Ministère de l'Enseignement Supereir et de la Recherche Scientifique
Université Djilali Bounnama de Khemis Miliana
Faculté des Sciences de la Nature et de la Vie et des Sciences de la Terre

---

N° 37…./FSNV-ST/PGRS/2026

Khemis Miliana, le 10/06/2026

EXTRAIT DE P.V DU CONSEIL SCIENTIFIQUE

Du 10/06/2026

Objet : Retour Expertise polycopié de cours

Suite à l'expertise du polycopié de cours du Dr RICHA Amina, intitulé **« Water Geochemistry & Aquatic Pollution»** réalisée par les experts cités dans le tableau ci-dessous. Le Conseil Scientifique de la Faculté tenu le 10/06/2026 a émis **un avis favorable.**

Nom et Prénom	Grade	Etablissement	Expertise
BOUDERBAIA Abdelkader	professeur	U. KHEMIS MILIANA	Avis favorable
BENKHELIFA Mohamed	professeur	U. MOSTAGANEM	Avis favorable

Le Président du Conseil Scientifique

كواش بن موسى
رئيس المجلس العلمي للكلية
علوم الطبيعة والحياة وعلوم الأرض

People's Democratic Republic of Algeria
Ministry of Higher Education and Scientific Research

Djilali Bounaama University Khemis Miliana
Faculty of Natural and life siences and earth sciences
Department of Ecology and Environment

HANDOUT

Water Geochemistry and Aquatic Pollution
WGAP
« Learning Materials and Self-Assessment Exercises »

Prepared by:
Dr. RICHA Amina

المجلس العلمي

Academic Year: 2025-2026

People's Democratic Republic of Algeria
Ministry of Higher Education and Scientific Research

Djilali Bounaama University Khemis Miliana

Faculty of Natural and life siences and earth sciences

Department of Ecology and Environment

HANDOUT

Water Geochemistry and Aquatic Pollution
WGAP
« Learning Materials and Self-Assessment Exercises »

Prepared by:
Dr. RICHA Amina

Academic Year: 2025-2026

Preface

This course handout for **Water Geochemistry and Aquatic Pollution** is intended for first-year Master's students in Bioclimatology and is also suitable for students in environmental sciences, hydrogeology, and related disciplines. It integrates fundamental principles of geochemistry with their environmental applications to provide a clear understanding of water rock interactions, pollutant behavior, and the processes that control water quality in natural systems.

Based on several years of teaching and field experience in hydrogeochemistry and environmental assessment, this handout offers both theoretical knowledge and practical tools to help students master the essential concepts of water geochemistry and aquatic pollution. Developed in accordance with the official Master's curriculum, it follows a progressive pedagogical approach that moves from fundamental principles to applied case studies.

Chapter I introduces the hydrological cycle and key concepts of water chemistry. Chapter II examines the fundamental geochemical processes governing water mineralization, chemical equilibria and stability diagrams. Chapter III explores the main sources and mechanisms of aquatic pollution including agricultural contaminants, industrial and urban pollutants and their impacts on ecosystems. Chapter IV focuses on analytical methods and water quality monitoring, covering physicochemical parameters and international and national water quality standards. Chapter V introduces geochemical modeling tools, particularly DIAGRAMS & PHREEQC presenting file structure, databases, and practical examples related to speciation, mineral saturation and transport processes. Chapter VI concludes with applied case studies. These studies strengthen students' ability to interpret environmental data and apply geochemical reasoning to real-world challenges. Overall, this handout aims to equip students with the scientific understanding and analytical skills necessary to evaluate water quality, diagnose contamination processes, and contribute effectively to environmental protection and sustainable water resource management.

This manuscript is written in a clear and structured style, supported by practical examples and applied case studies to facilitate comprehension of key concepts. Students, colleagues, and all readers are warmly invited to share their comments and suggestions regarding the content and format of this work at: **a.richa@univ-dbkm.dz**.

Your feedback is sincerely appreciated and will contribute to the continuous improvement of this material.

TABLE OF CONTENT

TABLE OF CONTENT

TABLE OF CONTENT

People's Democratic Republic of Algeria
Ministry of Higher Education and Scientific Research

Djilali Bounaama University Khemis Miliana

Faculty of Natural and life siences and earth sciences

Department of Ecology and Environment

HANDOUT

Water Geochemistry and Aquatic Pollution
WGAP
« Learning Materials and Self-Assessment Exercises »

Prepared by:
Dr. RICHA Amina

Academic Year: 2025-2026

Preface

This course handout for **Water Geochemistry and Aquatic Pollution** is intended for first-year Master's students in Bioclimatology and is also suitable for students in environmental sciences, hydrogeology, and related disciplines. It integrates fundamental principles of geochemistry with their environmental applications to provide a clear understanding of water rock interactions, pollutant behavior, and the processes that control water quality in natural systems.

Based on several years of teaching and field experience in hydrogeochemistry and environmental assessment, this handout offers both theoretical knowledge and practical tools to help students master the essential concepts of water geochemistry and aquatic pollution. Developed in accordance with the official Master's curriculum, it follows a progressive pedagogical approach that moves from fundamental principles to applied case studies.

Chapter I introduces the hydrological cycle and key concepts of water chemistry. Chapter II examines the fundamental geochemical processes governing water mineralization, chemical equilibria and stability diagrams. Chapter III explores the main sources and mechanisms of aquatic pollution including agricultural contaminants, industrial and urban pollutants and their impacts on ecosystems. Chapter IV focuses on analytical methods and water quality monitoring, covering physicochemical parameters and international and national water quality standards. Chapter V introduces geochemical modeling tools, particularly DIAGRAMS & PHREEQC presenting file structure, databases, and practical examples related to speciation, mineral saturation and transport processes. Chapter VI concludes with applied case studies. These studies strengthen students' ability to interpret environmental data and apply geochemical reasoning to real-world challenges. Overall, this handout aims to equip students with the scientific understanding and analytical skills necessary to evaluate water quality, diagnose contamination processes, and contribute effectively to environmental protection and sustainable water resource management.

