to the manufacturer’s technical specification, within the operational limits and restrictions indicated. Therefore, equipment must be operated by qualified and adequately trained workers.

The NR 31 [6] also requires that rural employers, or equivalent, must provide training on how to prevent accidents with pesticides to all workers directly exposed to them. The NR 31 requires that training must be provided to workers with direct exposure, and the program should consist of a minimum twenty hours distributed in a maximum of eight hours during normal working hours. This training should provide minimum knowledge about direct and indirect exposure to pesticides; signs and symptoms of intoxication and first aid procedures; labeling and safety signs; hygienic procedures during and after work; use of clothing and personal protective equipment; and cleaning and maintenance of clothing and personal protective equipment.

The NR 31 also provides that the rural employer must inform all employees about the use of pesticides in the establishment, such as the treated area: description of the general characteristics of the location area, type of application, including equipment to be used; trade name of the product used; toxicological classification; date and time of application; reentry interval; withdrawal period/grace period; protection measures required for workers in direct and indirect exposure; and measures to be taken in case of poisoning [6].

3.1.3.5. Emergency medical procedures

Labor legislation NR 31 [6] states that the rural employer must preserve the occupational health of workers, prevent, and control the injuries resulting from work accidents. The actions should be planned and implemented based on the identification of risks and paid by rural employers.

The rural or similar employer must ensure medical examinations and meet the deadlines and the schedule required. The required medical examinations are as follows: admission, held during the hiring process, before the worker takes on his responsibilities; periodic medical examination, held annually; medical examination upon return to work, held on the first day when the employee returns to work after being absent for longer than 30 days due to any illness or accident; medical examination upon changing function, provided that the worker is going to be exposed to a specific risk different than the previous; and dismissal medical examination, performed at the end of the employment contract [6].

Medical tests include clinical evaluation and complementary exams when necessary and depending on the risks. After each medical examination, the Occupational Health Certificate (OHC) must be issued in duplicate, containing the following data: full name of the worker, worker ID and function; exposure to occupational risks; indication of medical procedures that the worker underwent and when they were performed; and whether the worker is fit or unfit for the specific function to be performed. The OHC should have the doctor's registration number issued by the Medicine Regional Council and be dated and signed by the doctor who performed the examination. The first part of the OHC should be filed and be available for inspection while a copy is compulsorily given to the employee, upon receipt of signing the first via [6].

Other health actions at work must be planned and executed according to the needs and peculiarities. All rural establishments must be equipped with the necessary first aid material, according to the characteristics of the activity to be performed.

The employer should ensure the removal of the injured in an emergency, without cost to the employee. The employer must also allow workers access to health agencies for the purpose of prevention and prophylaxis of endemic diseases and the application of tetanus vaccine.

3.1.4. Hygiene, cleaning, maintenance, and safety of the environment

Occupational hygiene measures consist of actions and procedures to prevent, or minimize, environment and worker contamination with pesticides. These actions should be applied at all working stages.

The hygiene and cleaning measures are applied to machinery, pesticide application equipment, handling of pesticides, materials, and clothing. The occupational hygiene is also applied to workers, who must turn them into habits to reduce exposures and prevent contamination of the materials, equipment, and tools with pesticides.

Workers should be instructed to clean immediately after contamination occurs and to keep all components sanitized and clean. There are actions that should be performed before and after working with pesticides. For example, gloves should be decontaminated immediately after getting contaminated with pesticides during work.

Preventive health and environment safety after use of pesticides is also present in the Brazilian legislation for pesticide registration and labor. In the pesticide registration legislation, Decree Law no. 4074 [10] states that as a preventive safety measure, the agronomic prescription must have the diagnosis of plant health problem, the recommendation to read carefully the label, and the package leaflet of the recommended pesticides. The packaging and labeling of pesticides cannot be confused with toiletries, pharmaceuticals, food, diet, beverage, cosmetics, and perfumes. The package leaflet must be present in single packs and contain all the information on the label and instructions for use, poisoning signs, symptoms, and treatment.

