People's Democratic Republic of Algeria

Ministry of Higher Education and Scientific Research

University of Echahid Hamma Lakhdar - El Oued -

Faculty of Nature and Life Sciences

Department of Biology

Field: Nature and Life Sciences

Division: Biological Sciences

Course Title :

Plant Ecotoxicology

Prepared by:

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Intended for Students:

1st year of Master's Level

Specialty: Biodiversity and Plant Physiology

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Summary

Introduction

Plant Ecotoxicology is a crucial field of study within the Master's program in Biodiversity and Plant Physiology. This multidisciplinary field combines elements of ecology, toxicology, and plant biology to understand the impacts of contaminants on plants, their growth, development, and overall health. By investigating the responses of plants to various stressors, plant ecotoxicology provides valuable insights into the assessment of environmental risks and the development of sustainable solutions for a healthier ecosystem.

The subject matter delves into the complex interactions between plants and various environmental pollutants, including heavy metals, organic contaminants, and toxic gases. Students will explore the mechanisms by which plants absorb, accumulate, and respond to these toxins, as well as the effects on essential plant processes such as photosynthesis, growth, and central metabolism.

This course not only focuses on the direct impacts on plant life but also extends to broader environmental concerns. Topics such as forest decline, ozone depletion, and global warming are examined concerning their potential consequences for plant ecosystems. Additionally, the course touches on aspects of human toxicity, using cadmium as a case study to illustrate the interconnectedness of plant and human health.

By the end of this course, students will have gained valuable insights into the stress responses and protective mechanisms of plants against various pollutants. This knowledge is essential for understanding and addressing current environmental challenges, making it a vital component of the biodiversity and plant physiology curriculum.

The course combines theoretical knowledge with practical applications through lectures, lab work, and student presentations, providing a well-rounded approach to this critical area of environmental science.

Course 1.

Introduction to Plant Ecotoxicology

1.1 Definition and scope of ecotoxicology

Ecotoxicology is a multidisciplinary field that studies the effects of toxic chemicals on biological organisms, particularly at the population, community, and ecosystem levels. Plant ecotoxicology, a crucial subset of this field, focuses specifically on the impacts of pollutants on plants and plant-based ecosystems.

The scope of plant ecotoxicology is vast, encompassing effects from the molecular level to ecosystem-wide impacts. Key areas of study include:

a) Toxicant uptake: How plants absorb contaminants from their environment.

b) Distribution: The movement and allocation of toxicants within plant tissues.

c) Biotransformation: How plants metabolize and potentially detoxify harmful substances.

d) Effects on plant physiology: Changes in cellular processes and overall plant function.

e) Impacts on growth and reproduction: How pollutants affect plant development and propagation.

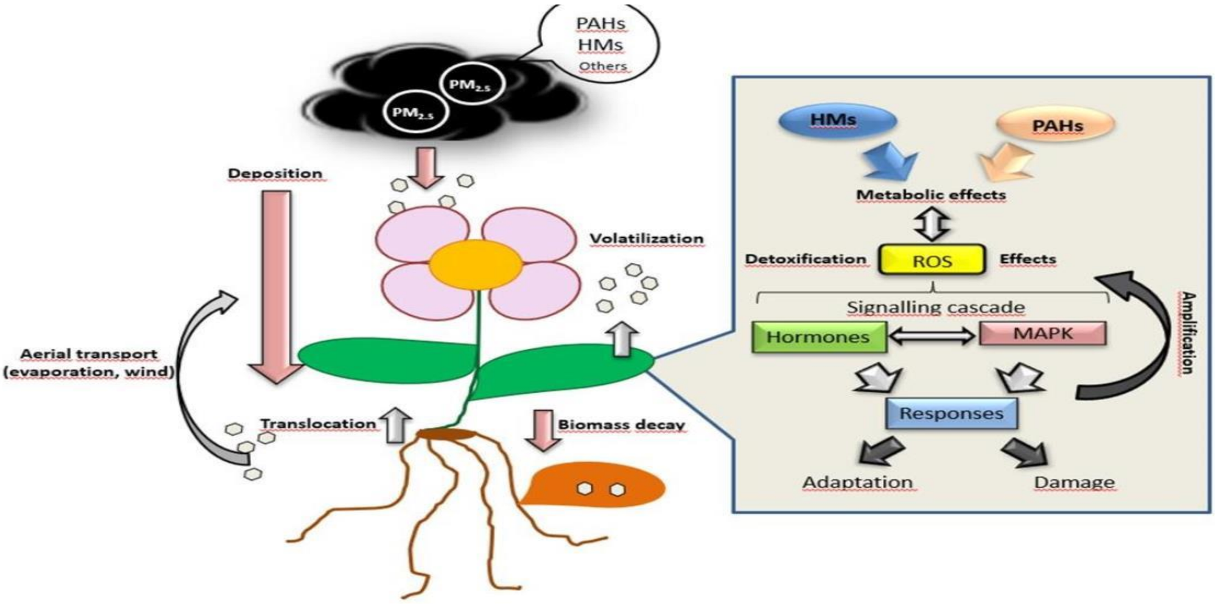

Figure 1. Biochemical and metabolic plant responses toward polycyclic aromatic hydrocarbons and heavy metals present in atmospheric pollution (Molina and Segura, 2021).

Plant ecotoxicology integrates knowledge from various disciplines, including:

- Ecology: Understanding the interactions between plants and their environment.

- Toxicology: Studying the adverse effects of chemicals on living organisms.

- Chemistry: Analyzing the structure, properties, and reactions of pollutants.

- Plant biology: Examining the physiological and molecular responses of plants to stress.

1.2 Importance of plant ecotoxicology in environmental science

The significance of plant ecotoxicology in environmental science cannot be overstated. Plants, as primary producers, form the foundation of terrestrial and many aquatic food webs. Their health and productivity have far-reaching consequences for entire ecosystems and, by extension, human well-being.

Key aspects highlighting the importance of plant ecotoxicology include:

a) Bioaccumulation: Plants can concentrate pollutants from their environment, potentially leading to higher levels of contaminants in herbivores and throughout the food chain. This process is particularly concerning for persistent organic pollutants (POPs) and heavy metals.

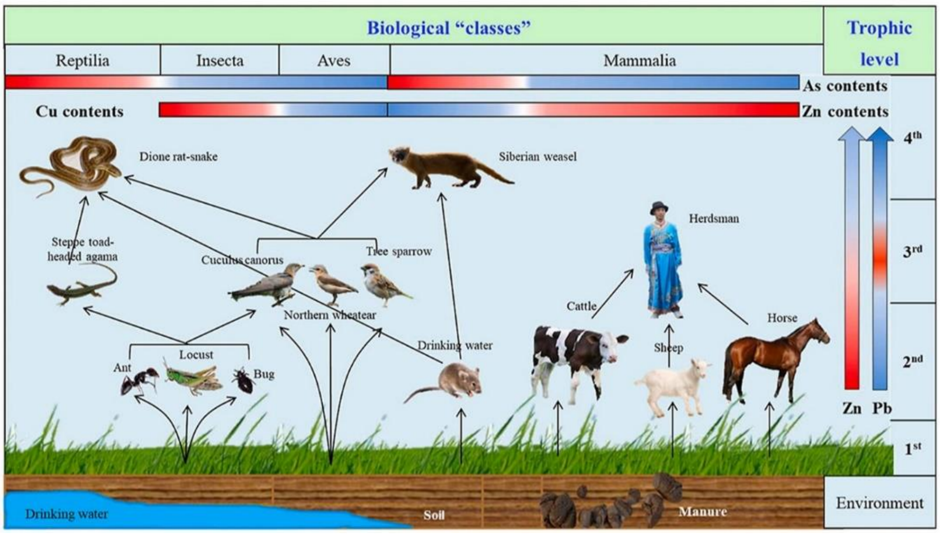

Figure 2. Distribution, bioaccumulation, and trophic transfer of heavy metals in the food web of grassland ecosystems, starting with plants (Zhang et al., 2021).

b) Ecosystem services: Plants provide crucial ecosystem services that can be disrupted by pollutants. These include:

- Oxygen production through photosynthesis

- Carbon sequestration, mitigating climate change

- Soil stabilization, preventing erosion

- Water cycle regulation

- Habitat provision for other organisms

c) Bioindicators: Plants can serve as early warning systems for environmental contamination. Certain species are particularly sensitive to specific pollutants, making them valuable bioindicators. For example, lichens are often used to monitor air quality due to their sensitivity to sulfur dioxide and other air pollutants.

d) Agricultural implications: Plant ecotoxicology has significant relevance to agriculture. Pollutants can affect crop yield, quality, and safety for human consumption.

e) Phytoremediation: Some plants can remove or neutralize contaminants in soil, water, or air. This natural process, known as phytoremediation, offers a potentially cost-effective and environmentally friendly method for cleaning up polluted sites.

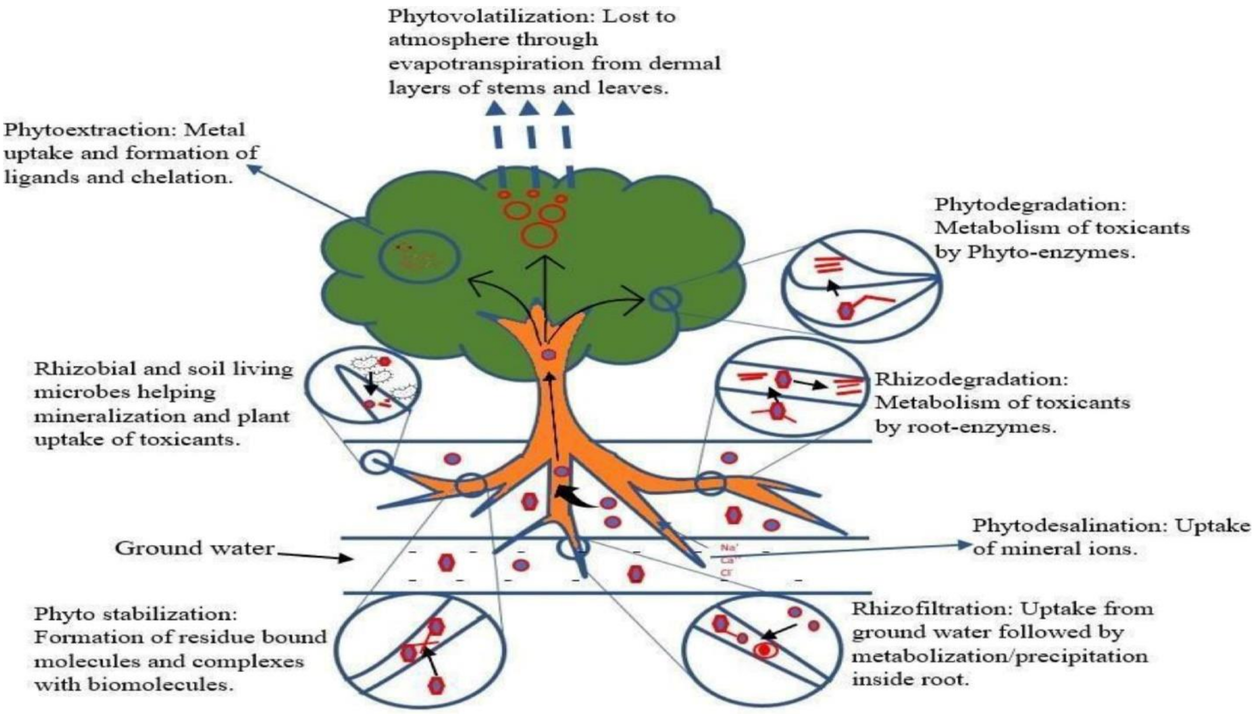

Figure 3. Diagram showing various phytoremediation mechanisms, including phytoextraction, phytodegradation, and phytostabilization (Kafle et al., 2022).

f) Biodiversity conservation: Pollutants can threaten plant species and communities, potentially leading to biodiversity loss. Plant ecotoxicology helps identify these threats and inform conservation strategies.

1.3 Historical perspective of plant ecotoxicology

The field of plant ecotoxicology has evolved significantly over time, shaped by growing environmental awareness and scientific advancements. Key milestones include:

19th century: Early observations of air pollution effects on plants were recorded, particularly in industrial areas. For instance, the impact of sulfur dioxide emissions on vegetation near smelters was noted.

1960s: Rachel Carson's seminal book "Silent Spring" (1962) highlighted the devastating effects of pesticides, particularly DDT, on ecosystems. While focused on animals, it sparked broader interest in chemical impacts on all living organisms, including plants.

1970s: Ecotoxicology emerged as a distinct field, with Rene Truhaut coining the term in 1969. This decade saw increased research on heavy metal pollution and its effects on plants.

1980s: Growing focus on acid rain and its impacts on forests. The phenomenon of "Waldsterben" (forest death) in Europe led to extensive research on the effects of atmospheric pollutants on trees.

Figure 4. Photograph showing forest decline due to acid rain in the Black Forest, Germany, from the 1960s to 1980s (URL: https://www.woodlands.co.uk/blog/flora-and-fauna/german-forest-dieback-waldsterben-2/)

1.4 Key concepts and terminology

Understanding plant ecotoxicology requires familiarity with several fundamental concepts and terms:

a) Toxicant: Any substance that can produce an adverse response in a living organism. In plant ecotoxicology, this includes both natural and synthetic chemicals that negatively affect plant health or function.

b) Xenobiotics: Chemical substances that are foreign to an organism or ecosystem. Many pollutants affecting plants are xenobiotics, such as synthetic pesticides or industrial chemicals.

c) Bioavailability: The proportion of a pollutant that is available for biological uptake. Factors affecting bioavailability include the chemical form of the pollutant, soil properties, and plant characteristics.

d) Bioaccumulation: The increase in concentration of a pollutant in an organism over time. Plants can bioaccumulate certain pollutants, particularly lipophilic organic compounds and some metals.

e) Biomagnification: The increasing concentration of a pollutant up the food chain. While this concept is more commonly applied to animals, plants play a crucial role as the initial step in many biomagnification processes.

f) Dose-response relationship: The change in effect on an organism caused by differing levels of exposure to a stressor.

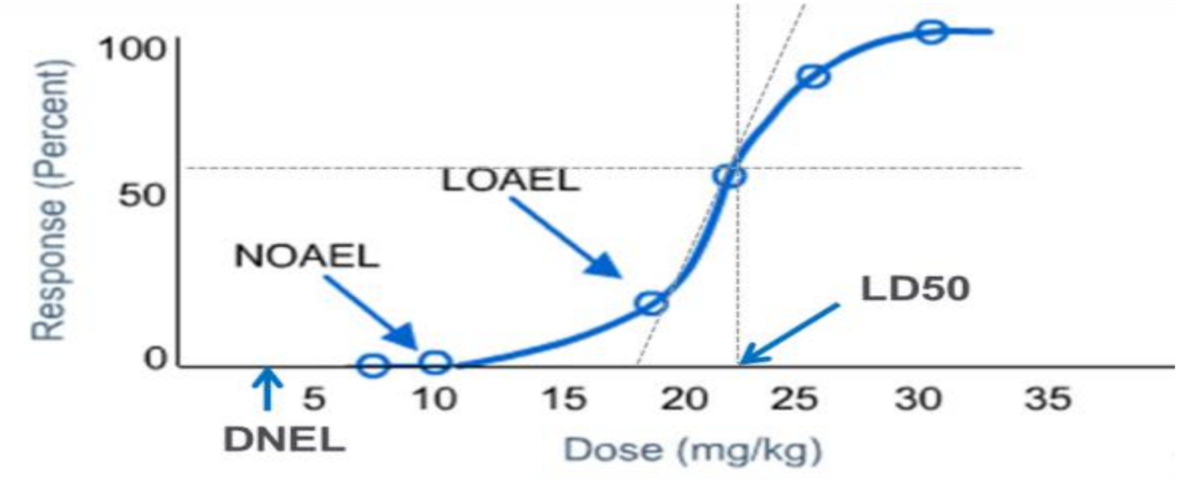

Figure 5. Graph showing a typical dose-response curve, highlighting key points such as NOAEL, LOAEL, and EC50. derived no-effect level (DNEL).
(URL: https://www.chemsafetypro.com/Topics/CRA/Toxicology_Dose_Descriptors.html).

g) LC50 and EC50: Lethal Concentration and Effective Concentration affecting 50% of a population. These metrics are used to quantify toxicity, with EC50 being more relevant for sublethal effects often observed in plants.

h) NOAEL and LOAEL: No Observed Adverse Effect Level and Lowest Observed Adverse Effect Level. These values are crucial for establishing safe exposure limits for plants.

i) Phytotoxicity: The degree of toxic effect by a compound on plant growth. This can manifest in various ways, such as reduced biomass, chlorosis, or altered root development.

j) Oxidative stress: An imbalance between the production of free radicals and the ability of the plant to detoxify them. Many pollutants induce oxidative stress in plants, leading to cellular damage.

k) Xenobiotic metabolism: The set of metabolic pathways that modify the chemical structure of xenobiotics. In plants, this often involves processes such as oxidation, reduction, and conjugation.

l) Biomarkers: Measurable indicators of some biological state or condition in plants. These can include biochemical, physiological, or morphological changes that indicate exposure to or effects of pollutants.

m) Hormesis: A phenomenon where a beneficial effect results from exposure to low doses of an agent that is otherwise toxic or lethal when given at higher doses. This concept is increasingly recognized as important in plant responses to certain pollutants.

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Course 2.

Fundamentals of Plant Biology and Chemistry

2.1 Basic plant anatomy and physiology

- Root system: Structure and functions (anchorage, water and nutrient uptake)

- Root cap, meristem, elongation zone, maturation zone

- Root hairs and their role in absorption

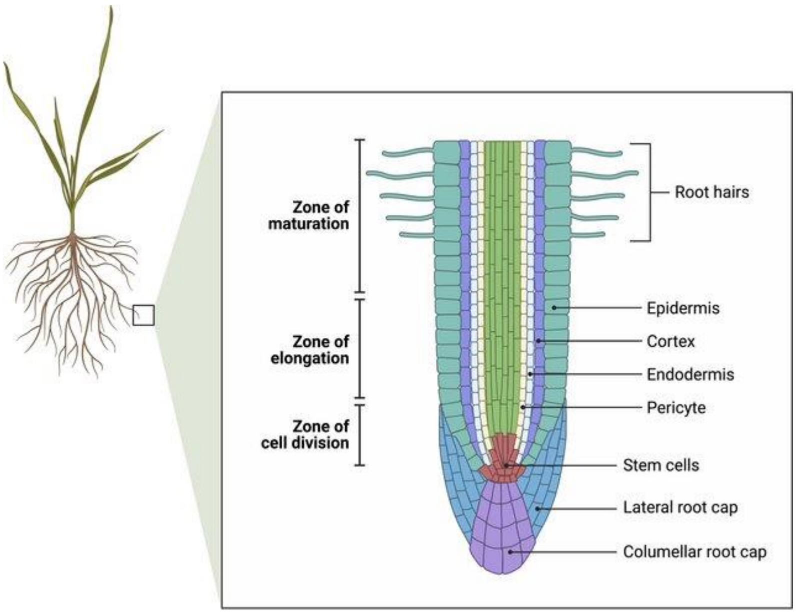

Figure 2.1. Longitudinal section of a typical root tip showing different zones (Shelden and Munns, 2023).

- Shoot system: Stem and leaves

- Vascular tissues: Xylem and phloem

- Leaf structure: Epidermis, mesophyll, stomata

- Cell types and tissues:
  - ✓ Parenchyma: Thin-walled cells involved in photosynthesis, storage, and secretion.
  - ✓ Collenchyma: Cells with unevenly thickened walls, provide structural support.
  - ✓ Sclerenchyma: Cells with thick, lignified walls for mechanical strength.

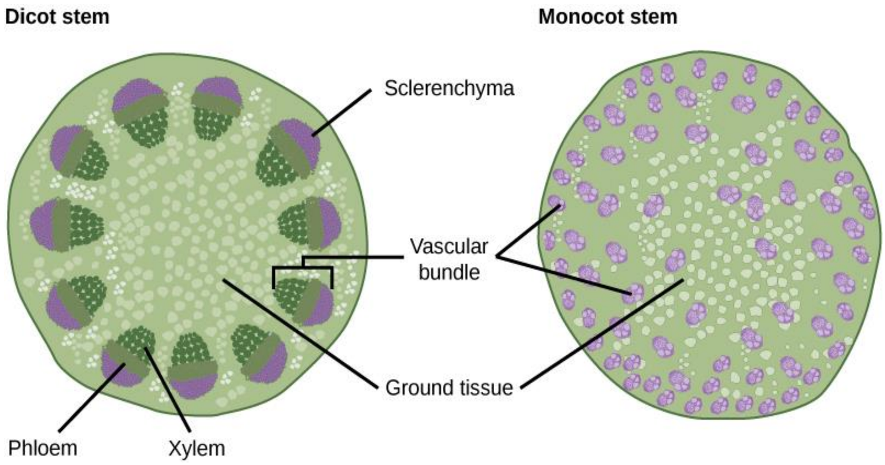

Figure 2.2. In (a) dicot stems, vascular bundles are arranged around the periphery of the ground tissue. The xylem tissue is located toward the interior of the vascular bundle, and phloem is located toward the exterior. Sclerenchyma fibers cap the vascular bundles. In (b) monocot stems, vascular bundles composed of xylem and phloem tissues are scattered throughout the ground tissue (URL: https://courses.lumenlearning.com/wm-biology2/chapter/plant-tissues-and-organs/)

- Plant cell structure: Cell wall, plasma membrane, organelles
- Differences between plant and animal cells

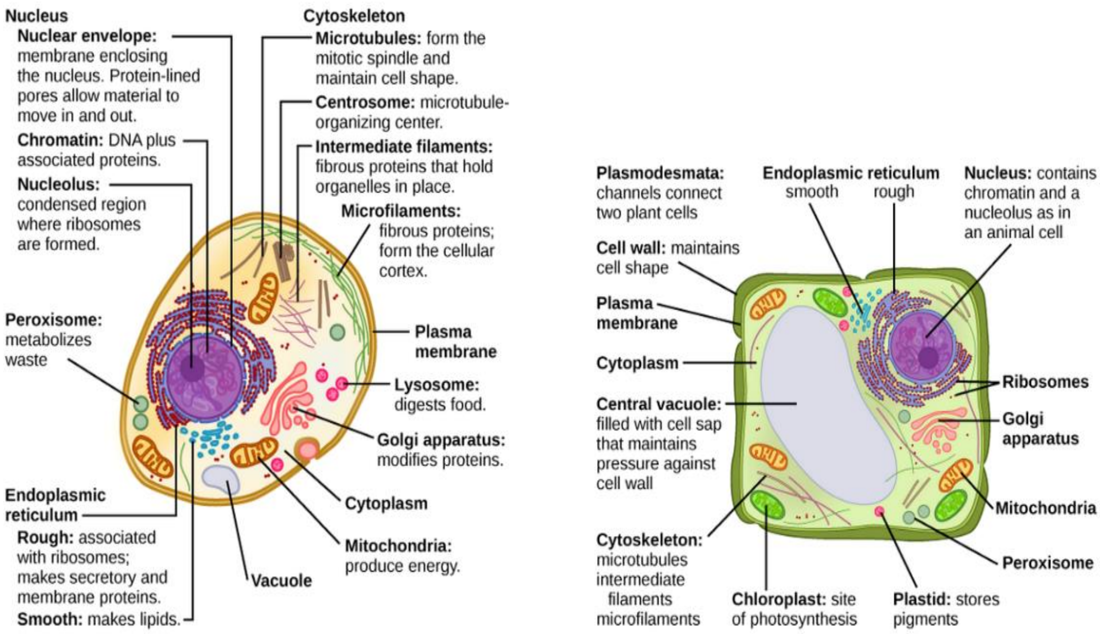

Figure 2.3. Diagram comparing plant and animal cell structures.
(URL: https://courses.lumenlearning.com/hccs-waymakerbiology1/chapter/animal-cells-versus-plant-cells/).

2.2 Plant growth and development processes

- Seed germination and early growth

- Primary and secondary growth

- Meristems: Apical, lateral, and intercalary

- Cell division, elongation, and differentiation

- Photomorphogenesis and light-mediated development

- Flowering and reproductive development

- Senescence and programmed cell death

2.3 Hormonal regulation in plants

- Auxins: Role in cell elongation, tropisms, apical dominance

- Cytokinins: Cell division, delay of senescence

- Gibberellins: Stem elongation, seed germination

- Abscisic acid: Stress responses, stomatal closure, seed dormancy

- Ethylene: Fruit ripening, abscission, stress responses

- Brassinosteroids: Cell elongation, vascular differentiation

- Jasmonates: Defense responses, seed germination

- Strigolactones: Branching inhibition, symbiotic associations

- Hormone interactions and crosstalk

2.4 Mineral nutrition and uptake mechanisms

- Essential macronutrients and micronutrients

- Roles of specific nutrients in plant metabolism

- Soil-root interface and rhizosphere

- Ion uptake mechanisms:

  - ✓ Passive uptake: Diffusion and mass flow
  - ✓ Active uptake: Carrier proteins and ion channels

- Nutrient transport within the plant

- Mycorrhizal associations and their role in nutrient uptake

- Nutrient deficiencies and toxicities

2.5 Photosynthesis and cellular respiration

- Photosynthesis:

✓ Light-dependent reactions: Photosystems I and II, electron transport chain
✓ Calvin cycle (light-independent reactions)
✓ C3, C4, and CAM photosynthetic pathways
✓ Factors affecting photosynthetic rate

- Cellular respiration:

✓ Glycolysis
✓ Citric acid cycle (Krebs cycle)
✓ Electron transport chain and oxidative phosphorylation
✓ Alternative respiratory pathways in plants

2.6 Basic chemistry concepts relevant to ecotoxicology

- Atomic structure and chemical bonding

- Organic compounds: Structure and functional groups

- pH and buffer systems

- Redox reactions and their importance in plant metabolism

- Chemical equilibrium and Le Chatelier's principle

- Basic thermodynamics: Enthalpy, entropy, and Gibbs free energy

- Principles of analytical chemistry relevant to toxicant detection

- Basics of biochemistry: Proteins, carbohydrates, lipids, nucleic acids

- Enzyme kinetics and inhibition

- Principles of spectroscopy and chromatography

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Course 3.

Toxic Substances and Their Sources

3.1 Classification of toxic substances

- Chemical classification:

- ✓ Inorganic toxicants: Heavy metals, metalloids, non-metal ions
- ✓ Organic toxicants: Pesticides, industrial chemicals, petroleum products
- ✓ Organometallic compounds

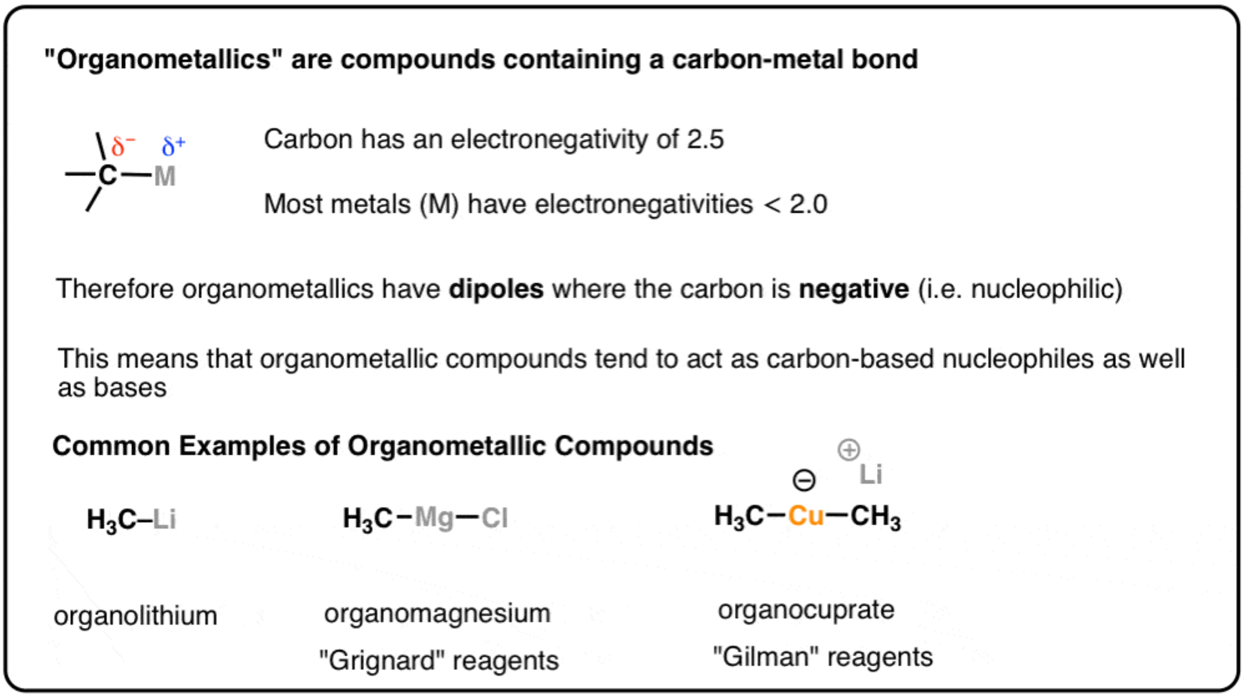

Figure 3.1. Examples of organometallic compounds include organolithium compounds, organomagnesium compounds (Grignard reagents) and organocuprates (Gilman reagents) (URL: https://www.masterorganicchemistry.com/2015/10/28/whats-an-organometallic/).

- Functional classification:

- ✓ Pesticides: Insecticides, herbicides, fungicides, rodenticides
- ✓ Industrial chemicals: Solvents, plasticizers, flame retardants
- ✓ Pharmaceuticals and personal care products
- ✓ Nanomaterials

- Classification by mode of action:

- ✓ Enzyme inhibitors
- ✓ Membrane disruptors
- ✓ Photosynthesis inhibitors
- ✓ Hormone mimics or disruptors

- Classification by persistence:

- ✓ Persistent organic pollutants (POPs)
- ✓ Non-persistent pollutants

- Classification by origin:

- ✓ Natural toxins
- ✓ Synthetic toxicants

3.2 Natural vs. anthropogenic sources of toxicants

- Natural sources:

- ✓ Volcanic emissions: Sulfur dioxide, heavy metals
- ✓ Mineral weathering: Arsenic, fluoride, radionuclides
- ✓ Forest fires: Polycyclic aromatic hydrocarbons (PAHs)
- ✓ Biological sources: Phytotoxins, microbial toxins
- ✓ Natural oil seeps

- Anthropogenic sources:

- ✓ Industrial processes: Chemical manufacturing, metal smelting
- ✓ Agriculture: Pesticides, fertilizers, animal waste
- ✓ Energy production: Fossil fuel combustion, nuclear power
- ✓ Transportation: Vehicle emissions, oil spills
- ✓ Waste management: Landfills, incineration
- ✓ Urban runoff: Road salts, automotive fluids
- ✓ Mining activities: Acid mine drainage, heavy metal contamination

3.3 Point and non-point pollution sources

- Point sources:

- Definition: Single, identifiable sources of pollution

- Examples:

- ✓ Industrial discharge pipes
- ✓ Wastewater treatment plant outfalls
- ✓ Oil spills from tankers
- ✓ Mine tailings

- Characteristics:

- ✓ Easier to monitor and regulate
- ✓ Often subject to specific permits and regulations

- Non-point sources:

- Definition: Diffuse sources of pollution, not from a single location

- Examples:

- ✓ Agricultural runoff
- ✓ Urban stormwater runoff
- ✓ Atmospheric deposition
- ✓ Erosion and sedimentation

- Characteristics:

- ✓ More challenging to monitor and control
- ✓ Require broader management strategies

3.4 Bioavailability and bioaccumulation of toxicants

- Bioavailability:

- Definition: The proportion of a toxicant that can be absorbed by an organism

- Factors affecting bioavailability:

- o Chemical form of the toxicant
- o Soil or water properties (pH, organic matter content, redox conditions)
- o Environmental conditions (temperature, light)
- o Biological factors (root exudates, microbial activity)

- Methods for assessing bioavailability:

- o Chemical extractions
- o Isotope dilution techniques
- o Diffusive gradients in thin films (DGT)
- o Bioindicators and bioassays

- Bioaccumulation:

- Definition: The net accumulation of a substance by an organism from all sources
- Processes involved:
    - Uptake: From water, soil, air, or diet
    - Distribution: Within the organism's tissues
    - Metabolism: Biotransformation of the toxicant
    - Excretion: Removal of the toxicant or its metabolites
- Bioaccumulation factors (BAF) and bioconcentration factors (BCF)
- Biomagnification: Increase in concentration up the food chain

- Factors influencing bioaccumulation:
    - Physicochemical properties of the toxicant (e.g., lipophilicity)
    - Environmental persistence
    - Species-specific factors (metabolism, excretion rates)
    - Trophic level and food web dynamics

- Implications of bioaccumulation:
    - Ecological impacts on higher trophic levels
    - Human health concerns through food chain contamination
    - Challenges in risk assessment and environmental monitoring

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Course 4.

Heavy Metal Contamination

4.1 Common heavy metals in the environment

Definition of heavy metals:

Heavy metals are generally defined as metallic elements with a density greater than 5 g/cm³. However, in environmental sciences, the term often includes metalloids like arsenic that can cause toxicity at low concentrations.

Environmentally significant heavy metals:

a) Lead (Pb):

- Atomic number: 82

- Common valence states: Pb^{2+}, Pb^{4+}

- Major sources: Historical use in gasoline, paint; battery manufacturing

b) Cadmium (Cd):

- Atomic number: 48

- Common valence state: Cd^{2+}

- Major sources: Phosphate fertilizers, industrial emissions

c) Mercury (Hg):

- Atomic number: 80

- Common valence states: Hg^0, Hg^{2+}, CH_3Hg^+ (methylmercury)

- Major sources: Coal combustion, artisanal gold mining

d) Arsenic (As) - technically a metalloid:

- Atomic number: 33

- Common valence states: As^{3+}, As^{5+}

- Major sources: Natural geological formations, wood preservatives

e) Chromium (Cr):

- Atomic number: 24

- Common valence states: Cr^{3+}, Cr^{6+}

- Major sources: Leather tanning, stainless steel production

f) Copper (Cu):

- Atomic number: 29

- Common valence states: Cu^{+}, Cu^{2+}

- Major sources: Mining, pesticides, plumbing materials

g) Zinc (Zn):

- Atomic number: 30

- Common valence state: Zn^{2+}

- Major sources: Galvanized products, tire wear, industrial emissions

h) Nickel (Ni):

- Atomic number: 28

- Common valence state: Ni^{2+}

- Major sources: Stainless steel production, battery manufacturing

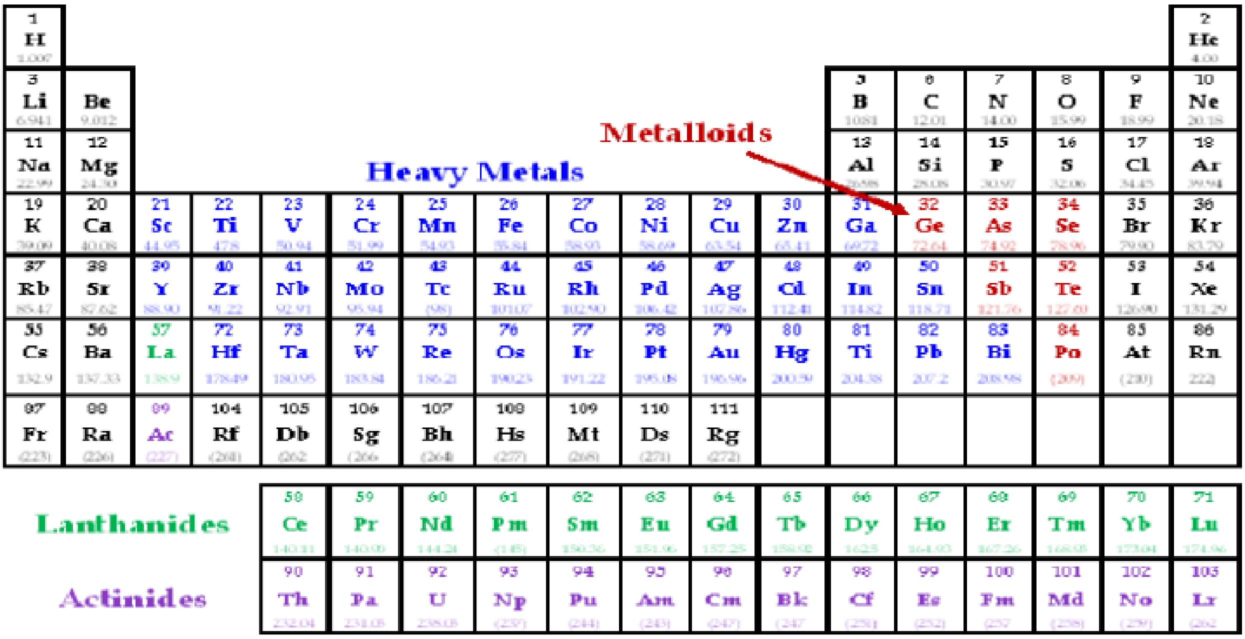

Figure 4.1. Periodic table highlighting common heavy metals of environmental concern (Hoodaji et al., 2012).

Essential vs. non-essential heavy metals for plants:

- Essential: Cu, Zn, Ni (in trace amounts)

- Non-essential: Pb, Cd, Hg, As, Cr (Cr^{3+} may be beneficial in trace amounts)

4.2 Sources of heavy metal pollution

Natural sources:

a) Weathering of metal-bearing rocks:

- Release of metals through physical and chemical weathering processes
- Influenced by rock type, climate, and topography

b) Volcanic eruptions:

- Release of metals in ash and gases
- Can cause local and global distribution of metals

c) Forest fires:

- Mobilization of metals stored in vegetation and soil organic matter
- Ash deposition can lead to increased metal concentrations in soil and water

Anthropogenic sources:

a) Mining and smelting operations:

- Extraction and processing of metal ores
- Tailings and waste rock disposal
- Acid mine drainage

b) Industrial processes:

- Electroplating: Release of Cr, Ni, Cu
- Battery manufacturing: Pb, Cd, Ni
- Pesticide production: Cu, As, Hg

c) Agricultural practices:

- Fertilizers: Cd contamination in phosphate fertilizers
- Pesticides: Historical use of lead arsenate, copper-based fungicides

d) Sewage sludge application:

- Concentration of metals in biosolids
- Land application leading to soil contamination

e) Fossil fuel combustion:

- Coal burning: Release of Hg, As, Se
- Oil combustion: Ni, V emissions

f) Vehicle emissions:

- Historical use of leaded gasoline
- Tire and brake wear: Zn, Cu, Pb

g) Electronic waste disposal:

- Improper recycling and disposal of e-waste
- Release of Pb, Cd, Hg, and other metals

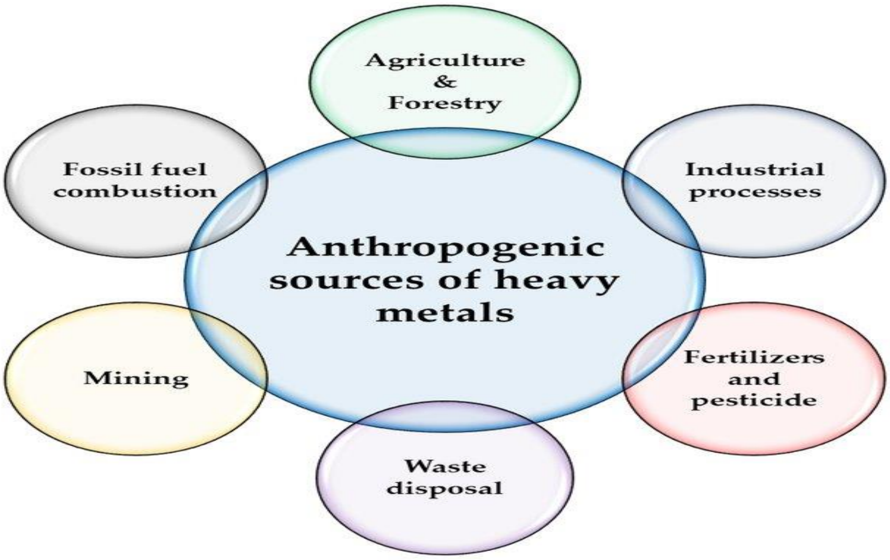

Figure 4.2. Major anthropogenic sources to global heavy metal pollution (Alengebawy et al., 2021).