This manuscript is written in a clear and structured style, supported by practical examples and applied case studies to facilitate comprehension of key concepts. Students, colleagues, and all readers are warmly invited to share their comments and suggestions regarding the content and format of this work at: **a.richa@univ-dbkm.dz**.

Your feedback is sincerely appreciated and will contribute to the continuous improvement of this material.

TABLE OF CONTENT

TABLE OF CONTENT

TABLE OF CONTENT

General Introduction

Water is essential for the functioning of terrestrial ecosystems and sustainable development. Its quality determines the health of ecosystems, agricultural productivity, and resource availability across various sectors, and the balance of bioclimatic environments. In a world experiencing rapid population growth, urbanization, industrialization, and climate disruptions, understanding the mechanisms that govern water chemistry is a scientific, societal, and environmental challenge.

Geochemistry is an indispensable tool for the qualitative and quantitative management of water resources, particularly for ensuring their sustainability and supporting adaptation to climate change. Geochemistry serves both as a science for understanding natural processes and as an environmental diagnostic tool.

Water geochemistry studies the origin, distribution, and evolution of chemical elements in aquatic environments. It aims to understand exchanges between water, rocks, the atmosphere, the biosphere, and human activities. Studying these interactions allows for the understanding of processes of transfer, transformation, and accumulation of nutrients and chemical elements, whether naturally occurring or resulting from anthropogenic pollution.

This module provides a comprehensive and integrated approach to the theoretical foundations of water geochemistry and its practical applications for managing water pollution and environmental modeling. It enables students to acquire the skills necessary to assess water quality, identify contamination sources and processes, and evaluate the impact of climate change on water geochemistry across different reservoirs, thereby developing essential competencies in environmental management.

The teaching is based on real case studies, experimental analyses, and the use of specialized software such as Diagrams and PHREEQC for simulating chemical equilibria and reactions in natural waters. This module allows students to acquire fundamental cross-disciplinary skills, beginning with understanding, interpreting, and modeling geochemical phenomena, thereby strengthening their ability to manage water resources effectively in a context of sustainable development and climate resilience, as well as to identify pollution sources.

Chapter I: Introduction to Water Geochemistry

1. Origin of Chemical Elements in Water

Natural water is never chemically pure. As it passes through different environmental compartments (atmosphere, soils, rocks, biosphere), it acquires chemical substances of diverse origins. These dissolved, colloidal, or particulate substances define water chemistry and its quality. The origin of these elements falls into three major categories: atmospheric, geological, and anthropogenic sources.

Atmospheric sources include marine aerosol deposits and desert dust, which influence the chemistry of surface waters. Geological sources result from the weathering of rocks and minerals, allowing for the mineralization of natural waters and determining their chemical composition. Anthropogenic inputs (pollution) also contribute to the alteration of these natural cycles. Understanding how these sources interact is essential to evaluate the influence of human activities on water quality and aquatic ecosystems, considering the effects of pollution and climate change. This evaluation requires an integrated approach that considers material fluxes and anthropogenic alterations of the hydrological cycle.

I.1.1. Atmospheric Inputs

The atmosphere is a primary pathway for enriching water with chemical elements. Precipitation (rain, snow, fog) introduces gases and particles from the air into water. These atmospheric inputs include sodium and chlorine (from marine spray) and nutrients such as calcium and magnesium (from Saharan dust).

- **Dissolved gases:** CO_2, O_2, N_2, SO_2, NO_x, NH_3, which directly affect the pH and redox potential of rainwater. These gases are important in water chemistry and impact aquatic ecosystem health.
- **Particles and aerosols:** marine salts (Na^+, Cl^-, Mg^{2+}, SO_4^{2-}), continental dust (Ca^{2+}, K^+, HCO_3^-), soot, atmospheric pollutants, and industrial fallout. These inputs are significant as they can provide major sources of cations and anions in surface waters, influencing their chemistry.

Rainwater serves as the primary source for many surface and groundwater systems before contact with soil and rocks. These air-water exchanges are essential for hydrogeochemical cycles (material fluxes, water quality). The interaction between the atmosphere and surface waters is crucial for assessing the effects of pollution and climate change on water quality.

Such interactions highlight the need for an integrated approach to studying hydrogeochemical cycles and anthropogenic effects on water quality and aquatic ecosystems. Understanding these processes is vital for developing sustainable water management strategies to cope with climate change and human pressures. Effective water management requires analyzing interactions between natural and anthropogenic inputs to mitigate human impacts on water resources.

I.1.2. Geological Inputs

The lithosphere is the major source of dissolved elements in natural waters. Upon contact with water and rock minerals, geochemical reactions occur, such as the weathering of silicates, which release Ca^{2+} and Mg^{2+} and modify water chemistry. This process is particularly noticeable in geological formations such as granites, where dissolved loads are primarily atmospheric in origin.

Chemical weathering (hydrolysis, dissolution, oxidation, and reduction) releases ions such as Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, SO_4^{2-}, Cl^{-}. These processes are important for understanding hydrogeochemical cycles and their effects on water quality. Anthropogenic geochemical processes can also impact water quality, highlighting the need for integrated water resource management.

Ion exchange between solid phases (clays, oxides) and aqueous solutions affects contaminant reactivity and mobility, influencing water quality. Understanding these processes is crucial for sustainable water management.

Precipitation or dissolution of secondary minerals (calcite, gypsum, iron and manganese oxides) controls cation and anion concentrations, influencing groundwater chemistry and quality.

These reactions control water mineralization and geochemical signatures, which depend on the type of rocks encountered (limestone, sandstone, basalt, granite, etc.) and the water-rock contact time.

I.1.3. Biological and Organic Inputs

Living organisms actively participate in elemental cycles within aquatic environments. Biological activity is thus a critical factor in regulating the chemical composition of natural waters.

