Co-funded by
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OpenEAT

Curriculum for specialists regarding contaminated cereals and related products

„I eat to live or I live to eat“

Project reference: 2024-1-RO01-KA220-VET-000249064

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CURRICULUM DESCRIPTION

Name of project: „ I eat to live or I live to eat“ (OpenEAT)
Project Reference : 2024-1-RO01-KA220-VET-000249064
Curriculum addressed to experts and specialists in agriculture, food technologies, food safety and nutritionists.

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Objectives	The curriculum establish the **cognitive skills and abilities** necessary to experts and specialists regarding the measures to reduce cereals contamination, methodologies to detect pesticides, heavy metals and toxic nitrogen compounds and the impact on health. Cognitive skills refer to ability necessary to use the scientific concepts belonging to the fundamental disciplines chemistry, biology and general technologies in order to develop new strategies for safety foods in context of Ukrainian conflict. Curriculum will presents theoretical and practical aspects regarding measures to reduce cereals contamination, methodologies to detect pesticides, heavy metals and toxic nitrogen compounds and the impact on health.
Cognitive skills	When designing a curriculum focused on **measures to reduce cereals contamination with pesticides, nitrogen compounds, and heavy metals**, it's essential to develop **cognitive skills** that enhance problem-solving, critical thinking, and decision-making. Here are the key cognitive skills to include: **1. Analytical Thinking** • Identifying contamination sources in cereals and their impact on health • Analyzing soil and crop data to detect contamination trends

	• Evaluating the effectiveness of different contamination reduction strategies **2. Critical Thinking** • Assessing risks associated with pesticide and heavy metal contamination • Comparing different agricultural practices for reducing contamination • Questioning and validating research findings on contamination control **3. Problem-Solving** • Developing innovative solutions for minimizing contamination • Adapting farming techniques to reduce chemical residues • Addressing regulatory compliance challenges in real-world scenarios **4. Decision-Making** • Choosing appropriate pest control strategies with minimal environmental impact • Balancing productivity and sustainability in cereal farming • Interpreting lab test results to make informed contamination control decisions **5. Scientific Inquiry and Research Skills** • Conducting field experiments on contamination mitigation • Reviewing scientific literature on pesticide and heavy metal reduction • Applying research methodologies to assess contamination levels **6. Systems Thinking** • Understanding the interactions between soil, water, crops, and contaminants • Recognizing the long-term effects of contamination on ecosystems and human health • Designing sustainable agricultural systems that minimize contamination risks
Professional skills	**Developing a curriculum to address measures for reducing contamination in cereals requires a blend of scientific, technical, and regulatory knowledge.** **1. Agricultural and Environmental Science Skills** • Understanding pesticide behavior in soil and crops • Knowledge of nitrogen cycle and fertilizer impact on cereals • Awareness of heavy metal contamination sources (industrial pollution, soil composition, irrigation) • Soil and crop monitoring techniques **2. Food Safety and Quality Control** • Hazard Analysis and Critical Control Points (HACCP) principles • Risk assessment for pesticide residues and heavy metals • Laboratory testing methods for contaminants (e.g., chromatography, spectroscopy) • International food safety regulations (EU, FAO, Codex

	Alimentarius) **3. Sustainable Farming and Precision Agriculture** • Best practices for pesticide application and reduction strategies • Integrated Pest Management (IPM) techniques • Organic and regenerative farming practices • Precision agriculture tools (drones, sensors, AI for monitoring soil health) **4. Regulatory and Compliance Knowledge** • Legal frameworks on pesticide use and residue limits • Maximum Residue Limits (MRLs) and regulatory standards • Certification requirements for organic and sustainable cereals **5. Data Analysis and Technology Use** • Statistical analysis of contamination levels • Use of Geographic Information Systems (GIS) for soil and water contamination mapping • AI and IoT applications in monitoring contamination
Competence units	**1. Contamination Sources and Risk Assessment** **Competences:** • Identify primary sources of contamination in cereals (pesticides, fertilizers, heavy metals) • Assess environmental and agricultural factors contributing to contamination • Analyze contamination pathways (soil, water, air) and their impact on food safety **Key Topics:** • Pesticide residue formation and persistence • Nitrogen compounds: overuse, runoff, and leaching • Heavy metal accumulation from industrial and natural sources • Risk assessment methodologies **2. Sustainable and Integrated Farming Practices** **Competences:** • Apply **Integrated Pest Management (IPM)** to reduce pesticide dependency • Implement **sustainable fertilization techniques** to minimize nitrogen compound contamination • Utilize soil remediation and conservation methods to reduce heavy metal uptake **Key Topics:** • Biological pest control and crop rotation • Precision agriculture for controlled fertilizer application • Soil pH management and bio-remediation techniques • Organic farming alternatives **3. Monitoring and Detection of Contaminants** **Competences:** • Conduct field and laboratory tests for pesticide residues, nitrates, and heavy metals • Use modern detection techniques (chromatography, spectrometry,

	biosensors) • Interpret contamination levels and suggest corrective actions **Key Topics:** • Laboratory testing methods (GC-MS, HPLC, ICP-MS) • Regulatory limits for contaminants (EU, Codex, FAO standards) • On-site rapid testing techniques **4. Regulatory Compliance and Food Safety Standards** **Competences:** • Apply **Maximum Residue Limits (MRLs)** and food safety regulations • Ensure compliance with national and international standards • Implement **Hazard Analysis and Critical Control Points (HACCP)** for contamination prevention **Key Topics:** • EU pesticide regulations, FAO Codex Alimentarius, WHO guidelines • Good Agricultural Practices (GAP) • HACCP principles for cereal production and storage **5. Technological and Digital Solutions for Contamination Reduction** **Competences:** • Utilize precision agriculture technologies (drones, sensors, AI) for contamination control • Apply GIS mapping to monitor contaminated areas • Implement smart irrigation and fertilization systems **Key Topics:** • AI and IoT applications in sustainable farming • GIS-based contamination mapping • Automated pesticide and fertilizer application systems **6. Sustainable Supply Chain and Consumer Awareness** **Competences:** • Manage post-harvest handling to prevent contamination • Ensure sustainable sourcing and traceability in cereal production • Educate stakeholders on contamination risks and mitigation strategies **Key Topics:** • Storage and transport contamination prevention • Blockchain and traceability technologies • Consumer education on food safety
Elements of innovation	The elements of innovation are due by the complementarity of the competencies that are intended to be implemented to the target groups and which relate to elements of agronomy, cereals protection, contaminants detection, analytical tools and health implication in order to manage the cereals contamination and to assure the food safety in context of Ukrainian conflict.
The impact	Implementing a well-structured curriculum on this topic can have **significant positive effects** across multiple areas, from agriculture and public health to environmental sustainability and economic benefits. Below are the key **impact areas**:

	1. Agricultural and Environmental Impact • Reduction of Soil and Water Contamination • Enhanced Crop Quality and Safety • Climate Resilience and Sustainability **2. Public Health and Food Safety Impact** • Safer Food Supply • Reduction in Health Risks • Increased Consumer Confidence **3. Economic and Industry Impact** • Higher Market Value for Contaminant-Free Cereals • Cost Reduction for Farmers • Efficient use of pesticides and fertilizers lowers input costs • Preventing contamination avoids potential financial losses from rejected exports • Job Creation and Technological Advancements • Demand for skilled professionals in precision agriculture, food safety, and environmental monitoring increases • Encouragement of agtech innovations such as AI-based contamination detection **4. Educational and Research Impact** **Capacity Building for Future Agricultural Experts** • Farmers, agronomists, and policymakers gain advanced knowledge on contamination reduction • Training on **data-driven decision-making** enhances agricultural efficiency **Encouragement of Scientific Innovation** • Research into **bioremediation, nanotechnology, and alternative pest control** advances sustainability • Increased collaboration between **universities, research institutions, and industry leaders** **Global Knowledge Exchange** • International partnerships facilitate learning from best practices in different regions • Integration of **e-learning platforms** allows knowledge sharing beyond local communities **5. Policy and Regulatory Impact** **Stronger Compliance with Food Safety Regulations** • Farmers and producers are better equipped to meet national and international standards • Government agencies improve monitoring and enforcement of contamination control policies **Informed Decision-Making for Policymakers** • Scientific data from the curriculum supports evidence-based policy development • Improved strategies for reducing **agricultural pollution and chemical overuse** **Empowerment of Local Communities**

	• **Citizen science initiatives** encourage public participation in food safety monitoring • Increased awareness leads to advocacy for stronger environmental and food safety regulations