4.3 Soil and water contamination by heavy metals

Soil contamination:

a) Adsorption and complexation with soil particles:

- Cation exchange capacity (CEC) of soil
- Formation of metal-organic complexes
- Precipitation of metal hydroxides and carbonates

b) Factors affecting metal mobility in soils:

- pH: Generally, lower pH increases metal solubility
- Organic matter: Can bind metals, reducing bioavailability

- Clay content: Higher clay content typically increases metal retention

  - Redox conditions: Influence metal speciation and solubility

c) Speciation of metals in soil solution:

- Free metal ions
- Inorganic complexes (e.g., chlorides, carbonates)
- Organic complexes (e.g., with humic substances)

d) Impact on soil microorganisms and fertility:

- Reduced microbial diversity and activity
- Altered nutrient cycling
- Impacts on symbiotic relationships (e.g., mycorrhizae)

Water contamination:

a) Surface water pollution:

- Runoff from contaminated soils
- Industrial discharge
- Atmospheric deposition

b) Groundwater contamination:

- Leaching of metals from contaminated soils
- Interaction with aquifer materials

c) Aquatic ecosystem impacts:

- Bioaccumulation in aquatic organisms
- Altered community structure
- Impacts on water quality and ecosystem services

d) Sediment contamination and resuspension:

- Accumulation of metals in bottom sediments
- Potential for release during disturbance events

Monitoring and assessment techniques:

- Soil and water sampling strategies
- Analytical methods: ICP-MS, AAS, XRF
- Biomonitoring using indicator species
- Geochemical modeling of metal speciation and transport

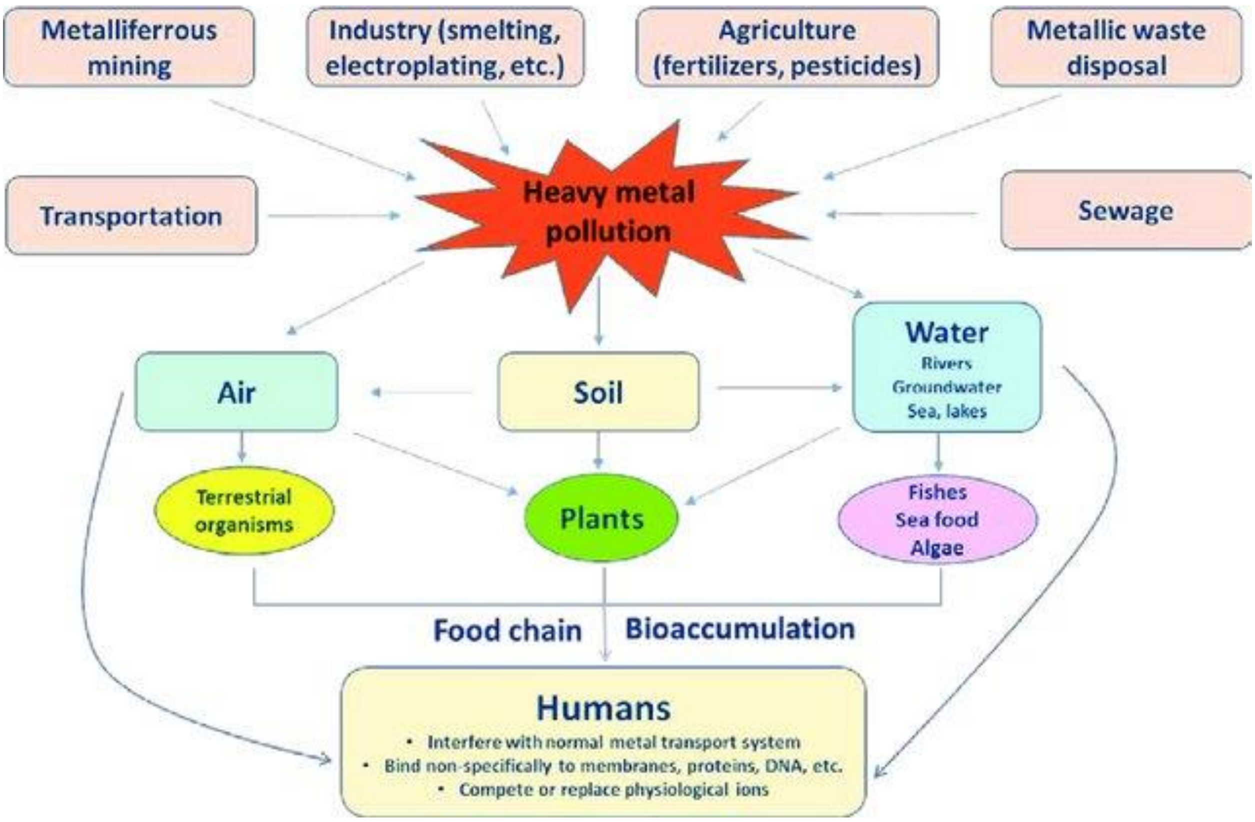

Figure 4.3. Schematic representation depicting the sources of heavy metal pollution and the impact on the environment and organisms (Farcasanu et al., 2018).

4.4 Absorption mechanisms of heavy metals by plants

Root uptake pathways:

a) Passive uptake through ion channels:

- Diffusion along electrochemical gradients
- Non-selective cation channels may allow metal entry

b) Active transport via carrier proteins:

- Metal-specific transporters (e.g., IRT1 for Fe, Zn, Cd)
- P-type ATPases for metal efflux and compartmentalization

Role of root exudates in metal solubilization:

- Organic acid secretion (e.g., citrate, malate)
- Phytosiderophore release for Fe acquisition (also affects other metals)

Mycorrhizal associations and their influence on metal uptake:

- Arbuscular mycorrhizae can alter metal bioavailability
- Potential for increased or decreased metal uptake depending on metal and fungal species

Foliar absorption of airborne metal particles:

- Deposition on leaf surfaces
- Uptake through stomata and cuticular penetration

Metal-specific uptake mechanisms:

- Strategy I (non-graminaceous plants): Proton extrusion and Fe^{2+} uptake
- Strategy II (graminaceous plants): Phytosiderophore release and Fe^{3+}-PS complex uptake

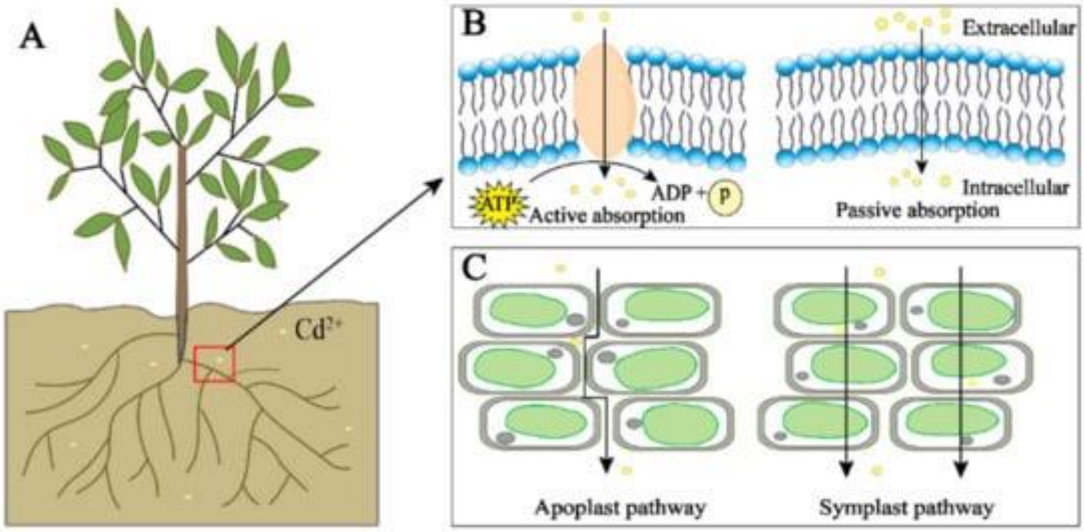

Figure 4.4. The root uptake of cadmium in plants. Cd (yellow) in the environment can enter plants through plant roots (**A**); when the concentration of Cd is low, ATP is consumed for active transport, and when the concentration is high, it directly enters cells for passive absorption (**B**); Cd is transported between cells by the apoplast and symplast pathways (**C**). (Yang et al., 2021).

4.5 Accumulation patterns in different plant tissues

Root accumulation and sequestration:

- Binding to cell wall components
- Sequestration in root vacuoles
- Formation of metal plaques on root surfaces

Translocation to aerial parts via xylem:

- Loading into xylem vessels
- Transport forms (free ions, organic complexes)

Leaf accumulation and compartmentalization:

- Sequestration in leaf vacuoles
- Binding to cell walls
- Trichome accumulation in some species

Stem and bark storage:

- Accumulation in woody tissues
- Potential for long-term metal storage

Reproductive tissue accumulation:

- Variability in metal translocation to seeds, fruits, and flowers
- Implications for food safety and seed viability

Hyperaccumulator plants and their unique distribution patterns:

- Definition: Plants that accumulate metals at levels 100 times higher than normal
- Examples: Thlaspi caerulescens (Cd, Zn), Pteris vittata (As)
- Potential applications in phytoremediation

Table 4.2. Examples of metal accumulation patterns in different plant species and tissues (Singh et al., 2012).

Vegetable crop	Metal uptake (mg/m^2 crop area)					Zn distribution in different plant parts (%)				Cu distribution in different plant parts (%)			
	Zn	Cu	Pb	Cd	Ni	Root	Stem	Leaf	Fruit	Root	Stem	Leaf	Fruit
Radish	28	16	2	3	4	78	NA	22	NA	60	NA	40	NA
Carrot	39	15	18	2	25	40	NA	60	NA	51	NA	49	NA
Potato	20	11	8	3	4	5	75	20	NA	9	77	14	NA
Onion	7	3	3	1	6	4	66	30	NA	5	73	22	NA
Spinach	13	5	3	3	2	17	NA	83	NA	25	NA	75	NA
Amaranthus	35	14	14	10	7	10	36	54	NA	22	39	39	NA
Fenugreek	5	4	2	1	1	10	45	45	NA	16	38	46	NA
Mustard	67	45	25	22	25	7	42	51	NA	7	55	38	NA
Cauliflower	80	28	45	8	57	18	4	40	38	45	4	26	25
Cabbage	56	18	45	9	38	17	30	53	53	17	33	50	NA
Soybean	15	19	6	1	4	2	16	12	70	3	39	20	38
Cluster bean	24	36	15	2	9	9	28	41	22	9	55	23	13
Tomato	48	14	9	3	14	23	48	25	4	16	36	37	11
Brinjal	58	28	29	4	20	32	40	25	3	27	37	27	9
Peas	47	11	14	1	10	1	15	15	69	3	9	19	69
Okra	36	19	18	5	14	6	45	29	20	10	24	25	41
Mean	36	18	16	5	15	17	31	38	32	20	40	34	29
CD at 5%	21	12	10	3	5	12	9	8	9	8	12	6	8

4.6 Effects on plant growth and development

Inhibition of seed germination:

- Reduced germination rates
- Delayed emergence
- Abnormal seedling development

Root growth inhibition and morphological changes:

- Reduced root elongation
- Increased lateral root formation
- Root tip browning and necrosis

Reduced biomass production:

- Decreased shoot and root dry weight
- Altered root-to-shoot ratio

Leaf chlorosis and necrosis:

- Interveinal chlorosis (e.g., Fe deficiency symptoms)
- Marginal and tip necrosis

Altered plant architecture and branching patterns:

- Reduced plant height
- Changes in branching and tillering

Delayed or inhibited flowering and fruit set:

- Late flowering or failure to flower
- Reduced fruit yield and quality

Premature senescence:

- Early leaf senescence and abscission
- Shortened overall lifespan

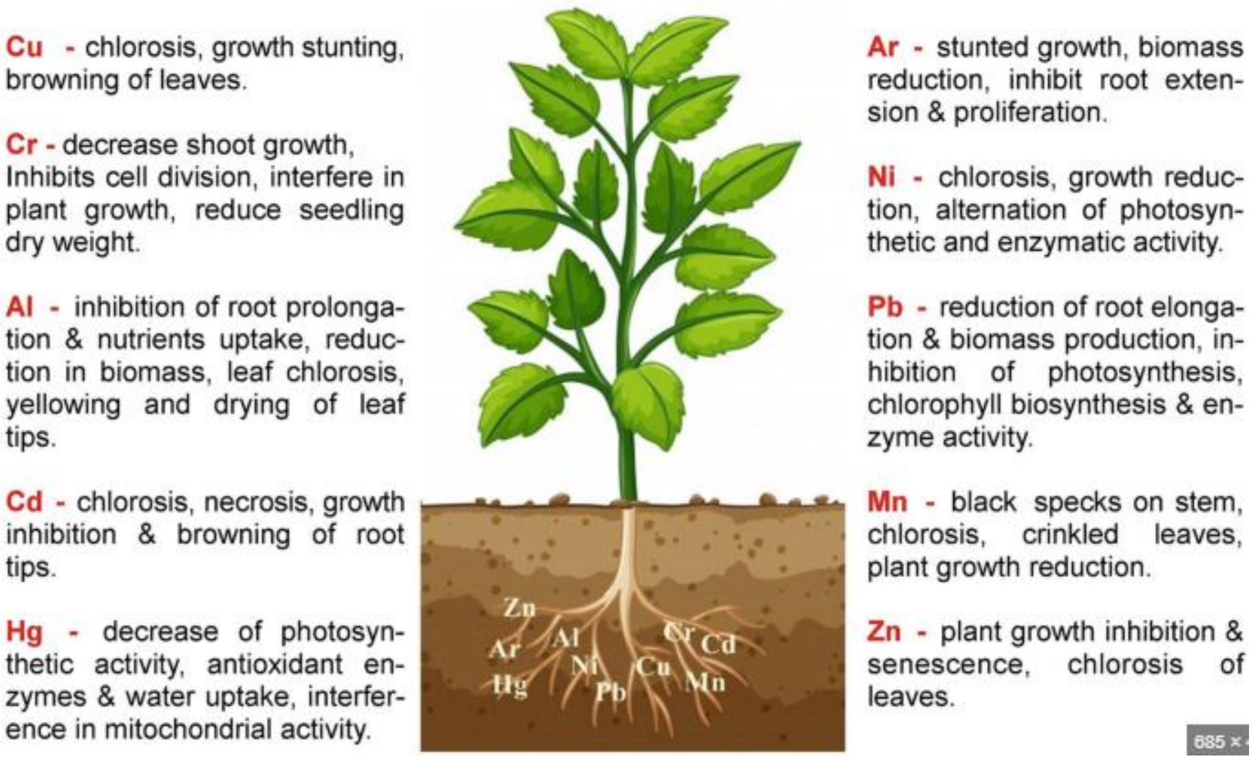

Figure 4.5. Physiological and molecular responses, and heavy metal toxicity symptoms in plants (Patel et al., 2021).

4.7 Impact on photosynthesis and chlorophyll content

Chlorophyll biosynthesis inhibition:

- Interference with enzyme activities in chlorophyll synthesis pathway
- Substitution of Mg^{2+} in chlorophyll molecule by heavy metals

Photosystem II damage:

- Alteration of PSII reaction center proteins
- Inhibition of oxygen evolution

Electron transport chain disruption:

- Interference with plastoquinone and cytochrome functions
- Altered electron flow between photosystems

Rubisco activity reduction:

- Direct inhibition of Rubisco enzyme
- Decreased CO_2 fixation rates

Stomatal function impairment:

- Changes in guard cell ion balance
- Altered stomatal conductance and transpiration

Chloroplast ultrastructure alterations:

- Thylakoid membrane disorganization
- Changes in grana stacking

Overall photosynthetic rate reduction:

- Decreased CO_2 assimilation
- Reduced photosynthetic efficiency (Fv/Fm ratio)

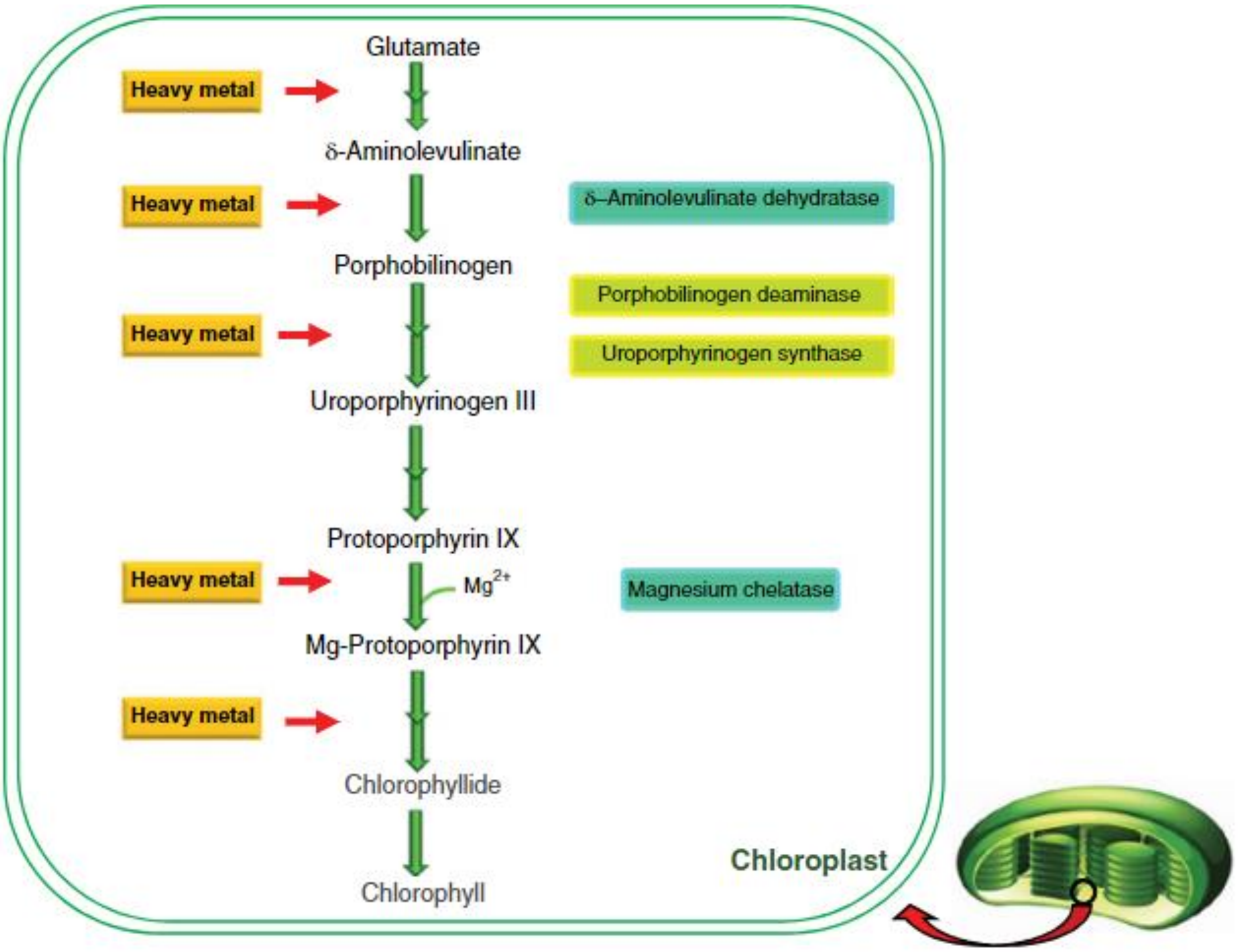

Figure 4.6. Diagram showing points of heavy metal impair several steps of chlorophyll biosynthesis process (Souri et al., 2019).

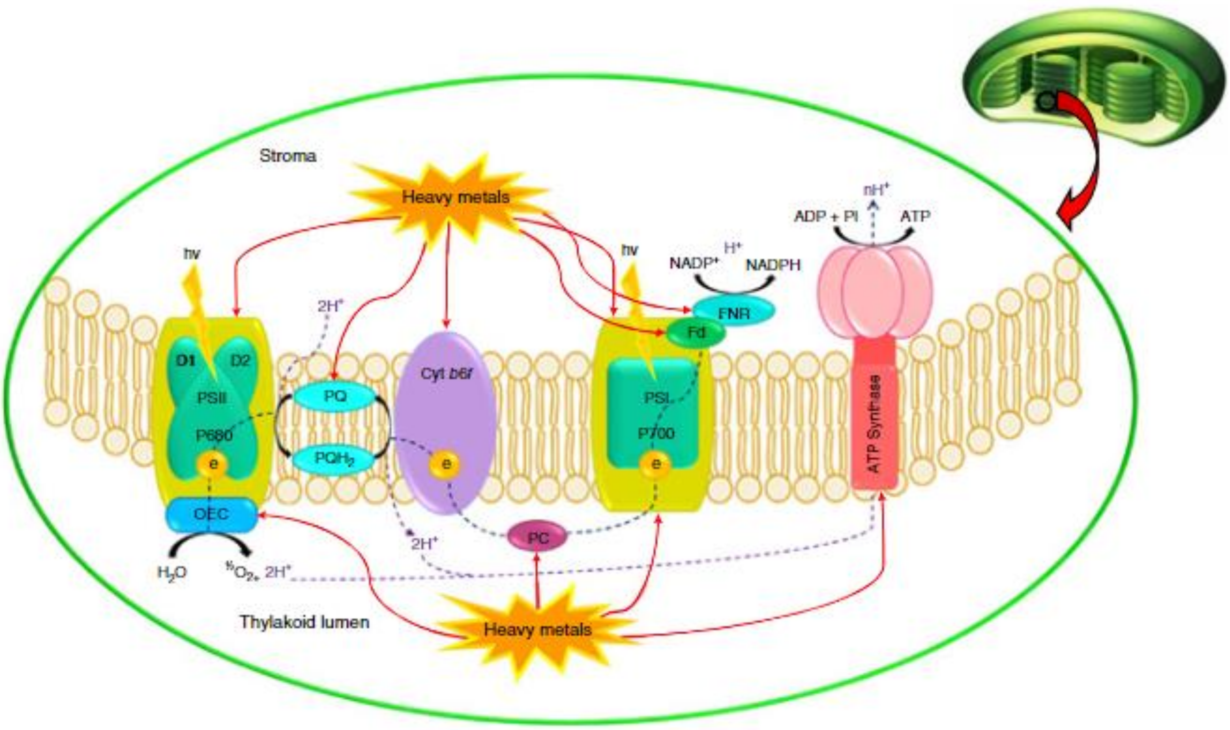

Figure 4.7. Overview of the light-dependent reactions of photosynthesis. The photosynthetic system of water photolysis involving manganese stabilizing protein (OEC); the reaction center of PSII (P680); PSII proteins (D1 and D2); the oxidized and reduced plastoquinone pools (PQ and PQH); plastocyanin (PC); the reaction center of PSI (P700); ferredoxin (Fd); ferredoxin NADP+ oxidoreductase (FNR); ATP Synthase. Dotted lines show the pathways of electron and proton transport. Red lines show the effect of heavy metals on the light-dependent reactions of photosynthesis. See insert for color representation of this figure (Souri et al., 2019).

4.8 Alterations in plant metabolism

Oxidative stress induction:

- Reactive oxygen species (ROS) generation: O_2^-, H_2O_2, OH•
- Lipid peroxidation: Membrane damage
- Protein oxidation: Enzyme inactivation
- DNA damage: Mutations, strand breaks

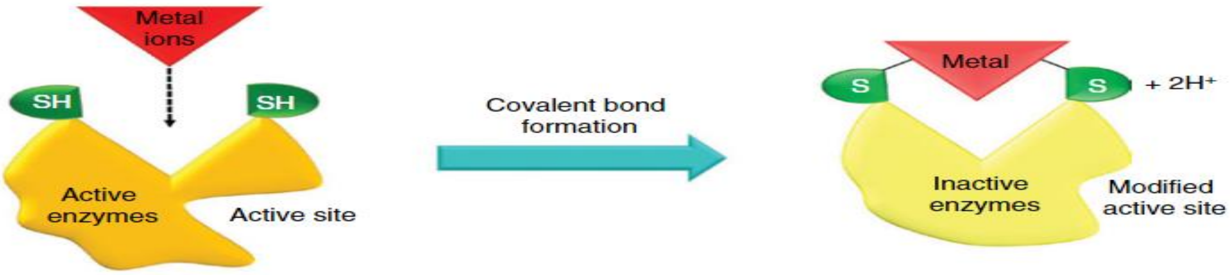

Figure 4.8. Interaction of heavy-metals with sulfhydryl (SH) group of enzymes. Above cartoon demonstrates how a divalent metal cation (e.g. Hg^{2+}, Pb^{2+}, Cu^{2+}, As^{2+}, and Cd^{2+}) acts as a non-competitive inhibitor of photosynthetic enzymes (URL. http://slideplayer.com/slide/6281587#).

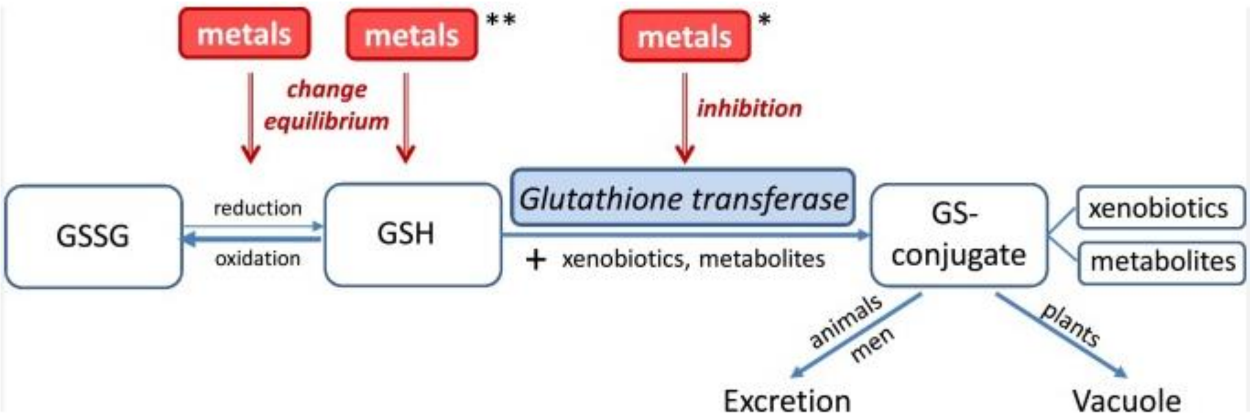

Figure 4.9. Inhibitory effect of metals on animal and plant glutathione transferases (Dobritzsch et al., 2020).

Antioxidant system responses:

- Enzymatic antioxidants: Superoxide dismutase (SOD), catalase (CAT), ascorbate peroxidase (APX)
- Non-enzymatic antioxidants: Glutathione, ascorbate, tocopherols

Nutrient uptake and assimilation disruption:

- Competition for uptake sites with essential nutrients
- Interference with nutrient transport and metabolism

Alterations in carbohydrate metabolism:

- Changes in sugar content and composition
- Effects on starch synthesis and degradation

Protein synthesis inhibition:

- Disruption of ribosomal function
- Altered amino acid metabolism

Changes in secondary metabolite production:

- Increased synthesis of stress-related compounds (e.g., phenolics)
- Alterations in plant defense chemicals

Phytochelatin and metallothionein synthesis:

- Induction of metal-binding peptides
- Role in metal detoxification and homeostasis

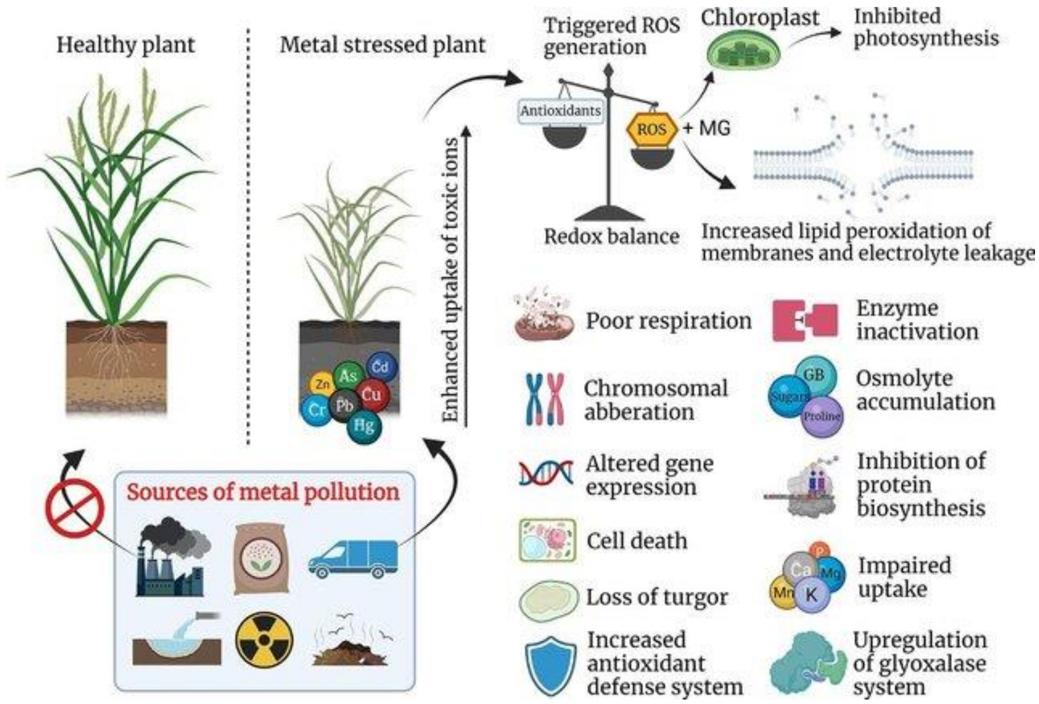

Figure 4.10. Schematic representation of phytotoxic effects of heavy metal(loid)s on plants and different defense responses in plants to tolerate metal toxicity (Hafeez et al., 2023).

4.9 Case study: Cadmium toxicity in plants and human health implications

Sources of cadmium contamination:

- Phosphate fertilizers
- Industrial emissions (e.g., battery manufacturing, metal plating)
- Sewage sludge application

Cadmium uptake and translocation in plants:

- Uptake via calcium and zinc transporters
- High mobility in the plant, readily translocated to shoots

Physiological and biochemical effects on plants:

- Growth inhibition: Reduced biomass, stunted roots
- Photosynthesis impairment: Chlorophyll degradation, PSII damage
- Oxidative stress induction: Increased ROS production
- Nutrient imbalances: Interference with Fe, Zn, and Ca uptake

Cadmium accumulation in edible plant parts:

- Variation among crop species and cultivars
- Higher accumulation in leafy vegetables and grains

Human health risks associated with cadmium exposure:

- Chronic kidney disease: Proximal tubule damage
- Osteoporosis: Interference with calcium metabolism
- Cardiovascular diseases: Hypertension, atherosclerosis
- Potential carcinogenic effects: Classified as Group 1 carcinogen by IARC

Regulatory limits for cadmium in food and environment:

- Codex Alimentarius Commission standards for food
- WHO guidelines for drinking water
- National and regional soil contamination limits

Strategies for mitigating cadmium contamination in agriculture:

- Soil amendments: Lime, organic matter, biochar
- Crop selection and rotation: Using low-accumulating varieties
- Phytoremediation approaches: Using hyperaccumulators for soil cleaning

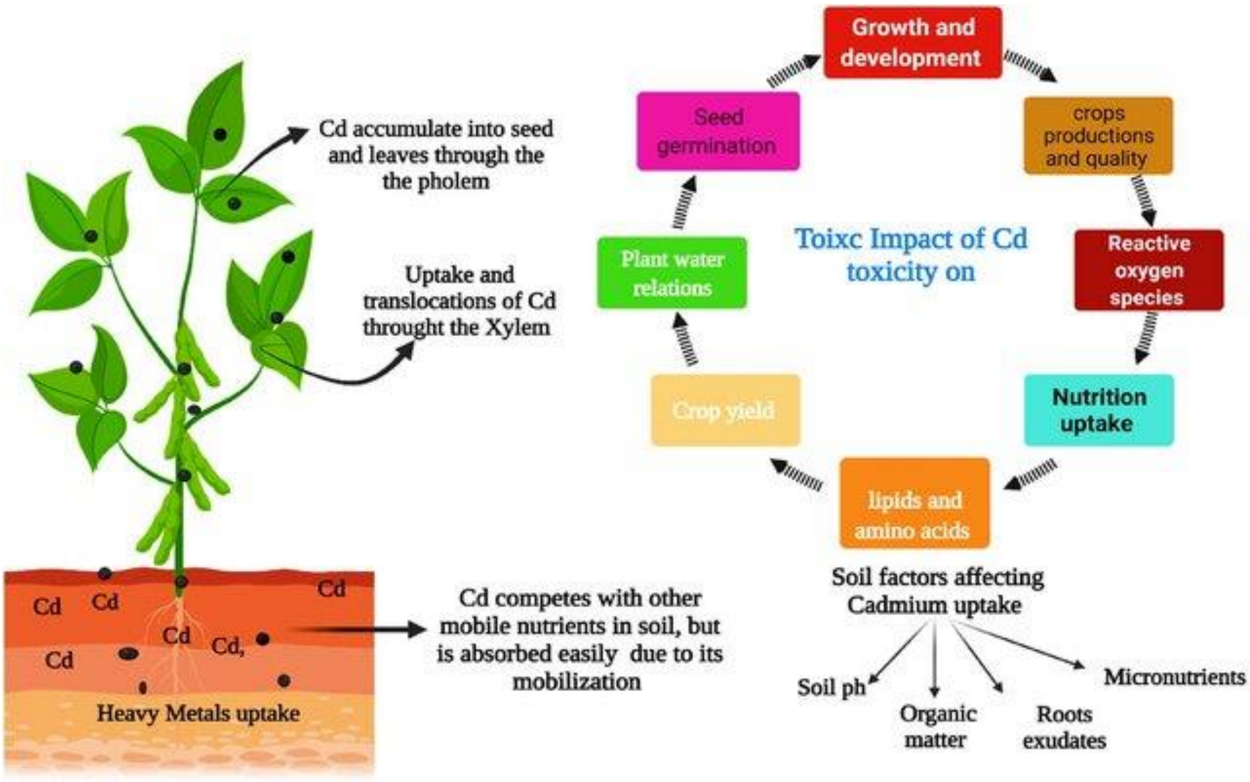

Figure 4.11. The absorption, transport, accumulation, and toxicity of cadmium (Cd) in plant species. Soil pH, micro-and macronutrients, and organic matter in soil are significant variables influencing plants' Cd uptake (Alsafran et al., 2023).

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Course 5.

Plant Stress Responses

5.1 Definition and types of stress in plants

Definition of stress: Any external factor that negatively influences plant growth, productivity, reproductive capacity, or survival. Stress in plants is often defined as a significant deviation from optimal growing conditions.

5.1.1. Categories of stress:

a) Abiotic stress: Environmental factors

b) Biotic stress: Living organisms

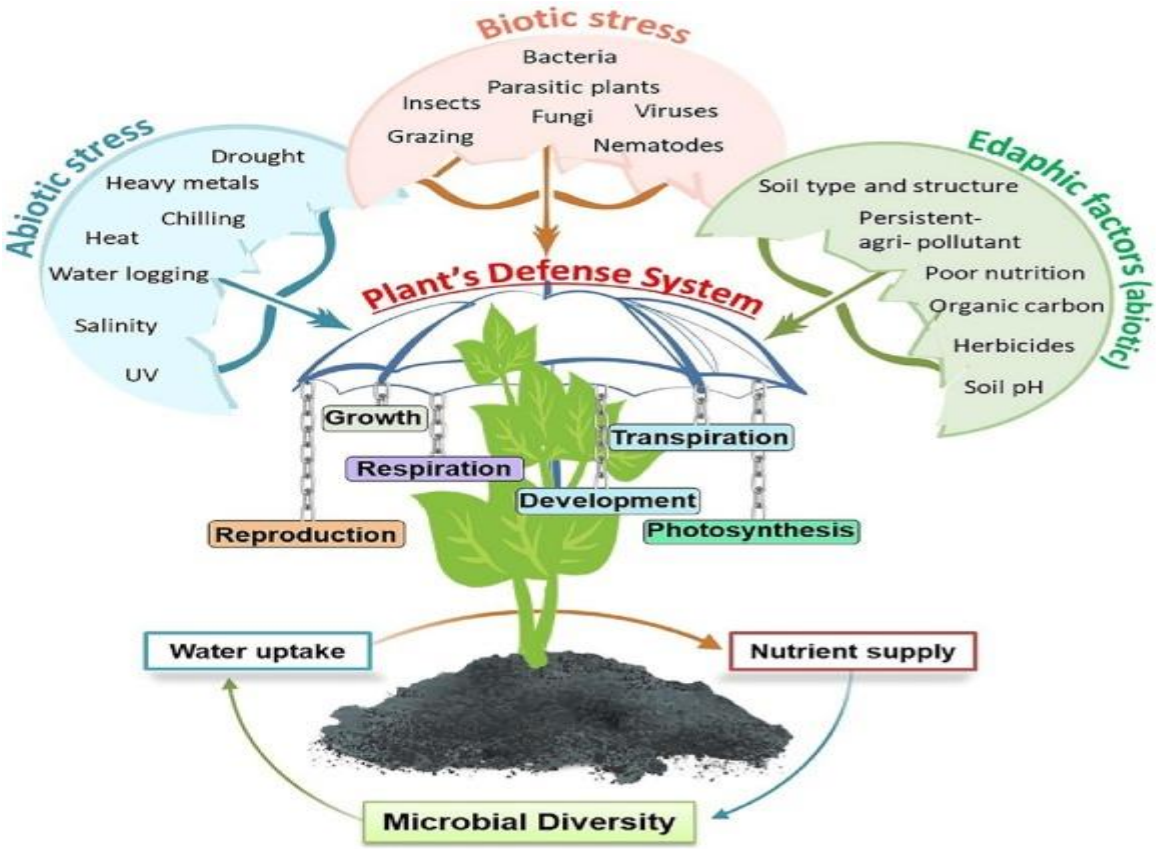

Figure 5.1. Diagram illustrating various abiotic and biotic stresses affecting plants (Nawaz et al., 2023).

5.1.2. Acute vs. chronic stress:

- Acute stress: Short-term, severe stress events

- Chronic stress: Long-term, persistent stress conditions

5.1.3. Concept of stress tolerance and adaptation:

- Stress tolerance: Ability to withstand stress without significant damage

- Adaptation: Long-term genetic changes that enhance survival under stress

- Acclimation: Short-term physiological adjustments to stress

5.2 Physiological and biochemical stress responses

5.2.1. Changes in water relations:

- Osmotic adjustment:
    - Accumulation of compatible solutes (e.g., proline, glycine betaine)
    - Increases in inorganic ion concentrations

- Alterations in stomatal conductance:
    - Stomatal closure to reduce water loss
    - Changes in guard cell ion fluxes

5.2.2. Photosynthetic responses:

- Adjustments in light-harvesting complexes:
    - Changes in chlorophyll a/b ratios
    - Alterations in antenna complex size

- Changes in carbon fixation pathways:
    - Shifts between C3, C4, and CAM metabolism
    - Adjustments in Rubisco activity and content

5.2.3. Respiratory changes:

- Increased respiration rates:
    - Enhanced energy demand for stress responses

- Alterations in the electron transport chain:
    - Alternative oxidase pathway activation

5.2.4. Hormonal responses:

- Abscisic acid (ABA) production:

- Stomatal closure
- Gene expression regulation

- Ethylene synthesis:

  - Senescence acceleration
  - Fruit ripening modulation

- Jasmonates and salicylic acid in defense responses:

  - Pathogen resistance
  - Herbivore defense signaling

5.2.5. Metabolic adjustments:

- Accumulation of compatible solutes:

  - Proline, glycine betaine, sugar alcohols

- Changes in carbohydrate metabolism:

  - Starch degradation
  - Increased soluble sugar content

- Alterations in nitrogen metabolism:

  - Changes in amino acid profiles
  - Adjustments in nitrate assimilation

5.2.6. Morphological responses:

- Changes in root-to-shoot ratio:

  - Increased root growth under drought

- Leaf area adjustments:

  - Leaf rolling or shedding

- Trichome development:

  - Enhanced protection against herbivores and excess light

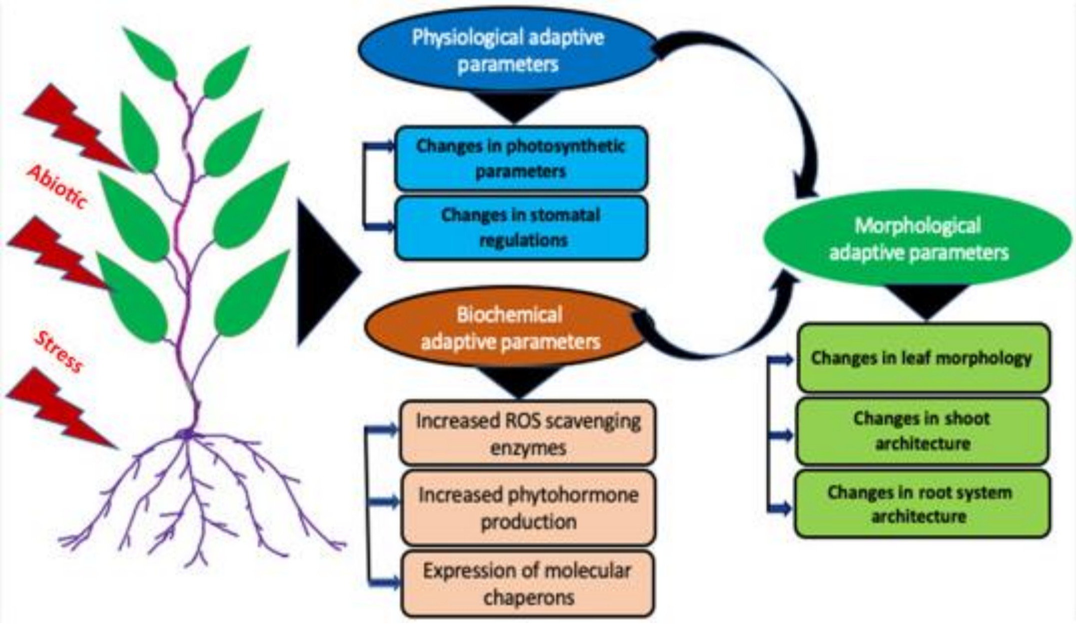

Figure 5.2. Schematic representation of major physiological and biochemical responses to stress in plants (Kashyap et al., 2021).