Interactions between organisms and their environment are essential to understanding aquatic ecosystem dynamics. These interactions influence biodiversity, as well as the structure and functioning of aquatic communities. Studies show that considering both biotic and abiotic interactions is crucial to predict ecological dynamics in these complex systems. Factors such as water temperature and community connectivity interact nonlinearly, influencing biogeochemical cycles and ecosystem responses to environmental changes.

- Aquatic plants and microalgae absorb and release elements such as carbon, nitrogen, phosphorus, and sulfur, regulating primary productivity and community composition, affecting overall ecological balance.
- Decomposition of organic matter releases dissolved organic compounds, humic and fulvic acids, which complex metals and modify water chemistry. These compounds influence metal bioavailability and toxicity to aquatic organisms and interact with essential nutrients like phosphorus and nitrogen, affecting algal bloom dynamics.
- Microorganisms catalyze numerous reactions (nitrification, denitrification, sulfate reduction, iron oxidation), influencing pH and redox potential. Understanding biological and chemical mechanisms is essential to assess human impacts on water quality and ecosystem health. Integrated approaches that consider complex biotic-abiotic interactions are critical for evaluating ecological quality in aquatic systems.

I.1.4. Anthropogenic Inputs

Human activities significantly alter chemical element fluxes into aquatic environments, potentially causing eutrophication with negative consequences for aquatic biodiversity and water quality.

- **Agricultural pollution:** fertilizers (NO_3^-, PO_4^{3-}), pesticides, lime amendments. Excess nutrients from agriculture are major drivers of eutrophication, leading to algal blooms, biodiversity loss, and potentially toxic cyanobacterial outbreaks. Sustainable agricultural practices and reduced urban nutrient discharges are essential to mitigate eutrophication.
- **Urban and domestic effluents:** organic matter, nutrients, detergents, microplastics. Combined with agricultural inputs, these exacerbate water quality and ecosystem health issues, necessitating urgent measures to preserve aquatic systems.
- **Industrial and mining effluents:** heavy metals, hydrocarbons, acids, salts. Industrial discharges, especially from mining, degrade water quality, threatening aquatic ecosystems and human health. Sustainable water management strategies are needed to protect ecosystems and future water supplies.

- **Anthropogenic atmospheric deposition:** sulfur and nitrogen oxides causing acid rain. These inputs disturb natural balances, increase ionic loads, and create ecotoxicological risks. Water geochemistry serves as an integrated management tool to mitigate these impacts and preserve aquatic ecosystem health. Public policies must enforce strict controls on industrial and urban discharges and consider cumulative impacts to develop sustainable strategies for restoring affected aquatic ecosystems.Here is a clear, academic English translation of your text, keeping the structure and references intact:
- **Industrial and mining effluents:** heavy metals, hydrocarbons, acids, and various salts. Industrial effluents, particularly those resulting from mineral extraction, can cause significant degradation of water quality, thereby affecting aquatic ecosystems (Moore & Luoma, 1990). These impacts highlight the importance of sustainable water resource management to preserve the health of aquatic ecosystems and ensure water quality for future generations.
- The impacts of anthropogenic activities on aquatic ecosystems emphasize the urgency of adopting sustainable practices to preserve water quality and biodiversity. Research should also focus on the long-term effects of these pollutants on the health of aquatic ecosystems in order to develop appropriate management strategies. Research efforts must concentrate on assessing the cumulative impacts of different pollution sources to better understand their effects on aquatic ecosystem health. Management strategies should also include public awareness initiatives to encourage sustainable behaviors and reduce pollutant inputs into aquatic environments.
- **Anthropogenic atmospheric deposition:** sulfur and nitrogen oxides responsible for acid rain. These atmospheric deposits contribute to water pollution, causing ecological imbalances and affecting the health of aquatic ecosystems.

  These inputs disrupt natural equilibria, increase ionic loads, and may generate major ecotoxicological risks for biodiversity and the ecosystems that depend on it. Water geochemistry is considered a tool for integrated water resource management and is therefore crucial for mitigating these impacts and preserving the health of aquatic ecosystems (Adjagodo et al., 2016). Public policies must include strict measures to control industrial and urban discharges in order to protect water quality and aquatic biodiversity (Rios et al., 2024). Management strategies should also take into account the cumulative effects of industrial and agricultural discharges in order to develop sustainable approaches for restoring affected aquatic ecosystems.

Research highlights that integrating environmental geochemistry into integrated water resource management is essential to mitigate the impacts of pollution on aquatic biodiversity and to ensure water quality and ecosystem health. A systemic and collaborative approach involving multiple stakeholders is necessary to address these complex challenges and promote the resilience of aquatic environments. Particular attention must be paid to effective implementation in order to manage pollutant inputs and protect aquatic ecosystems. Future research should focus on evaluating the long-term impacts of pollution and on developing sustainable management strategies for aquatic ecosystems.

Ecological restoration is essential to improve the resilience of aquatic ecosystems in the face of increasing anthropogenic pressures. Moreover, collaboration among researchers, managers, and decision-makers is crucial for developing effective and sustainable policies that protect aquatic biodiversity and improve water quality.

I.1.5. Synthesis: Diversity and Dynamics of Inputs

All these sources, both natural and anthropogenic, continuously supply aquatic environments. The chemical composition of a given water body therefore results from a dynamic balance among the following processes:

Inputs (precipitation, runoff, leaching, infiltration),
Transfer (flow, diffusion), and
Transformation (chemical, biological, or physical reactions).

Understanding the origin of chemical elements thus constitutes an essential first step for interpreting water analyses, assessing resource quality, and modeling geochemical processes in aquatic ecosystems.

Freshly fallen rainwater exhibits a certain degree of chemical reactivity and represents the primary driver of soil and rock weathering in temperate climates. Consequently, the chemical composition of groundwater is influenced by the lithology of geological formations, with notable variations depending on the types of rocks through which the water flows. These variations are reflected in the concentrations of major elements, which directly depend on the weathering of silicate minerals in crystalline and sedimentary rocks. Cations such as calcium and magnesium are particularly affected by these weathering processes, thereby exerting a strong influence on groundwater chemistry.