Activities hours

	Total hours	Theoretical	Practical	Individual study
	82	**48**	**24**	**10**

Subjects of Curriculum

Theoretical part	No of hours	Obs
Chapter 1. Introduction to Cereals Contamination Risks in Conflict-Affected Agriculture ● Understand the impact of military activities on soil and crop contamination ● Identify primary contaminants: pesticides, nitrogen compounds, and heavy metals ● Analyze the pathways of contamination in cereals and food systems ● Overview of **agricultural contamination risks** ● Sources of **heavy metal contamination (lead, arsenic, cadmium)** ● Effects of **pesticides and excessive nitrogen fertilizers** on soil and water	2 (LTT 1-3)	Each theoretical part consists in hours 8 hours x 2 days In total 16 hours /LTT
Chapter 2. Terms and definitions ● **General Terms Related to Contamination** ● **Heavy Metal Contamination Terms** ● **Nitrogen Compound Contamination Terms** ● **Pesticide Contamination Terms** ● **Conflict-Specific Agricultural Contamination Terms** ● **International and EU Regulatory Terms**	2 (LTT 1-3)	
Chapter 3. The International context of Ukrainian conflict and Legislation at national and European level ● **Regulatory limits and thresholds** (EU, FAO, Codex Alimentarius)	2 (LTT 1-3)	
Chapter 4. Measures necessary to reduce cereals contamination ● Measure to reduce pesticides content in cereals and cereal products ● Measure to reduce heavy metals contamination in cereals and cereal products ● Measure to reduce nitrogen compounds in cereals and cereal products	8 (LTT1)	
Chapter 5. The analytic methods to control the contaminants ● Analytical methods to detect pesticides content in cereals and cereal products ● Analytical methods to detect heavy metals contamination in cereals and cereal products ● Analytical methods to detect nitrogen compounds in cereals and cereal products	8 (LTT2)	
Chapter 6. The health risk regarding cereal and cereals product contamination ● The health risk of cereal and cereals products contaminated with pesticides	8 (LTT3)	

• The health risk of cereal and cereals products contaminated with heavy metals • The health risk of cereal and cereals products contaminated with nitrogen compounds		
Evaluation	2 (LTT1-3)	
Practical part Practical activities will be carried out in the partner universities' teaching laboratories, which present the necessary equipment's.	No of hours	Obs
i) Exchange best practices in managing of cereals and related products susceptible for contamination imported from Ukraine.	8 LTT1	Each practical part consists in 8 hours x 1 days (LTT 1-3)
ii) Exchange best practices regarding the detection of contaminants from cereals and cereal products.	8 LTT2	
iii) Exchange best practices regarding healthy and food security risks associated with consumption of cereals products contaminated with pesticides, heavy metals and nitrogen compounds.	8 LTT3	
Evaluation methods: The evaluation methods are set based on objective, semi-objective and subjective items. ***Objective items*** refer to the evaluation based on the dual, pair or multiple choice principles of a number of solutions offered to learners. ***Semi-objective items*** can be with short answer, complementary, or structured questions in which the student intervenes with solutions expressed in the partially rendered formulation. ***The subjective items*** refer to the free or structured essay, in which the learner freely expresses solutions to the requested problem or based on a required scheme. In the category of subjective items, is included also the solving of some problems on the topic taught.		
Assessment for the certification of competencies: will be done by means of tools and evidence developed in accordance with the provisions regarding the cognitive and professional skills, taking into account the performance criteria and the conditions of its applicability. Some evidence and evaluation tools will be able to take into account the integrated assessment of multiple competencies or more performance criteria from the same competency or from different competencies. The evaluation highlights the extent to which key competencies, general technical skills and specialized technical skills are shaped.		
List of teaching and research materials: The theoretical parts and also the practical parts will be exemplified by texts, pictures and videos, and the final teaching method will take into account the level of the target group to whom it addresses.		

EXTENDED CURRICULUM

Chapter 1. Introduction

1.1. Understand the impact of military activities on soil and crop contamination

Military activities can introduce a wide range of contaminants into the environment, impacting soil and subsequently, the crops grown within it. These contaminants can be broadly categorized as:

Heavy Metals: Munitions, military vehicles, dron warfare and other equipment can release heavy metals like lead, cadmium, chromium, lithium and depleted uranium into the soil. These metals can accumulate in plants, posing health risks to consumers.

Explosive Compounds: The detonation of explosives releases various chemical compounds, including nitroaromatics (e.g., TNT, RDX) and perchlorates, into the environment. These compounds can be toxic to plants and humans, and their persistence in soil can lead to long-term contamination.

Propellants and Fuels: Spills and leaks from military vehicles and storage facilities can contaminate soil with propellants (e.g., ammonium perchlorate) and fuels (e.g., hydrocarbons). These substances can negatively impact plant growth and development, and some may have carcinogenic properties.

Chemical and Biological Weapons: Although less common, the potential use of chemical or biological weapons poses a severe threat of widespread and long-lasting contamination. These agents can have devastating effects on human health and the environment.

Radioactive Materials: The use of depleted uranium munitions raises concerns about radioactive contamination. While the radiotoxicity of depleted uranium is debated, its chemical toxicity as a heavy metal is well established.

Unexploded Ordnance (UXO): UXO, including landmines and unexploded bombs, not only pose a direct physical danger but can also leach contaminants into the surrounding soil over time as they corrode.

The impact of these contaminants on soil and crops is multifaceted:

Soil Degradation: Contamination can alter soil properties, affecting its fertility, structure, and water-holding capacity, ultimately hindering plant growth.

Plant Uptake and Accumulation: Plants can absorb contaminants from the soil through their roots and translocate them to different parts, including the edible portions like grains. The level of accumulation depends on various factors, including the type of contaminant, its concentration in the soil, the plant species, and environmental conditions.

Food Chain Contamination: Contaminated crops can introduce these harmful substances into the food chain, affecting both human and animal health. Long-term exposure to low levels of contaminants can lead to chronic health problems.

Important considerations

The severity of soil and crop contamination depends on the type and intensity of military activities, soil type and climate.

The long-term effects of soil contamination caused by military activities can be difficult to assess and may not be fully understood for many years.

Addressing soil and crop contamination caused by military activities is essential to protect human health and the environment.

1.2. Identify primary contaminants: pesticides, nitrogen compounds, and heavy metals

Cereals, a globally significant food staple, are vulnerable to diverse contamination sources, posing substantial risks to human health. Pesticides, nitrogen compounds, and heavy metals are primary contaminants of particular concern due to their pervasive use, environmental persistence, and potential for adverse health outcomes.

1.2.1. Pesticides

These chemical agents are employed to manage pests that inflict crop damage or vector diseases. While essential for ensuring food security, pesticide residues in cereals represent a significant threat to human health.

The main pesticide classes include:

Organophosphates – Affect the nervous system by inhibiting acetylcholinesterase (e.g., chlorpyrifos, malathion, diazinon).

Carbamates – Similar to organophosphates but with reversible enzyme inhibition (e.g., carbaryl, aldicarb).

Organochlorines – Persistent in the environment, many are now banned (e.g., DDT, lindane).

Pyrethroids – Synthetic analogs of natural pyrethrins, used for insect control (e.g., permethrin, cypermethrin).

Neonicotinoids – Act on insect nervous systems, controversial for their impact on bees (e.g., imidacloprid, thiamethoxam).

Triazines – Common herbicides inhibiting photosynthesis (e.g., atrazine, simazine).

Sulfonylureas – Herbicides that disrupt plant amino acid synthesis (e.g., metsulfuron-methyl).

Phenoxy Herbicides – Used for broadleaf weed control (e.g., 2,4-D).

Dicarboximides – Fungicides that inhibit fungal growth (e.g., iprodione).

Strobilurins – Modern fungicides that disrupt mitochondrial respiration (e.g., azoxystrobin).

Each class has specific uses, toxicity profiles, and environmental impacts.

Health Impacts

The main health impacts of pesticide exposure on humans depend on the type of pesticide, dose, and duration of exposure. They include:

Acute Effects (Short-Term Exposure)

1. **Neurological Effects** – Headaches, dizziness, nausea, convulsions (e.g., organophosphates and carbamates inhibit acetylcholinesterase).
2. **Respiratory Issues** – Difficulty breathing, irritation, or asthma-like symptoms from inhalation exposure.
3. **Skin and Eye Irritation** – Rashes, burning sensation, or allergic reactions from dermal contact.
4. **Gastrointestinal Issues** – Vomiting, diarrhea, and abdominal pain due to ingestion.

Chronic Effects (Long-Term Exposure)

1. **Neurotoxicity** – Increased risk of neurodegenerative diseases like Parkinson's and cognitive decline.
2. **Carcinogenicity** – Some pesticides (e.g., organochlorines, glyphosate) are linked to cancer, including leukemia and non-Hodgkin's lymphoma.
3. **Endocrine Disruption** – Interference with hormonal systems, affecting reproductive health, thyroid function, and fetal development.
4. **Reproductive and Developmental Effects** – Reduced fertility, birth defects, and developmental disorders in children.
5. **Immune System Suppression** – Increased susceptibility to infections and autoimmune diseases.
6. **Liver and Kidney Damage** – Chronic exposure can lead to organ dysfunction due to bioaccumulation of toxic compounds.