5.3 Oxidative stress and reactive oxygen species (ROS)

5.3.1. Types of ROS:

- Superoxide radical (O2•-): Formed by one-electron reduction of O2

- Hydrogen peroxide (H2O2): Produced by dismutation of O2•-

- Hydroxyl radical (OH•): Highly reactive, formed from H2O2

- Singlet oxygen (1O2): Excited state of molecular oxygen

5.3.2. Sources of ROS in plants:

- Chloroplasts: Electron transport chain in photosystems

- Mitochondria: Respiratory electron transport chain

- Peroxisomes: Photorespiration and β-oxidation of fatty acids

- Plasma membrane-bound NADPH oxidases: Stress-induced activation

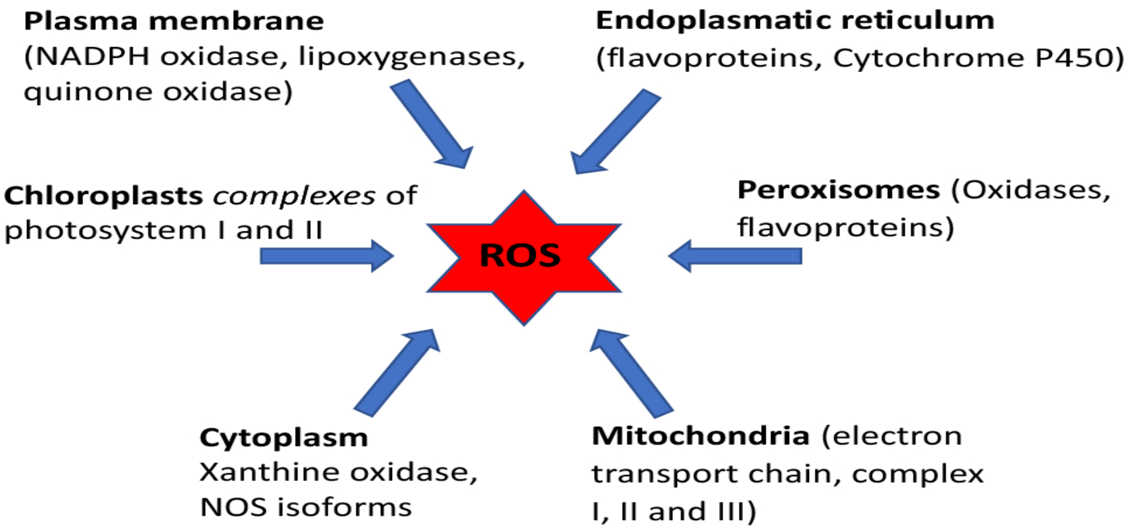

Figure 5.3. Diagram showing ROS production sites in plant cells (Jomova et al., 2023).

5.3.3. Dual role of ROS:

- Oxidative damage to cellular components:

  - Lipid peroxidation of membranes
  - Protein oxidation and enzyme inactivation
  - DNA damage and mutation
  - Pigment breakdown (e.g., chlorophyll degradation)

- Signaling molecules in stress responses:

  - Activation of stress-responsive genes
  - Regulation of programmed cell death
  - Mediation of systemic acquired resistance

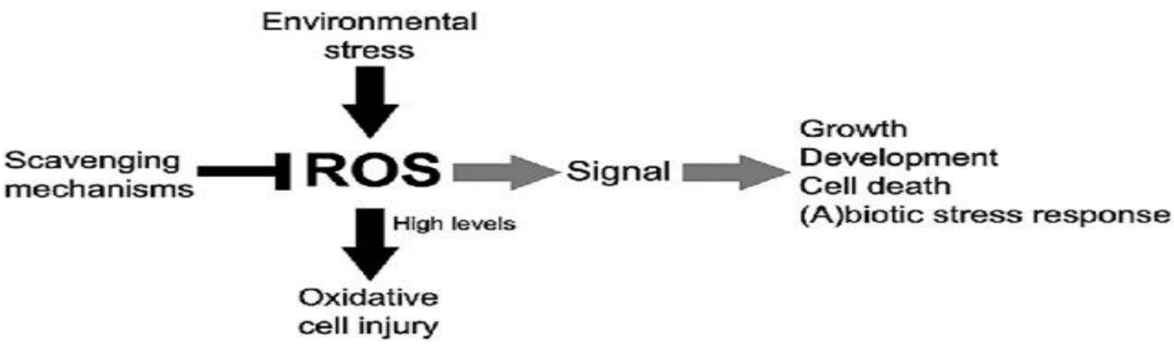

Figure 5.4. The double role of ROS. Environmental stress conditions induce over-production of ROS which, at high concentrations, can produce oxidative cell injuries. However, plants have a broad array of antioxidant systems that allow ROS to be used as a signal in distinct biological processes, such as growth and development, responses to biotic and abiotic stresses, and programmed cell death (PCD) (Del Río, 2015).

5.4 Antioxidant systems in plants

5.4.1. Enzymatic antioxidants:

- Superoxide dismutase (SOD):

  - Dismutates $O_2^{\bullet -}$ to H_2O_2
  - Multiple isoforms (Cu/Zn-SOD, Mn-SOD, Fe-SOD)

- Catalase (CAT):

  - Converts H_2O_2 to H_2O and O_2
  - Primarily located in peroxisomes

- Ascorbate peroxidase (APX):

  - Reduces H_2O_2 using ascorbate as electron donor
  - Key enzyme in ascorbate-glutathione cycle

- Glutathione reductase (GR):

  - Maintains reduced glutathione pool
  - NADPH-dependent reduction of oxidized glutathione

- Monodehydroascorbate reductase (MDHAR) and Dehydroascorbate reductase (DHAR):

  - Regeneration of reduced ascorbate

5.4.2. Non-enzymatic antioxidants:

- Ascorbic acid (Vitamin C):

  - Water-soluble antioxidant
  - Direct scavenging of ROS

- Glutathione:

  - Tripeptide thiol compound
  - Involved in ascorbate-glutathione cycle

- Tocopherols (Vitamin E):

  - Lipid-soluble antioxidants
  - Protection of membrane lipids

- Carotenoids:

  - Quenching of singlet oxygen

- Protection of photosynthetic apparatus

- Flavonoids and other phenolic compounds:

    - Diverse group of secondary metabolites
    - ROS scavenging and metal chelation

Ascorbate-glutathione cycle:

- Cyclic pathway for H2O2 detoxification
- Involves APX, MDHAR, DHAR, and GR

5.4.3. Regulation of antioxidant systems under stress:

- Transcriptional upregulation of antioxidant enzymes

- Post-translational modifications

- Compartment-specific responses

5.5 Heat shock proteins and stress tolerance

5.5.1. Classification of heat shock proteins (HSPs):

- HSP100: Large molecular chaperones, involved in protein disaggregation

- HSP90: Highly conserved, involved in signal transduction

- HSP70: Diverse functions, protein folding and import

- HSP60: Chaperonins, assist in protein folding

- Small HSPs: Diverse group, prevent protein aggregation

5.5.2. Functions of HSPs:

- Protein folding and refolding:

    - Assist in proper protein conformation
    - Prevent misfolding under stress conditions

- Prevention of protein aggregation:

    - Binding to partially denatured proteins
    - Maintaining proteins in soluble state

- Targeting proteins for degradation:

    - Recognition of irreparably damaged proteins

- Facilitating proteasomal degradation

5.5.3. HSP regulation:

- Heat shock factors (HSFs):

  - Transcription factors controlling HSP expression
  - Activated by various stresses

- Heat shock elements (HSEs):

  - Conserved DNA sequences in HSP promoters
  - Binding sites for HSFs

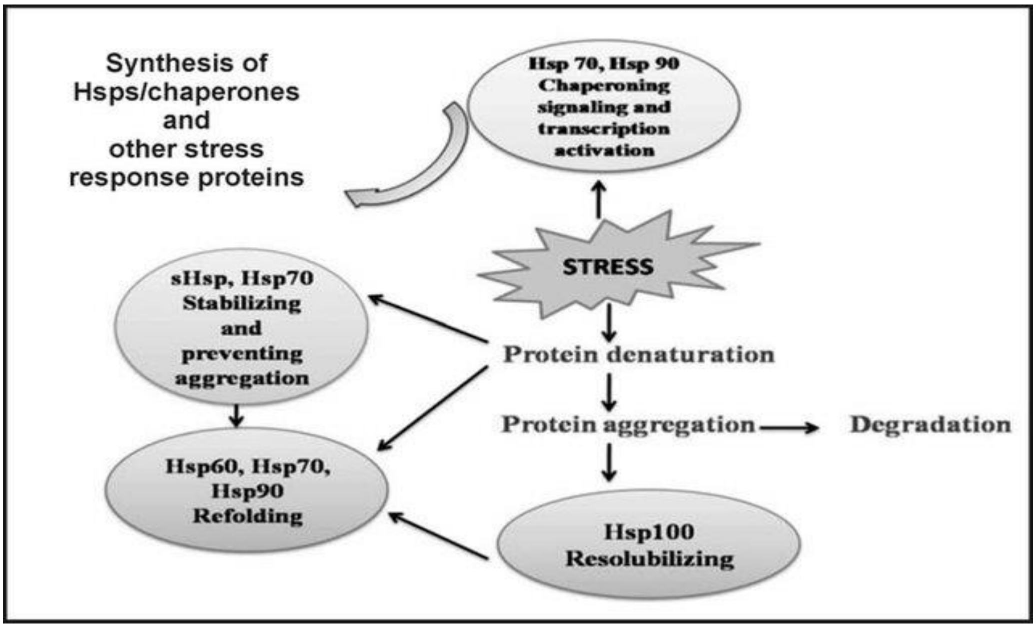

Figure 5.5. Function of various heat shock proteins (HSPs) under stress conditions (Sehgal et al., 2016).

5.5.4. Role of HSPs in cross-tolerance to multiple stresses:

- Protection against various abiotic stresses

- Involvement in pathogen resistance

5.6 Phytochelatins and metallothioneins in metal detoxification

5.6.1. Phytochelatins:

- Structure: (γ-Glu-Cys)n-Gly, where n = 2-11

- Synthesis: Catalyzed by phytochelatin synthase

- Phytochelatin synthase regulation :

- Post-translational activation by heavy metals
- Transcriptional regulation under prolonged stress

- Metal binding and sequestration :

  - Formation of metal-PC complexes
  - Vacuolar sequestration via ABC transporters

5.6.2. Metallothioneins :

- Types: Four main types in plants (MT1, MT2, MT3, MT4)

- Structure: Cysteine-rich, low molecular weight proteins

- Metal binding properties :

  - High affinity for various heavy metals
  - Involved in metal homeostasis and detoxification

- Gene regulation :

  - Metal-responsive elements in promoters
  - Developmental and tissue-specific expression

5.6.3. Comparison of phytochelatins and metallothioneins:

- PCs: Enzymatically synthesized, inducible

- MTs: Genetically encoded, constitutive and inducible

5.6.4. Role in heavy metal tolerance and hyperaccumulation:

- Chelation of excess metals

- Contribution to vacuolar sequestration

- Involvement in long-distance metal transport

5.7 Stress signaling pathways

5.7.1. Stress perception and signal transduction:

- Membrane-bound receptors:

  - Receptor-like kinases (RLKs)
  - Two-component histidine kinases

- Ion channels:

- Mechanosensitive channels
- Ligand-gated channels

- G-protein coupled receptors:

  - Involvement in various stress responses

5.7.2. Second messengers:

- Calcium signaling:

  - Cytosolic Ca^{2+} elevations
  - Calcium-dependent protein kinases (CDPKs)

- Reactive oxygen species (ROS) :

  - H_2O_2 as a signaling molecule
  - Redox-sensitive transcription factors

- Lipid signaling :

  - Phosphatidic acid production
  - Inositol phosphate signaling

5.7.3. Mitogen-activated protein kinase (MAPK) cascades:

- Three-tiered kinase modules (MAPKKK → MAPKK → MAPK)

- Involvement in various stress responses

5.7.4. Hormone-mediated signaling pathways:

- ABA-dependent pathways:

  - AREB/ABF transcription factors
  - SnRK2 protein kinases

- ABA-independent pathways :

  - DREB/CBF transcription factors
  - NAC and ZF-HD transcription factors

5.7.5. Cross-talk between different stress signaling pathways:

- Integration of multiple stress signals

- Shared signaling components and transcription factors

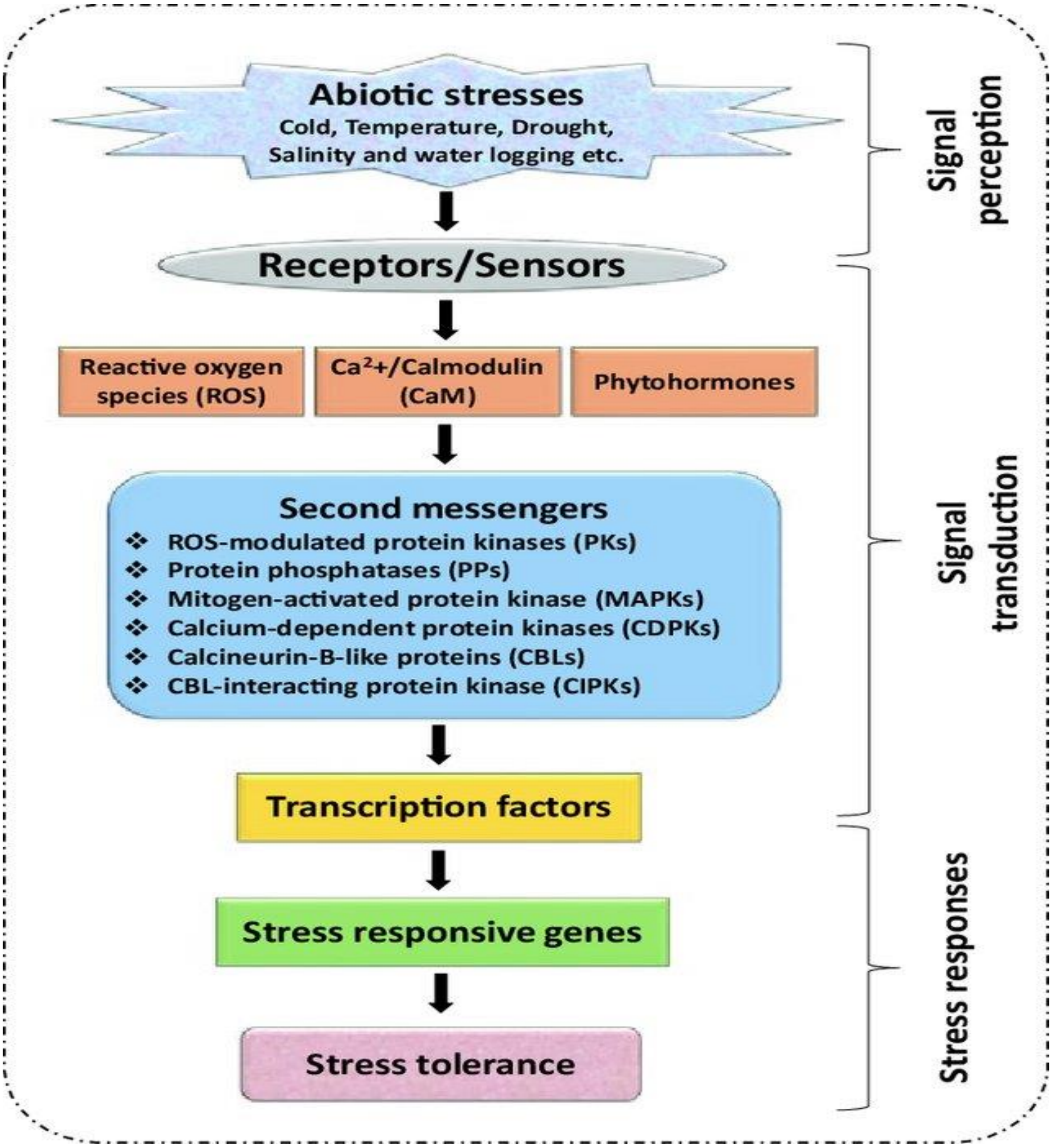

Figure 5.6. Overview of major stress signaling pathways in plants. Some key factors play a vital role in signaling pathways such as perception of stress, transcriptional regulation, expression of stress-responsive genes, and physiological responses for the development of abiotic stress tolerance plants (Raza et al., 2020).

5.8 Stress-induced gene expression

5.8.1. Transcription factors involved in stress responses:

- DREB/CBF family: Drought and cold responses

- AREB/ABF family: ABA-responsive gene expression

- MYB and MYC factors: Various stress responses

- NAC family: Senescence and stress responses

- WRKY family: Pathogen defense and abiotic stress

5.8.2. Cis-acting regulatory elements:

- Abscisic acid-responsive elements (ABRE)

- Dehydration-responsive elements (DRE)

- Heat shock elements (HSE)

5.8.3. Stress-responsive genes:

- Late embryogenesis abundant (LEA) proteins:
    - o Hydrophilic proteins, various protective functions

- Osmoprotectant biosynthesis genes :
    - o Proline, glycine betaine synthesis pathways

- Antioxidant enzyme genes :
    - o SOD, CAT, APX, etc.

- Ion transporter genes :
    - o Na^+/H^+ antiporters, K^+ channels

5.8.4. Epigenetic regulation of stress responses:

- DNA methylation changes under stress

- Histone modifications affecting gene accessibility

- Small RNAs in stress regulation:
    - o miRNAs and siRNAs modulating stress responses

5.8.5. Systems biology approaches to understanding stress-induced gene networks:

- Transcriptomics, proteomics, and metabolomics integration

- Network analysis of stress-responsive genes

- Identification of key hubs and regulatory modules

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Course 6.

Organic Contaminants (Xenobiotics)

6.1 Classification of organic pollutants

Organic contaminants, also known as xenobiotics, are typically man-made and can persist in ecosystems for extended periods, posing significant risks to plant and animal life.

6.1.1 Definition of xenobiotics

Xenobiotics are chemical substances found within an organism that are not naturally produced or expected to be present within that organism. In the context of plant ecotoxicology, xenobiotics refer to organic compounds that are introduced into the environment through human activities and can interact with plant systems in various ways.

6.1.2 Major classes of organic pollutants

Organic pollutants can be classified into several major categories based on their chemical structure, origin, and intended use.

Pesticides

They can be further categorized into:

a) Insecticides:

- Organochlorines (e.g., DDT, aldrin, dieldrin)
- Organophosphates (e.g., malathion, chlorpyrifos)
- Pyrethroids (e.g., permethrin, cypermethrin)

b) Herbicides:

- Phenoxy acids (e.g., 2,4-D, MCPA)
- Triazines (e.g., atrazine, simazine)
- Glyphosate and glyphosate-based formulations

c) Fungicides:

- Azoles (e.g., propiconazole, tebuconazole)
- Strobilurins (e.g., azoxystrobin, pyraclostrobin)

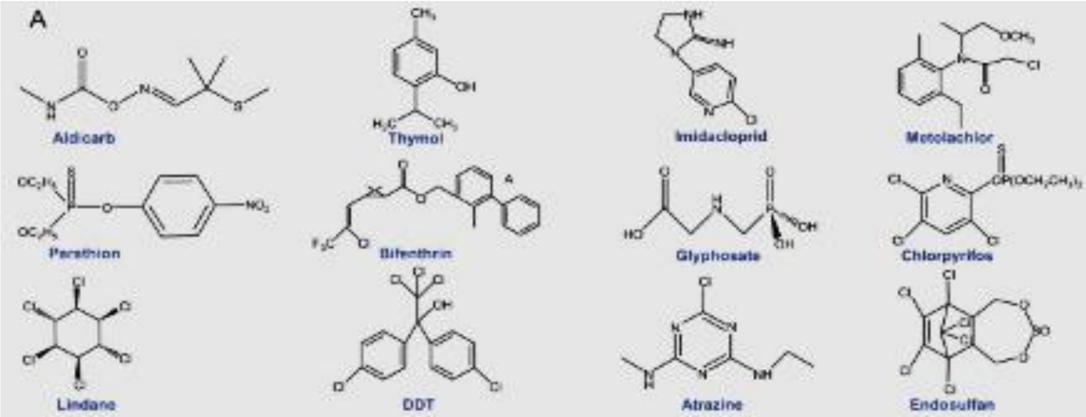

Figure 1. Chemical structures of common pesticides (Ahuja, 2022).

Industrial chemicals

Industrial chemicals encompass a wide range of organic compounds used in manufacturing processes, consumer products, and other industrial applications. Some important classes include:

a) Polychlorinated biphenyls (PCBs): These synthetic organic chemicals were widely used in electrical equipment, hydraulic fluids, and plasticizers before being banned due to their persistence and toxicity.

b) Dioxins and furans: These are highly toxic compounds that are primarily produced as byproducts of industrial processes, such as waste incineration and chlorine bleaching of paper pulp.

c) Phthalates: These chemicals are commonly used as plasticizers in various products, including plastics, cosmetics, and personal care items.

d) Bisphenols: Bisphenol A (BPA) and related compounds are used in the production of certain plastics and resins, with potential endocrine-disrupting effects.

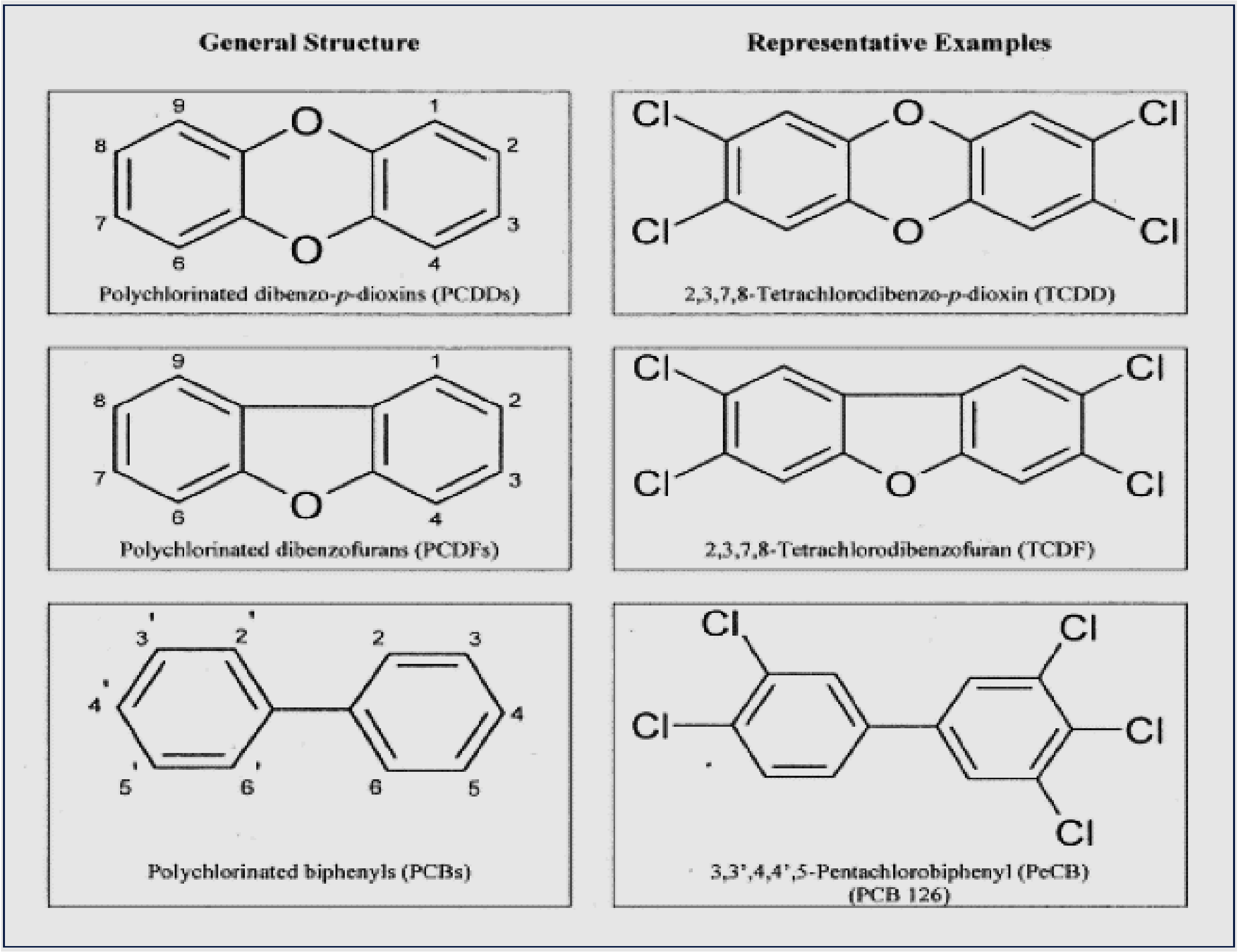

Figure 2. Molecular structures of common industrial organic pollutants (Johnston, 2016).

Petroleum hydrocarbons

Petroleum hydrocarbons are a complex mixture of organic compounds derived from crude oil and its refined products. These pollutants can enter the environment through oil spills, leaks from storage tanks, and incomplete combustion of fossil fuels. They include a wide range of compounds, from light, volatile substances to heavy, persistent molecules.

Polycyclic aromatic hydrocarbons (PAHs)

PAHs are a group of organic compounds composed of multiple aromatic rings. They are formed during the incomplete combustion of organic matter and are found in fossil fuels, tar, and various industrial products. PAHs are of particular concern due to their persistence in the environment and potential carcinogenic properties.

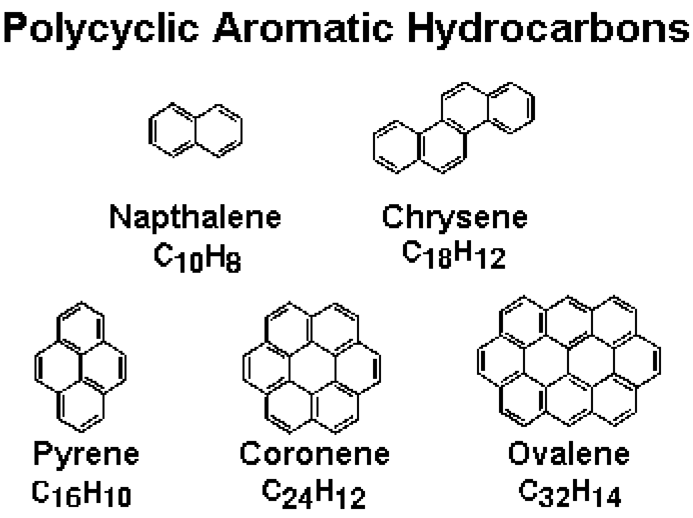

Figure 3. Examples of PAH structures (URL: https://users.physics.unc.edu/~gcsloan/research/pah_info.html).

Pharmaceuticals and personal care products (PPCPs)

PPCPs represent a diverse group of chemicals used in medications, cosmetics, and personal hygiene products. These compounds can enter the environment through wastewater treatment plants, improper disposal, and agricultural runoff. Examples include:

- Antibiotics
- Hormones and endocrine disruptors
- Analgesics and anti-inflammatory drugs
- UV filters and preservatives

Perfluoroalkyl substances (PFAS)

PFAS are a group of synthetic chemicals characterized by their strong carbon-fluorine bonds, which make them highly persistent in the environment. They have been widely used in consumer products, firefighting foams, and industrial applications due to their water and oil-repellent properties.

6.1.3 Classification based on chemical structure and functional groups

Organic pollutants can also be classified based on their chemical structure and functional groups. Some common structural classifications include:

- Aliphatic compounds (e.g., alkanes, alkenes, alkynes)
- Aromatic compounds (e.g., benzene derivatives, PAHs)

- Halogenated compounds (e.g., organochlorines, brominated flame retardants)

- Oxygenated compounds (e.g., alcohols, aldehydes, ketones, carboxylic acids)

- Nitrogen-containing compounds (e.g., amines, nitro compounds)

- Sulfur-containing compounds (e.g., thiols, sulfides)

6.1.4 Persistent organic pollutants (POPs)

Persistent organic pollutants (POPs) are a subset of organic contaminants that possess specific characteristics making them particularly problematic in the environment. The key features of POPs include:

a) Persistence: POPs are resistant to environmental degradation through chemical, biological, and photolytic processes, allowing them to remain intact in the environment for long periods.

b) Bioaccumulation: These compounds tend to accumulate in the fatty tissues of living organisms, leading to increasing concentrations as they move up the food chain (biomagnification).

c) Long-range transport: POPs can be transported over long distances through air and water currents, affecting ecosystems far from their original source.

d) Toxicity: Many POPs have been associated with adverse effects on human health and the environment, including carcinogenicity, reproductive disorders, and developmental abnormalities.

The Stockholm Convention on Persistent Organic Pollutants, an international environmental treaty, aims to eliminate or restrict the production and use of POPs. The treaty initially focused on 12 POPs, known as the "Dirty Dozen," which included:

- Aldrin; Chlordane; DDT; Dieldrin; Endrin; Heptachlor; Hexachlorobenzene; Mirex; Toxaphene; Polychlorinated biphenyls (PCBs); Polychlorinated dibenzo-p-dioxins (PCDDs); Polychlorinated dibenzofurans (PCDFs).

Since its inception, the Stockholm Convention has expanded to include additional POPs, recognizing the ongoing challenges posed by these persistent contaminants.

6.2 Sources and environmental fate of xenobiotics

The presence of xenobiotics in the environment is largely attributed to human activities.

6.2.1 Sources of xenobiotics

Xenobiotics enter the environment through various pathways, often as a result of human activities across different sectors:

- Agricultural activities

- Industrial processes and emissions

- Wastewater treatment plants

- Landfills and waste disposal sites

- Accidental spills and leaks

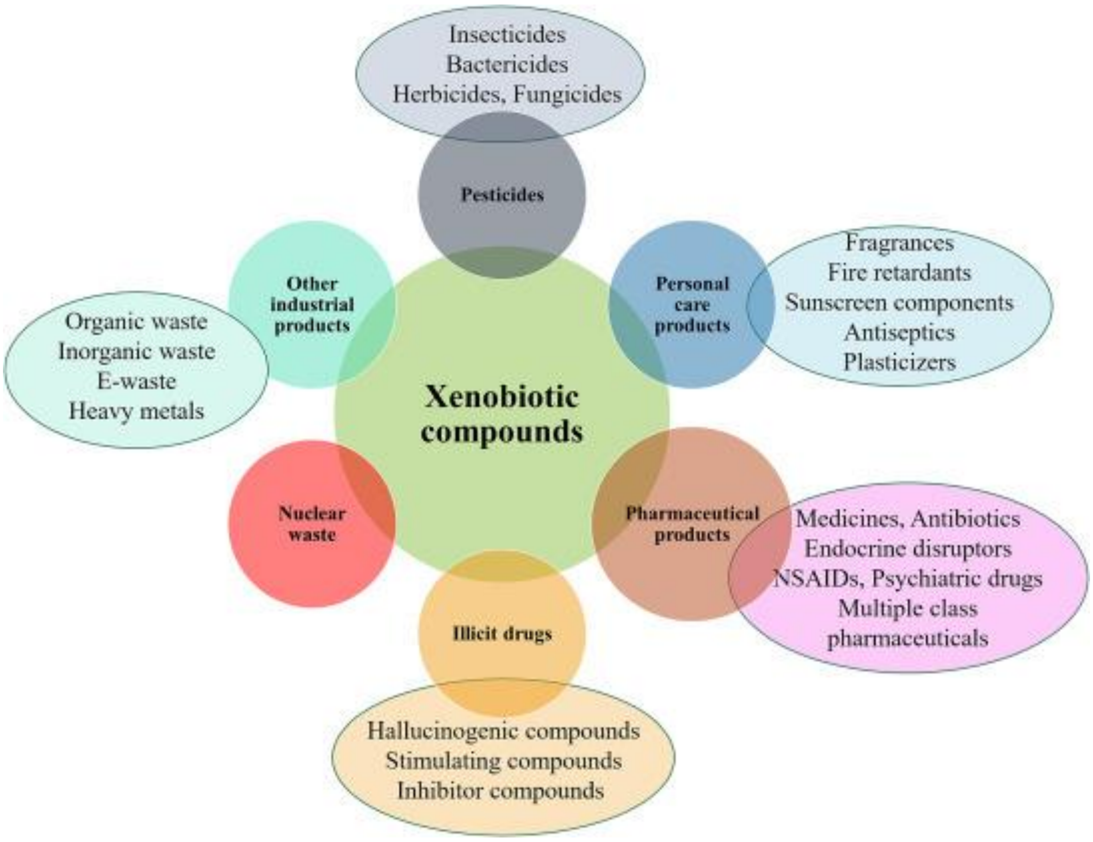

Figure 4. Major sources of xenobiotics in the environment (Priya et al., 2024).

6.2.2 Environmental distribution

Once released into the environment, xenobiotics can be distributed across different environmental compartments through various processes:

a) Air transport and deposition:

- Volatile organic compounds (VOCs) can be transported over long distances in the atmosphere

- Particulate matter can adsorb organic contaminants and facilitate their transport

- Wet and dry deposition processes transfer atmospheric pollutants to soil and water bodies

b) Water solubility and runoff:

- Water-soluble xenobiotics can be easily transported through surface water and groundwater systems

- Runoff from agricultural fields and urban areas can carry dissolved and particle-bound contaminants to water bodies

c) Soil adsorption and leaching:

- Organic contaminants can adsorb to soil particles, particularly those with high organic matter content

- Leaching of contaminants through soil profiles can lead to groundwater contamination

6.2.3 Fate processes

The fate of xenobiotics in the environment is governed by various physical, chemical, and biological processes that determine their persistence, transformation, and ultimate disposition:

a) Photodegradation:

- Direct photolysis: absorption of light energy leading to bond cleavage

- Indirect photolysis: reaction with photochemically generated reactive species (e.g., hydroxyl radicals)

- Factors affecting photodegradation:

  - Light intensity and spectral distribution

  - Presence of photosensitizers or quenchers

  - Chemical structure of the xenobiotic

b) Hydrolysis:

- Reaction of xenobiotics with water molecules, often catalyzed by acids or bases

- Important for the breakdown of esters, amides, and other hydrolyzable functional groups

- Influenced by pH, temperature, and the presence of dissolved ions

c) Biodegradation:

- Microbial degradation of xenobiotics through various metabolic pathways

- Can lead to partial or complete mineralization of organic contaminants

- Factors affecting biodegradation:

  - Chemical structure and bioavailability of the xenobiotic

  - Environmental conditions (temperature, pH, oxygen availability)

  - Presence and activity of microbial populations

d) Bioaccumulation and biomagnification:

- Accumulation of lipophilic xenobiotics in the fatty tissues of organisms

- Biomagnification occurs when contaminant concentrations increase at higher trophic levels in the food chain

- Bioaccumulation factors (BAFs) and octanol-water partition coefficients (Kow) are used to predict the potential for bioaccumulation

6.2.4 Factors affecting environmental persistence

The persistence of xenobiotics in the environment is influenced by various factors:

a) Chemical structure:

- Presence of halogen atoms (e.g., chlorine, fluorine) often increases stability

- Branching and ring structures can reduce biodegradability

- Functional groups can affect reactivity and susceptibility to degradation

b) Environmental conditions:

- pH: influences hydrolysis rates and speciation of ionizable compounds

- Temperature: affects reaction rates and microbial activity

- Light availability: impacts photodegradation processes

- Redox conditions: influence transformation pathways and microbial metabolism

c) Microbial activity:

- Presence of adapted microbial communities capable of degrading specific xenobiotics

- Availability of nutrients and co-substrates to support microbial growth

- Environmental factors affecting microbial activity (e.g., moisture, oxygen availability)

6.3 Absorption and translocation in plants

Plants can absorb xenobiotics from their surrounding environment through various pathways, primarily through roots and leaves. The extent of absorption and subsequent translocation within the plant depends on the properties of the xenobiotic and the plant species.

6.3.1 Root uptake mechanisms

Root uptake is a primary route for the absorption of xenobiotics from contaminated soil and water. Several mechanisms are involved in this process:

a) Passive diffusion:

- Lipophilic compounds can diffuse across cell membranes following concentration gradients
- Governed by Fick's law of diffusion
- Importance of the octanol-water partition coefficient (Kow) in predicting passive uptake

b) Carrier-mediated transport:

- Involves specific membrane proteins (transporters) that facilitate the movement of xenobiotics across cell membranes
- Can be active (requiring energy) or passive (following concentration gradients)

- Examples include:

- ABC transporters
- MATE transporters
- Organic anion transporting polypeptides (OATPs)

c) Factors affecting root uptake:

- ✓ Lipophilicity: compounds with moderate lipophilicity (log Kow between 0.5 and 3) are generally most easily absorbed
- ✓ Molecular size: smaller molecules are typically more readily absorbed
- ✓ Ionization state: neutral species are generally more easily absorbed than charged species
- ✓ Root surface area and morphology
- ✓ Soil properties (pH, organic matter content, clay content)
- ✓ Rhizosphere processes (e.g., root exudates, microbial activity)

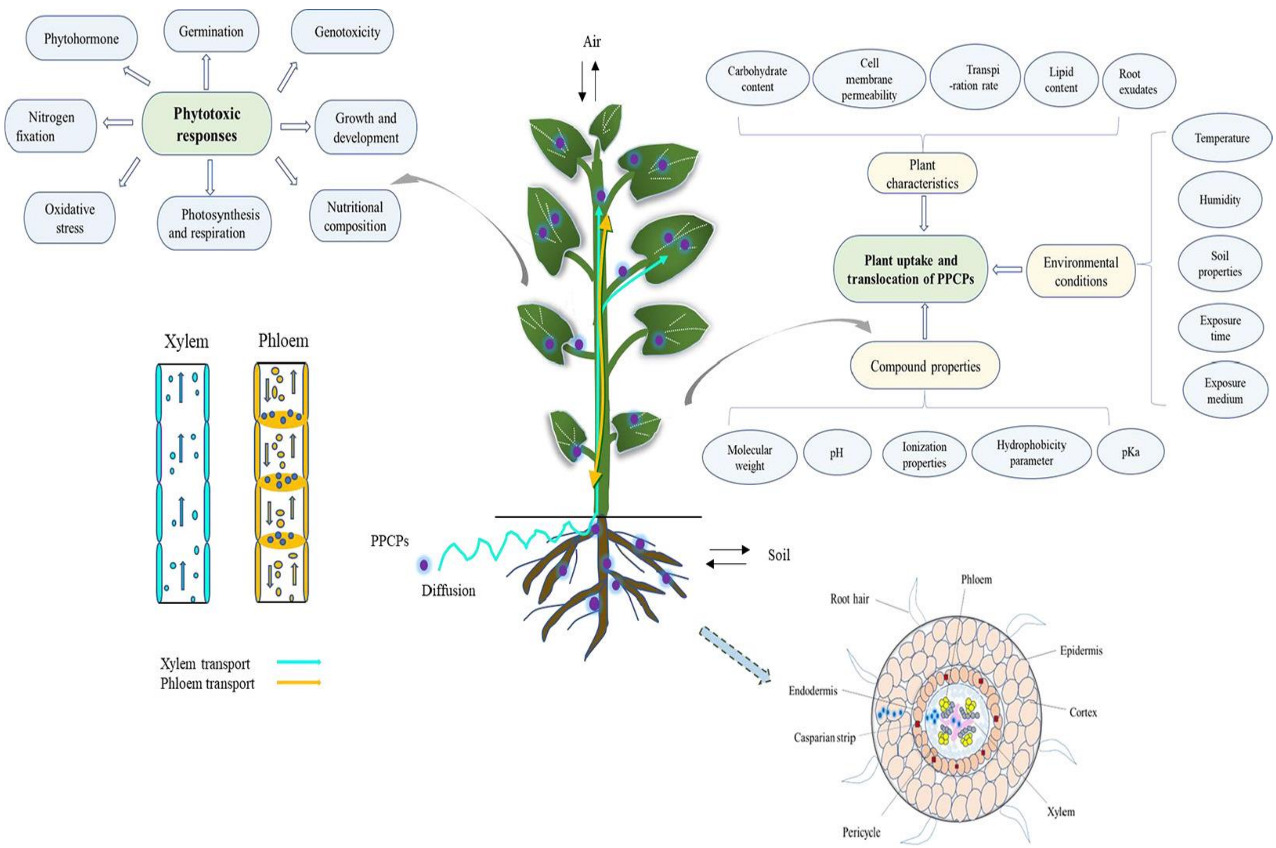

Figure 5. Schematic representation of root uptake mechanisms, accumulation, transport, metabolism and phytotoxic effects of pharmaceuticals and personal care products within plants (Wei et al., 2023).