Weathering processes are also responsible for natural variations in water chemistry, including parameters such as pH, calcium, and magnesium concentrations. Ion exchange plays a crucial role in the dynamics of these cations within aquifers. Ion exchange processes may also be influenced by the chemical composition of rainwater, which varies according to climatic and geological conditions.

Moreover, the chemical nature of rocks determines their relative resistance to water–rock interactions. This variability can lead to significant differences in groundwater quality, particularly with respect to mineralization and chemical reactivity.

Rock weathering induces the slow chemical breakdown of minerals, releasing dissolved matter into groundwater and surface waters. This dynamic of weathering and ion exchange is fundamental to understanding groundwater geochemistry, especially in crystalline terrains where cation composition is predominantly of geological origin. In such environments, groundwater cations mainly derive from geological sources, whereas anions are largely of atmospheric origin. Weathering processes and ion exchange thus contribute to the complexity of groundwater chemical composition, influencing both water quality and reactivity.As groundwater flows through subsurface environments, it progressively acquires dissolved elements at increasing concentrations until it reaches a state of equilibrium that defines its hydrochemical *facies*. This equilibrium results from complex interactions between dissolved constituents and aquifer minerals, thereby shaping groundwater chemistry.

Different rock types contain minerals with varying degrees of solubility. Consequently, mineral solubility directly affects groundwater chemical composition, influencing both water quality and reactivity. The chemical elements released are specific to the rock formations encountered, and the dominant ions present in water reflect the lithological characteristics of the aquifer. Therefore, understanding water–rock interactions is essential for evaluating groundwater mineralization and quality across different geological settings. These geochemical interactions are particularly pronounced in schist aquifers, where the dissolution of minerals such as albite and chlorite significantly influences cation composition in groundwater.

Here is a clear, academic English translation of your text, preserving the scientific tone and references and suitable for a thesis or peer-reviewed publication:

Factors Controlling the Aggressiveness of Water Toward Rocks

The chemical aggressiveness of water depends on several key factors:

- Température;
- pH;
- The load of already dissolved elements;

- The duration of water–rock contact (i.e., the residence time of water in the aquifer, linked to groundwater renewal by meteoric inputs).

These factors directly influence mineral dissolution and the modification of rock pore structure, thereby affecting aquifer hydrodynamics. Interactions among these factors may also lead to significant variations in rock permeability, consequently altering groundwater flow patterns within the aquifer. Such permeability changes can impact groundwater quality, particularly by facilitating contaminant migration.

Rainwater cannot be considered a form of “distilled water.” It contains various ions and dissolved elements that influence its chemical aggressiveness toward rocks, depending notably on soil geological composition and mineral oxidation processes. Thus, water chemistry, shaped by mineral oxidation and water–rock interactions, plays a crucial role in controlling the reactivity of water with its surrounding environment. These complex interactions highlight the importance of hydrochemistry in understanding dissolution and weathering processes within aquifers.

1. Rainwater contains natural and anthropogenic aerosols and dust particles. These particles can interact with water, modifying its chemical aggressiveness and influencing rock weathering processes within aquifers. Such interactions emphasize the need for an integrated approach to studying the effects of water on slope stability and aquifer dynamics. Hydrochemistry, as an analytical tool, enables a better understanding of these interactions and helps assess their impact on slope stability and water resource management.
2. The presence of dissolved carbon dioxide in rainwater induces acidic pH values of around 5, and often lowers**.** These acidic conditions promote mineral dissolution, particularly of calcite, and can therefore influence rock permeability within aquifers. Variations in pH and water chemical composition, especially those related to dissolved carbon dioxide, play a key role in rock weathering processes and aquifer dynamics. Weathering and dissolution processes are thus intensified by the presence of dissolved gases, underscoring the importance of hydrochemistry in evaluating environmental impacts.
3. Anthropogenic emissions of sulfur oxides, leading to the formation of dissolved sulfuric acid, contribute to increased acidity.

This enhanced acidity can have detrimental effects on groundwater quality and aquatic ecosystem health by promoting mineral dissolution and altering the geochemical properties of rocks. Furthermore, hydrochemical analysis of aquifers allows for a better understanding of how variations in pH and chemical composition affect slope stability and groundwater quality. These observations highlight the importance of monitoring pH changes and contamination impacts on aquifer dynamics to ensure the sustainability of water resources.

Altogether, these factors emphasize the need for proactive water resource management to preserve groundwater quality and maintain the stability of aquatic ecosystems. Integrating hydrochemical data into water resource management is essential for anticipating and mitigating environmental impacts related to variations in water quality.

I.3. Exogenous Factors Independent of Lithology: Examples of Dissolved Oxygen and Chloride Concentrations

Type of Aquifer

By definition, so-called unconfined aquifers are in equilibrium with the atmosphere and typically exhibit dissolved oxygen concentrations on the order of 5 to 10 $mg \cdot L^{-1}$, which are essential for sustaining aquatic life. In contrast, confined aquifers may display much lower levels of dissolved oxygen, significantly influencing groundwater geochemistry.

Confined aquifers, often characterized by anoxic conditions, can also affect mineral dissolution processes, such as iron mobilization, thereby further modifying groundwater chemical composition (*Hydrological and Geological Controls for the Joint Evolution of Dissolved Oxygen and Iron in Crystalline Rocks*, 2022). So-called captive aquifers exhibit a deficit in dissolved oxygen, which is consumed through the oxidation of organic matter or sulfides present within the aquifer. Oxygen is not replenished due to the lack of contact with the atmosphere via the unsaturated zone. This consumption of dissolved oxygen is frequently correlated with increased concentrations of iron and other redox-sensitive elements, thus influencing aquifer geochemistry. This dynamic highlights the importance of biogeochemical processes, in which oxygen consumption is often linked to significant chemical transformations, such as elevated iron concentrations. These interactions between dissolved oxygen and minerals underscore the crucial role of aquifers in biogeochemical cycles, influencing groundwater quality across diverse geological contexts.