Vulnerable Populations

- **Children and Pregnant Women** – More sensitive due to developing organs.
- **Farm Workers and Pesticide Applicators** – Higher exposure risk through occupational contact.

Regulatory limits and safety measures aim to minimize these risks, but exposure should be carefully controlled.

- **Regulatory Frameworks:** Numerous nations have implemented regulatory frameworks governing pesticide application and establishing maximum residue limits (MRLs) in cereals to mitigate consumer exposure (FAO/WHO, 2022).

1.2.2. Nitrogen Compounds

Nitrogen compounds, notably nitrates and nitrites, are naturally occurring substances that can also enter the food chain through agricultural practices, specifically the application of nitrogen-based fertilizers.

- **Sources of Contamination:** Excessive nitrogen fertilizer use can result in nitrate leaching into groundwater and surface water, subsequently contaminating irrigation water and cereal crops.
- **Health Implications:** Elevated nitrate levels in cereals present health risks, particularly for infants, as nitrates can be converted to nitrites, leading to methemoglobinemia, a condition impairing oxygen transport. Furthermore, nitrites can react with gastric amines to form carcinogenic nitrosamines (WHO, 2011).
- **Regulatory Measures:** The World Health Organization (WHO) has established guidelines for nitrate concentrations in potable water, and analogous regulations often apply to food products, including cereals.

1.2.3. Toxic trace elements

The expression "heavy metals" defines metallic elements that have a relatively high density compared to water and it is assumed that heaviness is associated to toxicity. Heavy metals are also considered trace elements as they are present in trace concentrations in the ppb range to less than 10 ppm in most environmental matrices. Previously, scientists used the term "heavy metals" when referring to trace elements. In fact, not all metals are essentially heavy (e. g. Al, Ni) and some elements are not metals (e. g. As, Se). That's why nowadays researchers prefer the term "(metallic) trace elements" or more simple, "trace elements".

Metals may be classified as essential and non-essential, depending on whether they exert a function in biochemical and physiological processes (Goyer et al., 2004). According to the World Health Organization (WHO) essential elements are I, Zn, Se, Fe, Cu, Cr and Mo. Other trace elements may/could have beneficial effects or be essential such as Mn, Co, As, Ni and V (Amiard et al., 2011). In fact, Cu and Fe are incorporated into a number of metalloenzymes involved in hemoglobin formation and carbohydrate metabolism (Henriques et al., 2017) while Zn plays an important role in cell division and growth, wound healing and breakdown of carbohydrates (Roohani et al., 2013). Non-essential trace elements such as Hg, Pb or Cd play no physiological role and are toxic at very small amounts (Goyer et al., 2004).

Toxic trace elements are naturally occurring elements generally characterized by high atomic weight and density, exhibiting toxic effects on biological systems. These contaminants can enter the food chain via various pathways, including industrial discharge, mining operations, and the use of contaminated irrigation water.

- **Representative toxic trace elements:** Arsenic, cadmium, lead, and mercury (mostly accidentally) are among the most concerning toxic trace elements in cereals. They can be incorporated by the cereal plants from contaminated soil and water sources.
- **Regulatory standards:** International organizations (European Union, etc.) as well as national authorities have established standards and guidelines for toxic trace elements concentrations in cereals to minimize human exposure.

1.3. Source of contamination

1.3.1. Source of contamination with pesticides

- **Agriculture**

Agriculture is the main economic sector where chlorinated pesticides were used, the effects of which are still felt today. The impact of pesticides used in agriculture on water is in the form of diffuse pollution, which is currently measured in groundwater and surface water.

Emissions of Persistent Organic Pollutants (POPs) used in the agricultural sector into the atmosphere occur from stationary sources, such as pesticide application on the ground and by burning, or from mobile sources mainly correlated with road vehicles (tractors and other means of transport).

- **Industry**

Emission sources in the industrial sector are mainly point-based. However, there are also some diffuse sources generated by the storage of solid and liquid waste from the production of pesticides. The existing stocks (including waste) of POPs are correlated with the quantities of POPs that are no longer used and that could be disposed of.

1.3.2. Source of contamination with nitrogen compounds

The amount of nitrates existing in the plant at a given time is the result of the balance between the amount absorbed and the amount used in proteinogenesis. Any factor likely to intervene in the metabolic chain, which ensures the transformation of nitric nitrogen into amino nitrogen and protein nitrogen, can influence the amount of free nitrates in the plant.

The sources of nitrate, nitrite and ammonium contamination of horticultural products are:

- **natural sources:** nitrates from soil, surface water, groundwater as a result of the natural decomposition of organic nitrogen by microorganisms and transformation into materials such as proteins in plants, animals. The natural occurrence of nitrates and nitrites in the environment is the consequence of the so-called "nitrogen cycle".
- **anthropogenic sources** given by the use of synthetic fertilizers in the fertilization of horticultural crops, agriculture and the application of waste resulting from these livestock farms on cultivated soils.
  - Excessive fertilization, with doses that exceed the plant's nitrogen requirement during the period of maximum consumption, leads to an increase in the nitrate content of the plant. The administration of nitrogen fertilizers, in the form of foliar fertilizer, leads to an increase in nitrate content, but during a short period after application, the nitrate level decreases to the pre-treatment value. The nitrate content of plants can be reduced by 20-25% by spraying crops with water in the pre-harvest period.
  - High levels of nitrates are found in crops grown on nitrogen-rich soils and humus, even in the absence of nitrogen fertiliser fertilisation. The problem of nutrient pollution starts at the household level, namely from the management and improper use of manure in agriculture. Organic farming promotes the use

of compost, fertilizer that is not harmful to the environment, is cheaper and easily accessible.

- **The genetic potential** of the plant causes nitrates to accumulate in the plant. The plant species characterized by the highest nitrate content are vegetables whose organ is consumed is the leaf.
- **Climatic conditions** (temperature, precipitation, light intensity) determine the level of nitrates in plants, as a result of the conditions under which the reduction reaction takes place. Among these, the lighting regime has a very important role, because it intervenes as a source that provides energy in the process of reducing nitrates in the plant (nitrate – nitrite – ammonium – amino acid).

1.3.3. Sources of heavy metal contamination (lead, arsenic, cadmium, antimony, chromium, nickel, zinc, mercury, aluminium)

Heavy element residues are the most persistent war residuals in the affected areas that contaminate air, soil and water. Their resident time in environment depends on redox properties. Sources of metal contamination are gunshot fumes and particles, bullet fragments, primers, detonators, military hardware, guns, ammunition, artillery and grenades, dron warfare.

Toxic trace elements contamination of crops primarily arises from the following sources:

(i) Soil contamination: Heavy metals like lead (Pb), arsenic (As), and cadmium (Cd) accumulate in agricultural soils due to industrial emissions, mining activities, and natural geological sources.

(ii) Irrigation water: Contaminated water from industrial discharge, wastewater irrigation, or naturally occurring high-metal groundwater can introduce heavy metals into the soil and plant system.

(iii) Atmospheric deposition: Airborne pollutants from industrial activities, vehicle emissions, burning of fossil fuels and exceptionally, (war) explosions emissions can settle on crops and soil, increasing metal concentrations.

(iv) Fertilizers and pesticides: Phosphate fertilizers and certain pesticides contain trace amounts of heavy metals, contributing to long-term soil accumulation.

(v) Waste and sludge Application: The use of sewage sludge, compost, or organic waste as soil amendments can introduce significant amounts of heavy metals into agricultural fields.

Once absorbed by plants, these metals can accumulate in edible parts, posing risks to human health.

1.4. Effects of pesticides and excessive nitrogen fertilizers on soil and water

The application of pesticides and excessive nitrogenous fertilizers in modern agriculture, while contributing to increased yields, poses significant threats to both soil and water quality, with consequent impacts on ecosystem health and potential detriments to human well-being.

Cereals, a globally dominant food source, exhibit particular vulnerability to contamination from these agrochemical inputs.

1.4.1. Pesticides

The utilization of pesticides for pest control can induce a range of unintended ecological consequences for both soil and water resources.