6.3.2 Foliar absorption

Foliar absorption is an important route for the uptake of airborne xenobiotics and those applied as foliar sprays (e.g., pesticides). Two main pathways are involved:

a) Cuticular penetration:

- Diffusion through the waxy cuticle covering leaf surfaces
- Influenced by:
- Cuticle thickness and composition
- Environmental conditions (temperature, humidity)
- Presence of adjuvants in foliar-applied formulations

b) Stomatal uptake:

- Entry through open stomata (leaf pores)
- More significant for gases and volatile organic compounds

- Affected by:

- Stomatal density and aperture
- Environmental factors influencing stomatal opening (light, CO_2 concentration, water availability)

6.3.3 Translocation pathways

Once absorbed, xenobiotics can be translocated within the plant through two main vascular systems:

a) Xylem transport:

- Primarily responsible for upward movement of water and solutes from roots to shoots
- Driven by transpiration pull and root pressure
- Important for the translocation of root-absorbed xenobiotics

b) Phloem mobility:

- Bidirectional transport of organic compounds throughout the plant
- Follows source-to-sink relationships
- Significant for the redistribution of xenobiotics within the plant

6.3.4 Factors influencing translocation

The extent and pattern of xenobiotic translocation within plants are influenced by several factors:

a) Chemical properties:

- Octanol-water partition coefficient (Kow): affects the balance between xylem and phloem transport
- pKa: influences the ionization state and membrane permeability
- Molecular size and polarity

b) Plant species and growth stage:

- Variations in vascular anatomy and transport processes among species
- Changes in source-sink relationships during plant development
- Differences in metabolism and compartmentalization capabilities

c) Environmental conditions:

- Temperature: affects transpiration rates and metabolic processes
- Light intensity: influences photosynthesis and phloem transport
- Water availability: impacts xylem flow and overall plant water status

6.4 Biotransformation and conjugation processes

Plants have evolved various mechanisms to detoxify and metabolize xenobiotics, often referred to as the "green liver" concept. These processes involve a series of enzymatic reactions that modify the chemical structure of xenobiotics, potentially reducing their toxicity and facilitating their sequestration or elimination.

6.4.1 Phase I reactions

Phase I reactions involve the introduction or modification of functional groups on the xenobiotic molecule, often making it more polar and reactive. The main types of Phase I reactions include:

a) Oxidation:

- Primarily catalyzed by cytochrome P450 monooxygenases (CYPs)
- Common reactions include hydroxylation, epoxidation, and N-dealkylation
- CYPs are diverse and can metabolize a wide range of substrates

b) Reduction:

- Less common than oxidation reactions
- Can be important for certain classes of xenobiotics (e.g., nitro compounds)
- Often catalyzed by NADPH-dependent reductases

c) Hydrolysis:

- Cleavage of ester, amide, or other hydrolyzable bonds
- Catalyzed by various esterases and amidases

6.4.2 Phase II conjugation reactions

Phase II reactions involve the conjugation of xenobiotics or their Phase I metabolites with endogenous molecules, typically increasing their water solubility and facilitating their sequestration or elimination. Major Phase II reactions include:

a) Glutathione conjugation:

Glutathione S-transferases (GSTs) catalyze the conjugation of glutathione to electrophilic xenobiotics or their metabolites. This process is crucial for the detoxification of many herbicides and other organic pollutants.

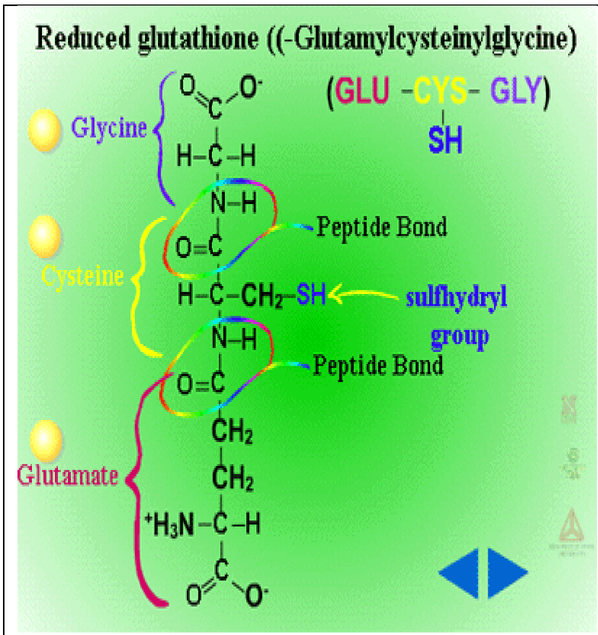

Fig. 19: Glutathione (γ-glutamylcysteinyl-ß-glycine)

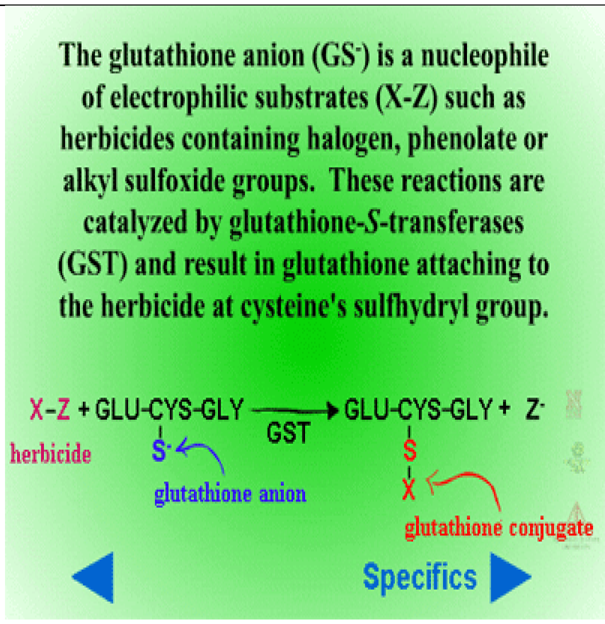

Fig. 20: Glutathione conjugation with herbicides (X) containing halogen, phenolate or alkyl sulfoxide groups (Z)

Figure 6. Glutathione conjugation reaction catalyzed by GST (URL: https://passel2.unl.edu/view/lesson/2aee31ac6c74/8)

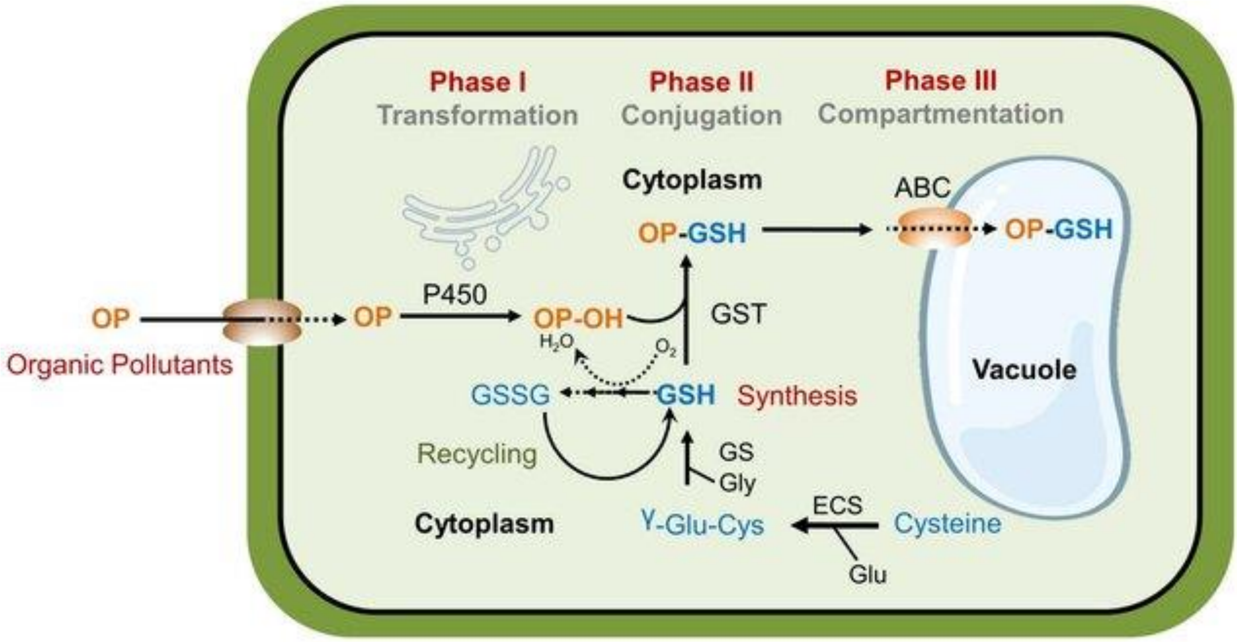

Figure 7. Mechanisms of organic pollutant detoxification in plants (Ahammed and Li, 2022).

Plant GSTs are encoded by large gene families, with 55 GST genes identified in Arabidopsis thaliana (Dixon and Edwards, 2010). The expression of many GST genes is induced by xenobiotic stress, highlighting their importance in plant defense mechanisms.

b) Glucose conjugation:

UDP-glucosyltransferases catalyze the addition of glucose to xenobiotics, forming O-glucosides or N-glucosides. This process is particularly important for the detoxification of phenolic compounds and certain hormones.

c) Malonate conjugation:

Malonylation is another important conjugation reaction in plants, often occurring after glucosylation. Malonate conjugates are generally more stable than glucose conjugates and are frequently found as end products of xenobiotic metabolism in plants.

d) Amino acid conjugation:

Some xenobiotics or their metabolites can be conjugated with amino acids, particularly aspartate and glutamate. This process is less common than other conjugation reactions but plays a role in the metabolism of certain plant hormones and some xenobiotics.

Enzymes involved in xenobiotic metabolism:

a) Glutathione S-transferases (GSTs):

As mentioned earlier, GSTs play a crucial role in Phase II metabolism. They are divided into several classes, each with distinct substrate specificities and functions.

b) UDP-glucosyltransferases:

These enzymes catalyze the transfer of glucose from UDP-glucose to various substrates, including xenobiotics. They are involved in the detoxification of many phenolic compounds and some herbicides.

c) Carboxylesterases:

These enzymes catalyze the hydrolysis of carboxylic esters and are important in the metabolism of certain insecticides and other xenobiotics containing ester bonds.

Compartmentalization of metabolites:

The final step in xenobiotic detoxification often involves the compartmentalization of conjugated metabolites, preventing them from interfering with cellular processes.

a) Vacuolar sequestration:

Many conjugated xenobiotics are transported into the vacuole, where they are isolated from the cytoplasm. This process involves specific transporters, such as ATP-binding cassette (ABC) transporters.

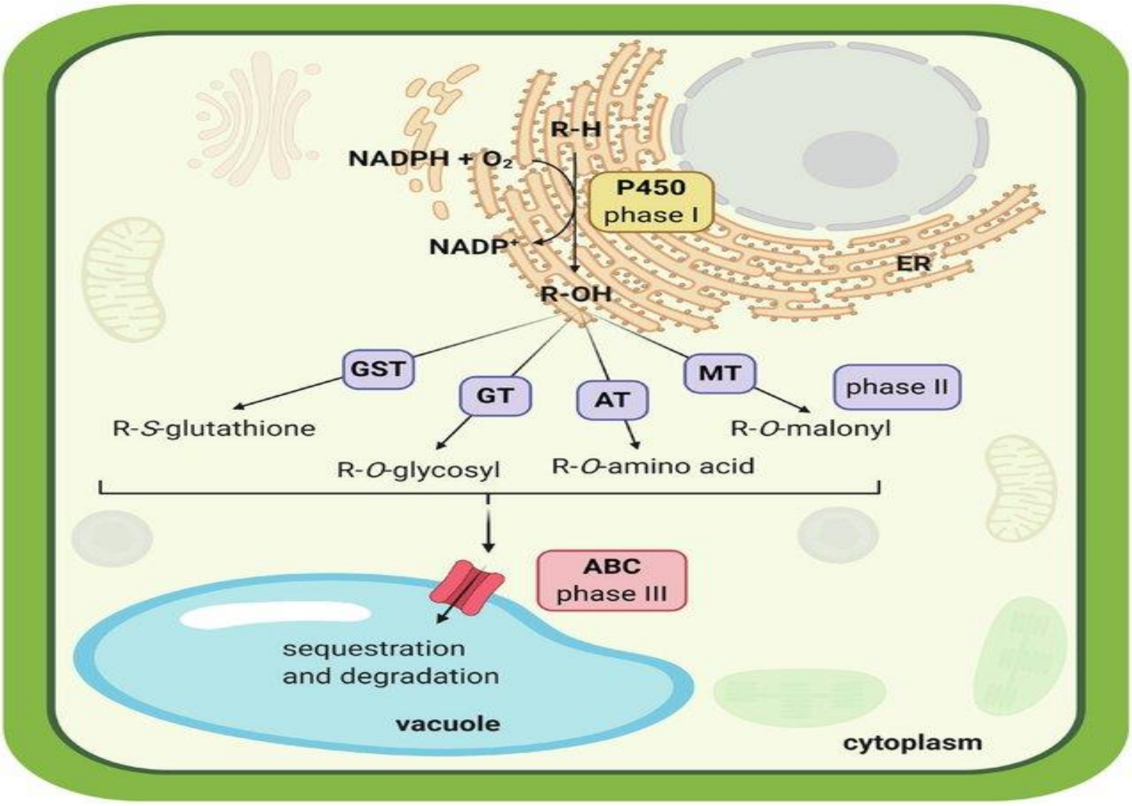

Figure 8. Summary of herbicide metabolism in a plant cell. Herbicides are normally taken through the three phases of metabolism as they are detoxified by plant cells. Typically, phase I introduces small functional groups on the structure of the active ingredient, phase II attaches a number of water-soluble metabolites via the action of several types of transferases, and phase III moves the conjugated metabolites to the vacuole (or the cell wall) for compartmentalization and further degradation. Active transport sometimes requires ABC transporters (or other transporter types) to move the herbicide metabolites across membranes. P450=cytochrome P450 monooxygenase, GST=glutathione-S-transferase, GT=glycosyl transferase, AT=amino acid transferase, MT=malonyl transferase, ABC=ATP-binding cassette, ER=Endoplasmic reticulum (Rigon et al., 2020).

b) Cell wall binding:

Some xenobiotic metabolites, particularly those derived from phenolic compounds, can be bound to cell wall components, effectively removing them from the cellular environment.

6.5 Effects on plant biochemistry and physiology

Organic contaminants can have profound effects on plant biochemistry and physiology, even at sublethal concentrations. These effects can manifest in various ways, depending on the nature of the contaminant and the plant species.

Membrane disruption and altered permeability:

Many organic contaminants, particularly lipophilic compounds, can partition into cellular membranes, altering their fluidity and permeability. This can lead to the disruption of membrane-bound processes and the leakage of cellular contents.

Interference with energy metabolism:

a) Inhibition of ATP synthesis:

Some xenobiotics can directly inhibit enzymes involved in ATP production, such as ATP synthase. For example, certain organotin compounds have been shown to inhibit ATP synthase in chloroplasts and mitochondria (Fotografiou and Economou-Amilli, 2009).

b) Uncoupling of oxidative phosphorylation:

Some organic contaminants, known as uncouplers, can dissipate the proton gradient across mitochondrial membranes, uncoupling electron transport from ATP synthesis. This leads to a decrease in ATP production and an increase in heat generation.

Oxidative stress induction:

Many xenobiotics can induce oxidative stress in plants by promoting the formation of reactive oxygen species (ROS) or by interfering with antioxidant systems. This can lead to damage to lipids, proteins, and nucleic acids.

Hormone imbalances and disruption of signaling pathways:

Some organic contaminants can mimic plant hormones or interfere with hormone synthesis, transport, or signaling. For example, certain phenoxy herbicides act as auxin mimics, leading to uncontrolled growth and eventual plant death.

Inhibition of key enzymes:

a) Acetolactate synthase (ALS):

ALS inhibitors, such as sulfonylurea and imidazolinone herbicides, block the biosynthesis of branched-chain amino acids, leading to plant death.

b) Acetyl-CoA carboxylase (ACCase):

ACCase inhibitors, including many grass-specific herbicides, interfere with fatty acid biosynthesis, causing membrane disruption and growth inhibition.

c) 5-enolpyruvylshikimate-3-phosphate (EPSP) synthase:

Glyphosate, one of the most widely used herbicides, inhibits EPSP synthase, disrupting the shikimate pathway and the biosynthesis of aromatic amino acids.

Alterations in nutrient uptake and assimilation:

Organic contaminants can interfere with nutrient uptake and assimilation processes in plants. For example, some herbicides can inhibit nitrate reductase, affecting nitrogen metabolism.

Impacts on protein synthesis and gene expression:

Xenobiotics can affect protein synthesis and gene expression through various mechanisms, including direct interactions with ribosomes, interference with transcription factors, or induction of stress response genes.

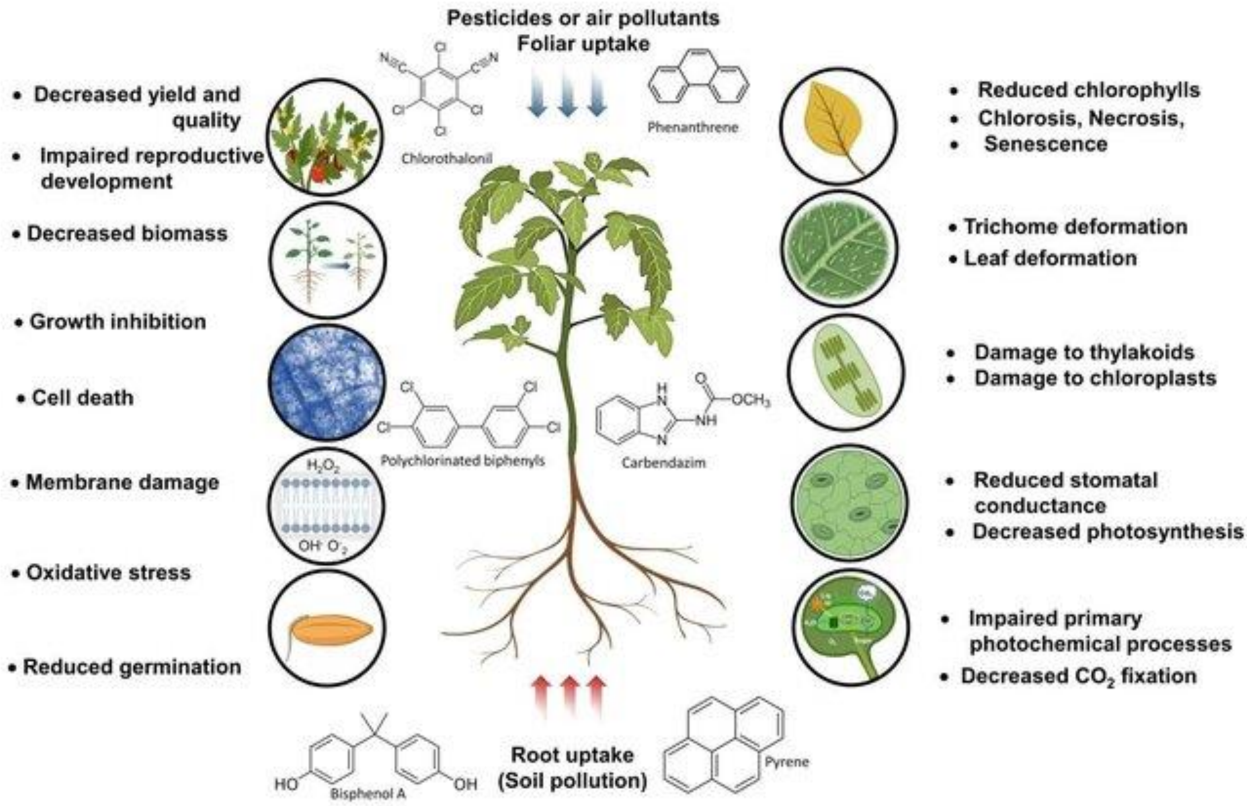

Figure 9. Deleterious effects of organic pollutants on plants and associated phytotoxicity (Ahammed and Li, 2022).

6.6 Herbicides: modes of action and plant responses

Photosystem II inhibitors (e.g., atrazine, diuron):

These herbicides bind to the QB binding site on the D1 protein of photosystem II, blocking electron transport. This leads to the generation of reactive oxygen species and ultimately to membrane damage and plant death.

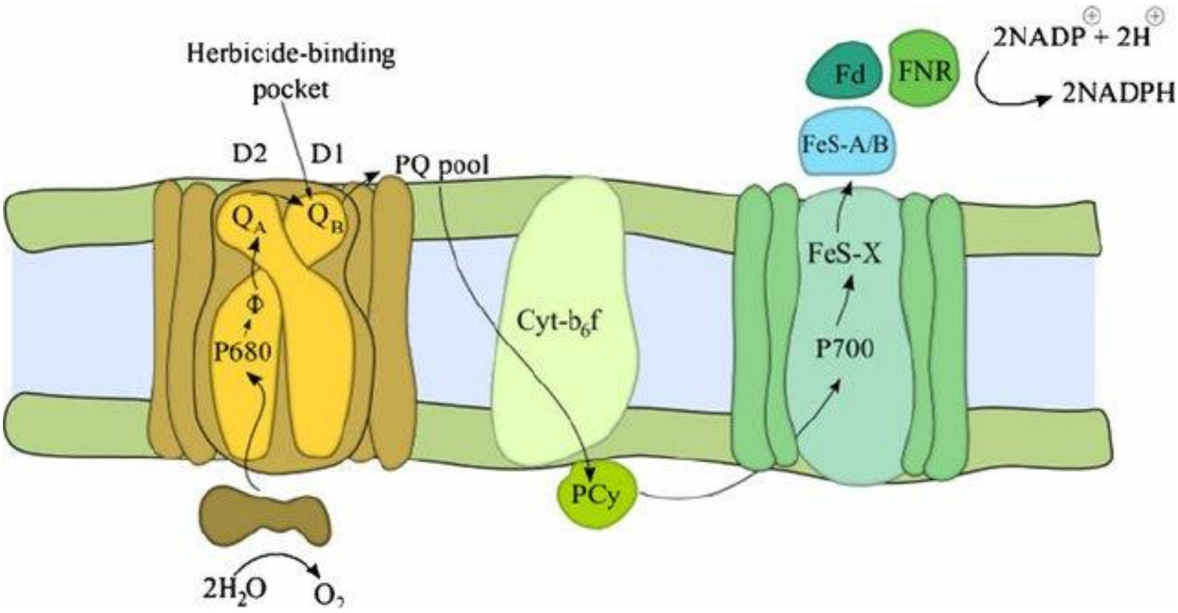

Figure 10. Herbicides, mechanism of action of Photosystem II inhibitors (Buonasera et al., 2011). The light-induced electron transport chain in the eukaryotic photosynthetic apparatus. The process starts at photosystem II (PSII), containing the chlorophyll P680 reaction center: here, water is split into molecular oxygen, electrons, and protons (H^+).

Auxin mimics (e.g., 2,4-D, dicamba):

These herbicides mimic the plant hormone auxin, leading to uncontrolled growth and eventual plant death. They are particularly effective against broadleaf weeds while leaving most grasses unaffected.

Amino acid synthesis inhibitors (e.g., glyphosate, imazethapyr):

As mentioned earlier, these herbicides inhibit key enzymes in amino acid biosynthesis pathways. Glyphosate inhibits EPSP synthase in the shikimate pathway, while imazethapyr inhibits acetolactate synthase in the biosynthesis of branched-chain amino acids.

Lipid synthesis inhibitors (e.g., fenoxaprop, sethoxydim):

These herbicides inhibit acetyl-CoA carboxylase (ACCase), a key enzyme in fatty acid biosynthesis. They are particularly effective against grass species.

Cellulose biosynthesis inhibitors (e.g., dichlobenil):

These herbicides interfere with cellulose synthesis, affecting cell wall formation and plant growth.

Carotenoid biosynthesis inhibitors (e.g., clomazone):

By inhibiting carotenoid biosynthesis, these herbicides lead to photooxidative damage in newly formed tissues, causing bleaching and plant death.

Plant responses to herbicides:

a) Physiological and biochemical changes:

Herbicide exposure can lead to various physiological and biochemical changes in plants, including alterations in photosynthesis, respiration, and metabolic pathways.

b) Oxidative stress and antioxidant responses:

Many herbicides induce oxidative stress in plants. In response, plants activate antioxidant defense mechanisms, including increased production of antioxidant enzymes and metabolites.

c) Development of herbicide resistance mechanisms:

Plants can develop resistance to herbicides through various mechanisms, including target-site mutations, enhanced metabolism, reduced uptake or translocation, and sequestration.

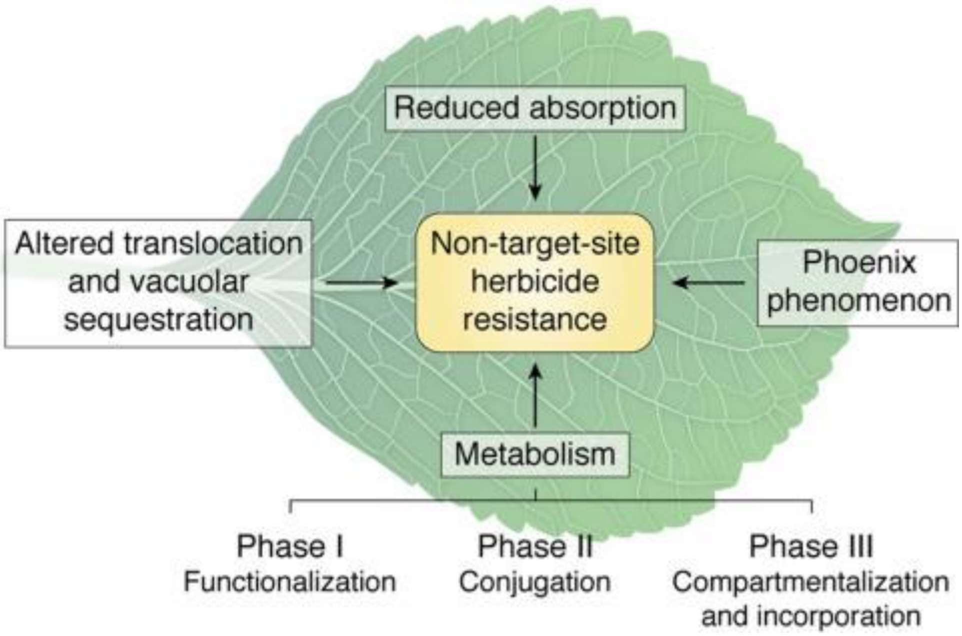

Figure 11. Major mechanisms of herbicide resistance in plants (Gaines et al., 2020). Summary of nontarget-site resistance (NTSR). Plants can evolve resistance to an herbicide by reducing its absorption, altering its translocation and/or sequestration, or developing a rapid necrosis of the foliage (phoenix phenomenon) or via degradation of the active ingredient through phases I, II, and III of metabolism.

6.7 Pesticides and their impact on non-target plants

While herbicides are designed to affect plants, other pesticides, such as insecticides and fungicides, can also have significant impacts on non-target plant species.

Direct phytotoxic effects of insecticides and fungicides:

Some insecticides and fungicides can cause direct damage to non-target plants. For example, copper-based fungicides can interfere with photosynthesis and cause oxidative stress in plants (Husak, 2015).

Indirect effects through:

a) Altered plant-pollinator interactions:

Insecticides can affect pollinator populations, indirectly impacting plant reproduction and community dynamics.

b) Impacts on beneficial soil microorganisms:

Pesticides can affect soil microbial communities, potentially disrupting symbiotic relationships between plants and microorganisms, such as mycorrhizal fungi.

c) Changes in plant community composition:

Selective pressure from pesticides can lead to shifts in plant community composition, potentially favoring tolerant or resistant species.

Sublethal effects on plant growth and development:

Even at concentrations that do not cause visible damage, pesticides can affect plant growth, development, and reproduction.

Bioaccumulation in non-target plants and implications for food webs:

Some pesticides can accumulate in plant tissues, potentially affecting herbivores and higher trophic levels in the food web.

Risk assessment approaches for non-target plant effects:

Evaluating the potential impacts of pesticides on non-target plants involves various approaches, including greenhouse studies, field trials, and ecological modeling.

6.8 Polycyclic aromatic hydrocarbons (PAHs) in the plant environment

PAHs are a class of organic pollutants of particular concern due to their persistence in the environment and potential toxicity.

Sources and formation of PAHs:

PAHs are primarily formed through incomplete combustion of organic matter. Major sources include industrial processes, vehicle emissions, and biomass burning.

Physical and chemical properties of PAHs:

PAHs are characterized by two or more fused aromatic rings. Their physical and chemical properties, such as water solubility and vapor pressure, vary with molecular weight and structure.

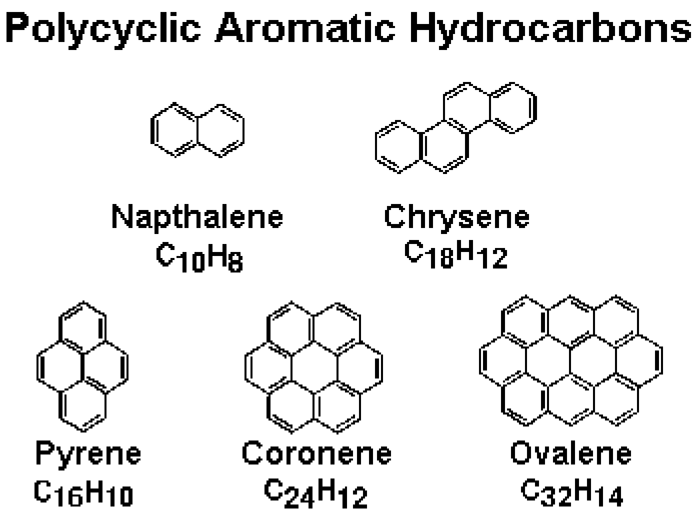

Figure 12. Structures of common PAHs found in the environment (URL: https://users.physics.unc.edu/~gcsloan/research/pah_info.html).

Environmental behavior and fate of PAHs:

In the environment, PAHs can undergo various processes, including volatilization, photodegradation, and microbial degradation. Their persistence generally increases with molecular weight.

Plant uptake and accumulation of PAHs:

a) Root uptake vs. foliar deposition:

Plants can take up PAHs from contaminated soil through their roots, but a significant portion of PAH accumulation in plants often occurs through foliar deposition of atmospheric PAHs.

b) Factors affecting bioavailability:

The bioavailability of PAHs to plants is influenced by various factors, including soil properties, PAH physicochemical characteristics, and plant species.

Metabolism and detoxification of PAHs in plants:

a) Cytochrome P450-mediated oxidation:

As with other xenobiotics, cytochrome P450 enzymes play a crucial role in the initial oxidation of PAHs in plants.

b) Conjugation and sequestration:

Oxidized PAH metabolites can undergo conjugation reactions, similar to those described earlier for other xenobiotics.

Effects of PAHs on plant physiology:

a) Phytotoxicity and growth inhibition:

PAHs can cause various phytotoxic effects, including reduced germination, stunted growth, and chlorosis.

b) Oxidative stress induction:

PAHs and their metabolites can induce oxidative stress in plants, leading to cellular damage.

c) Genotoxic effects:

Some PAHs and their metabolites can cause DNA damage in plants, potentially leading to mutations and other genetic effects.

PAHs in the food chain and human health implications:

The accumulation of PAHs in plants can lead to their entry into the food chain, potentially affecting human health.

Phytoremediation potential for PAH-contaminated soils:

Some plant species have shown potential for the phytoremediation of PAH-contaminated soils, either through direct uptake and metabolism or by enhancing microbial degradation in the rhizosphere.

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Course 7.

Atmospheric Pollutants and Their Effects

7.1 Major atmospheric pollutants affecting plants

Air pollution has become a significant environmental concern, with far-reaching impacts on plant life and ecosystems.

7.1.1 Overview of air pollution and its impact on vegetation

Air pollution refers to the presence of substances in the atmosphere that can have harmful effects on living organisms and the environment. Plants, being stationary and dependent on atmospheric gases for photosynthesis, are particularly vulnerable to air pollution. The impacts of air pollutants on vegetation can range from subtle physiological changes to visible injury and ecosystem-level alterations.

7.1.2 Primary vs. secondary air pollutants

Atmospheric pollutants can be categorized as primary or secondary pollutants:

a) Primary pollutants: These are emitted directly from sources into the atmosphere. Examples include:

- Sulfur dioxide (SO_2) from fossil fuel combustion
- Nitrogen oxides (NO_x) from vehicle exhaust and industrial processes
- Particulate matter (PM) from dust, smoke, and industrial emissions

b) Secondary pollutants: These are formed in the atmosphere through chemical reactions involving primary pollutants and other atmospheric constituents. Examples include:

- Ozone (O_3) formed from the reaction of NO_x and volatile organic compounds (VOCs) in the presence of sunlight
- Peroxyacetyl nitrate (PAN) produced in photochemical smog
- Sulfuric acid (H_2SO_4) formed from the oxidation of SO_2

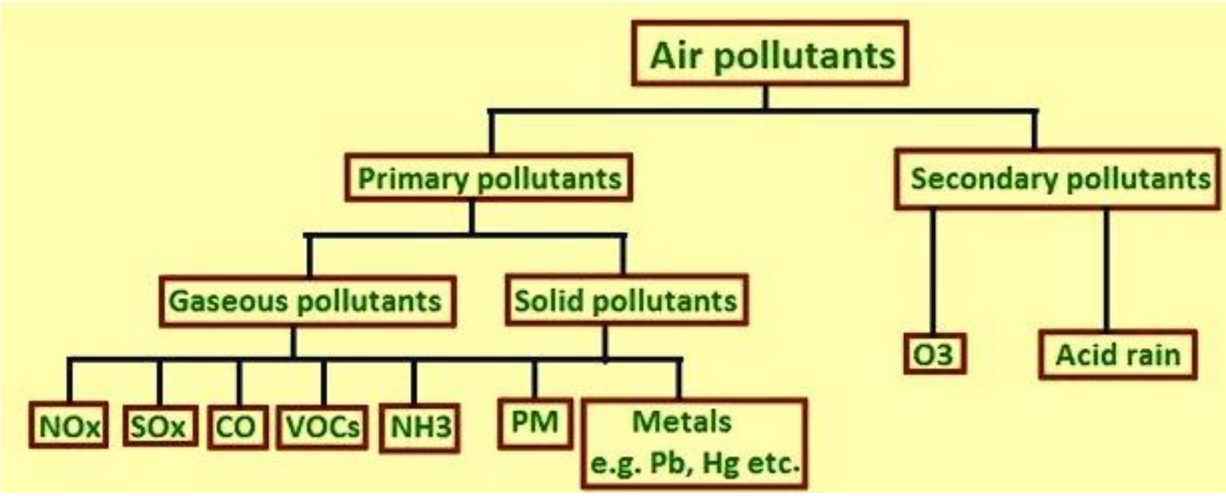

Figure 1. Schematic representation of primary and secondary air pollutants. Primary air pollutants are emitted directly into the air from sources. They can have effects both directly and as precursors of secondary air pollutants (URL: https://www.ispatguru.com/air-pollution-and-air-pollutants/).

7.1.3 Criteria air pollutants

The U.S. Environmental Protection Agency (EPA) has identified six criteria air pollutants that are regulated due to their widespread occurrence and potential to cause harm to human health and the environment. These pollutants are of particular concern for plant health:

a) Ozone (O3):

- A secondary pollutant formed through photochemical reactions
- Major component of urban smog
- Causes significant damage to vegetation, affecting crop yields and forest health

b) Nitrogen oxides (NOx):

- Primarily emitted as nitric oxide (NO) and nitrogen dioxide (NO2)
- Contribute to ozone formation and acid rain
- Can have both positive (fertilizing) and negative effects on plants

c) Sulfur dioxide (SO2):

- Primarily emitted from fossil fuel combustion and industrial processes
- Major contributor to acid rain
- Causes direct injury to plant foliage and affects soil chemistry

d) Particulate matter (PM):

- Classified based on size: PM10 (≤10 μm) and PM2.5 (≤2.5 μm)
- Sources include dust, smoke, and industrial emissions
- Can affect plant surfaces and indirectly impact soil properties

e) Carbon monoxide (CO):

- Produced by incomplete combustion of carbon-containing fuels
- Generally less directly harmful to plants compared to other criteria pollutants
- Can indirectly affect plants by influencing atmospheric chemistry

f) Lead (Pb):

- Historically emitted from leaded gasoline, now primarily from industrial sources
- Can accumulate in soils and be taken up by plants
- Toxic to plants at high concentrations

7.1.4 Other significant pollutants

In addition to the criteria air pollutants, several other atmospheric contaminants can significantly impact plant health:

a) Peroxyacetyl nitrate (PAN):

- A component of photochemical smog
- Highly phytotoxic, causing distinctive stippling on leaves

b) Volatile organic compounds (VOCs):

- Emitted from both natural (e.g., vegetation) and anthropogenic sources
- Contribute to ozone formation
- Some VOCs can directly affect plant physiology

c) Fluorides:

- Emitted from aluminum smelters, phosphate fertilizer plants, and brick kilns
- Can cause severe foliar injury and accumulate in plant tissues

d) Heavy metals in airborne particles:

- Include mercury (Hg), cadmium (Cd), and arsenic (As)
- Can be deposited on plant surfaces or taken up through roots
- Potential for bioaccumulation and toxicity

7.2 Ozone: formation, exposure, and plant responses

Tropospheric ozone (O3) is one of the most significant air pollutants affecting plants globally. Its formation, distribution, and impacts on vegetation are complex and multifaceted.

7.2.1 Tropospheric ozone formation

Ozone in the lower atmosphere (troposphere) is a secondary pollutant formed through photochemical reactions involving nitrogen oxides (NOx) and volatile organic compounds (VOCs) in the presence of sunlight.

The basic reactions involved in tropospheric ozone formation are:

1. NO2 + sunlight → NO + O

2. O + O2 → O3

3. O3 + NO → NO2 + O2

VOCs act as catalysts in this process, promoting the conversion of NO back to NO2 without consuming ozone, thus allowing ozone to accumulate.

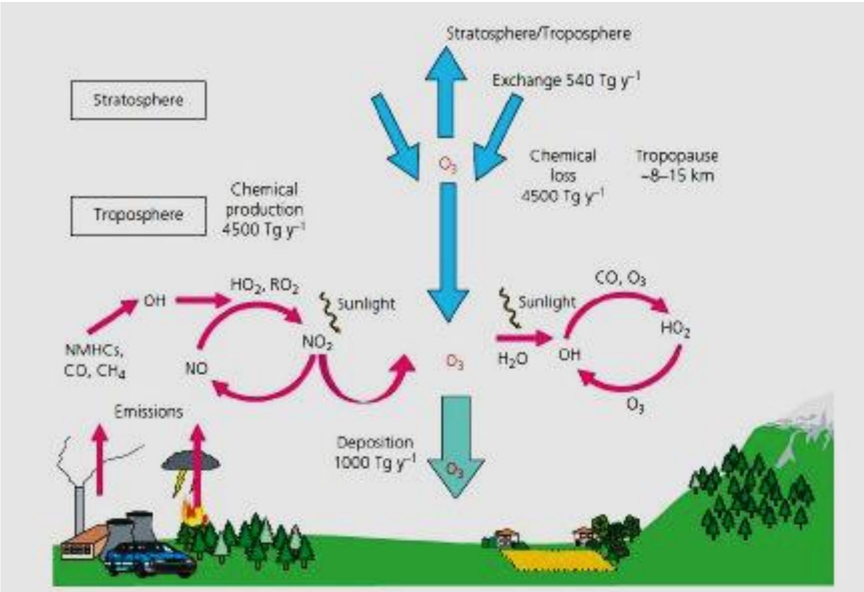

Figure 2. Schematic of tropospheric ozone formation (Kortsalioudakis et al., 2012).

Urban vs. rural ozone patterns:

- Urban areas: Higher NOx concentrations often lead to ozone depletion near emission sources

- Rural areas: Lower NOx levels allow for ozone accumulation, often resulting in higher ozone concentrations downwind of urban centers

7.2.2 Factors affecting ozone exposure

Several factors influence the exposure of plants to ozone:

a) Meteorological conditions:

- Temperature: Higher temperatures generally promote ozone formation
- Sunlight intensity: Crucial for photochemical reactions
- Wind patterns: Affect the transport and distribution of ozone and its precursors

b) Diurnal and seasonal variations:

- Daily cycle: Ozone concentrations typically peak in the afternoon
- Seasonal patterns: Highest levels often occur during summer months in temperate regions

c) Topography:

- Valley and basin formations can trap ozone and its precursors
- Elevation affects ozone concentrations and plant responses

7.2.3 Ozone uptake by plants

The impact of ozone on plants is determined not just by ambient concentrations but by the amount of ozone that enters the plant:

a) Stomatal conductance:

- Ozone primarily enters plants through stomata
- Factors affecting stomatal opening (light, humidity, CO2 concentration) influence ozone uptake

b) Flux-based approaches:

- Consider both ambient ozone concentration and stomatal conductance
- Provide a more accurate assessment of potential plant damage than concentration-based metrics alone

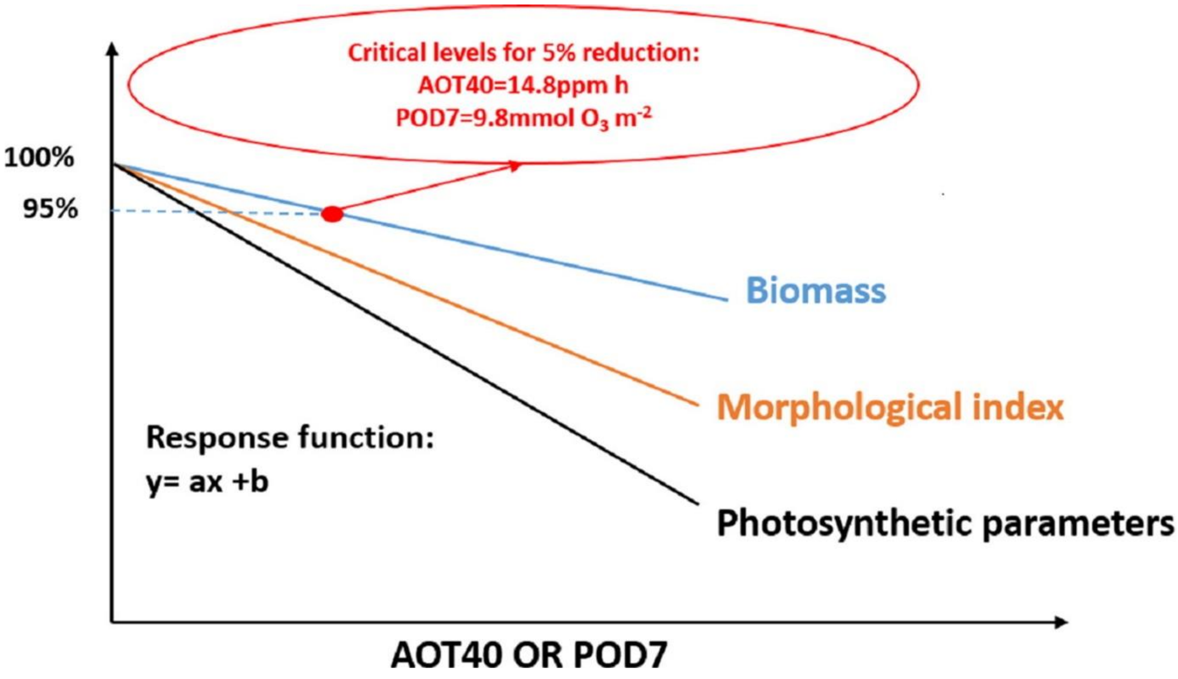

Figure 3. Ozone exposure-and flux-based response relationships with photosynthesis, leaf morphology and biomass in two poplar clones (Shang et al., 2017).