Overall, these processes emphasize the importance of understanding geochemical interactions for the sustainable management of groundwater resources.

Shallow - Deep Aquifers

Dissolved oxygen concentrations in groundwater are also influenced by aquifer depth. Depth affects not only oxygen availability but also geochemical interactions, particularly mineral dissolution processes such as iron mobilization, thereby altering water quality. The boundary between shallow and deep aquifers is generally located at approximately 30–40 m below the ground surface. These interactions may also be influenced by anthropogenic factors, highlighting the need to assess the patrimonial quality of groundwater resources in order to anticipate the impacts of human activities. This requires an integrated approach to understanding how anthropogenic pressures affect groundwater quality.

Distance from the Coast

Proximity to the sea strongly influences the chemical composition of precipitation and, consequently though to a lesser extent that of aquifers and surface water reservoirs. Chloride is one of the most sensitive parameters to marine influence. Near coastal areas, rainwater chloride concentrations can reach up to 40 $mg \cdot L^{-1}$, compared to approximately 2.5 $mg \cdot L^{-1}$ at higher elevations, such as in the Massif Central. Beyond 100 km from the coastline, marine influence on the chemical composition of rainwater can generally be considered negligible.

This spatial variability highlights the importance of assessing marine-derived inputs when studying groundwater geochemistry, particularly with respect to chloride concentrations and other dissolved constituents.

I.4. Major Elements: Origins and “Typical” Concentrations

I.4.1. Calcium (Ca^{2+})

Calcium is one of the major constituents of carbonate rocks, particularly limestones and chalks ($CaCO_3$), and plays an essential role in the formation of numerous minerals and biological structures. It is a key component of hard biomaterials, such as bones and shells, where it interacts with other ions to form complex structural frameworks. Calcium is widely present in sedimentary rocks, especially limestones and dolomites, where it significantly contributes to their mineral composition. It also plays a crucial role in the oceanic cycle, influencing the terrestrial mobility of elements and the composition of sediments. In addition, calcium is essential for plant health, as it participates in key physiological processes, including the regulation of cell membrane permeability and intracellular signaling. Chalk deposits, which are rich in calcium, are often used to improve soil quality, thereby promoting plant growth and increasing resistance to environmental stress.

Calcium carbonate

Limestone

Calcium is also abundant in other sedimentary rock types, such as gypsum ($CaSO_4 \cdot 2H_2O$)**,** as well as in certain igneous rocks. Gypsum, a hydrated calcium sulfate, is commonly regarded as a secondary mineral in various geological formations and has significant industrial applications. As an important source of calcium, gypsum plays a key role in multiple geochemical and biological processes, contributing to the regulation of water chemistry and nutrient availability. Here is a clear, technical English translation, suitable for a hydrogeology or geochemistry chapter:

Chalk

Calcium Silicate

Calcium concentrations vary depending on the type of aquifer. They are high (hundreds of $mg \cdot L^{-1}$) in carbonate aquifers and even higher in gypsiferous aquifers, as gypsum dissolves more readily than calcite. In contrast, calcium concentrations are lower (a few $mg \cdot L^{-1}$ to several tens of $mg \cdot L^{-1}$) in igneous rocks. This variability clearly illustrates the strong influence of the geological substrate on groundwater chemistry, particularly with respect to water hardness.

Details on calcium concentrations:

- **Carbonate aquifers (limestones, dolomites)**
  Dissolution of calcite ($CaCO_3$) releases calcium ions, resulting in typical concentrations of around 100 $mg \cdot L^{-1}$, which confer hard water characteristics.

- ➔ **Gypsiferous aquifers (gypsum, $CaSO_4 \cdot 2H_2O$)**

  Because gypsum is more soluble than calcite, it leads to very high concentrations of Ca^{2+} and sulfate, which may exceed several hundred $mg \cdot L^{-1}$, and in some cases more than 1,000 $mg \cdot L^{-1}$, rendering the water unsuitable for drinking.

- ➔ **Igneous rocks (granites, basalts)**

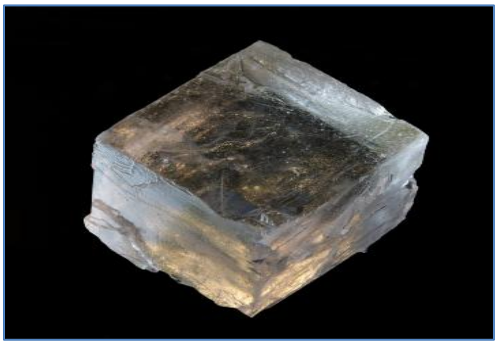
  These rocks contain less readily soluble calcium, resulting in lower concentrations, typically ranging from a few $mg \cdot L^{-1}$ to a few tens of $mg \cdot L^{-1}$.

I.4.2. Magnesium (Mg^{2+})

Magnesium (Mg^{2+}) is chemically similar to calcium, as the two elements are neighbors in the periodic table and share comparable chemical properties and regulatory mechanisms, although magnesium-bearing minerals are generally less soluble than calcium-bearing ones. Magnesium occurs in carbonate rocks (dolomitic limestones and dolomites), evaporitic formations (magnesium salts such as $MgSO_4$), and igneous rocks.

- In magnesian rocks (such as dolomites), Mg^{2+} concentrations are on the order of a few tens of milligrams per liter (mg/L).
- In magnesian carbonate rocks (e.g., dolomites), Mg^{2+} concentrations are on the order of a few tens of mg/L.

- Evaporite aquifers rich in magnesium minerals can contain high levels of magnesium, from a few hundred mg.L-1 to a few g.L-1.



- In igneous rocks, concentrations are generally lower, from a few mg.L-1 to a few tens of mg.L-1.