- **Edaphic Effects:**
  - **Biotic Disruption:** Pesticide application can negatively impact non-target soil organisms, including beneficial insects, earthworms, and microbial communities, resulting in diminished biodiversity and disruption of essential processes such as nutrient cycling and decomposition.
  - **Soil Contamination:** Persistent pesticide residues can accumulate within the soil matrix, potentially inhibiting plant growth and posing risks to organisms consuming contaminated plant material.
  - **Alteration of Soil Properties:** Certain pesticides can modify soil structure, water-holding capacity, and other physicochemical properties, potentially reducing soil fertility.
- **Aquatic Effects:**
  - **Water Contamination:** Pesticide runoff from agricultural fields can contaminate surface and groundwater resources, negatively impacting aquatic life and potentially infiltrating potable water sources.
  - **Ecotoxicity:** Pesticides can exhibit toxicity towards aquatic organisms, inducing harm or mortality in fish, invertebrates, and algae, thereby disrupting aquatic ecosystems.
  - **Sediment Contamination:** Pesticides can bind to sediment particles, accumulating in waterways and potentially posing protracted risks to aquatic life.

1.4.2. Excessive Nitrogen Fertilizers

While nitrogen fertilization can enhance crop productivity, its excessive application can exert detrimental effects on soil and water quality.

- **Edaphic Effects:**
  - **Soil Acidification:** Excessive nitrogen application can contribute to soil acidification, influencing nutrient bioavailability and potentially hindering plant growth.
  - **Nutrient Imbalance:** Elevated nitrogen levels can disrupt the equilibrium of other essential soil nutrients, potentially limiting plant growth and development.

- **Greenhouse Gas Emissions:** Nitrogen fertilizers can contribute to the emission of nitrous oxide (N2O), a potent greenhouse gas implicated in climate change.

- **Aquatic Effects:**
  - **Eutrophication:** Excessive nitrogen runoff can induce eutrophication in water bodies, characterized by algal blooms, oxygen depletion, and subsequent fish kills.
  - **Nitrate Contamination:** Elevated nitrate concentrations in drinking water can pose health risks, particularly for infants, leading to methemoglobinemia, a condition impairing oxygen transport.
  - **Groundwater Contamination:** Nitrates can leach into groundwater, contaminating drinking water supplies and potentially necessitating costly remediation efforts.

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Chapter 2. Terms and definitions

2.1. General Terms Related to Contamination

Contamination

The presence of **harmful substances** (chemical, biological, or physical) in food, soil, or water beyond acceptable levels, making them unsafe for consumption or use.

Food Safety

The **scientific discipline** focused on handling, preparing, and storing food in ways that **prevent contamination** and ensure it is safe for human consumption.

Maximum Residue Limits (MRLs)

The highest level of **pesticides or contaminants legally allowed** in food products, set by **Codex Alimentarius, EU, FAO, and national regulations**.

Risk Assessment

The process of **identifying, evaluating, and controlling potential hazards** in food and agriculture, particularly contamination caused by war-related environmental damage.

2. 2. Heavy Metal Contamination Terms

Heavy Metals

Toxic elements (e.g., lead, cadmium, mercury, arsenic) that **accumulate in soil and crops**, posing serious health risks when consumed.

Bioaccumulation

The gradual accumulation of **heavy metals** or toxic substances in plants, animals, or humans over time.

Phytoremediation

A process using **plants to absorb and neutralize heavy metals** from contaminated soils.

Lead (Pb) Contamination

Lead pollution in cereals caused by **military activities, ammunition, and industrial waste**, leading to **neurological and developmental disorders** when consumed.

Cadmium (Cd) Contamination

A **highly toxic heavy metal** that accumulates in soil due to **fertilizers, industrial emissions, and war debris**, affecting kidney function and bone health.

Arsenic (As) Contamination

Arsenic enters the food chain through **pesticides, water contamination, and war-related pollution**, leading to chronic poisoning and cancer risks.

Mercury (Hg) Contamination
Mercury contamination in agriculture results from **industrial emissions, explosives, and mining activities**, affecting neurological health and fetal development.

2.3. Nitrogen Compound Contamination Terms

Nitrogen Compounds
Chemical compounds containing **nitrogen** (e.g., nitrates, nitrites, ammonia) that **affect soil, water, and plant health** when used excessively.

Nitrate (NO_3^-) Pollution
High levels of **nitrates in water and soil**, often caused by **excessive fertilizer use and war-related industrial leaks**, leading to water contamination and health issues like **methemoglobinemia ("blue baby syndrome")**.

Nitrite (NO_2^-) Toxicity
Nitrites, derived from nitrates, are **highly toxic** and contribute to **carcinogenic nitrosamines** in food and drinking water.

Ammonia (NH_3) Contamination
Ammonia from **agricultural runoff, explosives, and industrial waste** can **acidify soil and water**, harming plant growth and aquatic ecosystems.

Eutrophication
The process where **excess nitrogen compounds** in water bodies cause **algae overgrowth**, leading to oxygen depletion and aquatic ecosystem collapse.

Denitrification
A natural process where **microbes convert nitrates into nitrogen gas**, reducing soil nitrogen levels and preventing pollution.

2.4. Pesticide Contamination Terms

Pesticides
Chemical substances used to **control pests, weeds, and diseases**, but they can leave **harmful residues** in food and the environment.

Organochlorine Pesticides (OCPs)
A class of **persistent, toxic pesticides** (e.g., **DDT, aldrin, dieldrin**) that accumulate in **soil, water, and food chains**.

Organophosphate Pesticides (OPs)
Highly toxic pesticides (e.g., **chlorpyrifos, malathion**) that **affect nervous system functions** and are subject to **strict EU regulations**.
Onicotinoids
A class of **systemic insecticides** linked to **bee population decline** and restricted under **EU law**.

Glyphosate
A **widely used herbicide** (found in **Roundup**) under scrutiny for its **potential carcinogenic effects**.
Pesticide Residue
The **trace amount of pesticide left** in food after treatment, which must remain below **Maximum Residue Limits (MRLs)** to be safe.

Integrated Pest Management (IPM)
A **sustainable farming approach** that minimizes pesticide use by combining **biological, physical, and chemical pest control methods**.

2.5. Conflict-Specific Agricultural Contamination Terms

War-Induced Soil Contamination
The pollution of agricultural land caused by **explosives, heavy metals, and industrial destruction during conflicts**.

Explosive Residue Contamination
Chemical contamination from **bombs, mines, and military debris**, affecting soil fertility and food safety.

Radiation Contamination
The presence of **radioactive materials** (e.g., uranium from depleted uranium shells) in agricultural areas, affecting long-term **soil and crop safety**.
Depleted Uranium (DU) Pollution
A **toxic and radioactive heavy metal** used in military ammunition that can **persist in soil for decades**, increasing **cancer and kidney disease risks**.

Post-Conflict Land Rehabilitation
The process of restoring war-damaged agricultural land through **soil decontamination, sustainable farming, and environmental recovery**.

2.6. International and EU Regulatory Terms

Codex Alimentarius
A global **food safety standard** that sets **maximum residue limits** for pesticides, heavy metals, and other contaminants in food.

EU Maximum Residue Limits (MRLs)
The **legal limits of contaminants** (e.g., heavy metals, pesticides) in food under **Regulation (EC) No 396/2005**.

EU Nitrates Directive (91/676/EEC)
European law that limits **nitrogen pollution from agriculture**, requiring farmers to follow **nutrient management plans**.

European Green Deal & Farm to Fork Strategy
EU initiatives to **reduce pesticide and fertilizer use by 50% by 2030**, promoting **organic farming and sustainable agriculture**.

Sanitary and Phytosanitary (SPS) Measures
WTO rules ensuring that food safety and contamination regulations **do not create unnecessary trade barriers**.

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Chapter 3. The International context of Ukrainian conflict and Legislation at national and European level

The war in Ukraine has disrupted global agriculture, given that Ukraine is one of the world's largest exporters of **wheat, maize, and barley**. The conflict has led to **soil degradation, contamination from military activities, trade restrictions, and food security challenges**.

3.1 Key International Impacts:

<u>Food Security and Global Grain Supply</u>

- Ukraine, along with Russia, accounts for **roughly 30% of global wheat exports**. The war has disrupted supply chains, leading to **higher food prices** and grain shortages, particularly in Africa and the Middle East.
- The **Black Sea Grain Initiative**, brokered by the UN and Turkey, was an attempt to ensure safe passage for grain exports, but its collapse further strained global food markets.

<u>Environmental and Agricultural Contamination</u>

- **Heavy metals, fuel residues, and unexploded ordnance** from military activities have **polluted Ukrainian farmlands**, increasing risks of contamination in cereals.
- Large-scale **bombardments and land destruction** have led to soil degradation, affecting long-term agricultural productivity.

<u>Disruptions in Agricultural Trade and Supply Chains</u>

- **Port blockades** and infrastructure damage have limited Ukraine's ability to export cereals, forcing reliance on alternative routes through **Poland, Romania, and the Baltic states**.
- **Sanctions against Russia** have disrupted the supply of fertilizers and agrochemicals, affecting global agricultural production.