7.2.4 Plant responses to ozone

Ozone exposure can lead to a wide range of responses in plants, from cellular-level changes to ecosystem-wide impacts:

a) Visible injury symptoms:

- Chlorosis: Yellowing of leaves due to chlorophyll degradation
- Necrosis: Death of plant tissue, often appearing as brown or black lesions
- Stippling: Small, darkly pigmented areas on leaf surfaces

b) Reduced photosynthetic capacity:

- Damage to chloroplast membranes and enzymes
- Decreased Rubisco activity and content
- Altered carbon allocation patterns

c) Accelerated senescence:

- Premature leaf aging and abscission
- Changes in hormonal balance, particularly increased ethylene production

d) Growth and yield reductions:

- Decreased biomass accumulation
- Reduced crop yields and quality

- Alterations in root-to-shoot ratios

7.2.5 Biochemical and molecular responses

At the cellular and molecular levels, ozone exposure triggers a complex series of responses:

a) Oxidative stress and antioxidant systems:

- Generation of reactive oxygen species (ROS)
- Activation of antioxidant enzymes (e.g., superoxide dismutase, catalase)
- Accumulation of non-enzymatic antioxidants (e.g., ascorbate, glutathione)

b) Ethylene signaling and programmed cell death:

- Increased ethylene biosynthesis
- Activation of programmed cell death pathways
- Role in the development of visible injury symptoms

c) Alterations in gene expression:

- Upregulation of defense-related genes
- Changes in expression of photosynthesis-related genes
- Activation of signaling cascades (e.g., MAPK pathways)

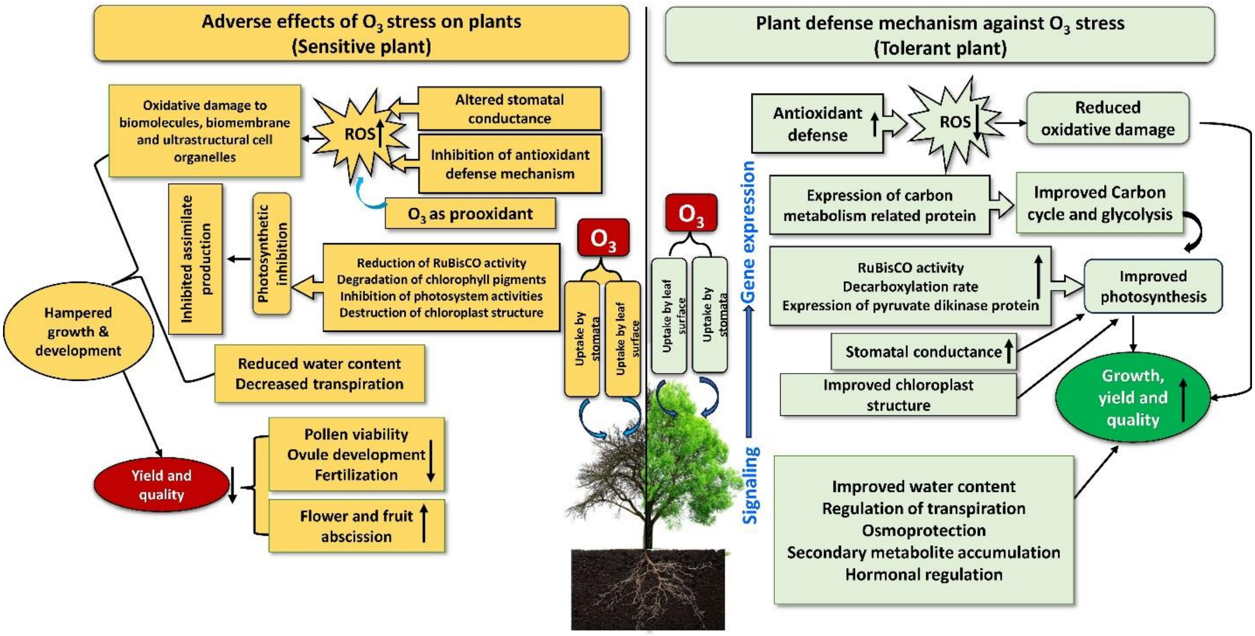

Figure 4. A schematic illustration of the response of sensitive and tolerant plants to ozone. The upward arrow inside boxes indicates increase and downward arrow indicates decrease (Nowroz et al., 2024).

7.2.6 Ozone sensitivity variations among plant species and cultivars

Plant species and even cultivars within a species can vary widely in their sensitivity to ozone:

a) Sensitive species:

- Many crops (e.g., soybean, wheat, potato)
- Certain tree species (e.g., aspen, birch)

b) Tolerant species:

- Some crops (e.g., barley, broccoli)
- Certain urban tree species (e.g., ginkgo, honey locust)

Factors influencing ozone sensitivity:

- Leaf characteristics (e.g., stomatal conductance, leaf thickness)

- Antioxidant capacity

- Growth rate and carbon allocation patterns

- Phenological stage at time of exposure

7.2.7 Ozone impacts on ecosystem level processes

Beyond individual plant responses, ozone can have significant impacts on ecosystem functioning:

a) Changes in species composition:

- Shift towards more ozone-tolerant species
- Potential loss of biodiversity

b) Alterations in biogeochemical cycles:

- Changes in carbon sequestration
- Impacts on nitrogen cycling

c) Interactions with other environmental stressors:

- Climate change (e.g., elevated CO2, drought)
- Other air pollutants (e.g., nitrogen deposition)

d) Feedback to atmospheric processes:

- Changes in VOC emissions from vegetation
- Alterations in surface energy balance

7.3 Nitrogen oxides: sources and phytotoxicity

Nitrogen oxides (NOx), primarily consisting of nitric oxide (NO) and nitrogen dioxide (NO2), are important air pollutants with significant impacts on plant health and ecosystem functioning.

7.3.1 Sources of nitrogen oxides (NOx)

NOx are emitted from both natural and anthropogenic sources:

a) Fossil fuel combustion:

- Vehicle exhaust
- Power plants
- Industrial boilers

b) Biomass burning:

- Forest fires
- Agricultural burning
- Residential wood burning

c) Lightning:

- Natural source of NOx in the upper troposphere
- Contributes to background NOx levels

d) Soil emissions:

- Microbial nitrification and denitrification processes
- Enhanced by nitrogen fertilizer application

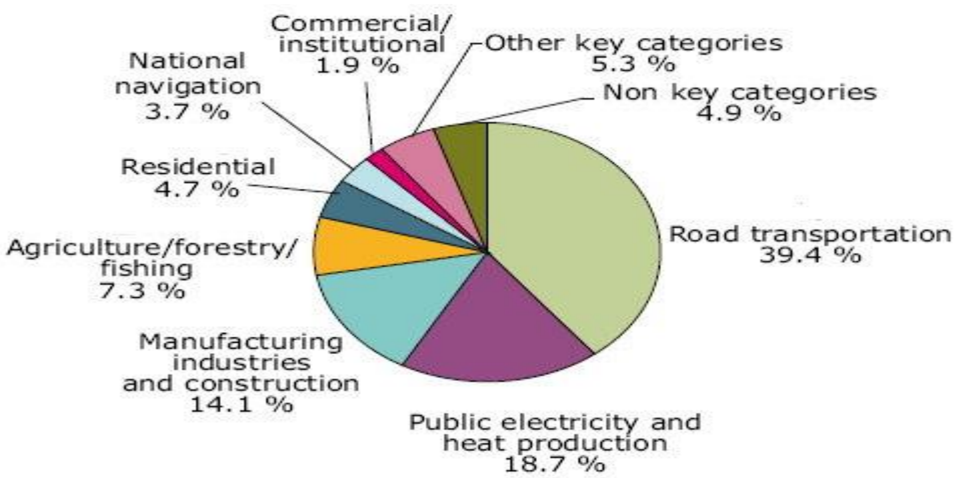

Figure 5. EU-27 emission sources of nitrogen oxides (NOx), 2006 (Popescu et al., 2010)

7.3.2 Chemistry of NOx in the atmosphere

The behavior and impacts of NOx in the atmosphere are influenced by various chemical reactions:

a) NO to NO2 conversion:

- ✓ $NO + O_3 \rightarrow NO_2 + O_2$
- ✓ $NO + RO_2 \rightarrow NO_2 + RO$ (where RO_2 is an organic peroxy radical)

b) Photolysis of NO2:

- ✓ NO_2 + sunlight $\rightarrow NO + O$
- ✓ $O + O_2 \rightarrow O_3$

c) Formation of nitric acid:

- ✓ $NO_2 + OH \rightarrow HNO_3$

d) Role in ozone formation:

- ✓ NOx acts as a catalyst in tropospheric ozone formation, as described in section 7.2.1

7.3.3 Direct effects of NOx on plants

While NOx are generally considered less phytotoxic than ozone or sulfur dioxide, they can still cause direct damage to plants:

a) Foliar injury and chlorosis:

- Accumulation of nitrite in leaves leading to chlorophyll degradation
- Development of interveinal chlorosis and necrotic lesions

b) Impacts on stomatal function:

- NO_2 can cause stomatal closure, reducing gas exchange
- Potential for increased water use efficiency in some cases

c) Alterations in nitrogen metabolism:

- Disruption of nitrate assimilation pathways
- Changes in amino acid composition

7.3.4 Indirect effects of NOx

The indirect effects of NOx on plants and ecosystems are often more significant than their direct phytotoxicity:

a) Contribution to acid rain formation:

- NOx react with water in the atmosphere to form nitric acid
- Leads to soil acidification and nutrient leaching

b) Eutrophication of ecosystems:

- Deposition of nitrogen compounds acts as a fertilizer
- Can lead to shifts in species composition favoring nitrophilous plants

c) Formation of secondary pollutants:

- Crucial role in tropospheric ozone formation
- Contribution to the formation of peroxyacetyl nitrate (PAN)

7.3.5 NOx as a source of nitrogen deposition

Atmospheric nitrogen deposition resulting from NOx emissions can have profound effects on ecosystems:

a) Impacts on nutrient cycling:

- Increased nitrogen availability in naturally nitrogen-limited ecosystems
- Potential for soil acidification and base cation leaching

b) Shifts in plant community composition:

- Favoring of nitrophilous species
- Potential loss of biodiversity, especially in sensitive habitats

c) Forest ecosystem responses:

- Initial growth stimulation in nitrogen-limited forests
- Potential for nitrogen saturation and decreased forest health over time

d) Impacts on agricultural systems:

- Both positive (fertilization effect) and negative (increased susceptibility to pests and diseases) impacts
- Interactions with crop management practices

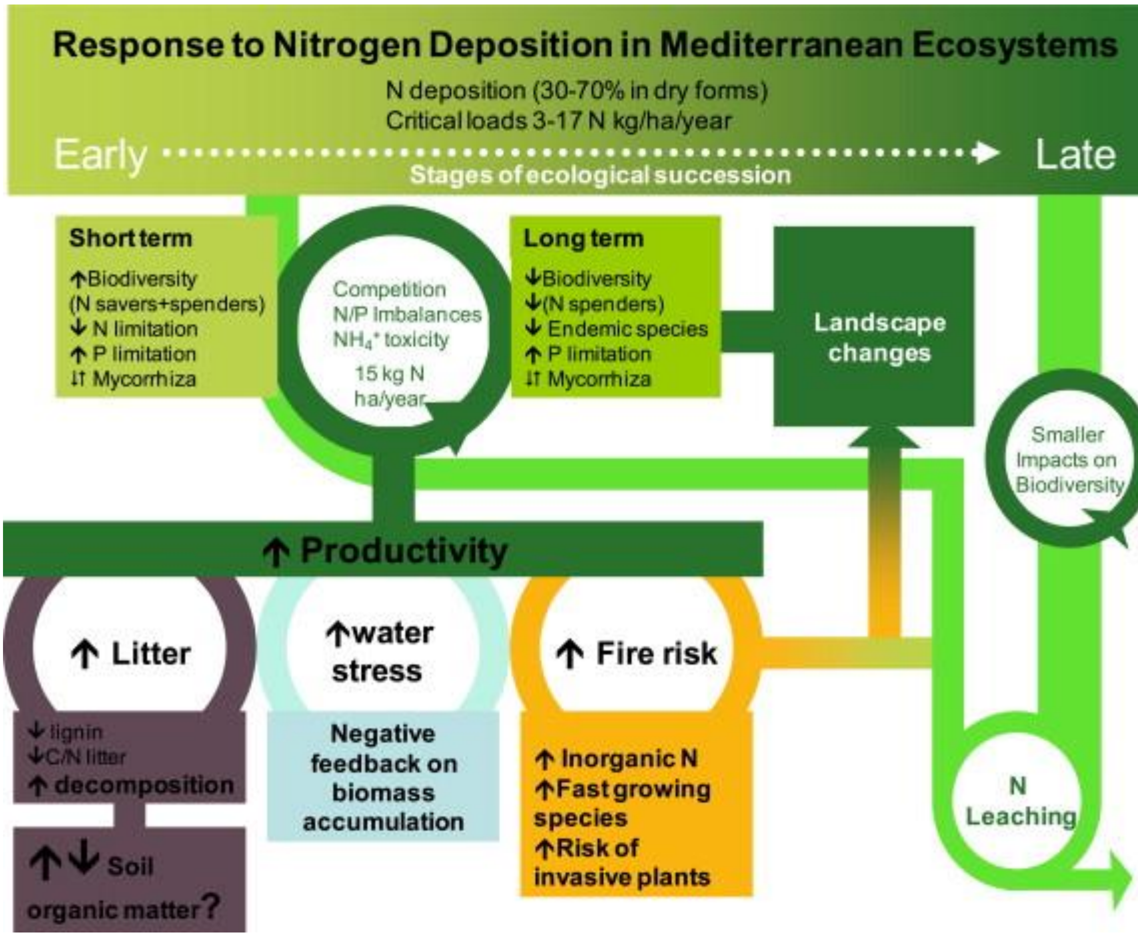

Figure 6. Nitrogen deposition effects on Mediterranean-type ecosystems (Ochoa-Hueso et al., 2011).

7.4 Sulfur dioxide: emissions and plant damage

Sulfur dioxide (SO2) has historically been one of the most significant air pollutants affecting plant life, particularly in industrialized regions. Although emissions have decreased in many developed countries due to regulatory efforts, SO2 remains a concern in many parts of the world.

7.4.1 Sources of sulfur dioxide (SO2)

SO2 is emitted from both natural and anthropogenic sources:

a) Coal and oil combustion:

- Power plants
- Industrial boilers
- Residential heating

b) Metal smelting:

- Copper, lead, and zinc smelting operations
- Processing of sulfur-containing ores

c) Volcanic emissions:

- Natural source of SO2
- Can cause significant local and regional air pollution events

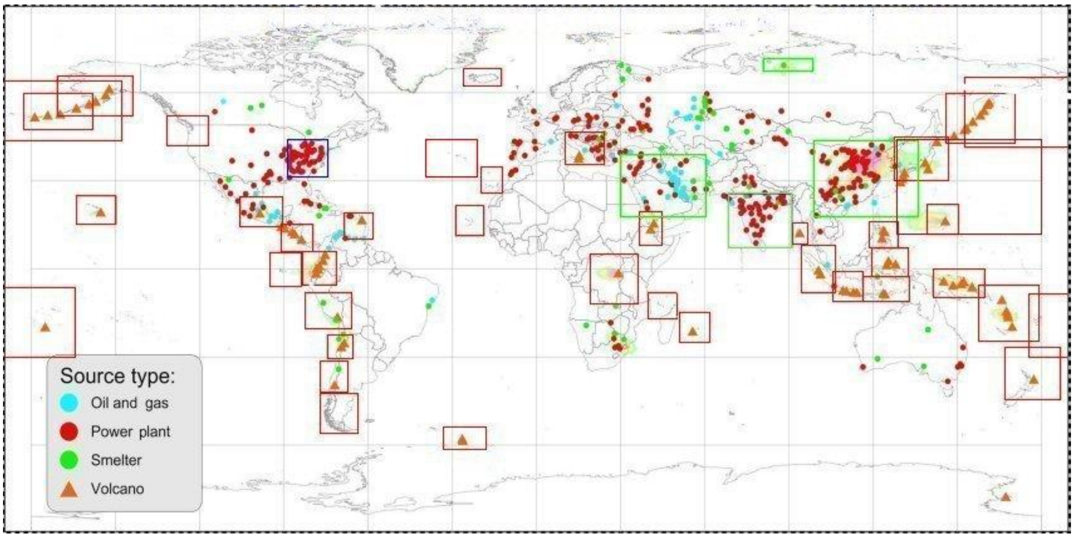

Figure 7. Global map of anthropogenic SO_2 emission sources (URL: https://so2.gsfc.nasa.gov/). SO_2 climatology from satellite instruments: Red = daily volcanic regions, green = daily pollution regions, blue = long-term pollution images.

7.4.2 Atmospheric chemistry of SO2

Once emitted, SO_2 undergoes various transformations in the atmosphere:

a) Oxidation to sulfuric acid:

- ✓ SO2 + OH → HOSO2
- ✓ HOSO2 + O2 → HO2 + SO3
- ✓ SO3 + H2O → H2SO4

b) Dry vs. wet deposition:

- Dry deposition: Direct absorption of SO2 gas by surfaces
- Wet deposition: Removal of SO2 and its oxidation products by precipitation

7.4.3 Plant uptake and metabolism of SO2

Plants can absorb SO2 directly from the atmosphere:

a) Stomatal absorption:

- Primary route of entry for SO_2 into plants
- Influenced by stomatal conductance and environmental conditions

b) Conversion to sulfite and sulfate:

- ✓ $SO_2 + H_2O \rightarrow H_2SO_3$ (sulfurous acid)
- ✓ $H_2SO_3 \rightarrow HSO_3^-$ (bisulfite) + H^+
- ✓ $HSO_3^- + 1/2\ O_2 \rightarrow SO_4^{2-}$ (sulfate) + H^+

7.4.4 Phytotoxic effects of SO2

SO_2 can cause a range of detrimental effects on plants:

a) Acute injury:

- Leaf necrosis and chlorosis
- Typically occurs at high concentrations or during short-term exposure events

b) Chronic effects:

- Reduced growth and yield
- Alterations in leaf anatomy and chlorophyll content
- Cumulative impacts from long-term, low-level exposure

c) Interactions with other pollutants:

- Synergistic effects with ozone, enhancing foliar injury
- Potential antagonistic effects with nitrogen oxides

7.4.5 Biochemical mechanisms of SO2 toxicity

At the cellular level, SO_2 toxicity is mediated through several mechanisms:

a) Disruption of photosynthesis:

- Inhibition of CO_2 fixation
- Damage to chloroplast membranes and thylakoid structure
- Reduction in chlorophyll content

b) Enzyme inhibition:

- Inactivation of key enzymes in carbon metabolism (e.g., ribulose-1,5-bisphosphate carboxylase/oxygenase)
- Interference with sulfur assimilation pathways

c) pH changes in cellular compartments:

- Acidification of the cytoplasm and chloroplast stroma
- Disruption of cellular homeostasis and metabolic processes

d) Oxidative stress:

- Generation of reactive oxygen species (ROS)
- Lipid peroxidation and membrane damage

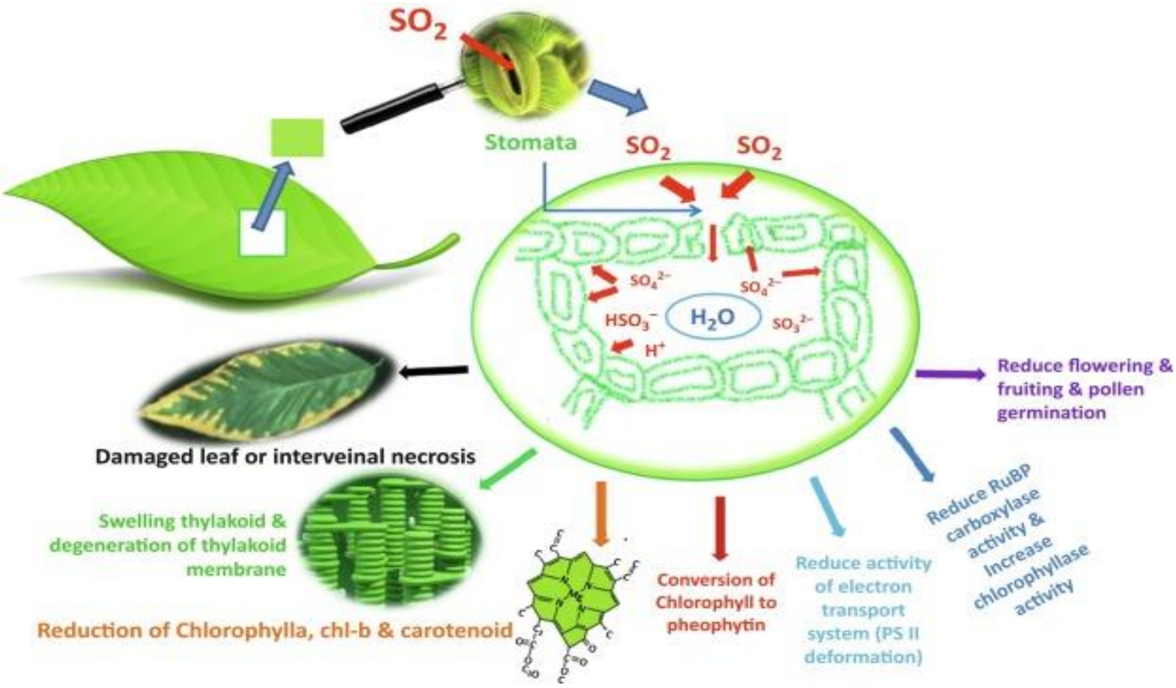

Figure 8. Plants response to SO2 or acid deposition (Jha and Yadav, 2023).

7.4.6 Differential sensitivity among plant species

Plant species vary widely in their sensitivity to SO2:

a) Sensitive species:

- Many lichens and bryophytes
- Certain crop plants (e.g., spinach, lettuce)
- Some coniferous trees (e.g., pine species)

b) Tolerant species:

- Many grasses
- Certain deciduous trees (e.g., oak, poplar)

Factors influencing SO2 sensitivity:

- Leaf characteristics (e.g., stomatal density, cuticle thickness)

- Cellular buffering capacity

- Sulfur metabolism and detoxification mechanisms

- Growth rate and life history traits

7.4.7 Historical perspective: SO2 pollution and forest decline

SO2 pollution has played a significant role in historical cases of forest decline:

a) "Waldsterben" (forest dieback) in Central Europe:

- Widespread forest damage observed in the 1970s and 1980s
- Initially attributed primarily to SO2 pollution
- Later recognized as a complex phenomenon involving multiple stressors

b) Smelter damage zones:

- Severe vegetation damage around metal smelting operations
- Classic examples include Sudbury (Canada) and Copper Basin (USA)

c) Decline of lichens in urban areas:

- Loss of sensitive lichen species as bioindicators of air quality
- Recovery of lichen communities following SO2 emission reductions

7.5 Peroxyacetyl nitrate (PAN) and photochemical smog

Peroxyacetyl nitrate (PAN) is a significant component of photochemical smog and can have severe impacts on plant health.

7.5.1 Formation of PAN in photochemical smog

PAN is formed through complex photochemical reactions involving hydrocarbons and nitrogen oxides:

a) Precursors and chemical reactions:

- ✓ CH3CHO (acetaldehyde) + OH → CH3CO (acetyl radical) + H2O
- ✓ CH3CO + O2 → CH3C(O)OO (peroxyacetyl radical)
- ✓ CH3C(O)OO + NO2 ⇌ CH3C(O)OONO2 (PAN)

b) Relationship with ozone formation:

- PAN formation competes with ozone production for NO2

- PAN can serve as a reservoir for NOx, influencing ozone formation downwind of urban areas

7.5.2 Characteristics of PAN

PAN has unique properties that influence its environmental behavior:

a) Stability and long-range transport:

- More stable than ozone at lower temperatures
- Can be transported long distances in the upper troposphere

b) Temperature dependence:

- Thermal decomposition increases with temperature
- Acts as a temporary reservoir for NOx, releasing it in warmer regions

7.5.3 Plant responses to PAN exposure

PAN can cause distinctive damage to vegetation:

a) Visible injury symptoms:

- Stippling and bronzing of leaf undersurfaces
- Typically affects younger, fully expanded leaves

b) Sensitivity variations among species:

- Many crops are highly sensitive (e.g., lettuce, spinach, tomato)
- Woody plants generally less sensitive than herbaceous species

7.5.4 Biochemical effects of PAN

At the cellular level, PAN toxicity involves:

a) Membrane damage:

- Lipid peroxidation
- Increased membrane permeability

b) Inhibition of photosynthesis and respiration:

- Disruption of electron transport chains
- Reduction in carbon fixation

7.5.5 PAN as an indicator of photochemical smog

PAN concentrations are often used as a marker for photochemical smog severity:

- Correlates with overall photochemical pollution levels

- Less reactive than ozone, providing a more stable indicator

7.5.6 Synergistic effects with other pollutants

PAN can interact with other air pollutants, potentially enhancing their phytotoxic effects:

- Synergistic injury with ozone

- Complex interactions with nitrogen oxides and sulfur dioxide

7.6 Particulate matter and its effects on plants

Particulate matter (PM) is a complex mixture of solid and liquid particles suspended in the air, with varying impacts on plant life.

7.6.1 Classification of particulate matter

PM is typically classified based on particle size:

a) Size fractions:

- PM10: Particles with a diameter of 10 micrometers or less
- PM2.5: Fine particles with a diameter of 2.5 micrometers or less
- Ultrafine particles: Less than 0.1 micrometers in diameter

b) Chemical composition:

- Organic compounds (e.g., soot, organic aerosols)
- Inorganic substances (e.g., sulfates, nitrates, metals)

7.6.2 Sources of particulate matter

PM can originate from both natural and anthropogenic sources:

a) Natural sources:

- Dust from arid regions
- Sea spray
- Volcanic ash
- Pollen and spores

b) Anthropogenic sources:

- Combustion processes (vehicles, power plants, industrial facilities)
- Agricultural activities (tilling, burning)
- Construction and demolition

7.6.3 Deposition of particulates on plant surfaces

Particles can accumulate on plant surfaces through various mechanisms:

a) Interception by foliage:

- Dependent on leaf surface characteristics (e.g., roughness, hairiness)
- Influenced by particle size and atmospheric conditions

b) Factors affecting deposition rates:

- Wind speed and turbulence
- Precipitation events
- Plant canopy structure

7.6.4 Direct effects on plants

Particulate matter can affect plants through several mechanisms:

a) Reduced light interception:

- Coating of leaf surfaces, reducing photosynthetically active radiation
- Potential shading effects in severe cases

b) Stomatal blockage:

- Physical obstruction of stomatal openings
- Interference with gas exchange and transpiration

c) Leaf temperature alterations:

- Changes in leaf surface albedo
- Potential impacts on energy balance and water relations

7.6.5 Indirect effects

PM can also have indirect impacts on plant health and ecosystem functioning:

a) Changes in soil chemistry through deposition:

- Alteration of soil pH
- Input of nutrients or potentially toxic elements

b) Impacts on plant-pollinator interactions:

- Interference with visual and olfactory cues
- Potential reduction in pollination efficiency

7.6.6 Particulates as carriers of toxic substances

PM can act as a vector for various pollutants:

a) Heavy metals:

- Accumulation of metals (e.g., lead, cadmium, zinc) on leaf surfaces
- Potential for foliar absorption or soil contamination

b) Organic pollutants:

- Adsorption of persistent organic pollutants (POPs) to particles
- Delivery of these compounds to plant and soil surfaces

7.6.7 Plant responses to particulate pollution

Plants have developed various adaptations to cope with particulate pollution:

a) Physiological adaptations:

- Increased leaf wax production
- Changes in stomatal density or behavior

b) Potential for biomonitoring:

- Use of plant species as indicators of particulate pollution levels
- Analysis of foliar dust loading and composition

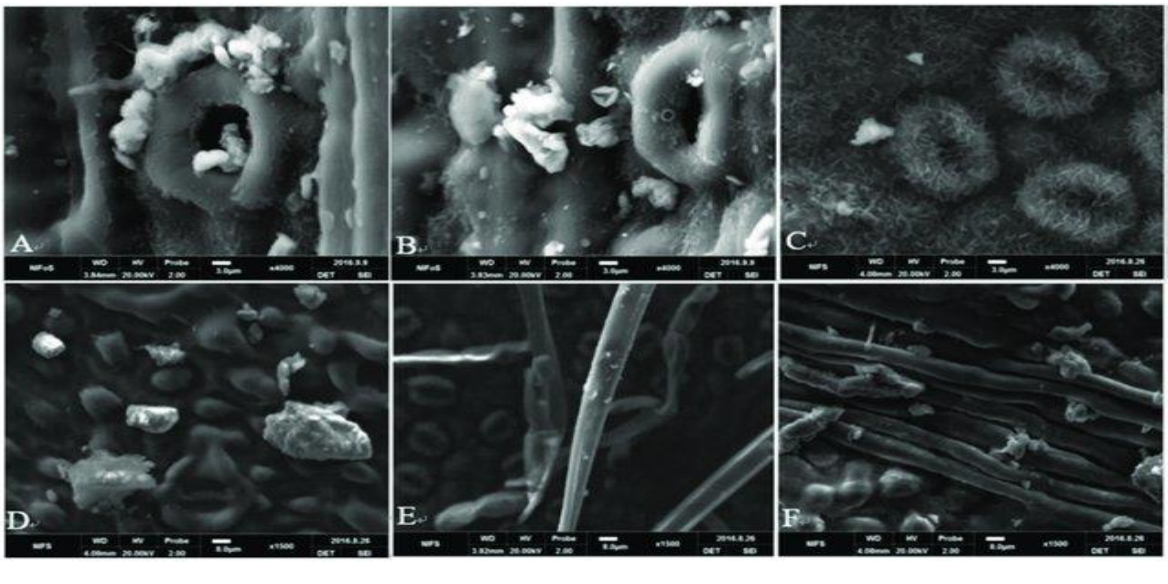

Figure 10. Scanning electron micrographs of particulate matter (PM) adsorbed on leaf surface. All dusty leaves of experimental species were collected, washed with water, filtered, and used for analysis. (A,B) PM in and around stomata; (C,D) PM in furrowed areas; (E,F) PM around trichomes (Jin et al., 2021).

7.7 Acid rain: formation, deposition, and ecological impacts

Acid rain, more broadly termed acid deposition, has been a significant environmental concern with far-reaching impacts on terrestrial and aquatic ecosystems.

7.7.1 Formation of acid rain

Acid rain results from the reaction of air pollutants with water, oxygen, and other chemicals in the atmosphere:

a) Conversion of SO2 and NOx to sulfuric and nitric acids:

- ✓ $SO_2 + H_2O \rightarrow H_2SO_3$
- ✓ $2\ NO_2 + H_2O \rightarrow HNO_2 + HNO_3$

b) Role of ammonia in neutralization:

- Ammonia can partially neutralize acids in the atmosphere
- Formation of ammonium sulfate and ammonium nitrate particles

7.7.2 Wet and dry acid deposition

Acid deposition occurs through both wet and dry processes:

a) Wet deposition:

- Acidic rain, snow, and fog
- pH typically ranges from 4.0 to 5.6

b) Dry deposition:

- Deposition of acidic gases and particles
- Often dominant in areas with low precipitation

7.7.3 Direct effects on plants

Acid deposition can directly impact plant tissues:

a) Foliar injury and nutrient leaching:

- Damage to leaf cuticles
- Leaching of base cations (e.g., calcium, magnesium) from foliage

b) Alterations in cuticle structure:

- Erosion of epicuticular waxes
- Increased susceptibility to other environmental stressors

c) Impacts on reproductive processes:

- Interference with pollen germination and pollen tube growth
- Potential effects on seed viability and germination

7.7.4 Soil-mediated effects

Many of the most significant impacts of acid deposition on plants are mediated through soil processes:

a) Soil acidification:

- Leaching of base cations
- Increased solubility of aluminum

b) Nutrient leaching and aluminum toxicity:

- Loss of essential nutrients (e.g., calcium, magnesium, potassium)
- Aluminum toxicity inhibiting root growth and nutrient uptake

c) Changes in microbial communities:

- Shifts in soil microbial composition and activity
- Potential impacts on nutrient cycling and decomposition processes

7.7.5 Ecosystem-level impacts

Acid deposition can lead to broad-scale changes in ecosystem structure and function:

a) Forest decline and dieback:

- Reduced forest productivity and increased tree mortality
- Changes in species composition favoring acid-tolerant species

b) Changes in species composition:

- Loss of acid-sensitive plant species
- Potential invasions by acid-tolerant exotic species

c) Impacts on aquatic ecosystems:

- Acidification of lakes and streams
- Loss of acid-sensitive aquatic organisms

7.7.6 Differential sensitivity of ecosystems to acid deposition

Ecosystems vary in their sensitivity to acid deposition:

a) Sensitive ecosystems:

- Areas with thin soils and slow-weathering bedrock (e.g., parts of the northeastern United States and southeastern Canada)
- High-elevation forests with high cloud deposition

b) More resistant ecosystems:

- Areas with deep soils and limestone bedrock
- Ecosystems adapted to naturally acidic conditions

7.7.7 Recovery processes and critical loads concept

As emissions of acid-forming pollutants have decreased in many regions, attention has turned to ecosystem recovery and prevention of future damage:

a) Recovery processes:

- Gradual increase in soil base saturation
- Recolonization by acid-sensitive species

b) Critical loads concept:

- Determination of the level of acid deposition an ecosystem can tolerate without long-term harmful effects
- Use in policy-making and emissions control strategies

7.7.8 Global trends in acid deposition and mitigation strategies

While acid deposition has decreased in North America and Europe due to emissions controls, it remains a significant issue in other parts of the world:

a) Increasing acid deposition in parts of Asia:

- Rapid industrialization and increasing energy consumption
- Challenges in implementing emissions control technologies

b) Mitigation strategies:

- Flue gas desulfurization in power plants
- Catalytic converters in vehicles
- Shift towards cleaner energy sources

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Course 8.

Forest Decline and Air Pollution

8.1 Historical perspective on forest decline

- Early observations of forest damage (1800s-1950s)

  - Smoke damage near industrial areas
  - "Waldsterben" in Central Europe

- Emergence of widespread forest decline (1970s-1980s)

  - Rapid increase in reported cases
  - Public and scientific concern

- Evolution of scientific understanding

  - From single-factor to multi-factor hypotheses
  - Development of long-term monitoring programs

- Changing perceptions of forest health

  - Shift from visual symptoms to ecosystem function

- Historical air pollution trends and forest health

8.2 Symptoms and patterns of forest dieback

- Visual symptoms of forest decline:

  - Crown thinning and transparency
  - Chlorosis and discoloration of foliage
  - Premature leaf or needle loss
  - Branch dieback and crown deformation

- Patterns of damage:

  - Elevation gradients in montane forests
  - Species-specific susceptibility
  - Age-related differences in tree response

- Temporal patterns:

  - Acute vs. chronic damage

- Seasonal variations in symptom expression

- Spatial patterns:
  - Regional differences in forest decline
  - Local topographic influences

- Below-ground symptoms:
  - Fine root mortality
  - Mycorrhizal associations changes

8.3 Air pollution as a contributing factor

- Major air pollutants implicated in forest decline:
  - Sulfur dioxide (SO_2)
  - Nitrogen oxides (NO_x)
  - Ozone (O_3)
  - Acid deposition

- Direct effects of air pollutants on trees:
  - Foliar injury and reduced photosynthesis
  - Altered carbon allocation patterns
  - Impacts on reproductive processes

- Indirect effects through soil processes:
  - Nutrient leaching and imbalances
  - Aluminum mobilization
  - Changes in soil microbial communities

- Long-range transport of pollutants
  - Impacts on remote forest ecosystems

- Challenges in establishing causal relationships
  - Complexity of forest ecosystems
  - Long-term nature of forest responses

8.4 Soil acidification and nutrient imbalances

- Mechanisms of soil acidification:
  - Acid deposition

- Base cation leaching
- Nitrification processes

- Changes in soil chemistry:

- Decreased pH and base saturation
- Increased aluminum availability
- Altered nutrient ratios (e.g., Ca:Al ratio)

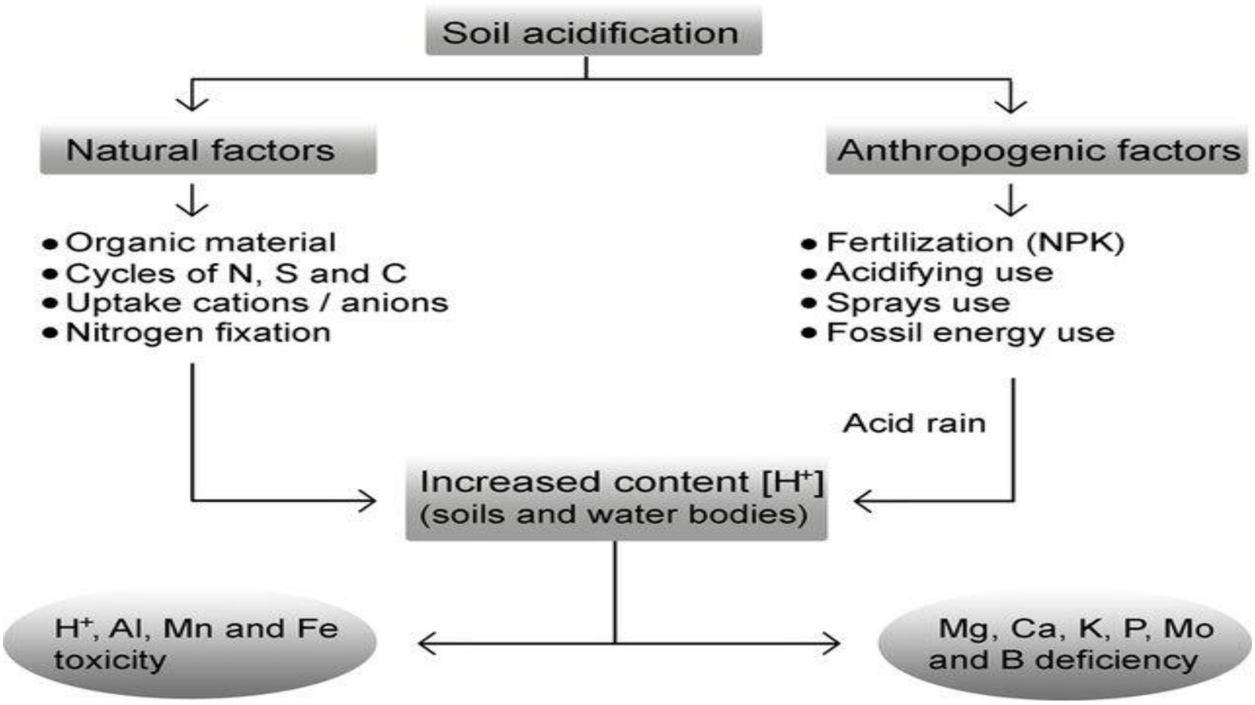

Figure 1. Soil acidification is a phenomenon determined by natural and anthropogenic factors. Bojórquez-Quintal et al., 2017). The decomposition of the organic matter, the imbalance of the N, S, and C cycles, the excess in the cation uptake on anions and the N fixation by the legumes influence the concentration of protons [H^+] in the soil solution. Anthropogenic factors such as the use of fertilizers (nitrogen, phosphorus, and potassium, NPK), the use of acidifiers and aerosols (H_2S, H_2SO_4, HF, and Cl_2), and the emission of gasses (CO_2, NO_2, and SO_2) into the atmosphere by use of fossil energy give rise to environmental pollution. Such molecules find their way into soil and water bodies in the form of acid rain, causing acidification of soils and the release of Al ions in a form easily absorbed by the plant root system, which is extremely toxic. Also, nutrient deficiency (P, Mg, and K) and toxicity by other metals (Mn and Fe) may occur.