I.4.3. Sodium (Na^+)

Sodium is mainly associated with igneous rocks. In sedimentary rocks, it is less abundant; however, the minerals that incorporate sodium can be highly soluble, such as halite (NaCl). The high solubility of halite in water, particularly in marine-influenced environments, contributes significantly to sodium enrichment in sedimentary formations.

Halite

Igneous rocks

The highest Na^+ concentrations are observed in aquifers containing soluble salts such as halite. For example, concentrations of approximately 250 $mg \cdot L^{-1}$ have been reported in the Jurassic aquifer of Lot-et-Garonne. These elevated sodium levels are influenced by mineral dissolution and groundwater circulation within sedimentary formations. In groundwater draining igneous rocks, Na^+ concentrations typically range from several tens of $mg \cdot L^{-1}$. Sodium levels may also vary as a result of the dissolution of silicate minerals, particularly sodium-rich feldspars, which contribute to Na^+ enrichment. Sodium feldspars play a major role in the hydrological cycle, contributing more than 20% of the total dissolved sodium in river waters. This sodium is largely released through the weathering of silicate minerals, especially sodic feldspars.

Finally, sodium is also abundant in sandy aquifers (e.g., sands derived from the erosion of ancient crystalline massifs), where Na^+ concentrations often reach several tens to several hundreds of mg·L⁻¹. These concentrations may be further influenced by saline intrusions and by sodium inputs resulting from mineral weathering within sedimentary formations.

I.4.4. Potassium (K^+)

Despite its abundance in certain igneous rocks and sedimentary rocks (such as clays and sandstones), potassium is generally present at low concentrations in groundwater. Nevertheless, chemical weathering processes can release potassium into aquifers, thereby influencing its concentration in groundwater.

Recent studies indicate that the use of potassium isotopes can provide valuable insights into water–rock interactions, particularly in CO_2-rich aquifers. The application of potassium isotopes in hydrogeochemical studies allows for a better understanding of the mechanisms governing potassium release and transport in aquifers, especially those affected by silicate weathering processes.

These studies highlight the importance of potassium isotopes for tracing potassium cycling in aquifers, particularly during clay incorporation and adsorption processes associated with silicate dissolution. Such findings open new perspectives for future research on potassium isotope behavior in various aquifer environments and their ability to identify potassium sources and transformation processes within hydrogeological systems.

Potassium concentrations generally do not exceed 10 $mg \cdot L^{-1}$ in groundwater. However, significant variations may occur depending on silicate dissolution processes and clay incorporation, which strongly influence potassium isotope dynamics in aquifers. These variations are particularly pronounced in aquifers where potassium adsorption onto clay minerals leads to decreased K^+ concentrations, thereby affecting K/Na ratios and $\delta^{41}K$ isotopic values. Higher potassium concentrations may nevertheless be observed in waters that have circulated through evaporitic formations rich in sylvite (KCl). Sylvite, being highly potassium-rich, can significantly influence groundwater chemical composition. Potassium isotope studies in such settings can provide critical information on the dissolution and adsorption processes that regulate potassium concentrations in aquifers.

Overall, these observations underscore the importance of investigating potassium transport and transformation mechanisms in aquifers, taking into account the complex interactions between solid and liquid phases. These mechanisms are essential for understanding how chemical weathering and adsorption processes influence potassium cycling in groundwater systems, particularly in relation to potassium isotopes.

I.4.5. Bicarbonate (HCO_3^-)

Bicarbonate ions are primarily formed through the dissolution of carbonate minerals by meteoric waters that become enriched in CO_2 during percolation through the soil. The concentration of bicarbonate in groundwater is strongly influenced by dissolved CO_2 levels, which largely originate from the mineralization of organic matter within the soil. As a result, bicarbonate dynamics in groundwater are closely linked to microbial activity and the decomposition of organic matter. This relationship highlights the importance of microorganisms in the carbon cycle and their role in regulating bicarbonate concentrations in groundwater.

In carbonate aquifers, bicarbonate concentrations typically reach several hundreds of $mg \cdot L^{-1}$. These concentrations may vary depending on the distance from recharge zones, as observed in the Aquia aquifer (United States), where HCO_3^- levels change along the hydrological gradient. Such variations illustrate how carbonate mineral dissolution and microbial activity interact to influence groundwater chemistry. Some mineral waters draining igneous rocks exhibit even higher bicarbonate concentrations, reaching several $g \cdot L^{-1}$, under the influence of deep-seated CO_2 and other geological processes. This demonstrates the diversity of bicarbonate sources within aquifer systems. These geological and biological processes indicate that groundwater chemical composition results from complex interactions among minerals, organic matter, and dissolved gases, particularly CO_2.

Overall, these interactions emphasize the central role of bicarbonate dynamics in aquifer systems, where carbonate mineral dissolution plays a key role in controlling groundwater chemistry. These observations highlight the need for further investigation into the relationships between geochemical and hydrological processes in aquifers in order to better understand their impact on groundwater quality.

Minerals containing magnesium are typically less soluble than calcium a mineral, which explains the generally lower concentrations of Mg^{2+} in groundwater. In magnesium-rich rocks, particularly dolomites, Mg^{2+} concentrations are commonly on the order of a few tens of milligrams per liter ($mg \cdot L^{-1}$). In magnesian carbonate rocks, such as dolomites, groundwater Mg^{2+} concentrations typically range within several tens of $mg \cdot L^{-1}$, reflecting the dissolution of dolomite and other magnesium-bearing minerals. Evaporitic aquifers rich in magnesium-bearing minerals may contain high magnesium concentrations, ranging from several hundred $mg \cdot L^{-1}$ to several $g \cdot L^{-1}$. In contrast, igneous rocks generally yield lower Mg^{2+} concentrations, typically from a few $mg \cdot L^{-1}$ to a few tens of $mg \cdot L^{-1}$, reflecting the lower solubility of magnesium-bearing silicate minerals. Here is a clear, structured, and academic English translation of Sections I.4.2 (completion), I.4.3, and I.4.4, harmonized with the previous subsections and suitable for a thesis or scientific publication:

Evaporitic minerals

Evaporitic aquifers rich in magnesium-bearing minerals may contain high magnesium concentrations, ranging from several hundred $mg \cdot L^{-1}$ to several $g \cdot L^{-1}$. In contrast, igneous rocks generally yield lower Mg^{2+} concentrations, typically from a few

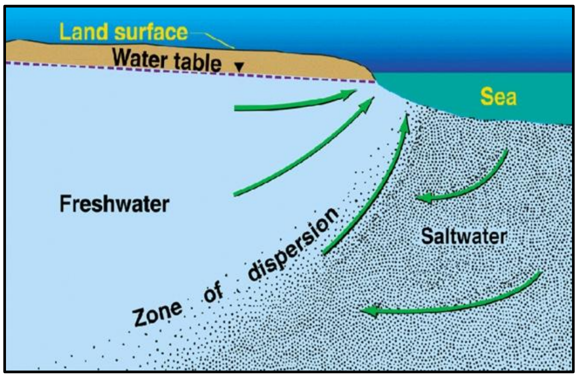
$mg\cdot L^{-1}$ to a few tens of $mg\cdot L^{-1}$, reflecting the lower solubility of magnesium-bearing silicate minerals.

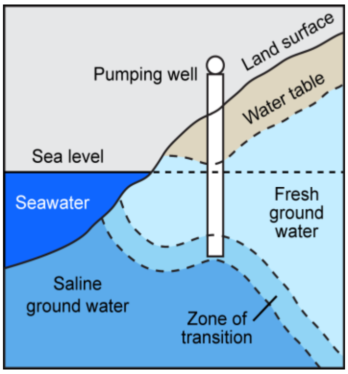
I.4.6. Chloride (Cl^-)

Regardless of lithology, chloride concentrations in groundwater are generally low. However, higher concentrations may be observed in certain regions, often due to the influence of surrounding rocks and climatic conditions.

In unconfined aquifers, chloride concentration is directly related to the chloride content of precipitation. Concentrations typically measured in unconfined groundwater are a few $mg\cdot L^{-1}$ and ultimately depend more on the distance from the coastline than on lithology, highlighting the importance of environmental factors in groundwater dynamics. Variations in salinity may also be influenced by processes such as evapotranspiration and interactions with neighboring aquifers. These interactions can contribute to increased salinity in groundwater, particularly in semi-arid regions where evapotranspiration is significant. Consequently, groundwater resource management in these areas requires special attention to minimize the impacts of salinization on water quality. Groundwater salinity is of particular concern in semi-arid zones, where evapotranspiration can exceed 85% of precipitation. Effective management is essential to preserve water quality and support local communities.

The dissolution of halite ($NaCl$) or the presence of a saline wedge (coastal aquifer) can lead to elevated chloride concentrations, ranging from several hundred $mg\cdot L^{-1}$ to several $g\cdot L^{-1}$. Therefore, groundwater resource management requires careful consideration to avoid the impacts of salinization, especially in coastal areas. Previous studies have shown that groundwater salinity can be exacerbated by factors such as seawater intrusion and inappropriate agricultural practices. In semi-arid regions, particular attention must be paid to water resource management to prevent the degradation of water quality. An integrated water resources management approach is crucial to mitigate the effects of salinization, taking into account interactions between aquifers and environmental factors.





I.4.7. Sulfate (SO_4^{2-})

In unconfined aquifers, the presence of sulfate is generally linked to the oxidation of pyrite (FeS_2), a sulfur-rich mineral found in all types of lithology (limestones, sands, igneous rocks). Pyrite oxidation also contributes to the release of nickel under certain geological conditions, as observed in studies of aquifers in northern France. This dynamic highlights the importance of pyrite in the trace element cycle and its influence on water quality in these aquifer systems. In this context, sulfate concentrations typically range from a few $mg \cdot L^{-1}$ to several tens of $mg \cdot L^{-1}$. In confined aquifers, sulfur is also present but in its reduced forms (H_2S).

Pyrite

Gypsum

Sulfates may also originate from the leaching of evaporitic formations (e.g., gypsum [$CaSO_4 \cdot 2H_2O$]). In confined aquifers, the dynamics of pyrite oxidation and sulfate leaching play a key role in groundwater quality. This complex interaction between pyrite and sulfates is essential for understanding variations in groundwater quality, particularly regarding nickel and sulfur. Understanding these processes is crucial for water resource management and minimizing pollution impacts, especially in aquifers containing pyrite and where denitrification processes occur, thereby influencing nickel remobilization and sulfate dynamics. Effective management of these resources requires continuous monitoring of chemical and isotopic parameters to prevent water quality degradation.

In some cases, sulfate concentrations can be very high, ranging from several hundred $mg \cdot L^{-1}$ to a few $g \cdot L^{-1}$. Such high sulfate levels can have significant implications for aquatic biodiversity and the health of local ecosystems. Further research is needed to assess the impact of elevated sulfate concentrations on aquatic organisms and surrounding ecosystems. Previous studies have shown that high sulfate concentrations can impair the reproduction of aquatic species, underscoring the importance of monitoring these levels in aquifers.

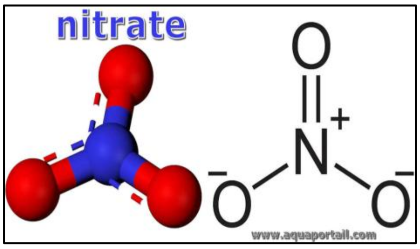
I.4.8. Silica (SiO_2)

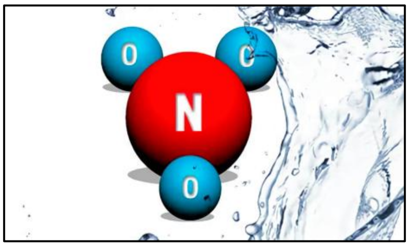
Silicon is nearly absent from carbonate rocks; consequently, in carbonate aquifers, silica concentrations generally do not exceed a few $mg \cdot L^{-1}$. However, in nitrate-rich environments, silica concentrations may increase due to silicate hydrolysis, a process enhanced by organic inputs. In contrast, silicon is very abundant in igneous rocks, sandstones, and clays.