The labor legislation NR 31 [6] states that all workers should be informed regarding the use of pesticides about the treated area, description of the general characteristics of the area and the location; type of application, including the equipment used; trade name of pesticide; toxicological classification; date and time of application; reentry interval; protective measures required for workers in direct and indirect exposure; and the measures to be taken in case of intoxication.

The preservation, maintenance, cleaning, and use of the equipment may only be performed by previously trained and protected persons. Equipment should be cleaned without contaminating wells, rivers, streams, and any other water collections NR 31 [6].

3.2. Protective measures

If the working conditions remained unsafe ($MOS < 1$) after the pesticide registration and labor legislation requirements were met and the preventive measures were put in place, the protective measures should be implemented intensively enough to make the working environment safe ($MOS \geq 1$).

Protective measures aim to isolate or neutralize the risks. They are grouped into collective that control the risk at the source (generation) and on the path (propagation or trajectory) and individual, which controls the risk directly on the exposure routes in the worker’s body (receiver).

Unsafe working conditions are compromised by defects, failures, technical irregularities, and lack of safety devices, therefore exposing to danger the physical integrity and/or health of the workers, facilities, and equipment. For example, lack of adequate protection when operating machinery and equipment [3].

For unsafe working conditions ($MOS < 1$), the need for exposure control (NEC) can be calculated using the formula proposed by Machado-Neto [23]:

$$NEC = (1 - MOS < 1) \times 100 (\%).$$

NR 31 requires that the employer must adopt collective protection measures to control the risks at the source, followed by personal protective measures at no cost to the worker, to complement when risk factors persist temporarily [6].

3.2.1. *Collective protection*

Collective protection measures can act on toxicity and/or exposure, considering the two main risk factors of poisoning with pesticides.

3.2.1.1. *Controlling herbicide toxicity*

The pesticide toxicity is controlled by replacing the pesticide with a less toxic one, with higher NOEL value (Table 2). The higher the NOEL value, the greater the safe dose and greater MOS value.

Pesticide formulation	Common name	g i.a. /L	NOEL, mg/kg/day	Registration holder
Gesapax 500 SC	Ametryn	500.0	2.0	Syngenta Proteção De Cultivos Ltda.
Aurora 400 EC	Cafentrazona-ethyl	400.0	3.0	FMC Química Do Brasil Ltda
Gamit Star EC	Clomazone	800.0	14.0	FMC Química Do Brasil Ltda
Roundup Original SL	Glyphosate	480.0	30.0	Monsanto Do Brasil Ltda
Dual Gold EC	Metolachlor	960.0	7.5	Syngenta Proteção De Cultivos Ltda.
Boral 500 SC	Sulfentrazone	500.0	12.0	FMC Química Do Brasil Ltda
Butiron SC	Tebutiurom	500.0	7.0	Milenia Agrociências S.A.
Combine 500 SC	Tebutiurom	500.0	7.0	Dow Agrosciences Industrial Ltda
DMA 806 BR SL	2.4D	806.0	1.0	Dow Agrosciences Industrial Ltda.
Callisto SC	Mesotrione	480.0	1.8	Syngenta Proteção De Cultivos Ltda.

Table 2. Commercial formulations of herbicides, active ingredients, and their concentrations in the formulations, NOEL values TGA [31], and registration holders in Brazil.

3.2.1.2. Controlling worker exposure to herbicides

The collective protective measures that control exposure are applied to the components of the working environment. The first may be the automation of potentially contaminating operations performed by the worker; however, very rarely this action can be applied. For example, closed systems for preparing and supplying the mixture of pesticide with the carrier.

The main measure of collective protection, when working with pesticides in field conditions, is to isolate the risk areas or the worker doing the job. The isolation of the risk area can be achieved by using a bar protection adapted to the sprayer bar pulled by the tractor used for applying nonselective herbicide in eucalyptus culture (Figure 4). The spray bar was reduced to 2.5 m in length and covered with sturdy plastic blades at the front, sides, and rear (Figure 4). The bar has been adapted to apply nonselective pesticide over a 2.0-m-wide area on the weeds between the rows in areas planted with 1.0-m-tall young eucalyptus plants [24].