- Impacts on nutrient cycling:

- Reduced base cation availability
- Phosphorus immobilization
- Nitrogen saturation in some ecosystems

- Effects on root systems:

- Fine root mortality and reduced growth
- Altered mycorrhizal associations

- Consequences for tree health:

    - Nutrient deficiencies and imbalances
    - Increased susceptibility to other stressors

- Soil acidification recovery processes

    - Natural recovery mechanisms
    - Liming and other mitigation strategies

8.5 Interactions between air pollutants and other stressors

- Climate-related stressors:

    - Drought and heat stress
    - Frost damage and winter injury
    - Extreme weather events

- Biotic stressors:

    - Insect pests and pathogens
    - Invasive species

- Anthropogenic factors:

    - Forest management practices
    - Land-use changes

- Synergistic effects:

    - Combined impacts of ozone and drought
    - Interactions between acid deposition and nutrient cycling

- Predisposing, inciting, and contributing factors in decline

- Complexity of multi-stressor interactions in forest ecosystems

8.6 Case studies of forest decline in Europe and North America

- European case studies:

- Black Forest decline in Germany
  - History and symptoms
  - Role of SO_2 and acid rain
  - Recovery and current status
- Carpathian Mountain forests
  - Transboundary pollution impacts
  - Species-specific responses
- Mediterranean forest declines
  - Interactions with climate change and fire regimes

- North American case studies:

- Red spruce decline in the Northeastern US
  - High elevation forests
  - Winter injury and acid deposition interactions
- Sugar maple decline in the Northeastern US and Eastern Canada
  - Soil calcium depletion
  - Multiple stressor interactions
- Western forest declines
  - Ozone impacts in the San Bernardino Mountains
  - Interactions with bark beetle outbreaks

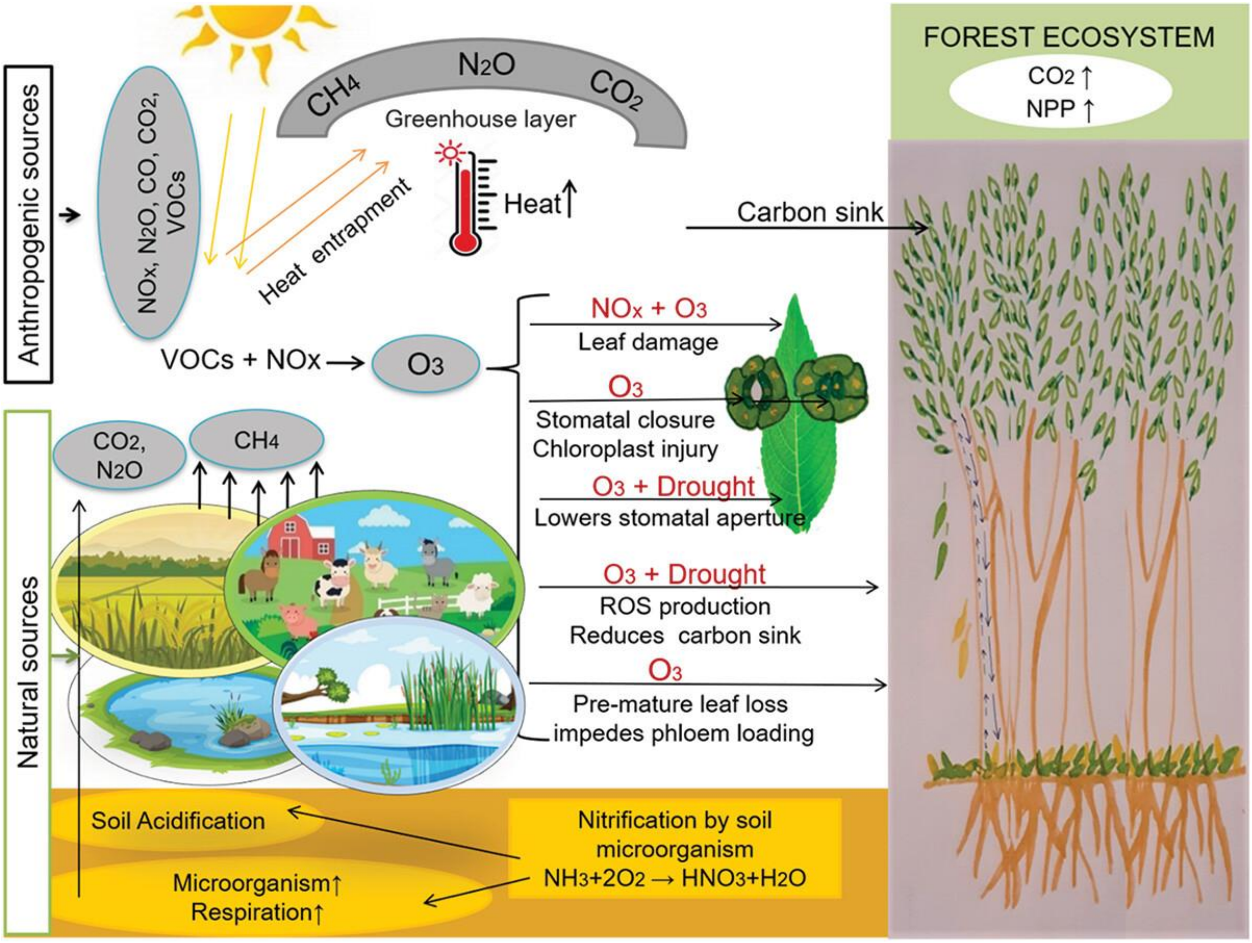

Figure 2. Integrated effects of air pollution and climate change on forests (Sonwani et al., 2022).

- Lessons learned from case studies:

- Importance of long-term monitoring
- Value of multi-disciplinary approaches
- Challenges in scaling from individual trees to landscapes

- Recovery and resilience:

- Examples of forest recovery following air quality improvements
- Factors influencing recovery potential
- Implications for forest management and conservation

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Course 9.

Ozone Depletion and UV Radiation

9.1 The ozone layer: structure and function

The stratospheric ozone layer is a crucial component of Earth's atmosphere, playing a vital role in protecting life on the planet from harmful ultraviolet radiation.

Stratospheric ozone layer:

The ozone layer is primarily located in the stratosphere, between 15 and 35 km above Earth's surface. Ozone (O_3) is a molecule composed of three oxygen atoms and is formed through a series of photochemical reactions known as the Chapman cycle (Chapman, 1930).

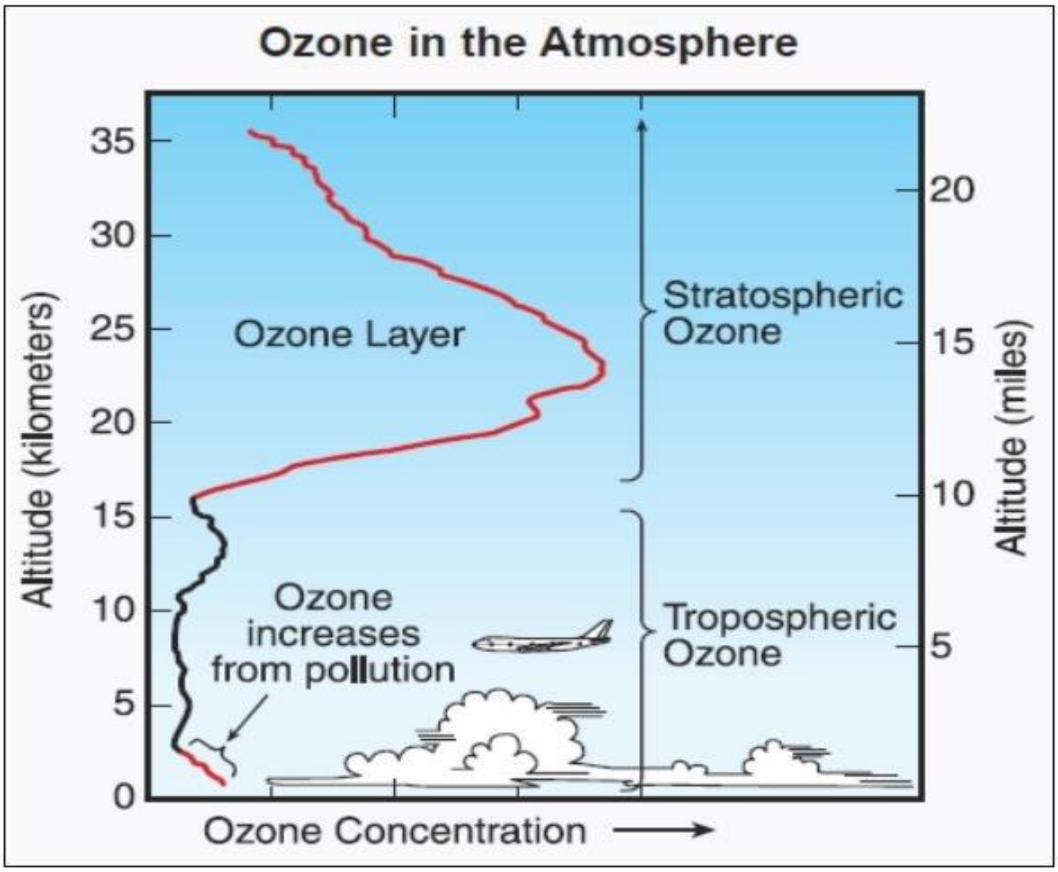


Figure 9.1. Vertical profile of ozone concentration in the atmosphere with the indication of the ozone layer (Source: www.scienceschool.org).

Ozone concentration variations:

Ozone concentrations in the stratosphere are not uniform and exhibit significant variations:

a) Latitudinal differences: Ozone concentrations are generally higher at mid to high latitudes and lower near the equator.

b) Seasonal fluctuations: Ozone levels typically peak in spring and reach their minimum in autumn in each hemisphere.

c) Natural fluctuations: Solar cycles, volcanic eruptions, and atmospheric circulation patterns can all influence ozone concentrations on various timescales.

Functions of the ozone layer:

a) UV radiation absorption: The primary function of the ozone layer is to absorb harmful ultraviolet radiation, particularly UV-B (280-315 nm wavelength). This absorption protects life on Earth from the damaging effects of UV radiation.

b) Thermal regulation: Ozone absorption of UV radiation also plays a role in heating the stratosphere, contributing to the temperature inversion that defines this atmospheric layer.

Ozone monitoring techniques:

a) Ground-based measurements: Instruments such as Dobson spectrophotometers and ozone sondes provide localized, high-precision measurements of total column ozone and vertical ozone profiles.

b) Satellite observations: Satellites equipped with instruments like the Total Ozone Mapping Spectrometer (TOMS) and the Ozone Monitoring Instrument (OMI) provide global coverage of ozone distribution.

Historical discoveries and research milestones:

Key milestones in ozone research include the discovery of the ozone layer by Charles Fabry and Henri Buisson in 1913, the development of the Chapman cycle theory in 1930, and the shocking discovery of the Antarctic ozone hole by Farman et al. in 1985.

9.2 Ozone-depleting substances and their sources

The depletion of stratospheric ozone is primarily caused by human-made chemicals known as ozone-depleting substances (ODS).

Major ozone-depleting substances (ODS):

a) Chlorofluorocarbons (CFCs): These compounds, such as CFC-11 and CFC-12, were widely used in refrigerants, aerosol propellants, and foam blowing agents.

b) Hydrochlorofluorocarbons (HCFCs): Developed as transitional replacements for CFCs, HCFCs have lower ozone-depleting potential but still contribute to ozone depletion.

c) Halons: Used primarily in fire extinguishers, halons contain bromine and are particularly effective at destroying ozone.

d) Carbon tetrachloride: This compound was used in various industrial applications and as a solvent.

e) Methyl chloroform: Also known as 1,1,1-trichloroethane, this substance was used as a solvent and cleaning agent.

f) Methyl bromide: Used as a pesticide and fumigant, methyl bromide is a significant source of bromine in the stratosphere.

Figure 9.2. Chemical structures of major ozone-depleting substances (URL: https://www.acquiscompliance.com/blog/ozone-depleting-substances-ods/).

Natural sources of ozone-depleting compounds:

While human-made ODS are the primary concern, some natural sources also contribute to stratospheric chlorine and bromine:

a) Volcanic eruptions: Large eruptions can inject significant amounts of chlorine and other halogens into the stratosphere.

b) Oceanic emissions: Marine organisms produce small amounts of halogenated compounds that can reach the stratosphere.

Anthropogenic sources:

The primary human activities that have released ODS into the atmosphere include:

a) Refrigerants and air conditioning

b) Aerosol propellants

c) Foam blowing agents

d) Solvents and cleaning agents

e) Fire extinguishants

Chemical properties of ODS:

ODS are particularly harmful to the ozone layer due to their specific chemical properties:

a) Stability: These compounds are extremely stable in the troposphere, allowing them to persist long enough to reach the stratosphere.

b) Long atmospheric lifetimes: Many ODS have atmospheric lifetimes of decades to centuries, leading to long-term impacts on the ozone layer.

c) Catalytic ozone destruction mechanisms: Once in the stratosphere, ODS break down under UV radiation, releasing chlorine or bromine atoms that catalytically destroy ozone molecules. A single chlorine atom can destroy thousands of ozone molecules before being removed from the stratosphere (Molina and Rowland, 1974).

9.3 Formation and dynamics of the ozone hole

The "ozone hole" refers to a severe depletion of ozone in the stratosphere, particularly over the Antarctic region during the Southern Hemisphere spring.

Definition of the "ozone hole":

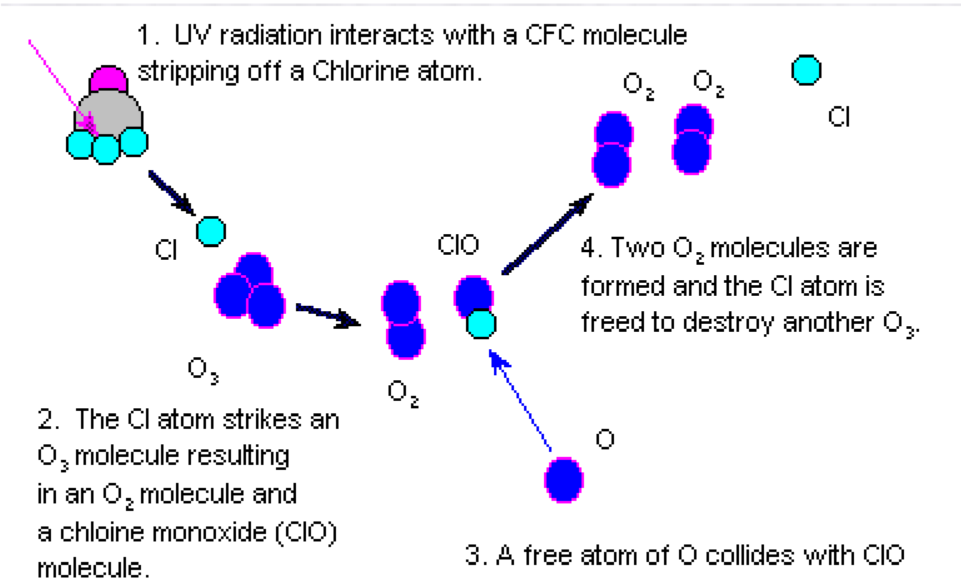
The term "ozone hole" is typically used when the ozone column density falls below 220 Dobson Units (DU), representing a loss of about one-third of the total column ozone compared to historical levels.

Seasonal formation process:

a) Polar stratospheric clouds (PSCs): During the cold, dark polar winter, temperatures in the stratosphere drop low enough for PSCs to form. These clouds provide surfaces for unique chemical reactions.

b) Heterogeneous chemistry on PSC surfaces: Inactive forms of chlorine (HCl and $ClONO_2$) react on PSC surfaces to produce more reactive forms (Cl_2 and HOCl).

c) Chlorine activation and catalytic ozone destruction: When sunlight returns in spring, it photolyzes these reactive chlorine species, initiating catalytic ozone destruction cycles.



chlorofluorocarbons (CFCs)

Figure 9.3. Schematic of ozone hole formation process in the Antarctic (URL: https://cimss.ssec.wisc.edu/wxwise/ozone/OZONE2.html).

Geographical and temporal characteristics:

a) Antarctic vs. Arctic ozone depletion: The ozone hole is much more pronounced over Antarctica due to colder temperatures and a more stable polar vortex. Arctic ozone depletion is generally less severe and more variable.

b) Seasonal variations and long-term trends: The Antarctic ozone hole typically forms in August and reaches its maximum extent in September-October before breaking up in November-December.

Factors influencing ozone hole dynamics:

a) Stratospheric temperature: Colder temperatures promote PSC formation and enhance ozone depletion.

b) Polar vortex strength: A stronger, more isolated polar vortex leads to more severe ozone depletion.

c) Solar cycles and volcanic eruptions: These factors can influence stratospheric temperatures and chemistry, affecting ozone depletion processes.

Monitoring and measurement techniques:

Ozone hole dynamics are monitored using a combination of ground-based, balloon-borne, and satellite instruments, providing a comprehensive view of ozone depletion processes.

Recovery projections and Montreal Protocol impacts:

The Montreal Protocol, signed in 1987, has been highly successful in reducing ODS emissions. As a result, the ozone layer is expected to recover to 1980 levels by the mid-21st century in mid-latitudes and by the late 21st century in polar regions (WMO, 2018).

9.4 Increased UV-B radiation and its effects on plants

The depletion of stratospheric ozone leads to increased UV-B radiation reaching Earth's surface, which can have significant impacts on plant life.

UV radiation spectrum and penetration to Earth's surface:

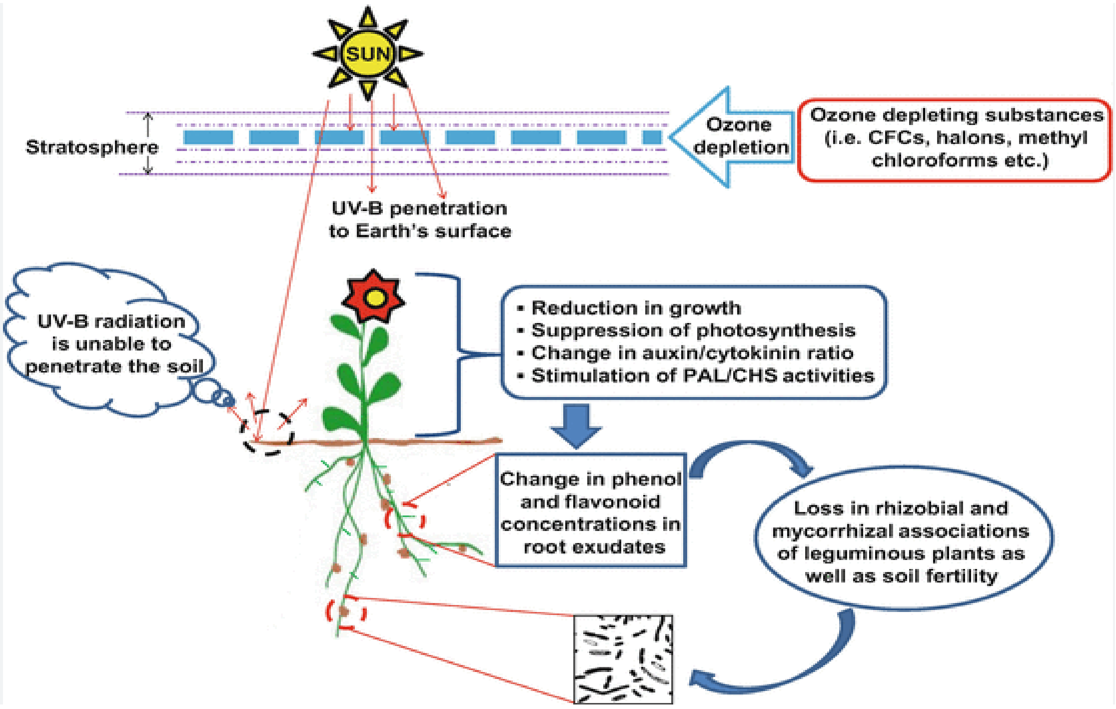
UV radiation is typically divided into UV-A (315-400 nm), UV-B (280-315 nm), and UV-C (100-280 nm). While the ozone layer completely blocks UV-C and most UV-B, ozone depletion leads to increased UV-B penetration.

Direct effects on plant molecules:

a) DNA damage: UV-B radiation can cause the formation of cyclobutane pyrimidine dimers (CPDs) and other photoproducts in DNA, potentially leading to mutations if not repaired.

b) Protein denaturation: UV-B can damage proteins directly or through the generation of reactive oxygen species (ROS).

c) Lipid peroxidation: UV-B induced ROS can initiate lipid peroxidation in cellular membranes, affecting membrane integrity and function.



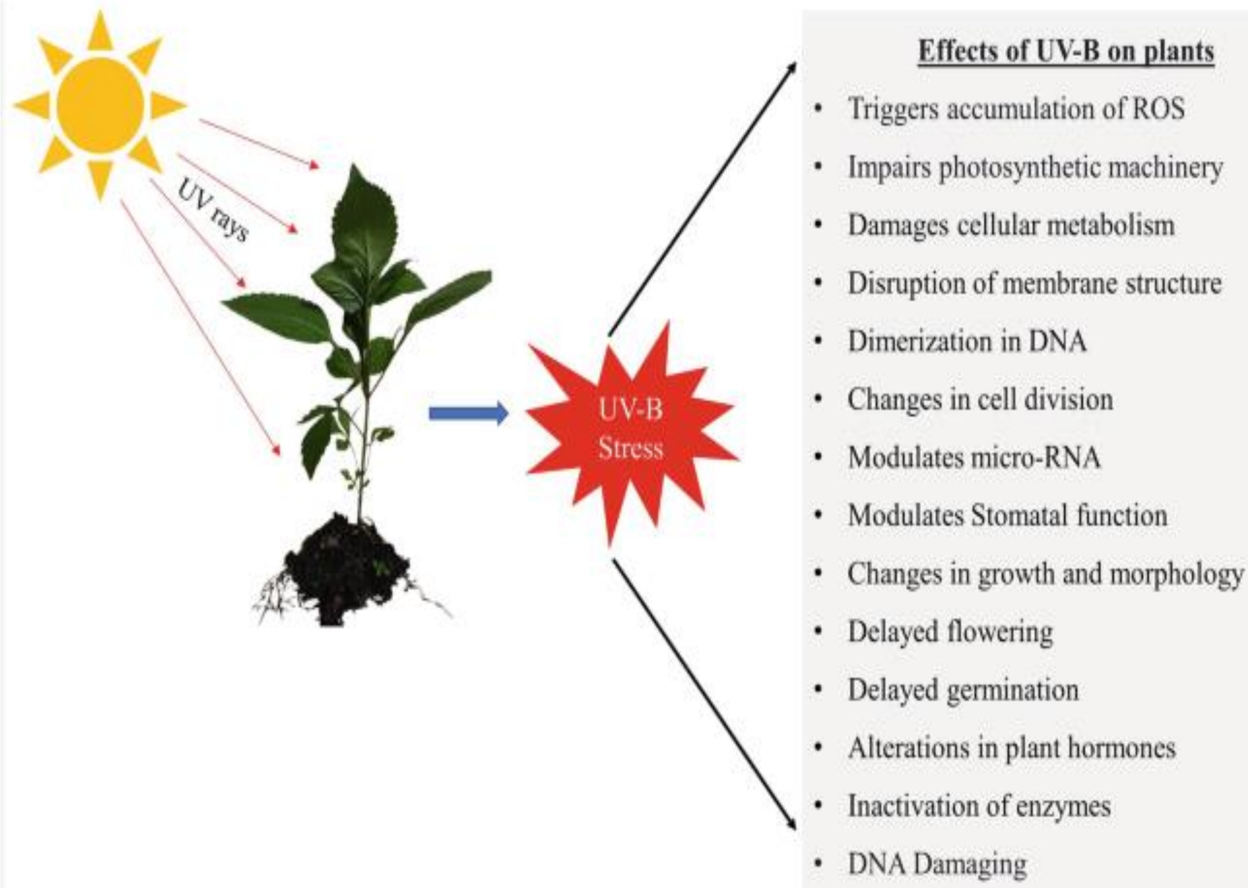


Figure 9.4. Molecular targets of UV-B radiation in plant cells

Physiological and morphological effects:

a) Reduced photosynthetic efficiency: UV-B can damage photosystem II and reduce the efficiency of carbon fixation.

b) Alterations in leaf structure: Plants may develop thicker leaves or cuticles as a protective response to increased UV-B.

c) Changes in plant height and branching patterns: UV-B exposure can lead to reduced plant height and increased branching in some species.

Effects on plant development:

a) Delayed flowering and reduced seed production: UV-B stress can alter reproductive timing and reduce overall reproductive output.

b) Alterations in pollen viability and germination: UV-B can negatively impact pollen quality and germination rates.

Species-specific sensitivity and elevation effects:

Plant species vary widely in their sensitivity to UV-B radiation. High-elevation plants often show greater tolerance due to evolutionary adaptation to naturally higher UV-B levels.

Interactions with other environmental factors:

The effects of UV-B on plants can be modulated by other environmental factors:

a) CO2 concentration: Elevated CO2 may partially mitigate some UV-B effects by increasing overall plant growth and carbon allocation to protective compounds.

b) Water availability: Drought stress can exacerbate UV-B impacts on plants.

c) Temperature: Higher temperatures may increase plant sensitivity to UV-B stress.

9.5 Plant adaptations to UV stress

Plants have evolved various mechanisms to cope with UV stress, ranging from molecular to morphological adaptations.

UV-screening compounds:

a) Flavonoids and other phenolic compounds: Plants accumulate UV-absorbing compounds, particularly in epidermal layers, to screen out harmful UV-B radiation.

b) Accumulation in epidermal layers: The localization of these compounds in the upper leaf layers provides effective UV screening while minimizing impacts on photosynthesis.

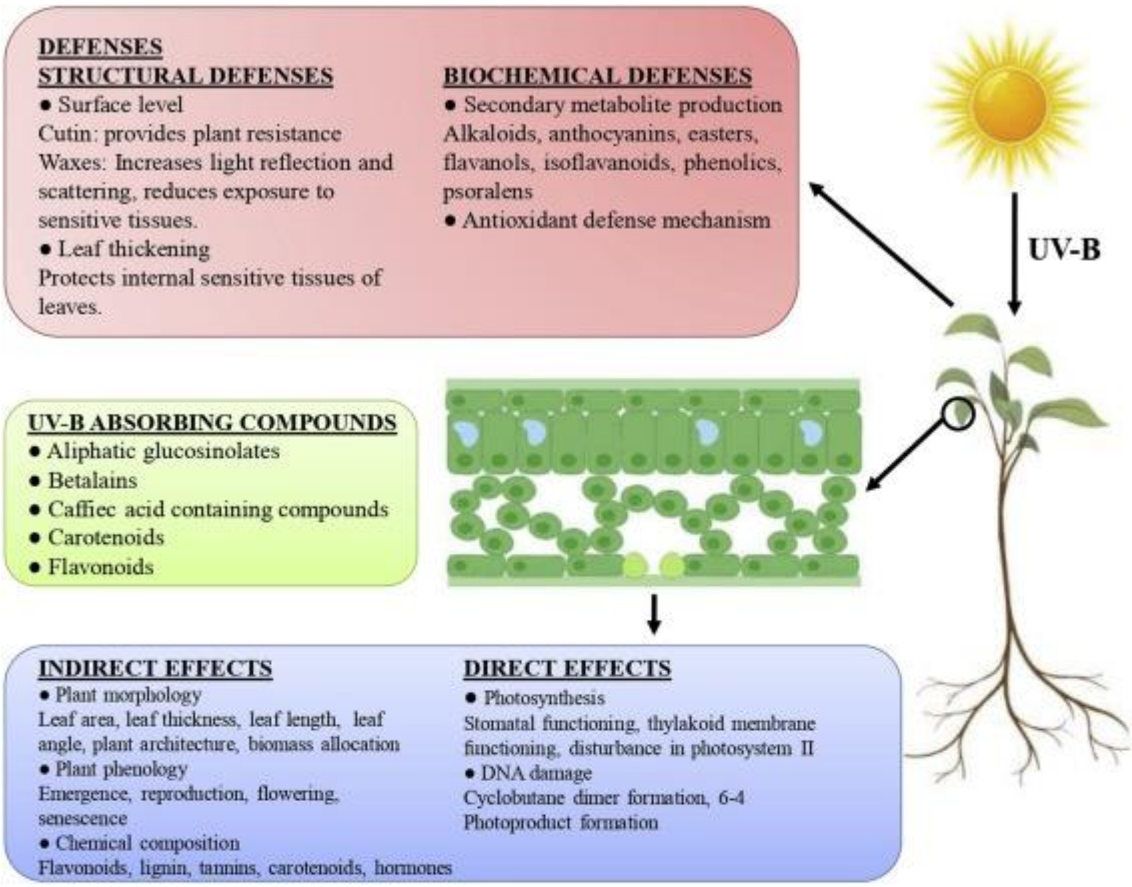


Figure 9.5. Cross-section of a leaf showing UV-screening compound accumulation in epidermal layers.

Antioxidant systems:

a) Enzymatic antioxidants: Plants upregulate enzymes such as superoxide dismutase, catalase, and peroxidases to neutralize UV-induced ROS.

b) Non-enzymatic antioxidants: Compounds like ascorbate and glutathione play crucial roles in maintaining cellular redox balance under UV stress.

DNA repair mechanisms:

a) Photoreactivation: Photolyase enzymes can directly reverse UV-induced DNA damage using light energy.

b) Excision repair pathways: Plants employ nucleotide excision repair and base excision repair to remove and replace damaged DNA sections.

Morphological adaptations:

a) Leaf orientation changes: Some plants alter leaf angle to reduce direct UV exposure.

b) Increased leaf thickness: Thicker leaves can provide greater UV protection to underlying tissues.

c) Enhanced trichome production: Increased leaf hair density can scatter UV radiation.

Physiological acclimation:

a) Upregulation of stress response genes: UV exposure triggers the expression of various stress-related genes, enhancing overall stress tolerance.

b) Alterations in resource allocation: Plants may shift resource allocation towards protective mechanisms at the expense of growth.

Ecosystem-level adaptations:

a) Changes in species composition: Long-term UV stress can lead to shifts in plant community composition, favoring more UV-tolerant species.

b) Shifts in plant-pollinator interactions: UV-induced changes in floral traits or flowering times can affect plant-pollinator relationships.

9.6 Ecological implications of ozone depletion

The effects of increased UV-B radiation due to ozone depletion extend beyond individual plants to influence entire ecosystems and global processes.

Effects on primary productivity:

a) Potential reductions in crop yields: Increased UV-B can negatively impact agricultural productivity, although the extent varies widely among crop species and cultivars.

b) Impacts on forest growth and carbon sequestration: UV-B effects on forest ecosystems could influence global carbon cycling and climate change mitigation efforts.

Alterations in plant community composition:

a) Shifts in competitive balance between species: Differential UV-B sensitivity among plant species can alter competitive dynamics and lead to changes in community structure.

b) Potential loss of UV-sensitive species: Highly UV-sensitive species may be at risk of local extinction in areas of severe ozone depletion.

Impacts on plant-herbivore interactions:

a) Changes in plant defensive compounds: UV-B stress often increases the production of phenolic compounds, which can affect plant palatability and nutritional quality for herbivores.

b) Altered palatability and nutritional quality: Changes in plant biochemistry due to UV stress can ripple through food webs, affecting herbivore populations and higher trophic levels.

Effects on soil processes:

a) Changes in litter decomposition rates: UV-induced changes in leaf chemistry can alter decomposition rates and nutrient cycling in ecosystems.

b) Impacts on soil microbial communities: Increased UV-B penetration can affect soil surface microbial communities, potentially influencing various soil processes.

Aquatic ecosystem effects:

a) Phytoplankton productivity changes: UV-B can negatively impact phytoplankton, the base of many aquatic food webs.

b) Ripple effects through aquatic food webs: Changes in phytoplankton communities can have cascading effects on zooplankton, fish, and other aquatic organisms.

Global biogeochemical cycles:

a) Potential alterations in carbon and nitrogen cycling: UV-B induced changes in plant productivity and soil processes could influence global biogeochemical cycles.

b) Interactions with climate change processes: The effects of UV-B stress on plants may interact with other climate change factors, potentially amplifying or mitigating certain impacts.

Long-term ecological consequences:

a) Biodiversity implications: Differential species responses to UV-B stress could lead to changes in biodiversity at various scales.

b) Ecosystem resilience and stability: The cumulative effects of UV-B stress may influence overall ecosystem resilience to other environmental perturbations.

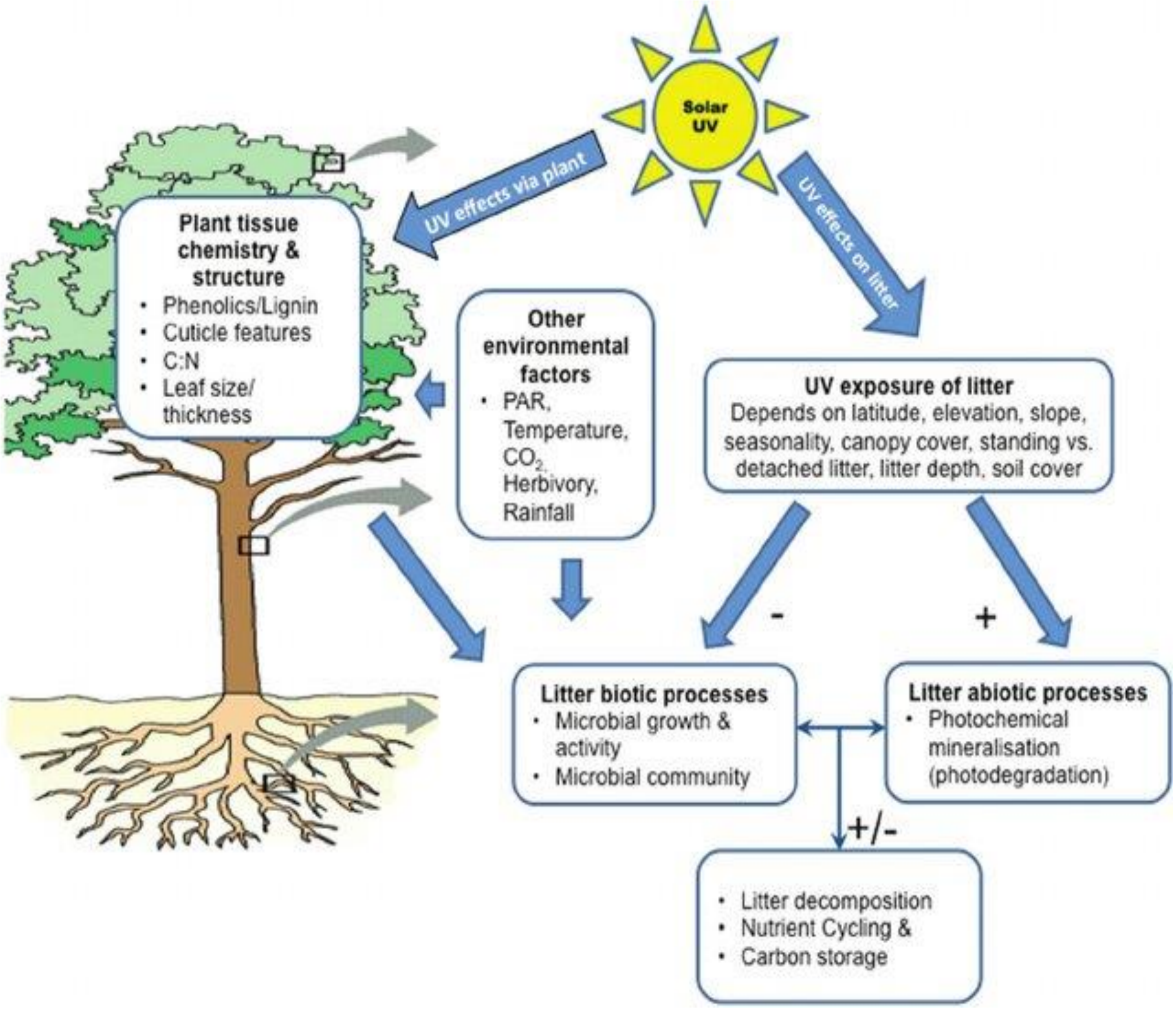


Figure 9.6. Conceptual model of the direct and indirect effects of solar UV radiation (290 – 400 nm) on the decomposition of terrestrial leaf litter, including potential interactions with other environmental factors. Bornman et al., 2015). The total exposure of litter to UV radiation will depend on a combination of climatic, landscape/vegetation, and species-specific factors. UV radiation generally reduces rates of biotic decomposition, whereas abiotic processes tend to enhance decomposition. Both processes exhibit distinct wavelength sensitivities (as seen from action spectra) depending on the underlying chromophores and mechanisms involved. Indirect effects of UV radiation are primarily mediated by those on leaf chemistry and structure, leading, e.g., to decreasing attractiveness of the litter for decomposing microbes. The role played by UV radiation on decomposition can depend also on other environmental factors interacting with biotic and abiotic processes and leaf chemistry and structure. The net effect of solar UV radiation on rates of decomposition, nutrient cycling, and carbon storage will depend on the combined effects of biotic and abiotic processes and may be positive, negative or neutral. PAR, photosynthetically active radiation (400 – 700 nm).

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Course 10.

Climate Change and Plant Ecosystems

10.1 Greenhouse effect and global warming

- Basic principles of the greenhouse effect

  - Natural vs. enhanced greenhouse effect
  - Major greenhouse gases (CO2, CH4, N2O, water vapor)

- Historical trends in atmospheric CO2 concentrations

  - Pre-industrial levels vs. current concentrations
  - Ice core records and long-term climate history

- Global temperature trends

  - Observed temperature increases
  - Regional variations in warming patterns

- Climate change projections

  - The Intergovernmental Panel on Climate Change (IPCC) scenarios and models
  - Projected temperature increases and their uncertainties

- Feedback mechanisms in the climate system

  - Albedo changes
  - Ocean circulation alterations
  - Permafrost thawing and methane release

10.2 Carbon dioxide enrichment and plant responses

The increasing atmospheric CO_2 concentration has direct and indirect effects on plant physiology and growth. CO_2 is a substrate for photosynthesis, and its increased availability can potentially enhance plant productivity. However, plant responses to elevated CO_2 are complex and vary depending on species and environmental conditions.

C3 and C4 plants respond differently to increased CO2 concentrations due to their distinct photosynthetic pathways. C3 plants, which include most trees and crops like wheat and rice, generally show a more pronounced response to elevated CO_2. This is because the enzyme Rubisco, which catalyzes the first major step of carbon fixation, is not CO_2-saturated under current atmospheric conditions in C3 plants. Elevated CO_2 can increase carboxylation efficiency and reduce photorespiration, leading to enhanced photosynthetic rates.

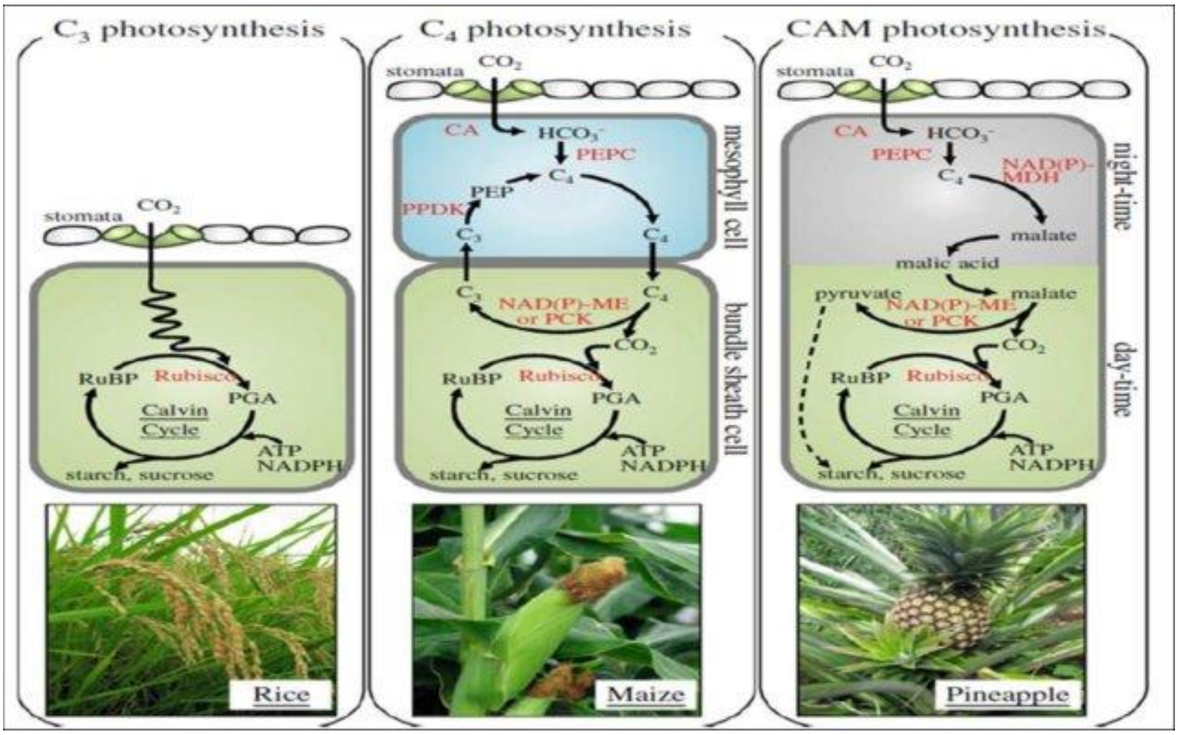

Figure 1. Pathway difference in C3, C4 and CAM plants (Yamori et al., 2014). Photosynthesis and Climate Change Adaptation : "C3, C4, and CAM.