3.2 Ukrainian National Legislation on Contamination and Food Safety

Ukraine's regulatory framework aligns with **European Union (EU) standards**, as part of its efforts toward **EU accession and agricultural trade compliance**. The key areas of focus include **pesticide use, nitrate pollution control, and heavy metal contamination regulations**.

Key Ukrainian Laws and Regulations

Law on **Pesticides and Agrochemicals (2002, amended)**

- Regulates **use, registration, and disposal** of pesticides and fertilizers
- Requires compliance with **EU residue limits** in food products

Law on Environmental Protection (1991, amended)

- Defines regulations on **soil pollution, chemical contamination, and industrial waste management**
- Sets standards for heavy metal and nitrate contamination in agriculture

Law on Food Safety and Hygiene (2014, amended to align with EU standards)

- Establishes **Maximum Residue Limits (MRLs) for pesticides and contaminants**
- Regulates food production, storage, and distribution for domestic and export markets

National Action Plan on Nitrate Pollution Reduction

- Implements measures to **prevent excessive nitrogen compound runoff** into soil and water
- Supports farmers in adopting **sustainable fertilization techniques**

Strategy for Sustainable Agriculture and Rural Development (2020-2030)

- Encourages **climate-resilient and environmentally friendly farming practices**
- Promotes **precision agriculture and bioremediation** to reduce contamination risks

3.3 European Legislation and Regulations on Agricultural Contamination

As Ukraine seeks **closer integration with the EU**, it must comply with strict **European food safety, environmental protection, and trade laws**.

Key EU Regulations Relevant to Cereal Contamination:

- ➢ **EU Pesticides and Agrochemicals Regulations**

Regulation (EC) No 1107/2009 – Governs the **authorization and use of pesticides** in the EU

Regulation (EU) 2019/1381 – Introduces stricter **transparency in food risk assessment**

Impact on Ukraine:

- Ukrainian grain exports to the EU must meet **pesticide residue limits** under **Regulation (EC) No 396/2005**
- Ukraine must phase out **banned EU pesticides** such as neonicotinoids

- ➢ **EU Nitrate and Heavy Metal Regulations**

Nitrates Directive (91/676/EEC) – Limits nitrogen compound pollution in water bodies

Heavy Metals in Food Regulation (EU) 2023/915 – Sets strict **cadmium, lead, arsenic limits** in cereals

Impact on Ukraine:

- Farmers must implement **best management practices (BMPs)** to **reduce nitrogen runoff**
- Compliance with **EU heavy metal thresholds** is necessary for exports

- ➢ **EU Food Safety and Trade Laws**

General Food Law (Regulation (EC) No 178/2002) – Establishes the basis for EU food safety policy

EU Maximum Residue Limits (MRLs) for Contaminants in Food (Regulation (EC) No 1881/2006, updated 2022) – Sets limits for contaminants in cereals

Impact on Ukraine:

- Ukrainian cereal producers must **test for contaminants before export**
- Strict traceability is required to meet **HACCP and food safety certification standards**

- **EU Sustainable Agriculture and Green Deal Policies**

Farm to Fork Strategy (2020) – Aims to reduce pesticide and fertilizer use by **50% by 2030**
Common Agricultural Policy (CAP) 2023-2027 – Supports **eco-friendly farming** through subsidies
Impact on Ukraine:

- Ukraine must align its **sustainable farming practices** with EU Green Deal goals

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Chapter 4. Measures necessary to reduce cereals contamination

Cereals are a fundamental component of the global food supply, but their contamination with harmful substances, including pesticides, heavy metals, and nitrogen compounds, poses significant health and environmental risks. To ensure food safety and sustainability, it is essential to implement effective measures that minimize contamination at every stage of production-from soil management and fertilization to harvesting, storage, and processing.

4.1. Measure to reduce pesticides content in cereals and cereal products

Application of Good Agricultural Practices (GAPs) during cereals production

Plant protection products are "pesticides" that protect crops or desirable or useful plants. They are used in agriculture as well as in other sectors. Contain at least one active substance to protect plants or plant products against pests/diseases, and improve the productivity in field and postharvest, avoiding also the contamination by mycotoxins produced by some fungal species, that can be present in the derivative products.

The pesticides include, amongst others: herbicides, fungicides, insecticides, acaricides, nematicides, molluscicides, growth regulators, repellents, rodenticides and biocides and for each a wide range of synthetic chemical compounds. The use of pesticides is allowed in integrated agriculture rather than in organic ones. The use of pesticides in integrated agriculture must be done by applying the Integrated Pest Management (IPM). This latter takes into account on agronomic, mechanical, physical, and biological principles, resorting to selective synthetic pesticide use when addressing situations cannot be successfully managed with other means. Crop rotation, using resistant/tolerant cultivars and certified seed as well as the use of beneficial organisms are common practices to minimize applications with chemicals. When pesticides are used, it is necessary to respect their Maximum Residue Levels (MRLs) as enforced by different authoritative bodies, and in accordance with the "Good Agricultural Practice". For the use of pesticides, anti-resistance strategies must also be applied to maximize the effectiveness by reducing their application. Overall, pest monitoring by using observations in the field, classic and molecular diagnostic methods as well as forecasting systems allow scheduling the pest management, taking into account threshold levels considering the crop and the climatic conditions of the reference area. In detail, methods such as hyperspectral imaging and PCR-based tests enable prompt and precise pathogen detection, enabling preventive steps prior to disease outbreaks. New technologies are coming in the cereals management. With the unpredictable nature of weather conditions, it is often difficult to estimate the effects of disease in each season. New tools to predict likely disease risks, devise appropriate control measures, and better decision making with cereal disease management are available and such tools can help growers be proactive rather than reactive with regards to disease management. Nevertheless, remote sensing technologies, such as satellite and drone imagery, and IoT offer an affordable way to monitor and manage disease on a wide scale. Biological control agents and natural substances including resistance inducers can limit the severity of cereals pathogens, limiting the use of pharmaceuticals. The strategies for the integrated protection of cereals from pests and diseases must be done also considering the possibility that these crops can be affected by fungal diseases producing mycotoxins, that can contaminate grains and derivative products. According to recent studies, the most important mycotoxins occurring on cereals are deoxynivalenol (DON), zearalenone (ZEN), aflatoxins (AFs), ochratoxin A (OTA), T-2/HT-2 toxins and fumonisins (FUMs). These secondary metabolites are produced by various fungi species belonging essentially to the *Aspergillus*, *Penicillium* and *Fusarium* genera. The monitoring of these fungal pathogens in the field allows to better schedule their protection strategies avoiding the mycotoxins contamination on cereals and derivatives. Various household and industrial preparations like washing, blanching, peeling, and thermal treatments have been found effective for reducing pesticide residues. Novel technologies like cold plasma, pulsed electric field, irradiation, ultrasonication have been applied to degrade pesticide residues and mycotoxins depending on the type of pesticide and processing parameters, considering also that their dissipation can occur with milling and cooking procedures. Anyway, it is fundamental the appropriate management of the crop in field to prevent accumulation of pesticide residues and mycotoxins in postharvest and into the derivative products.

The reduction of contaminants in cereals requires a comprehensive approach that includes:

●**Sustainable Agricultural Practices:** Using environmentally friendly farming techniques to limit the accumulation of harmful substances.

●**Precision Farming Technologies:** Implementing AI-driven monitoring systems to optimize fertilizer and pesticide application.

● **Regulatory Compliance:** Ensuring adherence to food safety standards and environmental guidelines.

●**Post-Harvest Processing and Testing:** Applying advanced grain cleaning, detoxification, and

laboratory testing to detect and remove contaminants.

By integrating these measures, cereal production can become safer, more sustainable, and aligned with global food security goals.

4.1.1.Integrated Pest Management (IPM)

IPM is a comprehensive approach that combines various pest control methods to minimize pesticide use. It includes:

●**Biological control:** Using natural predators and microorganisms to suppress pest populations.

●**Agronomic practices:** Crop rotation, intercropping, and resistant crop varieties to reduce pest outbreaks.

●**Mechanical control:** Traps, barriers, and manual removal of pests.

●**Chemical control as a last resort:** Applying pesticides only when necessary and in minimal doses.

4.1.2. Selection of Environmentally Friendly Pesticides

Instead of traditional chemical pesticides, safer alternatives should be used:

●**Biopesticides:** Derived from natural sources such as bacteria, fungi, or plant extracts.

●**Low-toxicity chemicals:** Pesticides with rapid degradation in the environment and minimal impact on non-target species.

●**Precision application:** Targeted spraying techniques to avoid excessive pesticide use.