The total exposure of the tractor driver without individual protection, but with protected spray bar, was 838.88 mg/day of glyphosate and MOS of 8.62 [24]. Therefore, the protection of the spray bar made the tractor driver work safe, with acceptable poisoning risk and tolerable exposure levels.



Figure 4. Sprayer bar protected with plastic blades attached to the bar used to apply nonselective herbicide between plant rows in eucalyptus plantation areas [24].

Although affected by several factors, occupational exposure to pesticides is directly related to the concentration of active ingredient in the sprayed mixture and the effective exposure time

during the work day [1]. Therefore, another way of changing an unsafe working condition to safe is to limit the working hours to the number of hours during which it is safe to perform the activity (TST). This parameter can be calculated using the following formula proposed by Machado-Neto [23]:

$$SWT = MOS \times eet,$$

where SWT indicates safe working time (h); MOS, margin of safety; and eet, effective exposure time (h).

The calculated SWT values lead to two situations:

1. If $MOS \geq 1$, the SWT is greater than the considered exposure time and reaffirms the safety of working conditions under study. For safe conditions, the SWT expresses their safety levels.
2. If $MOS < 1$, the SWT is less than the exposure time of the workday. Therefore, the calculation enables to restrict daily exposure to the SWT, using it as a collective safety measure.

3.2.1.3. Individual protection

The personal protective measures only control the exposure and consist of using PPE to complement the protection of collective and preventive measures. PPE should be used when proven by the employer that is technically unfeasible to adopt collective protection measures or when they are insufficient [6].

Labor legislation NR 31 provides that the rural employer must adopt at least the following personal protective measures: supply the PPE and work clothing appropriate to the risks undertaken without causing thermal discomfort to the worker. Provide PPE and work clothing in perfect working order and properly cleaned, replacing them as necessary. It should be made clear that their decontamination at the end of each workday is the responsibility of the rural employer. Instruct on the correct use of protective devices. Provide a suitable place for safekeeping of personal clothing. Provide water, soap, and towels for personal hygiene. Ensure that any protection device or contaminated clothing be taken out of the workplace. Ensure that no device or protective clothing is reused before due decontamination. Forbid the use of personal clothing when applying pesticides [6].

The same legislation further states that it is mandatory to supply PPE to the workers for free in the following circumstances: when the collective protection measures are technically proven unfeasible or when they do not offer complete protection against the risks resulting from work and while the collective protection measures are being implemented and to meet emergency situations. PPE should be appropriate to the risks and kept in perfect condition and operation. The employer must require and train the employee to use PPE [6].

PPE control exposures on the workers' body surface via dermal and respiratory routes. Respiratory exposure is controlled with respirators equipped with filters for particles or

particles and vapors, with activated carbon. Dermal exposure is controlled with PPE made of porous and nonporous materials, or impervious. Waterproof materials are plastic coated, laminated, and rubberized; for hand protection, waterproof gloves; feet protection, waterproof rubber boots; leg protection, aprons; and plastic goggles with side shield. The porous materials are various types of fabric impregnated with carbon-fluorine compounds, which repel the water droplets of the spray mist. These porous materials are used to make the hood, long-sleeved shirts, and pants.

There is no need to use any PPE when working conditions are classified as safe ($MOS \geq 1$); however, PPE could always be recommended as accident preventive measure. The noncontrolled dermal exposure was reduced by 99%, from 838.88 to 8.62 mg/day of glyphosate in the case of the tractor driver applying glyphosate in eucalyptus plantations with the protective plastic cover over the sprayer bar (Figure 4) and wearing PPE consisting of a set of water-repellent parts (hood, long-sleeved shirt and pants), gloves, and waterproof boots. MOS increased from 8.62 to 103.24 [24]. The use of PPE made the working condition of the tractor driver even more secure.

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