Direct effects of elevated CO2 on plants include:

1. Increased photosynthetic rates: Many plants show higher rates of carbon fixation under elevated CO2 conditions.

2. Enhanced water use efficiency: Plants often reduce stomatal conductance in response to higher CO2, leading to improved water use efficiency.

3. Altered plant growth and biomass allocation: Elevated CO2 can lead to increased biomass production, with changes in allocation patterns between roots, stems, and leaves.

However, long-term exposure to elevated CO2 can lead to acclimation responses in plants. Photosynthetic down-regulation may occur, where plants adjust their photosynthetic capacity to the new CO2 environment. This can involve reductions in Rubisco content and activity, as well as changes in leaf nitrogen content.

The effects of elevated CO2 on plant-water relations are particularly important in the context of climate change. Reduced stomatal conductance can lead to decreased transpiration rates, potentially altering local and regional water cycles. This interaction between CO_2 and water use has implications for agriculture and natural ecosystems, especially in water-limited environments.

Elevated CO_2 can also affect plant chemical composition. Changes in C:N ratios and protein content have been observed in many species, which can impact nutritional quality for herbivores and decomposition processes. Additionally, some plants show altered production of secondary metabolites under elevated CO_2 conditions, which may influence plant defense mechanisms and ecological interactions.

The CO_2 fertilization effect, where increased atmospheric CO_2 leads to enhanced plant growth, has been observed in many studies. However, this effect is often limited by other factors, particularly nutrient availability. Nitrogen is especially important, as increased carbon fixation requires additional nitrogen for protein synthesis. In natural ecosystems and agricultural systems without additional fertilization, nitrogen limitation can constrain the potential benefits of elevated CO_2.

10.3 Temperature effects on plant physiology and phenology

Rising temperatures associated with climate change have profound effects on plant physiology and phenology. These effects can be both direct, through impacts on metabolic processes, and indirect, through alterations in phenological timing and ecological interactions.

Temperature directly affects plant metabolism by influencing enzyme kinetics and biochemical reactions. Generally, biochemical reaction rates increase with temperature up to an optimum point, beyond which they decline due to enzyme denaturation and other stress responses. This relationship is often described by the Q_{10} coefficient, which represents the factor by which reaction rates change for every 10°C increase in temperature.

Photosynthesis is particularly sensitive to temperature changes. Each plant species has an optimal temperature range for photosynthesis, which reflects its evolutionary history and adaptation to specific environments. As temperatures increase beyond this optimum, photosynthetic rates decline due to various factors:

1. Increased photorespiration in C3 plants

2. Enzyme denaturation

3. Damage to photosynthetic apparatus, particularly photosystem II

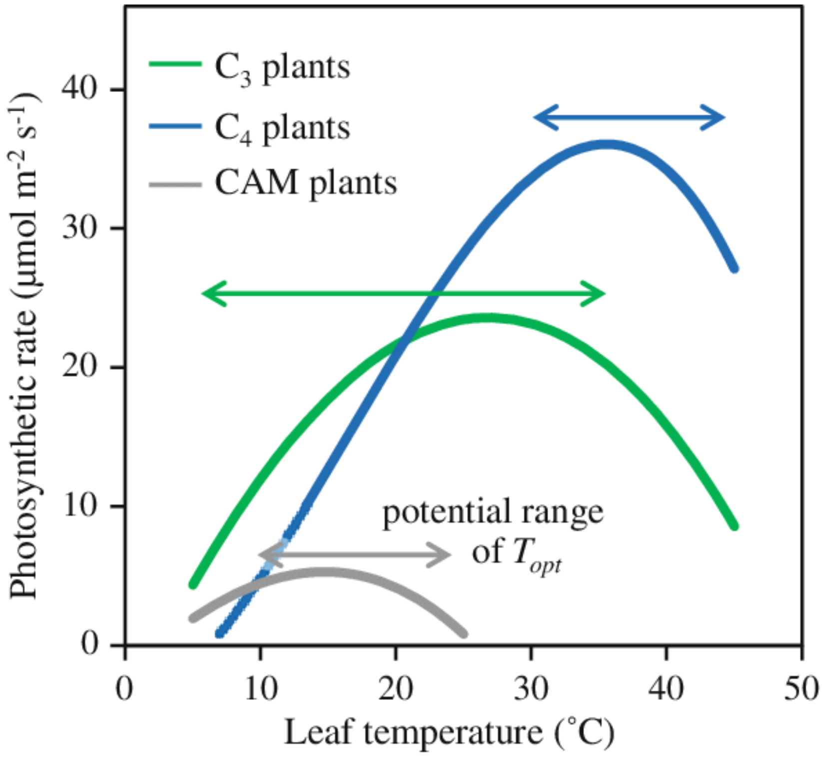

Figure 2. Typical temperature responses of photosynthesis in C 3, C 4 , and CAM plants (Yamori et al., 2014). Temperature responses of photosynthesis are pooled from the published data and are averaged in C 3 , C 4 , and CAM plants, respectively (86 C 3 herbaceous plants, 31 C 4 plants, and 27 CAM plants). In CAM plants, data for CO 2 fixation rate at night was pooled. From the pooled data, the potential range of optimum temperature for photosynthesis is indicated in C 3 , C 4 , and CAM plants, respectively

Respiration rates also increase with temperature, potentially affecting the overall carbon balance of plants. If respiration increases more rapidly than photosynthesis with rising temperatures, it could lead to reduced net carbon gain and potentially carbon loss from plants and ecosystems.

Temperature increases also affect plant water relations. Higher temperatures lead to increased evaporative demand, which can result in water stress if plants cannot maintain adequate water uptake. This can lead to stomatal closure, reducing CO2 uptake and potentially leading to carbon starvation under prolonged stress conditions. Additionally, high temperatures can increase the vulnerability of plant hydraulic systems to cavitation, further compromising water transport.

One of the most visible effects of warming on plants is changes in phenology, the timing of life cycle events. Numerous studies have documented shifts in plant phenology in response to climate change, including:

1. Earlier spring events: Bud burst, leaf-out, and flowering are occurring earlier in many species.

2. Delayed autumn events: Leaf senescence and dormancy onset are often delayed.

3. Extended growing seasons: The combination of earlier spring and later autumn events results in longer growing seasons in many regions.

These phenological changes can have cascading effects on ecosystems. For example, earlier flowering might lead to mismatches with pollinator activity, potentially affecting plant reproduction and pollinator populations. Similarly, changes in the timing of leaf-out can affect herbivore populations and their predators, altering food web dynamics.

Temperature also affects plant reproduction in various ways. High temperatures can reduce pollen viability and interfere with fertilization processes. Seed development and maturation are also temperature-sensitive, with potential impacts on seed quality and germination rates.

For many temperate and boreal plant species, winter temperatures play a crucial role in regulating life cycles. Chilling requirements, which are periods of cold temperature necessary for proper bud break and flowering, may not be met under warming conditions. This can lead to irregular growth patterns and reduced productivity. Conversely, reduced frost occurrence can benefit some species by reducing frost damage, but it may also allow pest populations to survive winter in greater numbers.

The ability of plants to adapt to these temperature changes will be crucial for their survival and distribution under future climate scenarios. While some species may be able to adjust through phenotypic plasticity or rapid evolution, others may face local extinction or be forced to migrate to more suitable climates.

10.4 Altered precipitation patterns and plant water relations

Climate change is expected to significantly alter precipitation patterns globally, with some regions experiencing increased rainfall while others face more frequent and severe droughts. These changes in water availability have profound implications for plant water relations and ecosystem functioning.

Projected changes in precipitation patterns vary widely by region:

1. Many mid-latitude and subtropical dry regions are expected to experience less rainfall.

2. Mid-latitude wet regions are projected to receive more precipitation.

3. The frequency and intensity of extreme precipitation events are likely to increase in many areas.

Plants respond to water stress through a variety of mechanisms aimed at maintaining water balance and avoiding damage. Key responses include:

1. Stomatal regulation: Plants can rapidly close stomata to reduce water loss through transpiration. While this helps conserve water, it also reduces CO2 uptake, potentially limiting photosynthesis.

2. Osmotic adjustment: Plants can accumulate solutes in their cells to maintain turgor pressure under water-limited conditions. This allows them to continue extracting water from increasingly dry soil.

3. Xylem embolism and hydraulic failure: Under severe drought, air bubbles can form in the xylem, disrupting water transport. If extensive, this can lead to hydraulic failure and plant death.

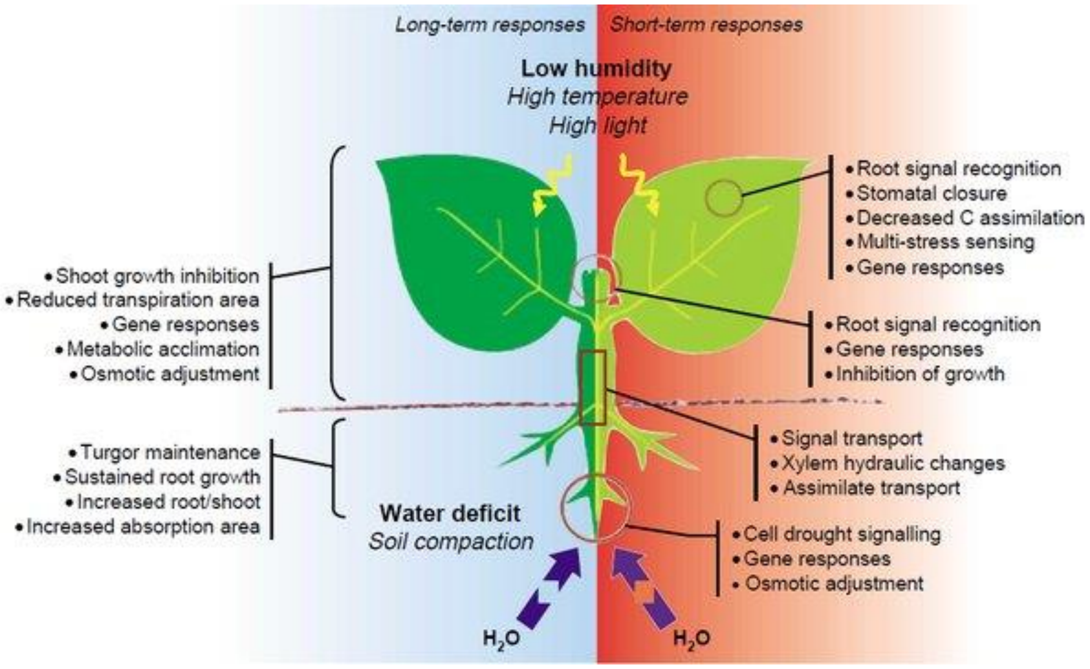

Figure 3. Plant responses to water stress (Santos et al., 2009).

Adaptations to altered water availability can occur at various levels:

1. Root system architecture: Plants may allocate more resources to root growth, particularly deep roots, to access water in deeper soil layers.

2. Leaf area adjustments: Reducing leaf area through leaf shedding or producing smaller leaves can help plants conserve water.

3. Water use efficiency improvements: Some plants may evolve or acclimate to use water more efficiently, producing more biomass per unit of water transpired.

Changes in precipitation patterns also affect nutrient uptake and cycling. Drought can reduce nutrient mobility in soil, limiting plant access to essential elements. Conversely, increased precipitation can lead to nutrient leaching, potentially reducing soil fertility over time. Mycorrhizal associations, symbiotic relationships between plant roots and fungi, play a crucial role in nutrient and water uptake and may become even more important under changing climate conditions.

The interaction between altered precipitation patterns and elevated CO2 is complex. Higher CO2 concentrations can improve water use efficiency, potentially ameliorating some effects of drought stress. However, this effect may be limited, particularly under severe or prolonged drought conditions.

10.5 Extreme weather events and their impact on vegetation

Climate change is increasing the frequency and intensity of extreme weather events, which can have severe impacts on vegetation and ecosystems. These events include heat waves, droughts, floods, storms, and wildfires.

Heat waves can cause significant physiological stress in plants, leading to reduced growth, reproductive failure, and in severe cases, mortality. Prolonged exposure to extreme high temperatures can damage cellular structures, denature proteins, and disrupt membrane integrity. Heat stress can also lead to the production of reactive oxygen species, causing oxidative damage to plant tissues.

Forest die-offs associated with heat waves and droughts have been observed in many parts of the world. These events can lead to rapid ecosystem shifts, potentially transforming forests into shrublands or grasslands.

Droughts, especially when prolonged, can have devastating effects on vegetation. Short-term drought responses include stomatal closure and leaf rolling to reduce water loss. However, long-term drought can lead to cavitation in the xylem, leaf shedding, and eventually plant death. Severe droughts can trigger large-scale vegetation die-back and, in extreme cases, contribute to desertification processes.

Floods and waterlogging present different challenges for plants. Excess water in the soil leads to oxygen depletion in the root zone, causing root hypoxia or anoxia. This can impair root function, reduce nutrient uptake, and lead to the accumulation of toxic compounds in the soil. Prolonged flooding can cause root death and, ultimately, mortality of flood-intolerant species. Additionally, floods can cause soil erosion and nutrient leaching, affecting long-term site productivity.

Storms and high winds can cause direct physical damage to vegetation, including defoliation, branch breakage, and uprooting of trees. Such damage can create gaps in forest canopies, altering light regimes and potentially facilitating the establishment of different species. In coastal areas, storms surge and salt spray can have severe impacts on vegetation not adapted to saline conditions.

Wildfires, while natural components of many ecosystems are increasing in frequency and intensity due to climate change. Fires can cause immediate mortality of non-fire-adapted species and have long-lasting effects on ecosystem structure and composition. Post-fire recovery can lead to significant vegetation shifts, especially if changing climate conditions favor different species than those present before the fire.

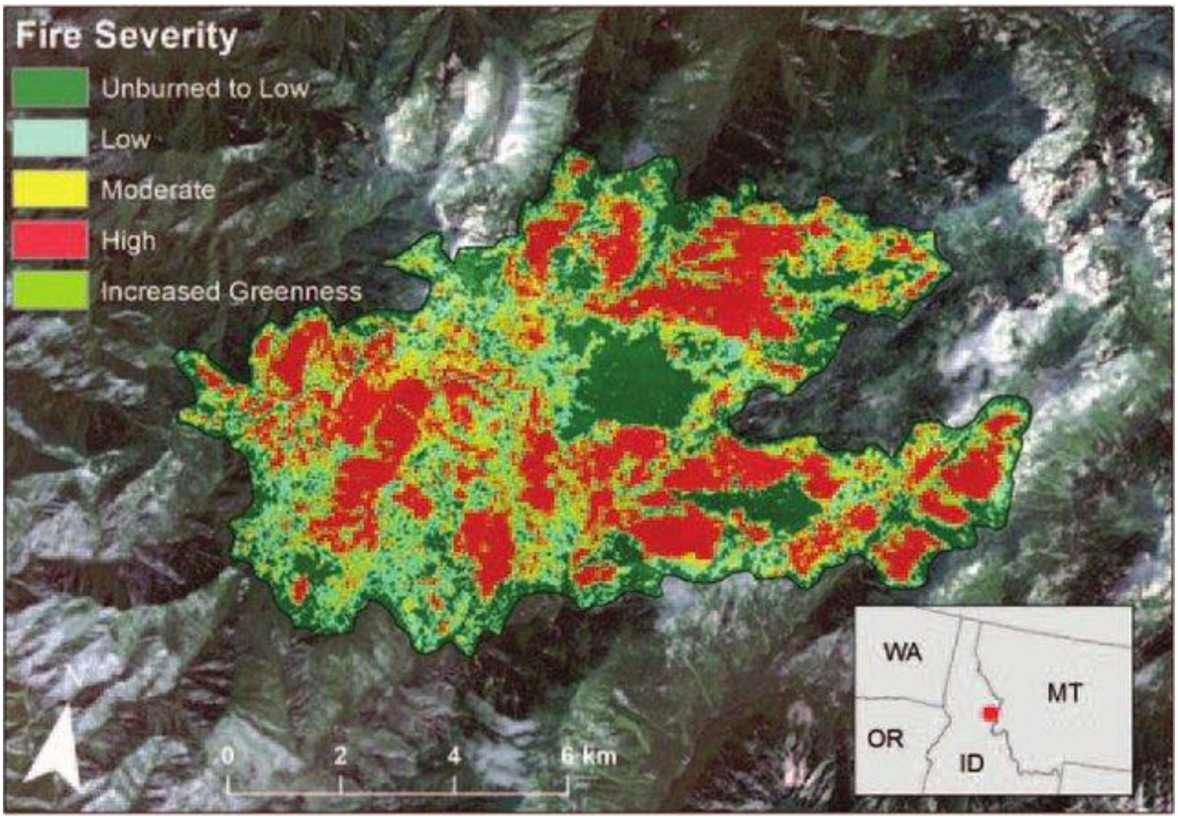

Figure 4. Remote sensing data derived from satellite imagery have greatly advanced our ability to conduct research on wilderness fires. Shown here are consistently derived and readily available data describing categories of burn severity as differences in the Normalized Burn Ratio index between prefire and postfire images. Data shown are from the MTBS 1 project for a fire in 1988 in the Selway-Bitterroot Wilderness (Miller and Aplet, 2016).

10.6 Shifts in plant community composition and distribution

- Range shifts
  - Latitudinal and altitudinal migrations
  - Limitations to migration (dispersal, habitat fragmentation)
- Changes in competitive interactions
  - Altered plant-plant competition
  - Invasive species dynamics
- Phenological mismatches
  - Plant-pollinator desynchronization
  - Herbivore-plant interactions
- Community reassembly
  - Novel ecosystems and no-analog communities
  - Loss of foundation species
- Biome shifts
  - Potential for rapid ecosystem transitions
  - Tipping points and irreversible changes
- Biodiversity implications
  - Extinction risks for specialized and endemic species
  - Potential for evolutionary adaptations

10.7 Interactions between climate change and other stressors

- Synergies with air pollution
  - Ozone and elevated temperature interactions
  - Nitrogen deposition and CO2 fertilization
- Pest and pathogen dynamics
  - Range expansions of pests and diseases
  - Altered plant defense mechanisms
- Land-use change interactions
  - Habitat fragmentation and climate change
  - Agricultural intensification and adaptation

- Nutrient cycling alterations
    - Changes in decomposition rates
    - Nitrogen and phosphorus availability
- Feedbacks with soil processes
    - Soil organic matter decomposition
    - Microbial community shifts
- Cumulative effects and ecosystem resilience
    - Multiple stressor interactions
    - Thresholds and tipping points in ecosystems

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Course 11.

Biomonitoring and Phytoremediation

11.1 Principles of biomonitoring using plants

Biomonitoring is a critical tool in environmental science that involves the use of living organisms to assess the quality of the environment. In the context of plant ecotoxicology, biomonitoring using plants offers unique advantages and insights into environmental conditions. The primary objectives of biomonitoring are to detect the presence of pollutants, assess their biological effects, and monitor changes in environmental quality over time.

There are two main types of biomonitoring:

1. Active biomonitoring: This involves the deliberate introduction of known plant species into an area of interest. These transplant studies allow for controlled exposure periods and standardized comparisons across different sites.

2. Passive biomonitoring: This utilizes naturally occurring plants in the environment. It provides information on long-term exposure and effects under real-world conditions.

Plants offer several advantages as biomonitors:

1. Wide distribution and stationary nature: Plants are found in most terrestrial and aquatic environments and remain in one location, allowing for site-specific assessments.

2. Accumulation of pollutants: Many plant species can accumulate pollutants over time, providing an integrated measure of exposure.

3. Cost-effectiveness and ease of sampling: Compared to chemical analysis of environmental samples, plant-based biomonitoring can be more economical and straightforward.

Biomonitoring can be conducted at various levels of biological organization:

1. Molecular and biochemical responses: These include changes in enzyme activities, gene expression, or metabolite profiles. They often provide early warning signs of environmental stress.

2. Physiological and morphological changes: Observable alterations in plant growth, photosynthetic efficiency, or leaf structure can indicate pollutant effects.

3. Population and community-level effects: Changes in species abundance, diversity, or community composition can reflect long-term or severe environmental impacts.

Integrating biomonitoring with traditional chemical monitoring approaches can provide a more comprehensive understanding of environmental quality. While chemical analyses offer precise quantification of pollutant levels, biomonitoring reveals the biological relevance and effects of these pollutants.

Spatial and temporal considerations are crucial in designing effective biomonitoring programs. Spatial variation in pollutant distribution and environmental conditions must be accounted for in sampling designs. Temporal aspects, including seasonal changes and long-term trends, are important for interpreting biomonitoring data accurately.

11.2 Selection of plant species for biomonitoring

The choice of plant species is critical for successful biomonitoring. Ideal biomonitor species should meet several criteria:

1. Abundance and wide distribution: The species should be common enough to allow for widespread sampling and comparisons across different areas.

2. Tolerance to pollutants of interest: The plant should be able to survive in polluted environments while still showing measurable responses to pollutant exposure.

3. Accumulation capacity: For certain types of biomonitoring, the ability to accumulate pollutants without severe toxic effects is important.

4. Ease of identification and sampling: Species that are easily recognizable and can be sampled without complex procedures are preferable.

Different plant groups are often used for specific types of biomonitoring:

1. Mosses and lichens: These are excellent biomonitors for air pollution due to their lack of root system and reliance on atmospheric deposition for nutrients.

2. Aquatic macrophytes: Plants like duckweed (Lemna sp.) or water hyacinth (Eichhornia crassipes) are useful for monitoring water pollution in freshwater systems.

3. Trees: Long-lived tree species can provide information on long-term pollution trends and are particularly useful in urban environments.

4. Grasses and herbs: These are often used for soil contamination studies due to their rapid growth and extensive root systems.

It's important to consider species-specific accumulation patterns when interpreting biomonitoring data. Different plant species may accumulate pollutants at different rates or in different plant tissues, affecting the interpretation of results.

The choice between native and introduced species for biomonitoring depends on the specific goals of the study. Native species provide information on local ecosystem impacts, while introduced species may offer standardization across different regions.

For comparative studies across different areas or time periods, the use of standardized species is often beneficial. This approach allows for more direct comparisons by minimizing variation due to species-specific responses.

11.3 Biomarkers and bioindicators in plant ecotoxicology

Biomarkers and bioindicators are essential tools in plant ecotoxicology, providing insights into the biological effects of environmental pollutants.

Biomarkers are measurable biological responses to environmental stressors. They can be classified into several types:

1. Biochemical biomarkers: These include changes in enzyme activities (e.g., antioxidant enzymes), stress proteins (e.g., heat shock proteins), or other cellular components.

2. Physiological biomarkers: Measures such as photosynthetic efficiency (often assessed through chlorophyll fluorescence) or respiration rates can indicate plant stress.

3. Morphological biomarkers: Visible changes like leaf damage, chlorosis, or growth inhibition can serve as biomarkers of pollutant exposure.

Molecular biomarkers have gained increasing attention in recent years:

1. Gene expression changes: Alterations in the expression of stress-responsive genes can provide early indications of pollutant effects.

2. Protein biomarkers: Proteomic approaches can reveal changes in protein abundance or post-translational modifications in response to pollutants.

3. Metabolomic approaches: Analysis of metabolite profiles can offer insights into pollutant-induced changes in plant metabolism.

Bioindicators, on the other hand, are species or groups of species whose presence, absence, or condition reflects environmental quality. They can be individual species that are particularly sensitive to certain pollutants or entire plant communities whose composition changes in response to environmental stress.

Effective biomarkers should meet several criteria:

1. Specificity: The biomarker should respond primarily to the stressor of interest.

2. Sensitivity: It should show detectable changes at environmentally relevant pollutant levels.

3. Dose-dependent responses: The magnitude of the biomarker response should correlate with the level of pollutant exposure.

4. Relevance to higher levels of biological organization: Ideally, the biomarker should be linked to effects at the population or ecosystem level.

Integrating multiple biomarkers in assessment can provide a more comprehensive picture of pollutant effects. This approach, sometimes called a "biomarker suite," can help overcome the limitations of individual biomarkers and provide more robust conclusions.

However, the use of biomarkers also faces challenges:

1. Natural variability: Biomarker responses can be influenced by factors other than pollutant exposure, such as season, plant age, or genetic variation.

2. Interpretation of complex mixtures: In real-world environments, plants are often exposed to multiple pollutants, making it difficult to attribute biomarker responses to specific contaminants.

3. Extrapolation to higher levels of organization: Linking molecular or cellular biomarker responses to ecological effects remains a significant challenge.

11.4 Phytoremediation: concepts and applications

Phytoremediation is an innovative and environmentally friendly approach to cleaning up contaminated environments using plants. It harnesses the natural abilities of plants to take up, accumulate, or degrade various pollutants.

The main mechanisms of phytoremediation include:

1. Phytoextraction: Plants absorb contaminants from the soil and accumulate them in harvestable plant tissues.

2. Phytodegradation: Plants or associated microorganisms break down organic pollutants into less toxic substances.

3. Phytostabilization: Plants reduce the mobility and bioavailability of pollutants in the environment, preventing their spread.

4. Phytovolatilization: Plants take up pollutants and release them into the atmosphere in a modified, less toxic form.

5. Rhizofiltration: Plant roots absorb or adsorb pollutants from water and aqueous waste streams.

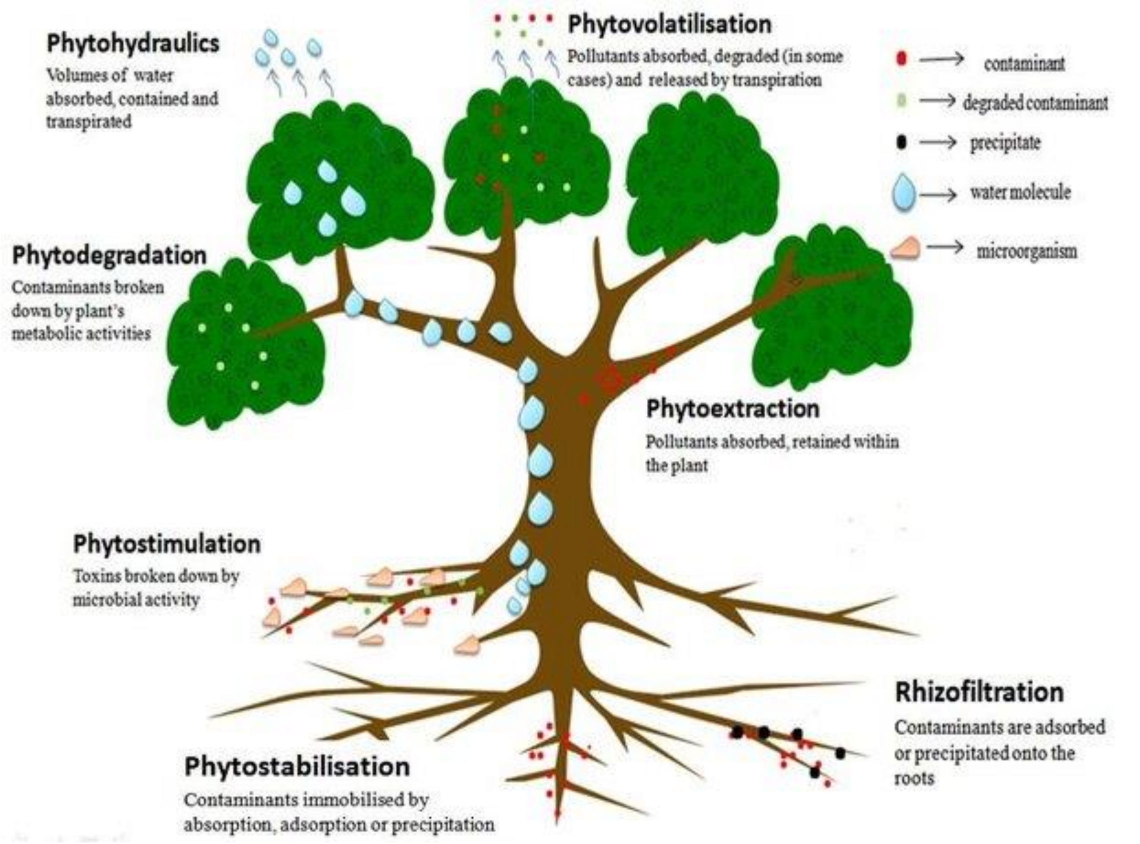

Figure 1. Overview of the basic mechanism of action of the different phytoremediation technologies (Jyrwa et al., 2016).

Phytoremediation offers several advantages:

1. Cost-effectiveness: It is generally less expensive than traditional engineering-based remediation methods.

2. Environmental friendliness: As a solar-driven process, it has minimal environmental impact and can enhance soil quality.

3. In situ application: Phytoremediation can be applied without removing contaminated soil or water, reducing disturbance to the site.

4. Public acceptance: As a "green" technology, phytoremediation often receives positive public perception.

However, phytoremediation also faces limitations:

1. Time required: The process can take several growing seasons to achieve significant contaminant reduction.

2. Depth limitations: Phytoremediation is most effective for shallow contamination within the root zone of plants.

3. Potential for food chain contamination: There is a risk that contaminated plant material could be consumed by animals.

Phytoremediation has been applied in various environments:

1. Soil remediation: Used for cleaning up sites contaminated with heavy metals, organic pollutants, or radionuclides.

2. Water treatment: Applied in constructed wetlands for treating wastewater or in rhizofiltration systems for removing pollutants from aqueous streams.

3. Air quality improvement: Certain plants can help remove air pollutants, particularly in urban environments.

11.5 Phytoextraction of heavy metals

Phytoextraction is a promising approach for remediating soils contaminated with heavy metals. It relies on the ability of certain plants, known as hyperaccumulators, to take up and concentrate high levels of metals in their tissues.

Metal hyperaccumulator plants possess several key characteristics:

1. High metal uptake capacity: They can accumulate metals at concentrations 100-1000 times higher than non-hyperaccumulator plants.

2. Rapid growth and high biomass production: This allows for efficient metal removal from the soil.

3. Tolerance to high metal concentrations: Hyperaccumulators have evolved mechanisms to detoxify or sequester high levels of metals.

Some well-known hyperaccumulator species include:

1. Thlaspi caerulescens (Alpine pennycress): Accumulates high levels of cadmium and zinc.

2. Alyssum bertolonii: Known for its ability to hyperaccumulate nickel.

3. Pteris vittata (Chinese brake fern): Efficiently accumulates arsenic.

The efficiency of phytoextraction depends on several factors:

1. Bioavailability of metals: Only the fraction of metals that is available for plant uptake can be extracted.

2. Root exudates and rhizosphere processes: Plants can modify the rhizosphere to enhance metal solubility and uptake.

3. Translocation to aboveground tissues: Efficient transport of metals from roots to shoots is crucial for phytoextraction.

Various approaches have been developed to enhance phytoextraction efficiency:

1. Chelate-assisted phytoextraction: Adding chelating agents to the soil can increase metal solubility and plant uptake.

2. Genetic engineering: Modifying plants to enhance metal uptake, translocation, or tolerance can improve phytoextraction performance.

After harvesting metal-rich plant biomass, proper processing and disposal are crucial. Options include incineration, composting, or recovery of valuable metals through phytomining.

11.6 Phytodegradation of organic pollutants

Phytodegradation involves the breakdown of organic pollutants by plants or their associated microorganisms. This process is particularly useful for remediating sites contaminated with petroleum hydrocarbons, chlorinated solvents, or pesticides.

Plants possess several enzyme systems capable of degrading organic pollutants:

1. Cytochrome P450 monooxygenases: These enzymes can oxidize a wide range of organic compounds.

2. Peroxidases: Important in the degradation of phenolic compounds and some aromatic hydrocarbons.

3. Carboxylesterases: Involved in the breakdown of certain pesticides and other ester-containing compounds.

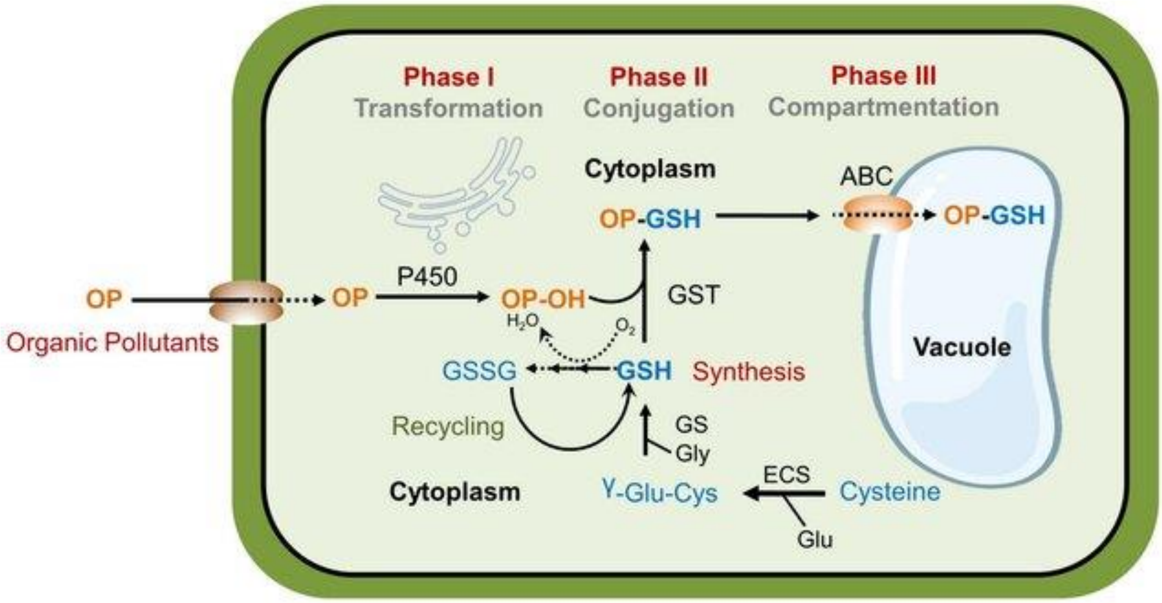

Figure 2. Simplified diagram of plant enzymatic systems involved in organic pollutant degradation (Ahammed et al., 2022).

Rhizosphere-enhanced biodegradation is a crucial aspect of phytodegradation. Plant roots release exudates that stimulate microbial activity in the rhizosphere, enhancing the degradation of organic pollutants.

The metabolic pathways for degrading common organic pollutants can be complex:

1. Petroleum hydrocarbons: Often involve initial oxidation followed by further breakdown of smaller molecules.

2. Chlorinated solvents: May undergo reductive dechlorination followed by oxidation of the resulting hydrocarbons.

3. Pesticides: Degradation pathways vary widely depending on the specific pesticide structure.

Factors influencing phytodegradation efficiency include:

1. Chemical structure of the pollutant

2. Environmental conditions (temperature, moisture, oxygen availability)

3. Plant species and associated microbial communities

Genetic engineering approaches have been explored to enhance plant degradation capacities, such as introducing mammalian cytochrome P450 genes into plants.

Integration of phytodegradation with microbial remediation approaches can offer synergistic benefits, combining the strengths of both plant and microbial degradation processes.

11.7 Rhizofiltration and constructed wetlands

Rhizofiltration is a phytoremediation technique that uses plant roots to absorb or adsorb pollutants from water. It is particularly effective for removing metals and certain organic compounds from aqueous waste streams.

Plant species used in rhizofiltration include:

1. Aquatic macrophytes: Plants like water hyacinth (*Eichhornia crassipes*) or duckweed (*Lemna* sp.) that naturally grow in water.

2. Terrestrial plants with high root biomass: Species like sunflower (Helianthus annuus) or Indian mustard (Brassica juncea) can be grown hydroponically for rhizofiltration.

Mechanisms of contaminant removal in rhizofiltration systems include:

1. Root adsorption and absorption: Pollutants can bind to root surfaces or be taken up into root tissues.

2. Precipitation and complexation: Root exudates can cause pollutants to precipitate or form stable complexes.

3. Microbial degradation in the rhizosphere: Plant roots support microbial communities that can degrade certain pollutants.

Constructed wetlands are engineered systems that use natural processes involving wetland vegetation, soils, and associated microbial communities to treat wastewater. Types of constructed wetlands include:

1. Surface flow wetlands: Water flows over the soil surface through vegetation.

2. Subsurface flow wetlands: Water flows through a porous medium (e.g., gravel) planted with wetland vegetation.

3. Vertical flow wetlands: Water is applied intermittently to the surface and percolates vertically through the substrate.

Design considerations for constructed wetlands include:

1. Hydraulic loading rate

2. Retention time

3. Plant species selection

4. Substrate composition

Constructed wetlands have been successfully applied in various contexts, including:

1. Municipal wastewater treatment

2. Agricultural runoff management

3. Industrial effluent treatment

4. Stormwater management in urban areas

11.8 Challenges and limitations of phytoremediation

- Time constraints:
  - Slow growth rates of plants
  - Long-term nature of remediation projects

- Depth limitations of root systems

- Bioavailability constraints:
  - Aging of contaminants in soil
  - Strong soil adsorption

- Potential for food chain transfer of contaminants

- Climate and seasonal limitations

- Regulatory and public perception challenges

- Economic considerations:
  - Land use during remediation
  - Comparison with conventional remediation technologies

- Genetic stability of engineered plants

- Disposal of contaminated plant biomass

- Need for site-specific optimization

- Research needs and future directions:
  - Improving plant-microbe interactions
  - Enhancing contaminant uptake and tolerance

- Developing multi-purpose phytoremediation systems

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Course 12.

Ecotoxicological Risk Assessment

12.1 Principles of ecological risk assessment

Ecological risk assessment is a structured approach used to evaluate the likelihood of adverse ecological effects resulting from exposure to one or more environmental stressors. Its primary objectives are to provide a scientific basis for decision-making in environmental management and to support the development of policies and regulations aimed at protecting ecosystem health.

The ecological risk assessment process typically consists of four main components:

1. Problem formulation: This initial step involves defining the problem, identifying the stressor(s) of concern, and determining the ecosystem components at risk.

2. Exposure assessment: This phase quantifies the spatial and temporal distribution of the stressor(s) in the environment and evaluates the likelihood of contact or co-occurrence with ecological receptors.

3. Effects assessment: This stage involves determining the relationship between stressor levels and ecological effects, often through toxicity testing or field studies.

4. Risk characterization: The final step integrates exposure and effects information to estimate risks and evaluate their significance.

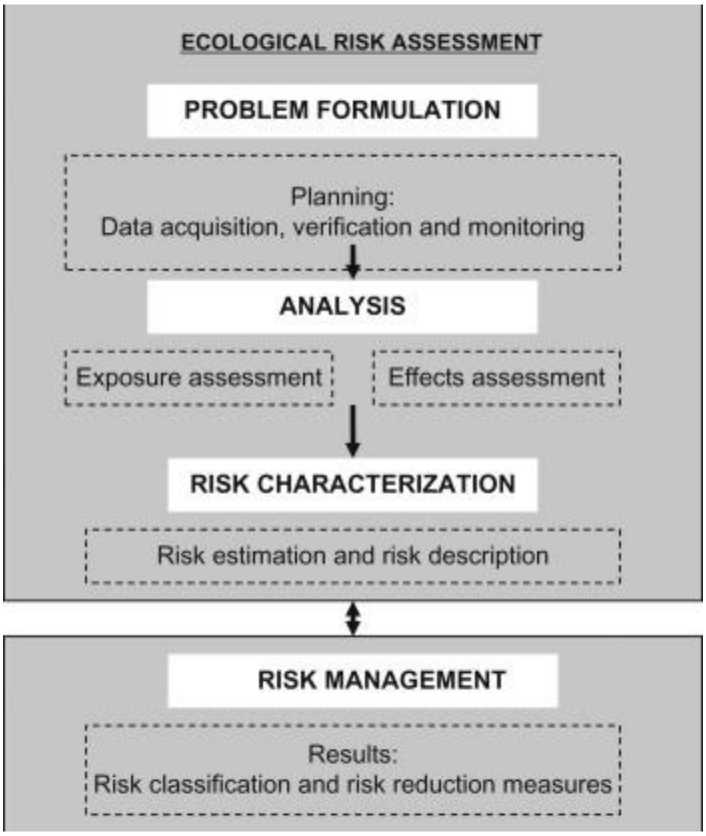

Figure 1. Ecological Risk Assessment process of Pesticides Used in Agriculture (Ying et al., 2018).

A crucial element in problem formulation is the development of a conceptual model. This model is a visual representation or written description of the hypothesized relationships between ecological entities and the stressors to which they may be exposed. It helps in identifying key relationships and focusing the assessment on the most relevant pathways and receptors.