4.1.3. Optimization of Pesticide Application Methods and Timing

Ensuring proper pesticide use reduces residues in the final product:

- **Adhering to recommended doses:** Avoiding excessive application.
- **Following weather conditions:** Applying pesticides in optimal weather to prevent drift and runoff.
- **Pre-harvest intervals:** Ensuring a sufficient period for pesticide degradation before harvesting.

4.1.4. Monitoring Pesticide Residues in Soil and Water

To prevent pesticide accumulation and environmental contamination, the following measures should be implemented:

- **Buffer zones:** Areas of vegetation near water bodies to absorb pesticide runoff.
- **Soil management:** Regular testing and using bio-remediation techniques to remove pesticide residues.
- **Water filtration systems:** Preventing contamination of irrigation and drinking water sources.

4.1.5. Post-Harvest Treatment and Detoxification of Grain

Several techniques can reduce pesticide residues in harvested grain:

- **Cleaning and washing:** Removes surface residues.
- **Thermal processing:** Heat treatment to degrade pesticides.
- **Ozonation and UV treatment:** Chemical-free methods to break down pesticide molecules.

4.1.6. Monitoring and Laboratory Control

Regular testing ensures grain safety before it reaches consumers:

- **Chromatographic and spectrometric analysis:** Detecting pesticide residues in grain samples.
- **Random sampling:** Conducted at different stages (field, storage, distribution).
- **Compliance with regulatory limits:** Ensuring pesticide residues do not exceed safe levels.

4.1.7. Implementation of Organic Farming

Transitioning to organic farming reduces pesticide use by:

- Using compost and organic fertilizers: Enhancing soil fertility naturally.
- Employing natural pest control: Beneficial insects, companion planting, and biopesticides.
- Avoiding synthetic chemicals: Only approved organic substances are used.

Farmer Training and Awareness Programs

Education is key to reducing pesticide use:

- **Workshops and seminars:** Teaching best practices for pesticide application and alternative methods.
- **Demonstration farms:** Showing the effectiveness of sustainable techniques.
- **Accessible guidelines:** Providing farmers with clear pesticide reduction strategies.

4.1.8. Consumer Awareness and Food Safety Recommendations

Consumers can also take steps to minimize pesticide exposure:

●Proper washing and peeling: Reducing surface pesticide residues.
●Choosing certified organic products: Ensuring lower pesticide levels.
●Following cooking methods that reduce pesticides: Some pesticides degrade with heat.

4.1.9. Strengthening Government Control and Certification

Effective regulation ensures compliance with safety standards:

●Harmonization with international norms (e.g., EU, Codex Alimentarius).
●Regular inspections of farms and storage facilities.
●Stronger penalties for excessive pesticide use and contamination.
●Encouraging certification programs for pesticide-free or organic grains.

Implementing these measures will reduce pesticide residues in grain crops, protect human health, and promote environmentally friendly agriculture.

4.2. Measure to reduce heavy metals contamination in cereals and cereal products

Good agricultural practices during cereals production

Risk mitigation measures related to the presence of heavy metals include soil testing for heavy metals and possible remediation through phytoremediation, rotation of cereals with crops that absorb heavy metals, or the addition of soil amendments such as lime, biochar or organic matter to reduce the bioavailability of metals.

Control of inputs used during production is also recommended, in particular checking that irrigation water is free from contamination by metals such as cadmium and lead. Cadmium-rich phosphate fertilizers should also be avoided and organic fertilizers (such as manure) should be tested for metal contamination.

Measures to be taken during grain processing

Monitoring supply chains is crucial, with raw materials and processed products regularly analyzed for the presence of heavy metals.

4.2.1. Control of Contamination Sources

●Regular monitoring of soil, water, and air to identify sources of heavy metals.
●Detection and restriction of contaminated fertilizers, pesticides, and wastewater in agriculture.

4.2.2. Agrochemical Soil Analysis

●Periodic testing of soil for heavy metal content.
●Use of only certified fertilizers and composts with low levels of toxic elements.

4.2.3. Liming and Application of Organic Fertilizers

●Use of lime materials to reduce the bioavailability of heavy metals in soil.
●Application of organic matter (humus, biochar) to bind heavy metals and reduce their mobility.

4.2.4. Cultivation of Crops Resistant to Heavy Metal Accumulation

●Use of crop varieties and hybrids with a low ability to accumulate heavy metals in grains.

4.2.5. Phytoremediation – Biological Soil Purification

●Cultivation of phytoremediation plants (sunflower, mustard, alfalfa) to absorb and remove heavy metals from the soil.

4.2.6. Proper Selection of Fields for Cultivation

●Avoiding grain cultivation on contaminated or industrial lands.

●Monitoring areas near industrial zones and highways.

4.2.7. Control and Purification of Irrigation Water

●Testing irrigation water for heavy metal content.

●Use of filtration systems and other water purification technologies.

4.2.8. Optimization of Grain Storage and Processing Technologies

●Use of safe storage materials to avoid contact with metal surfaces that may release toxic elements.

●Removal of surface contamination through cleaning and washing before processing.

4.2.9. Laboratory Control of Grain Product Quality

●Regular monitoring of heavy metal content in grains, flour, cereals, and other products.

●Implementation of safety standards in accordance with national and international regulations.

4.2.10. Regulation and Government Oversigh

●Implementation of stricter environmental regulations and control over compliance.

●Introduction of certification for products regarding heavy metal content.

4.2.11. Development of Organic Farming

●Encouraging the transition to environmentally friendly farming methods.

●Avoiding synthetic fertilizers and pesticides that may contain heavy metals.

The implementation of these measures will help reduce heavy metal contamination in grain crops, enhance food safety, and minimize the negative impact on human health and the environment.

4.3. Measure to reduce nitrogen compounds in cereals and cereal products

Nitrogen compounds such as nitrates, nitrites, and biogenic amines can accumulate in cereals and cereal products due to agricultural practices, environmental contamination, or microbial activity during processing and storage. While some nitrogen compounds are beneficial indicators of protein content, others—especially in excessive amounts—may pose health risks. To ensure food safety and quality, it is essential to implement effective strategies aimed at reducing unwanted nitrogen compounds. These include optimizing fertilization practices, selecting low-uptake cereal varieties, improving post-harvest handling, controlling storage conditions (temperature, humidity, and ventilation), and applying targeted processing methods that inhibit microbial growth and enzymatic degradation. Together, these measures contribute to safer, healthier cereal-based products while supporting sustainable agricultural and production systems.

Good agricultural practices during cereals production

Mitigation measures include the use of precision farming techniques, where soil is regularly tested to monitor nitrogen levels and fertilization is adjusted accordingly, applying only the necessary amount of nitrogen fertilizer and opting for slow-release or organic fertilizers to minimize nitrogen run-off.
Good practice to maintain soil organic matter, the use of compost and green manure to improve nitrogen retention, and crop rotation with legumes to naturally fix nitrogen in the soil can also help.
Controlled irrigation with drip techniques can also help prevent nitrogen leaching into groundwater.
Finally, the use of nitrification inhibitors with fertilizers can slow the conversion of ammonium to nitrate, reducing nitrogen losses.

Measures to be taken during grain processing

It is important to ensure that grain is stored under low humidity conditions to reduce microbial degradation and the formation of toxic nitrogen compounds.
Detoxification techniques such as soaking, germination, heat treatments and fermentation (e.g., sourdough fermentation) can also be used to reduce some nitrogen compounds.

4.3.1. Optimization of Nitrogen Fertilization

- Application of fertilizers based on plant needs and soil analysis to prevent excessive nitrogen accumulation.
- Use of slow-release and stabilized nitrogen fertilizers to reduce nitrate leaching.

4.3.2. Crop Rotation and Legume Integration

- Incorporation of nitrogen-fixing legumes into crop rotations to naturally enrich the soil with nitrogen and reduce synthetic fertilizer use.
- Alternating cereal crops with deep-rooted plants to improve nitrogen uptake.

4.3.3. Precision Farming and Smart Fertilization Techniques

- Implementation of precision agriculture technologies (drones, sensors, AI) to optimize nitrogen fertilizer application.
- Use of variable-rate application (VRA) to distribute nitrogen efficiently based on real-time plant requirements.

4.3.4. Use of Nitrification Inhibitors

- Adding nitrification inhibitors to fertilizers to slow down nitrogen conversion and reduce nitrate leaching into groundwater.

4.3.5. Controlled Irrigation Management

- Avoiding excessive irrigation, which can wash nitrogen compounds out of the soil.
- Implementing drip irrigation and other water-efficient technologies to minimize nitrogen runoff.

4.3.6. Organic Fertilization and Composting

- Substituting synthetic fertilizers with compost, manure, and other organic fertilizers that release nitrogen more gradually.
- Promoting microbial activity in the soil to enhance nitrogen efficiency.

4.3.7. Soil Health Improvement and Cover Crops

●Growing cover crops (e.g., clover, mustard) to absorb excess nitrogen and prevent nitrate leaching.

●Increasing soil organic matter to improve nitrogen retention.

4.3.8. Proper Grain Storage and Processing Techniques

●Ensuring optimal drying and storage conditions to prevent nitrogen compound transformations that could increase nitrates in cereals.

●Washing and processing grains to remove surface contaminants.

4.3.9. Monitoring and Laboratory Testing

●Regular analysis of soil, water, and grain samples to monitor nitrate and nitrogen compound levels.

●Compliance with food safety regulations for acceptable nitrogen compound levels in cereal products.

4.3.10. Regulatory Policies and Environmental Protection Measures

●Strengthening government regulations on nitrogen fertilizer use.

●Encouraging certification programs for low-nitrate cereals and cereal products.

By implementing these measures, nitrogen compound contamination in cereals and cereal products can be significantly reduced, improving food safety and environmental sustainability.

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Chapter 5. The analytic methods to control the contaminants

5.1. Analytical methods to detect pesticides content in cereals and cereal products

Methods for the analysis of pesticides can be generally classified in 4 groups: chromatographic techniques, spectroscopic techniques, mass spectrometry techniques, immunoassay techniques and capillary electrophoresis. The conventional analytical methods are gas chromatography (GC) and high performance liquid chromatography (HPLC) coupled with various detectors (UV, FD, DAD). Different types of detectors are used depending on the class of analyzed pesticides (ECD-for halogenated compounds, FPD for sulfur and phosphorus containing pesticides, NPD for compounds with nitrogen and phosphorus). FID is suitable for detection of all pesticides. MS and tandem MS are superior in comparison to other detectors. Pesticide residue analyses require complex sample preparation that involves extraction and clean-up procedures to ensure good extraction of targeted substances and avoid co-extraction of undesired interfering compounds. The QuEChERS sample preparation technique is extensively used for the multiresidue analysis in various food matrices. This technique has gained popularity due to simplicity, speed, ability to extract broad spectrum of pesticides and reduced consumption of organic solvents. Cereals are complex matrices due to presence of fat and high proportion of solids and some modifications of the QuEChERS technique are recommended to improve extraction efficiency, selectivity and sensitivity. Besides QuEChERS, liquid-liquid and solid-phase extractions are extracting methods of importance in pesticide analysis. QuEChERS is compatible with GC and LC coupled with MS or MS/MS.

5.2. Analytical methods to detect heavy metals contamination in cereals and cereal products

The most frequently used analytical techniques in food-analyzing laboratories to determine heavy element contamination in food are: Flame Atomic Absorption Spectrometry—FAAS and Graphite Furnace Atomic Absorption Spectrometry— GF-AAS. Many other methods exist, such as Inductively Coupled Plasma Atomic Emission Spectrometry—ICP-AES, Inductively coupled plasma-Mass Spectrometry—ICP-MS, High-resolution Continuum Source Graphite Furnace Atomic Absorption Spectrometry—HR-CS-GFAAS; Anion Exchange Chromatography Coupled to Inductively Coupled Plasma-Mass Spectrometry—AEC-ICP-MS; Microwave Induced Plasma Optical Emission Spectrometry—MIP OES; Electrochemical methods (potentiometry, etc.), Atomic fluorescence spectroscopy - AFS and X-ray absorption spectroscopy (XAS).

Sample preparation includes drying, milling, sample breakdown by dry, wet and microwave digestion.

5.3. Analytical methods to detect nitrogen compounds in cereals and cereal products

The detection and quantification of nitrogen-containing compounds in cereals and cereal-based products are essential for assessing nutritional quality—especially protein content—as well as ensuring food safety by monitoring undesirable nitrogenous substances such as nitrates, nitrites, or biogenic amines. Several analytical methods are routinely employed in both research and industry laboratories to achieve these objectives, each with its own strengths and limitations.

The Kjeldahl Method

The Kjeldahl method is one of the oldest and most widely used techniques for determining the total nitrogen content in foodstuffs, including cereals. The principle of the method involves the digestion of the sample with concentrated sulfuric acid, which converts organic nitrogen into ammonium sulfate. After digestion, the solution is made alkaline and the liberated ammonia is distilled and quantified through titration. Since nitrogen is a key component of proteins, this value is then used to estimate protein content using a specific conversion factor.

The Kjeldahl method remains a reference method due to its accuracy and broad applicability. It is standardized by organizations such as AOAC and ISO and is commonly used in quality control laboratories across the food industry.

Dumas Combustion Method (Elemental Analysis)

An alternative to the Kjeldahl method is the Dumas method, which determines total nitrogen content through high-temperature combustion. In this process, the sample is burned in an oxygen-rich environment, converting nitrogen to molecular nitrogen (N_2), which is then measured using a thermal conductivity detector. The method is faster and does not require strong acids or bases, making it safer and more environmentally friendly. However, like the Kjeldahl method, it does not distinguish between protein and non-protein nitrogen.

UV-Visible Spectrophotometry

UV-Vis spectrophotometry is frequently used to detect inorganic nitrogen compounds such as nitrates and nitrites in cereal samples. One of the most commonly employed procedures is the Griess reaction, which is specific for nitrite. In this method, nitrite reacts with sulfanilic acid and a coupling agent to form a colored azo dye, whose intensity can be measured spectrophotometrically at around 540 nm.

For nitrates, which do not react directly in the Griess reaction, a reduction step is usually required to convert them to nitrites. Alternatively, direct UV absorption methods can be employed, particularly in the 220–275 nm range. This method is relatively simple and cost-effective, though care must be taken to minimize interference from other matrix components.

High-Performance Liquid Chromatography (HPLC)

HPLC is a powerful technique that allows for the separation and quantification of a wide range of nitrogen compounds in cereals, including free amino acids, biogenic amines, urea, and small peptides. Detection is typically carried out using UV, fluorescence, or mass spectrometry, depending on the specific analytes and derivatization reagents used.

For example, amino acids can be derivatized with o-phthalaldehyde (OPA) or dansyl chloride to enhance detection sensitivity. HPLC is particularly valuable for nutritional profiling and monitoring fermentation or spoilage processes in cereal products.

Ion Chromatography

Ion chromatography (IC) is highly effective for the determination of inorganic nitrogen species such as nitrate and nitrite. It is particularly useful when very low detection limits are required or when analyzing complex cereal matrices. IC systems can separate ions based on their charge and size, and detect them with high sensitivity and specificity, making the method suitable for regulatory compliance testing in food safety.

Gas Chromatography (GC) and GC-Mass Spectrometry (GC-MS)

Gas chromatography, often coupled with mass spectrometry (GC-MS), is used for the detection of volatile nitrogen-containing compounds such as biogenic amines. These compounds may form during the spoilage of cereals or fermentation processes and can serve as indicators of product quality.

Prior to analysis, the amines are usually derivatized to improve their volatility and detection. This technique offers excellent sensitivity and specificity, although it requires more advanced instrumentation and sample preparation compared to spectrophotometric methods.

Capillary Electrophoresis (CE)

Capillary electrophoresis is an emerging technique for the analysis of nitrogen compounds, offering high resolution and requiring minimal amounts of sample and reagents. It is suitable for the analysis of amino acids, nitrates, and nitrites. While not yet as commonly used as HPLC or ion chromatography, CE is gaining popularity in academic and high-precision analytical settings due to its efficiency and green chemistry profile.

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Chapter 6. The health risk regarding cereal and cereals product contamination

6.1. The health risk of cereal and cereals products contaminated with pesticides

Consumption of cereals and cereal products contaminated with pesticides can pose various health risks, depending on the type and amount of pesticides, the duration of exposure and the general health status of the individual.

Potential health risks

Acute toxicity: Some pesticides can cause acute poisoning, manifested by nausea, vomiting, diarrhea, headaches, dizziness, convulsions or even death if exposed to high doses.

Long-term effects: Long-term exposure to pesticides, even at low doses, can increase the risk of chronic conditions such as:

- **Cancer**: Certain pesticides are considered carcinogens or may contribute to the development of cancer, especially leukemia, non-Hodgkin's lymphoma and breast cancer.
- **Neurological diseases**: Pesticide exposure can affect the nervous system, increasing the risk of Parkinson's, Alzheimer's and other neurodegenerative diseases.
- **Hormonal disorders**: Some pesticides can disrupt the endocrine system, affecting fertility, development and thyroid function.
- **Respiratory problems**: Inhalation or exposure to certain pesticides can cause asthma, bronchitis and other respiratory problems.
- **Immune system damage**: Some studies suggest that pesticides may weaken the immune system, making the body more susceptible to infection.
- **Developmental problems in children**: Pregnant women exposed to pesticides may have babies with low birth weight, birth defects or developmental delays.