Assessment endpoints are explicit expressions of the environmental values to be protected. These are often expressed in terms of important ecological entities (e.g., species, populations, communities) and their attributes. Measurement endpoints, on the other hand, are measurable responses to a stressor that are related to the assessment endpoints.

Ecological risk assessments often follow a tiered approach:

1. Screening-level assessments: These use conservative assumptions and simple analyses to quickly identify potential risks.

2. Refined assessments: These incorporate more site-specific data and more complex analyses to provide a more realistic evaluation of risks.

3. Site-specific assessments: These involve detailed field studies and advanced modeling to provide a comprehensive understanding of risks at a particular location.

Uncertainty analysis is a critical component of risk assessment. It involves identifying and, where possible, quantifying uncertainties at each stage of the assessment. Common sources of uncertainty include natural variability, measurement error, and model uncertainty.

The weight-of-evidence approach is often used in ecological risk assessment to integrate multiple lines of evidence. This approach considers the strength, consistency, and coherence of different types of data to reach conclusions about risks.

Regulatory frameworks and guidelines, such as those provided by the U.S. Environmental Protection Agency (EPA) or the Organisation for Economic Co-operation and Development (OECD), provide standardized approaches for conducting ecological risk assessments. These frameworks ensure consistency and comparability in risk assessments across different contexts.

12.2 Toxicity testing methods for plants

Toxicity testing is a fundamental component of effects assessment in ecological risk assessment. For plants, various types of toxicity tests are employed, depending on the specific endpoints of interest and the nature of the stressor:

1. Acute toxicity tests: These short-term tests (usually 24-96 hours) assess immediate effects of high doses of a stressor.

2. Chronic toxicity tests: These longer-term tests (weeks to months) evaluate effects of prolonged exposure, often at lower concentrations.

3. Seed germination and root elongation tests: These rapid tests assess effects on early plant development stages.

4. Whole plant growth tests: These evaluate effects on overall plant growth and biomass production.

5. Biochemical and physiological endpoint tests: These assess specific cellular or metabolic responses to stressors.

Standardized test protocols have been developed by various organizations to ensure consistency and reproducibility in toxicity testing. Key sources of standardized methods include:

1. OECD Guidelines for the Testing of Chemicals

2. International Organization for Standardization (ISO) standards

3. National regulatory test methods (e.g., U.S. EPA test guidelines)

The selection of test species is crucial in plant toxicity testing. Considerations include:

1. Relevance to the ecosystem of concern

2. Sensitivity to the stressor

3. Ease of cultivation and measurement

4. Standardization and comparability with existing data

Common test species include crop plants (e.g., lettuce, corn, soybean) and wild species (e.g., duckweed, ryegrass). Both monocots and dicots are often included to represent different plant types.

Exposure routes in plant toxicity testing can include:

1. Soil exposure: Plants are grown in contaminated soil or artificial soil amended with the test substance.

2. Hydroponic systems: Plants are exposed to the test substance in nutrient solutions.

3. Foliar application: The test substance is applied directly to plant leaves.

Endpoints measured in plant toxicity tests can be categorized as:

1. Morphological: Growth parameters (e.g., height, leaf area), biomass production

2. Physiological: Photosynthetic efficiency, transpiration rates, nutrient uptake

3. Biochemical: Enzyme activities, stress marker levels (e.g., malondialdehyde for lipid peroxidation)

4. Reproductive: Seed production, pollen viability, fruit development

12.3 Dose-response relationships and threshold levels

Understanding the relationship between the dose of a stressor and the response of an organism is fundamental to ecotoxicology. The dose-response relationship describes how the effect on an organism change with increasing dose or concentration of a stressor.

Dose-response curves can take various forms:

1. Monotonic responses: The response consistently increases or decreases with increasing dose.

2. Non-monotonic responses: The response changes direction over the dose range. An example is hormesis, where low doses stimulate a beneficial response while higher doses are inhibitory.

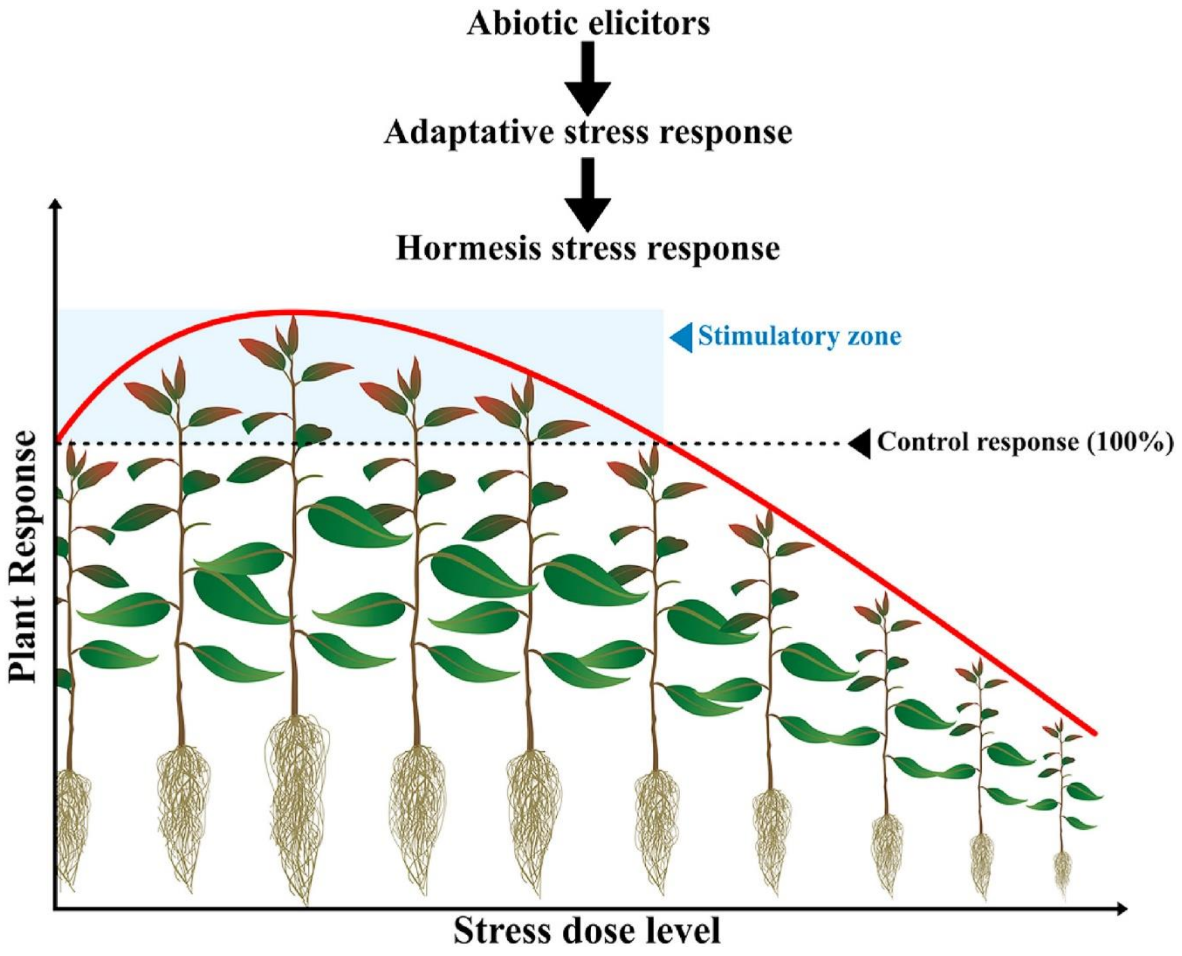

Figure 2. Hormesis induction through abiotic elicitors of plant (Agathokleous et al., 2019).

Statistical analysis of dose-response data is crucial for deriving toxicity metrics. Common approaches include:

1. Probit analysis: Used for quantal responses (e.g., mortality)

2. Logistic regression: Suitable for both quantal and continuous responses

3. Benchmark dose modeling: Estimates the dose that produces a predetermined change in response

Key toxicity metrics derived from dose-response data include:

1. EC50 (median effective concentration): The concentration that causes a 50% effect in the measured endpoint.

2. NOEC (no observed effect concentration): The highest tested concentration that does not cause a statistically significant effect.

3. LOEC (lowest observed effect concentration): The lowest tested concentration that causes a statistically significant effect.

The concept of thresholds is important in ecotoxicology, although it can be challenging to define true thresholds for biological responses. Relevant threshold concepts include:

1. Threshold of toxicological concern (TTC): A level of exposure below which no significant adverse effects are expected.

2. Critical effect dose (CED): The dose at which adverse effects first appear.

Challenges in determining thresholds for plant responses include natural variability in plant populations, the potential for low-dose effects, and difficulties in detecting small effect sizes.

12.4 Bioassays and their applications in plant ecotoxicology

Bioassays are tests that use living organisms to detect or measure the presence and effects of substances in the environment. In plant ecotoxicology, bioassays play a crucial role in assessing the potential impacts of pollutants on plant life.

Commonly used plant bioassays include:

1. Lemna growth inhibition test: Uses duckweed to assess effects on aquatic plants.

2. Arabidopsis gene expression assays: Utilizes changes in gene expression as sensitive indicators of stress.

3. Tradescantia micronucleus test: Assesses genotoxicity by observing micronucleus formation in pollen mother cells.

4. Allium cepa chromosome aberration test: Evaluates genotoxicity by observing chromosomal abnormalities in onion root tips.

Applications of bioassays in plant ecotoxicology include:

1. Screening of environmental samples: Rapid assessment of potential toxicity in water, soil, or air samples.

2. Toxicity identification evaluation (TIE): A stepwise process to identify specific toxicants in complex mixtures.

3. Monitoring of remediation progress: Assessing the effectiveness of cleanup efforts over time.

4. Regulatory compliance testing: Ensuring that environmental quality standards are met.

Advantages of plant bioassays include their sensitivity, ecological relevance, and ability to integrate the effects of multiple stressors. However, limitations include potential variability in responses and difficulties in extrapolating results to field conditions.

Integration of bioassays with chemical analysis provides a powerful approach for environmental assessment. While chemical analysis identifies and quantifies specific pollutants, bioassays reveal their biological effects and potential interactions.

High-throughput screening approaches, such as microplate-based assays and automated image analysis, are increasingly being applied to plant bioassays. These methods allow for rapid testing of multiple samples or conditions, enhancing the efficiency of ecotoxicological assessments.

12.5 Species sensitivity distributions

Species sensitivity distributions (SSDs) are statistical models that describe the variation in sensitivity of different species to a particular stressor. SSDs are powerful tools in ecological risk assessment, allowing for the estimation of the proportion of species potentially affected at different stressor levels.

Construction of an SSD requires toxicity data for multiple species, typically represented by EC50 or NOEC values. Key considerations in data selection include:

1. Taxonomic diversity: Representing a range of plant types

2. Ecological relevance: Including species relevant to the ecosystem of concern

3. Data quality: Using reliable and standardized toxicity test results

Statistical methods for fitting SSDs include:

1. Log-normal distribution: Assumes toxicity values are log-normally distributed

2. Log-logistic distribution: Often provides a better fit for ecotoxicological data

From the fitted SSD, protective concentrations can be derived:

1. HC5 (hazardous concentration for 5% of species): The concentration at which 5% of species are potentially affected.

2. PAF (potentially affected fraction): The proportion of species potentially affected at a given concentration.

Applications of SSDs in risk assessment include:

1. Derivation of environmental quality standards: HC5 values are often used as a basis for setting protective limits.

2. Comparative toxicity assessment: SSDs allow for comparison of the relative toxicity of different substances.

Limitations of the SSD approach include:

1. Data requirements: Constructing robust SSDs requires toxicity data for multiple species.

2. Representativeness: The species tested may not fully represent the ecosystem of concern.

3. Extrapolation challenges: Difficulties in relating laboratory-derived data to field conditions.

12.6 Ecological modeling in risk assessment

Ecological models are increasingly used in risk assessment to predict the potential impacts of stressors on populations, communities, and ecosystems. These models can integrate complex interactions and provide insights into long-term and indirect effects that may be difficult to assess through empirical studies alone.

Types of ecological models used in risk assessment include:

1. Population dynamics models: Simulate changes in population size and structure over time.

2. Food web models: Represent trophic interactions and energy flow through ecosystems.

3. Landscape-level models: Incorporate spatial heterogeneity and movement of organisms or contaminants.

4. Toxicokinetic-toxicodynamic (TKTD) models: Describe the uptake, distribution, and effects of toxicants in organisms.

Incorporation of toxicity data into ecological models can occur at various levels, from simple dose-response relationships to complex mechanistic descriptions of toxicant effects on physiological processes.

Spatially explicit modeling approaches are particularly valuable in plant ecotoxicology, as they can account for heterogeneity in contaminant distribution and habitat characteristics.

Dynamic energy budget (DEB) theory provides a framework for modeling how organisms acquire and utilize energy, and how these processes are affected by toxicants. DEB models are increasingly applied in ecotoxicology to link individual-level effects to population-level outcomes.

Model validation and uncertainty analysis are crucial steps in ecological modeling. Validation involves comparing model predictions with independent data, while uncertainty analysis assesses the impact of uncertainties in model inputs and structure on the outputs.

Applications of ecological models in risk assessment include:

1. Predicting long-term effects of contaminants on plant populations and communities
2. Assessing potential for recovery following exposure
3. Evaluating the effectiveness of different management scenarios
4. Extrapolating from laboratory toxicity data to field-level effects

12.7 Risk characterization and management strategies

Risk characterization is the final step in the risk assessment process, integrating the results of exposure and effects assessments to estimate risks and evaluate their significance.

Quantitative risk characterization methods include:

1. Hazard quotient approach: Compares exposure levels to toxicity thresholds
2. Probabilistic risk assessment: Incorporates variability and uncertainty in exposure and effects

Qualitative risk characterization approaches may be used when quantitative data are limited, often employing expert judgment and weight-of-evidence evaluations.

Uncertainty and variability are important considerations in risk characterization. Sources of uncertainty should be clearly identified and, where possible, quantified.

Risk management options based on the results of risk characterization may include:

1. Source control and emission reduction
2. Environmental remediation
3. Habitat modification to reduce exposure or enhance resilience
4. Regulatory actions and policy development

Effective risk communication is crucial for translating complex scientific findings into actionable information for stakeholders. This involves:

1. Clear presentation of risk assessment results and uncertainties
2. Engagement with diverse stakeholders
3. Tailoring communication strategies to different audiences

Adaptive management approaches are increasingly applied in ecological risk assessment and management. These involve iterative cycles of implementation, monitoring, and adjustment of management strategies based on new information.

Emerging challenges in plant ecotoxicological risk assessment include:

1. Assessing mixture toxicity: Understanding and predicting the effects of complex chemical mixtures

2. Incorporating climate change interactions: Evaluating how climate change may modify contaminant effects and plant responses

3. Addressing nanomaterials and emerging contaminants: Developing appropriate methods for assessing novel stressors

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Course 13.

Regulatory Framework and Environmental Policy

13.1 International conventions on environmental protection

- United Nations Framework Convention on Climate Change (UNFCCC)
    - Kyoto Protocol
    - Paris Agreement
- Convention on Biological Diversity (CBD)
- Stockholm Convention on Persistent Organic Pollutants
- Basel Convention on Hazardous Wastes
- Rotterdam Convention on Prior Informed Consent
- Vienna Convention for the Protection of the Ozone Layer
    - Montreal Protocol on Substances that Deplete the Ozone Layer
- UNECE Convention on Long-range Transboundary Air Pollution
- Ramsar Convention on Wetlands
- Implementation mechanisms and compliance monitoring
- Challenges in international environmental governance

13.2 National and regional regulations on pollutants

- United States:
    - Clean Air Act
    - Clean Water Act
    - Toxic Substances Control Act (TSCA)
    - Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA)
- European Union:
    - REACH (Registration, Evaluation, Authorization and Restriction of Chemicals)
    - Water Framework Directive
    - Industrial Emissions Directive
    - Plant Protection Products Regulation
- Other regional frameworks:
    - China's Environmental Protection Law
    - Canada's Environmental Protection Act

  - Australia's National Environment Protection Measures
- Comparison of regulatory approaches across different regions
- Harmonization efforts and mutual recognition agreements

13.3 Environmental quality standards for soil and water

- Soil quality standards:
  - Heavy metal limits
  - Organic contaminant thresholds
  - Microbiological criteria
- Water quality standards:
  - Drinking water guidelines (WHO, national standards)
  - Surface water quality criteria
  - Groundwater protection standards
- Sediment quality guidelines
- Ecological soil screening levels (Eco-SSLs)
- Derivation methodologies for environmental quality standards:
  - Use of toxicity data and safety factors
  - Background concentration considerations
- Site-specific standard development
- Challenges in setting standards for emerging contaminants

13.4 Air quality guidelines and their ecological relevance

- World Health Organization (WHO) Air Quality Guidelines
- National Ambient Air Quality Standards (NAAQS) in various countries
- Critical levels for vegetation protection:
  - Ozone exposure indices (AOT40, W126)
  - Sulfur dioxide and nitrogen oxide thresholds
- Particulate matter standards and their relevance to plants
- Deposition-based critical loads for ecosystems
- Challenges in relating human health-based standards to ecological effects
- Incorporating climate change considerations in air quality guidelines

13.5 Risk-based approaches in environmental management

- Risk-based corrective action (RBCA) framework
- Tiered approach to risk assessment and management
- Site-specific risk assessment in contaminated land management
- Environmental impact assessment (EIA) and strategic environmental assessment (SEA)
- Ecological risk assessment in pesticide registration
- Incorporating ecosystem services in risk-based decision making
- Probabilistic risk assessment approaches
- Adaptive management strategies in environmental policy
- Cost-benefit analysis in environmental decision making

13.6 The role of ecotoxicology in policy-making

- Scientific input in regulatory processes:
  - Toxicity testing for chemical registration
  - Derivation of environmental quality standards
  - Ecological risk assessment for policy decisions
- Challenges in translating ecotoxicological research into policy:
  - Dealing with scientific uncertainty
  - Balancing precautionary principle with evidence-based decision making
- The role of ecotoxicologists in policy advisory bodies
- Ecotoxicological considerations in emerging areas of environmental concern:
  - Nanomaterials regulation
  - Microplastics pollution
  - Endocrine disruptors policy
- Integration of mixture toxicity concepts in regulatory frameworks
- Biomonitoring and bio-indicators in compliance assessment
- Future directions in ecotoxicology-informed environmental policy:
  - Systems biology approaches
  - Adverse outcome pathways (AOPs) in regulatory toxicology
  - High-throughput screening and computational toxicology

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Course 14.

Emerging Contaminants and Future Challenges

14.1 Nanomaterials and their environmental fate

- Nanomaterials: materials with at least one dimension between 1-100 nm
- Environmental concerns: Complex behavior in environment due to size and properties
- Effects on plants: Can accumulate in tissues and potentially cause harm
- Challenges: Need for standardized detection methods and appropriate regulations
- Research needs: Understanding long-term impacts and improving analytical techniques

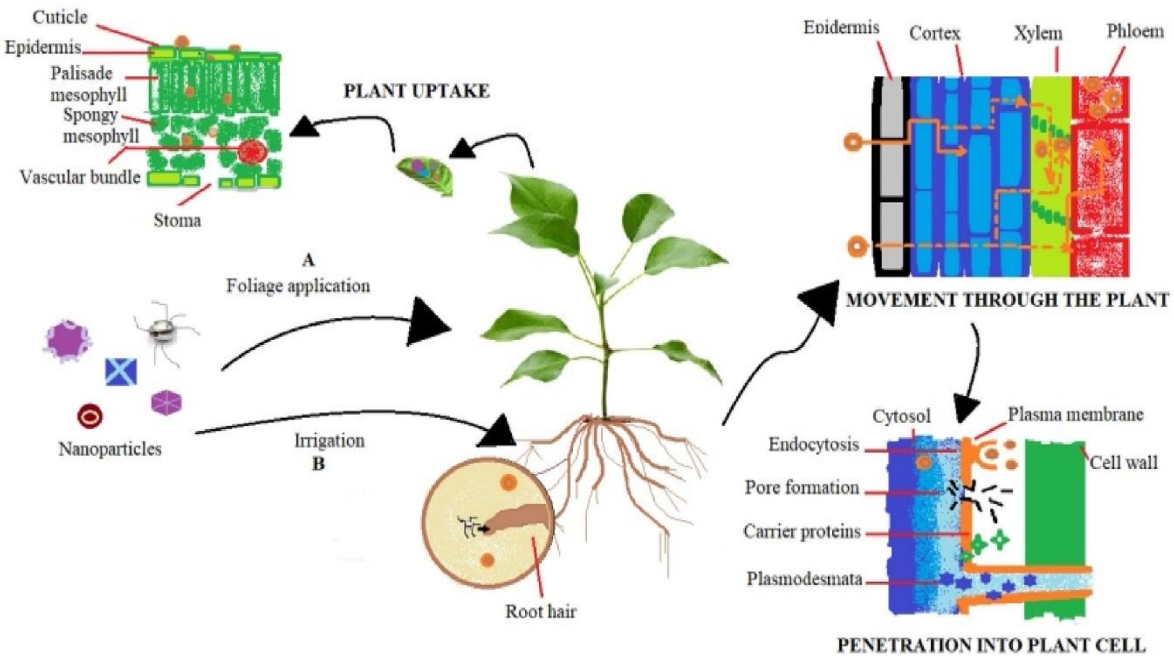

Figure 1. Mechanism of uptake and translocation in plants (A) Uptake of nanoparticles via foliar application. Penetration of nanoparticles into leaf's cuticle and further entry into palisade, spongy mesophyll and ultimately in vascular bundles (B) Uptake of nanoparticles through roots, they get penetrated in root hairs then into channels (xylem and phloem) by apoplastic and symplastic pathways (Tripathi et al., 2017).

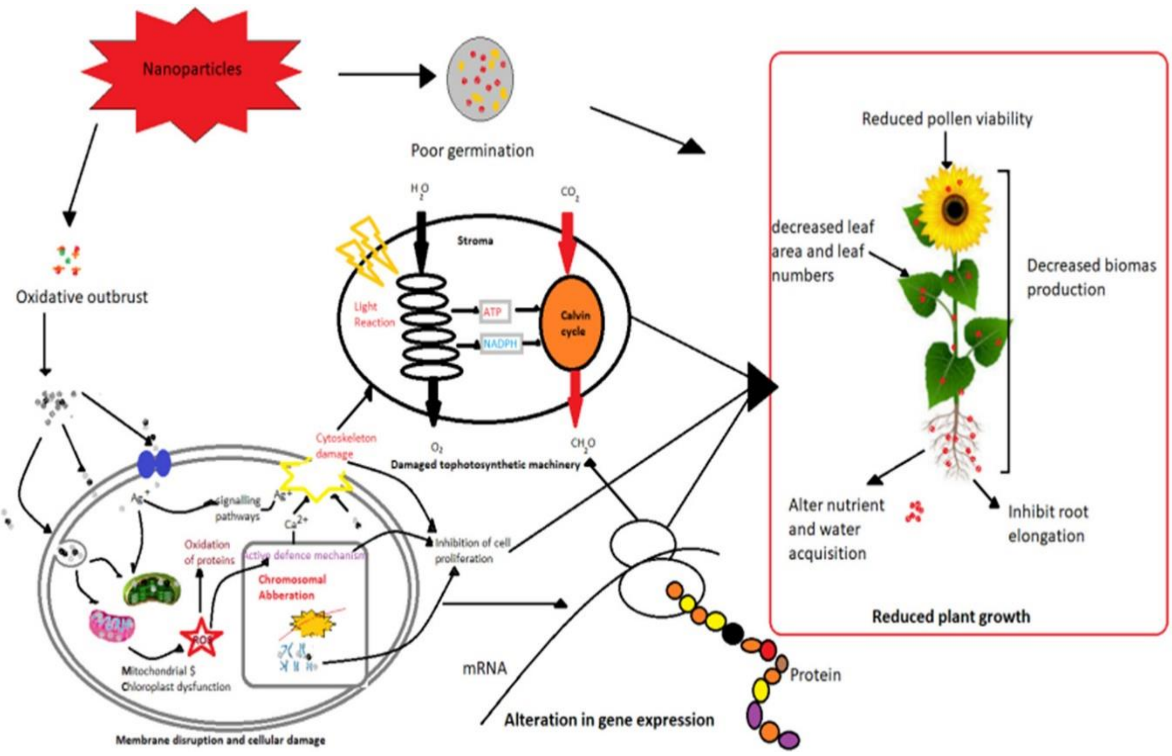

Figure 2. Phytotoxic effects of nanoparticles on development and growth in plant **(**Balážová et al. 2018).

14.2 Microplastics in terrestrial ecosystems

- Sources: Enter soil through various pathways including human activities
- Concerns: Can change soil properties and carry other pollutants
- Plant effects: Possible uptake and interference with normal plant functions
- Challenges: Difficult to detect in soil and assess long-term consequences
- Research priorities: Developing better detection methods and studying ecosystem impacts

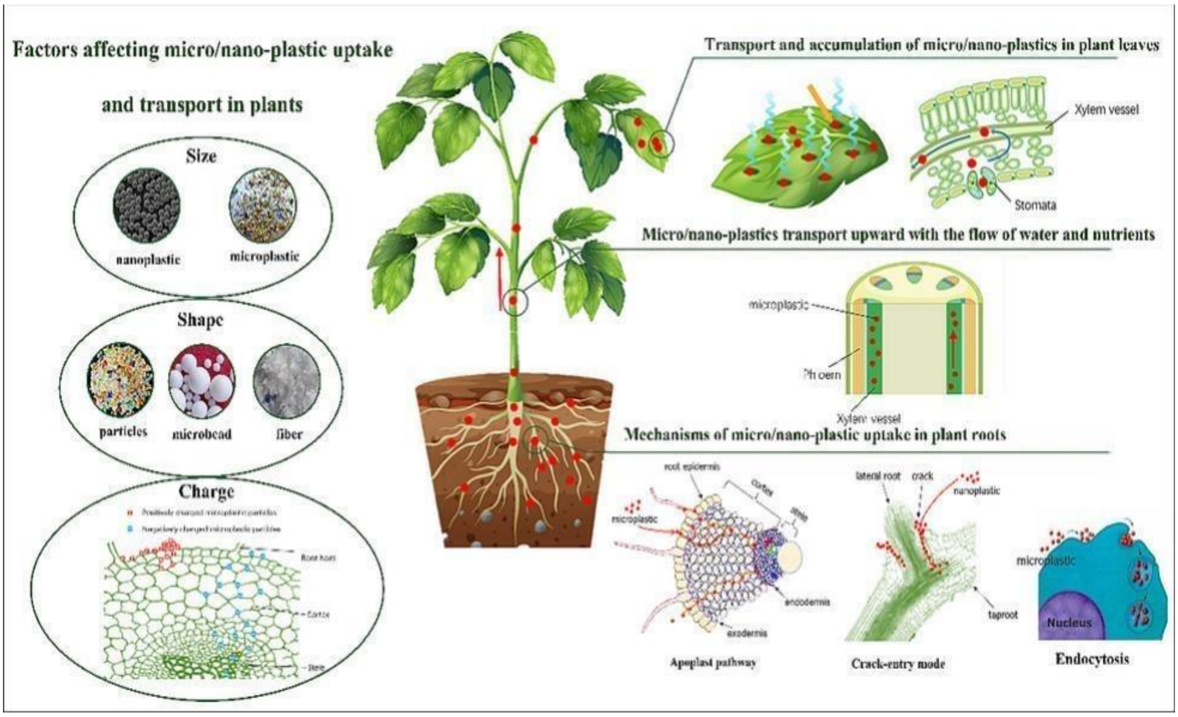

Figure 3. Uptake and transport of micro/nanoplastics in terrestrial plants: Detection, mechanisms, and influencing factors (Yu et al., 2023).

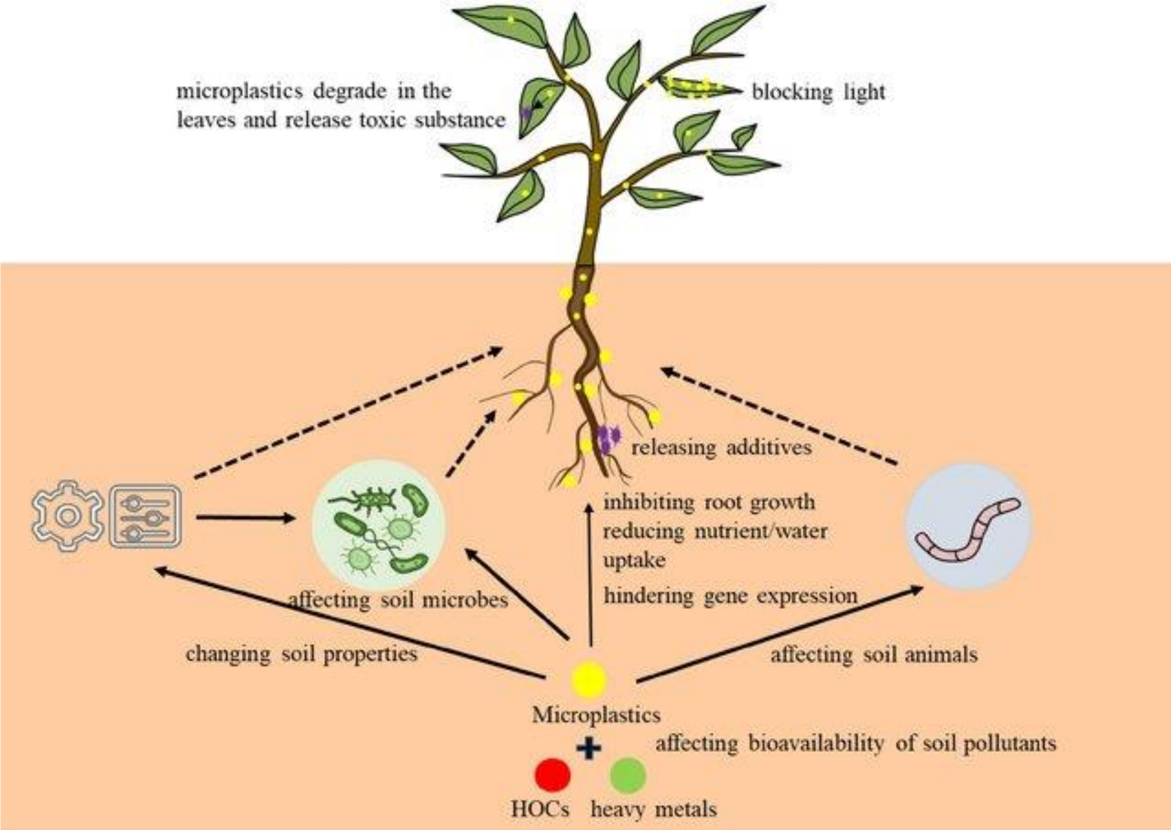

Figure 4. Inhibitory mechanism sof microplastics on plants. The solid arrows refer to the direct influencing mechanism; the dotted arrows refer to the indirect influencing mechanism (Li et al., 2022).

14.3 Pharmaceutical and personal care products (PPCPs) in the environment

- Sources: Primarily from human use and improper disposal
- Concerns: Many persist in environment and can accumulate in organisms
- Plant impacts: Can be taken up by plants and disrupt their processes
- Challenges: Wide variety of compounds with complex interactions
- Research needs: Improving removal from wastewater and understanding broader ecological effects

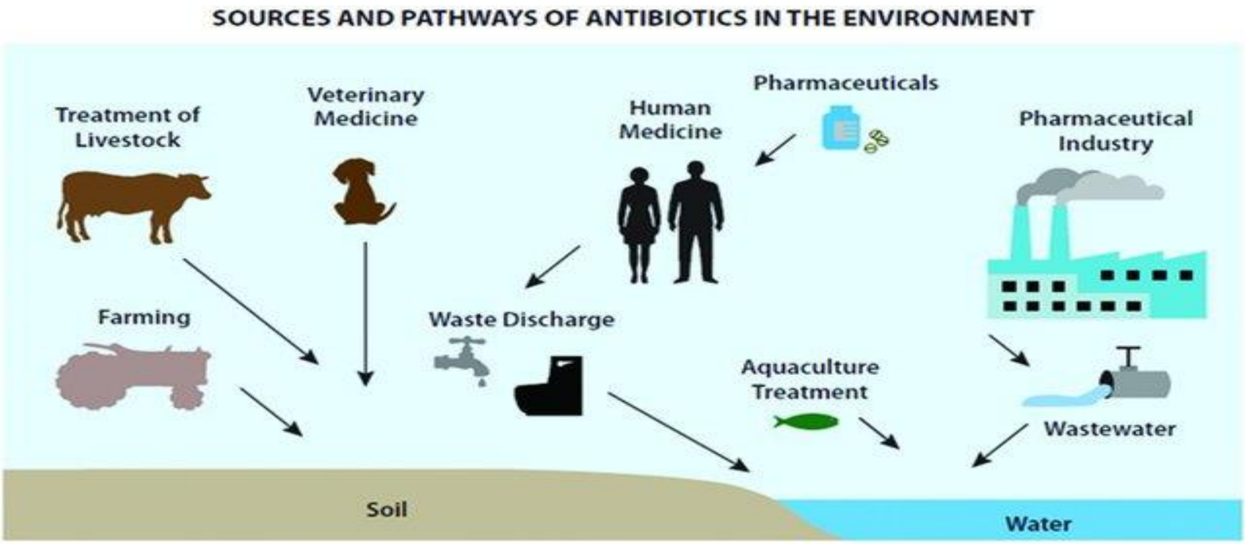

Figure 5. Sources and pathways of pharmaceuticals and personal care products in the environment (Kurwadkar et al., 2015).

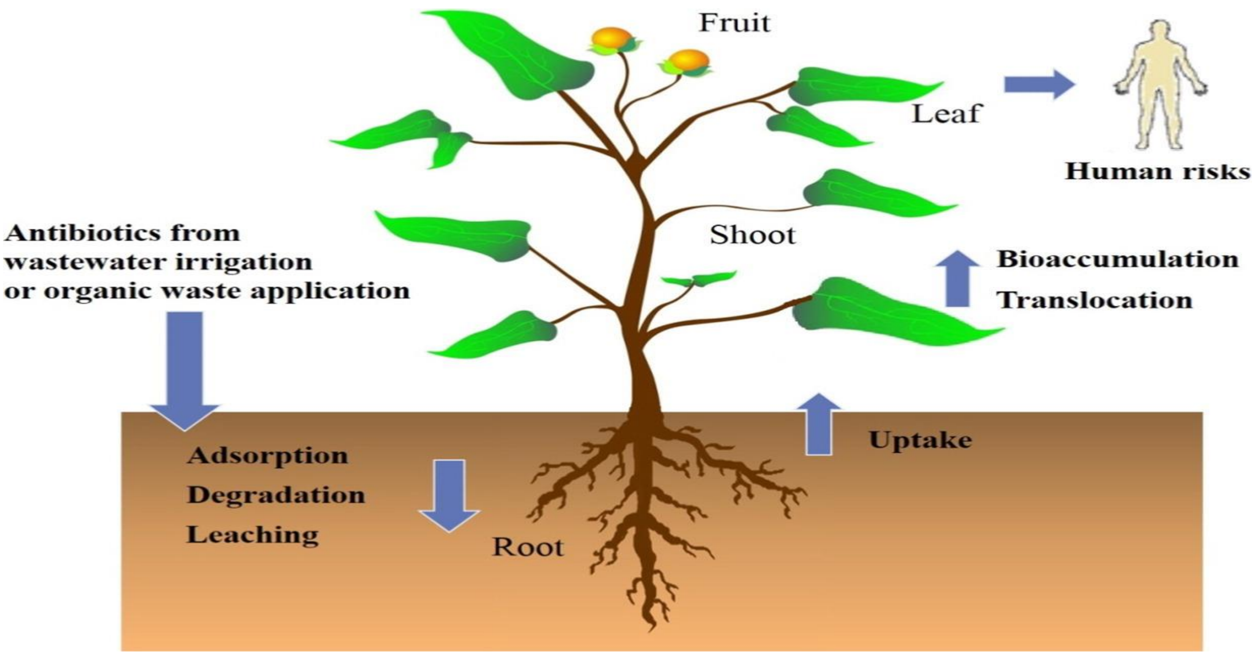

Figure 6. Sources and fate of antibiotics in soil and their uptake by edible crops (Pan and Chu, 2017).

14.4 Endocrine disruptors and their effects on plants

- Impact: Interfere with plant hormone systems, affecting growth and development
- Examples: Include both synthetic and natural compounds
- Ecological implications: Can have wider effects on plant-animal interactions
- Challenges: Complex mechanisms and effects, even at low doses
- Research priorities: Understanding molecular effects and long-term consequences

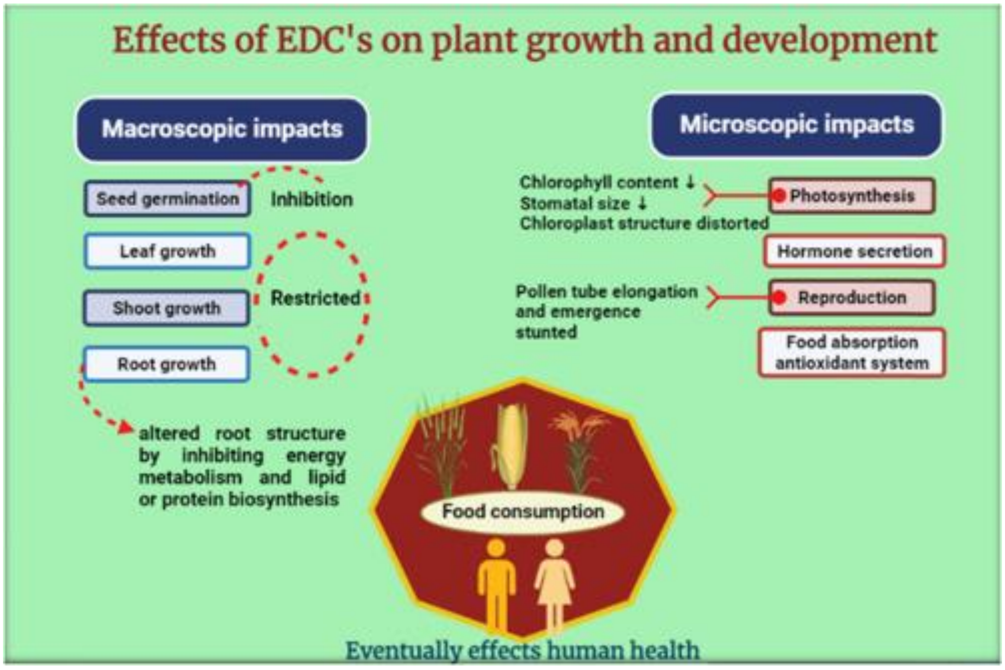

Figure 7. Endocrine-disrupting chemicals (EDCs) exposure-induced alteration in the germination, growth, and physiological trait of the plant (Saraswat, et al., 2024).

14.5 Combined effects of multiple stressors

- Complexity: Pollutants can interact in various ways when combined
- Factors: Include both pollutants and environmental conditions
- Challenges: Difficult to study due to numerous possible combinations
- Research needs: Developing methods to study multiple stressors efficiently

14.6 Climate change and pollutant interactions

- Effects: Climate change can alter how pollutants behave and affect plants
- Factors: Changes in temperature, rainfall, and CO_2 levels all play a role
- Challenges: Long-term nature of climate change complicates study
- Research priorities: Integrating climate and pollutant models for better predictions

14.7 Future directions in plant ecotoxicology research

- Focuses on advancing understanding of pollutant effects on plants
- Emphasizes new technologies, complex interactions, and ecosystem-level impacts
- Aims to improve prediction and mitigation of pollution effects on plant ecosystems

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Annex

Program of the Subject matter

Intitulé du Master : Biodiversité et physiologie végétale
Semestre *:* S2
Intitulé de l'UE :UEM1
Intitulé de la matière : Ecotoxicologie Végétale
Crédits : 5
Coefficients :3
Objectifs de l'enseignement (*Décrire ce que l'étudiant est censé avoir acquis comme compétences après le succès à cette matière – maximum 3 lignes).*

Connaissances préalables recommandées (*descriptif succinct des connaissances requises pour pouvoir suivre cet enseignement – Maximum 2 lignes).*Un peu de chimie de base... Une certaine connaissance de processus centraux (croissance et développement de plantes, régulation hormonale, nutrition minérale)

Contenu de la matière :

Effets de substances toxiques sur les végétaux, par exemple des métaux lourds contaminant des sols et des eaux terrestres (absorption, accumulation, effets sur des paramètres spécifiques aux plantes tels que la photosynthèse, la croissance et le métabolisme central, etc.;

Aspects de toxicité humaine avec l'exemple du cadmium) ;

Le phénomène de stress et des réactions de protection ;

Les contaminants organiques ("xénobiotiques"), leur absorption et les effets biochimiques et physiologiques ;

Les gaz toxiques (l'ozone, les oxydes d'azote et du soufre, le peroxyacétylnitrate, le "smog" chimique en général) ;

Les raisons putatives pour le dépérissement des forêts ;

Le trou d'ozone et l'échauffement terrestre - conséquences possibles pour les écosystèmes végétaux...

Mode d'évaluation : Exposés, Comptes rendus de TD/TP, Examen écrit, Rattrapage