Factors influencing risk

Type of pesticide: Different pesticides have different degrees of toxicity and can cause different health effects.

Amount of pesticide: The greater the amount of pesticide ingested, the greater the health risk.

Duration of exposure: Repeated or prolonged exposure to pesticides may increase the risk of long-term effects.

Individual health status: People with weakened immune systems, pregnant women, young children and people with certain pre-existing medical conditions may be more vulnerable to the harmful effects of pesticides.

6.2. The health risk of cereal and cereals products contaminated with heavy metals

Toxic heavy metals such as cadmium, mercury, lead, and arsenic may not only compete with essential minerals (e.g., calcium, magnesium, and iron) for cellular uptake, but also exhibit an affinity for vital cellular constituents, including structural proteins, enzymes, and nucleic acids, potentially disrupting their respective functions. The consumption of cereals and cereal products contaminated with heavy metals poses a wide range of health risks, the manifestation of which depends on a number of factors, including the type and concentration of the heavy metal, the duration of exposure and the physiological state of the individual. Heavy metals are harmful even at small concentrations due to their long biological half-lives, persistent nature and potential to accumulate in body organs.

Health Risks of Heavy Metal Contamination in Cereals and Cereal Products

Cereals and cereal products can accumulate heavy metals such as **lead (Pb), arsenic (As), and cadmium (Cd)** from contaminated soil, water, and air. Chronic exposure to these metals through food consumption poses significant health risks.

Acute toxicity: Exposure to certain heavy metals, such as mercury and arsenic, can trigger acute poisoning, characterized by symptoms such as nausea, vomiting, diarrhoea, headache, dizziness, convulsions and, in extreme cases, death.

Long-term effects: Even long-term exposure to low doses of heavy metals can increase the incidence of severe chronic diseases:

- **Cancer**: Certain heavy metals, such as arsenic, cadmium and lead, are classified as carcinogenic or may contribute to the development of neoplasms, especially skin, lung, bladder and kidney cancers.
- **Neurological diseases**: Exposure to heavy metals can affect the nervous system, and has been implicated in the etiology of neurodegenerative disorders such as Parkinson's disease and Alzheimer's disease.
- **Kidney disorders**: Cadmium and lead can damage kidney function, increasing the risk of kidney failure.
- **Bone problems**: Lead can interfere with calcium metabolism, promoting osteoporosis and fractures.
- **Cardiovascular system impairment**: Some heavy metals can negatively influence blood pressure and heart rate, increasing the risk of cardiovascular disease.
- **Developmental problems in children**: Exposure to heavy metals during pregnancy can have negative consequences on fetal development, including low birth weight, congenital malformations and neurodevelopmental delays.

More specific (depending on the element) health risks of heavy metal contamination in cereals and cereal products are provided below.

➢ **Lead (Pb)**

- **Neurological Damage** – Particularly harmful to children, causing cognitive impairment, reduced IQ, and developmental delays.
- **Cardiovascular Effects** – Increased risk of hypertension and heart disease.
- **Kidney Damage** – Long-term accumulation may lead to kidney dysfunction.

➢ **Arsenic (As)**

- **Carcinogenicity** – Long-term exposure to inorganic arsenic is linked to cancers (skin, lung, bladder).
- **Skin Disorders** – Hyperpigmentation, lesions, and keratosis.
- **Neurological and Cardiovascular Effects** – Increased risk of cognitive decline, diabetes, and cardiovascular diseases.

➢ **Cadmium (Cd)**

- **Kidney Toxicity** – Major target organ; chronic exposure leads to kidney failure.
- **Bone Weakness** – Causes calcium depletion, leading to osteoporosis and fractures.
- **Carcinogenicity** – Classified as a human carcinogen, linked to lung and prostate cancer.

Vulnerable Populations

- **Infants and Children** – More susceptible to neurological damage and developmental disorders.
- **Pregnant Women** – Risk of heavy metals crossing the placenta, affecting fetal development.
- **Elderly Individuals** – Higher risk of kidney damage and bone-related diseases.

Regulatory Limits and Prevention

Strict regulatory limits are set by organizations like **EFSA, WHO, and FDA** to control heavy metal levels in food. Preventive measures include soil and water monitoring, controlled fertilizer use, and processing techniques to reduce contamination in cereals.

Toxic manifestations

Acute toxicity: Exposure to certain heavy metals, such as mercury and arsenic, can trigger acute poisoning, characterized by symptoms such as nausea, vomiting, diarrhoea, headache, dizziness, convulsions and, in extreme cases, death.

Long-term effects: Even long-term exposure to low doses of heavy metals can increase the incidence of severe chronic diseases:

- **Cancer**: Certain heavy metals, including arsenic, cadmium, and lead, are recognized as carcinogenic or are implicated in the development of neoplasms, particularly carcinomas of the skin, lung, bladder, and kidney.
- **Cardiovascular dysfunction**: Certain heavy metals have been associated with deleterious effects on the cardiovascular system, including alterations in blood pressure and heart rate, thereby potentially increasing the risk of cardiovascular disease.
- **Neurological diseases**: Exposure to heavy metals can affect the nervous system, and has been implicated in the etiology of neurodegenerative disorders such as Parkinson's disease and Alzheimer's disease.
- **Kidney disorders**: Cadmium and lead can damage kidney function, increasing the risk of kidney failure.
- **Bone problems**: Lead can interfere with calcium metabolism, promoting osteoporosis and fractures.
- **Developmental problems in children**: Exposure to heavy metals during pregnancy can result in adverse developmental outcomes, including low birth weight, congenital malformations, and neurodevelopmental delays.
- Liver toxicity: By dysregulating the antioxidant system in the human organism, heavy metals cause oxidative stress in liver that may lead to inflammation, induce carcinogenic changes and liver failure.
- Metabolic effects and systemic organ toxicity: By binding to proteins in biological systems and by undergoing redox reactions, heavy metals disrupt cell control mechanisms and cause dysfunction of cellular antioxidant mechanisms, lead to generation of reactive oxidation species that additionally cause DNA damage and degrade and inactivate biomolecules.

Risk factors

Type of heavy metal: Each heavy metal has a specific toxic profile, causing distinct health effects.

Heavy metal concentration: The higher the amount of heavy metal ingested, the higher the health risk.

Duration of exposure: Repeated or prolonged exposure to heavy metals increases the risk of long-term effects.
Health status of the individual: People with a weak immune system, pregnant women, young children and people with certain pre-existing medical conditions are more vulnerable to the harmful effects of heavy metals.

6.3. The health risk of cereal and cereals products contaminated with nitrogen compounds

The presence of nitrogenous contaminants in cereals presents a significant threat to public health. These compounds, including nitrates, nitrites, and amines, can derive from various anthropogenic sources such as fertilizers, pesticides, and wastewater discharge.

Mechanisms of Contamination

Contamination of cereals with nitrogen compounds can occur throughout the production and processing continuum:

- **Pre-Harvest:** The over-application of nitrogen-based fertilizers can result in elevated nitrate concentrations within the soil matrix, subsequently leading to increased uptake and accumulation in plant tissues.
- **Post-Harvest:** Suboptimal storage conditions can foster the growth of microorganisms capable of converting nitrates to nitrites and amines.
- **Processing:** Certain processing techniques, including roasting and fermentation, may induce the formation of amine compounds.

Adverse Health Outcomes

Consumption of cereals contaminated with nitrogenous compounds can lead to a spectrum of adverse health outcomes, the severity of which is dependent on both the concentration of the contaminant and the duration of exposure. Key health risks include:

- **Methemoglobinemia:** Nitrites can oxidize hemoglobin to methemoglobin, a non-oxygen-carrying form of the protein. This can impair oxygen delivery to tissues, resulting in cyanosis, fatigue, and dyspnea.
- **Carcinogenicity:** Specific amines can react with nitrites in the acidic environment of the stomach to produce nitrosamines, compounds recognized for their carcinogenic potential.
- **Systemic Toxicity:** Exposure to nitrogenous compounds has been implicated in the development of various other health complications, including neurological, cardiovascular, and reproductive dysfunction.

Mitigation Strategies

Effective mitigation of nitrogen compound contamination in cereals necessitates the implementation of preventive and control measures across all stages of production and processing:

- **Optimized Fertilizer Application:** The judicious use of nitrogenous fertilizers, tailored to specific crop requirements, is essential to minimize soil nitrate accumulation and subsequent plant uptake.
- **Controlled Storage Practices:** Maintaining appropriate storage conditions that inhibit microbial proliferation and the formation of nitrogenous byproducts is crucial.

- **Comprehensive Quality Assurance:** Regular monitoring of nitrogen compound levels in cereals and cereal-derived products through analytical testing is necessary to ensure consumer safety.

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