Nevertheless, silicate minerals are often poorly weatherable, so the concentrations measured in these environments remain relatively low, typically ranging from a few $mg \cdot L^{-1}$ to about 10–20 $mg \cdot L^{-1}$. In silicate-rich settings, weathering processes can be influenced by factors such as pH and organic matter composition, which affect silica availability. Under these conditions, silica may also interact with existing cations and anions, thereby influencing nutrient dynamics in soils. This dynamic is essential for understanding the role of silicates in plant nutrition and the balance of terrestrial ecosystems.

I.4.9. Nitrates (NO_3^-)

The nitrate ion is the most oxidized form of nitrogen. Natural sources of nitrate mainly include precipitation and interactions with soils and vegetation. Under natural conditions, nitrate concentrations in groundwater are low, generally not exceeding a few $mg \cdot L^{-1}$. It is commonly accepted that concentrations higher than 10 $mg \cdot L^{-1}$ indicate anthropogenic inputs, such as fertilizer leaching and domestic or industrial discharges. Nitrates may also originate from the oxidation of organic nitrogen, a process that generates acidity and affects exchangeable cations in soils. This dynamic can have significant consequences for groundwater quality, particularly by increasing the concentrations of heavy metals such as nickel, due to interactions with organic nitrogen inputs. A reduction in nitrogen inputs could therefore lower both nitrate and heavy metal concentrations in groundwater, highlighting the importance of nitrogen management in preserving groundwater quality.





Other studies show that sustainable nitrogen management is essential to reduce the risk of leaching into aquifers, which can improve water quality. Thus, an integrated approach that considers nitrogen sources and geochemical interactions is crucial for maintaining aquifer health. A better understanding of hydrochemical processes and interactions between cations and anions is necessary to optimize groundwater resource management. This management should also include the assessment of natural nitrate concentrations and their relationship with environmental factors such as altitude and soil type.

I.4.10. Total Mineralization

Total mineralization of water refers to the overall concentration of dissolved ions. It is expressed either in $mg \cdot L^{-1}$ of dry residue (obtained by evaporating one liter of water at 180 °C) or in $\mu S \cdot cm^{-1}$ as electrical conductivity, which serves as a proxy for total salinity. Total mineralization is an important indicator of water quality and is influenced by factors such as salinity and the presence of dissolved minerals. Total mineralization can also be affected by anthropogenic activities, particularly pollution and seawater intrusion, which alter the ionic composition of water and increase its level of mineralization. Studies have shown that anthropogenic pollution and marine water intrusion are major factors influencing water mineralization in urbanized areas. In particular, groundwater in urbanized zones, such as the Abidjan District, exhibits high concentrations of nitrates and chlorides as a result of anthropogenic pollution and seawater intrusion, leading to increased total mineralization.

The total mineralization of groundwater is closely controlled by the lithology of the geological formations through which it flows. Waters originating from sedimentary-dominated environments, such as those of the Ben Haroun region (Mila Province), mainly circulate within limestone and marly formations characterized by high solubility. This hydrogeological setting significantly influences the chemical composition of groundwater, which is often enriched in calcium and sulfate ions. This ionic richness results from water–rock interactions, enhanced by the dissolution of minerals within these geological formations.

The dissolution processes of carbonates and evaporites promote substantial enrichment in major ions, particularly Ca^{2+}, Mg^{2+}, HCO_3^-, and SO_4^{2-}, leading to high total mineralization.

These chemical constituents are governed by cation exchange processes and water–rock interactions, thereby influencing the overall quality of regional water resources. Such interactions are essential for understanding groundwater quality dynamics, especially in the context of aridity and agricultural activities that further intensify mineralization. In contrast, waters from regions dominated by magmatic geological formations, such as the Djurdjura massif (Tikjda, Kabylia), flow through crystalline rocks (granites and gneisses) that are chemically resistant to weathering. This limits water–rock interactions, resulting in low concentrations of dissolved ions and low to moderate total mineralization.

This comparison clearly illustrates the major influence of geological context on the chemical composition and mineralization of groundwater in Algeria, particularly in regions subjected to increasing anthropogenic pressures.

Another illustrative example is the comparison between Evian and Volvic waters:

Evian: Rich in Ca^{2+} and Mg^{2+}, making it beneficial for bone growth and meeting mineral requirements. Its composition results from circulation through mineral-rich glacial alluvial deposits.

Volvic: Characterized by low total mineralization and a high silica content, making it ideal for light hydration or low-mineral diets. It flows through volcanic rocks (basalt), which strongly influence its mineral composition.

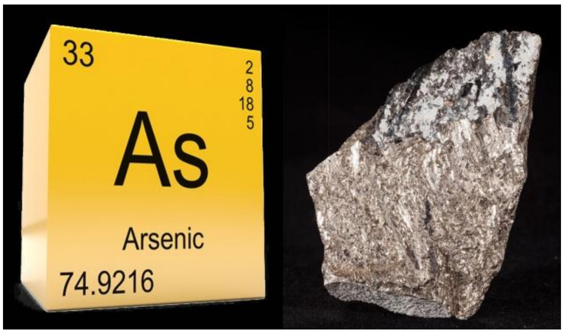
This comparison highlights how the nature of geological formations controls water–rock interactions and, consequently, the mineral signature of groundwater.

Ion / Mineral	**Evian (mg/L)**	**Volvic (mg/L)**	**Remarks**
Calcium (Ca^{2+})	80	11	Evian is very rich in calcium, beneficial for bone health
Magnesium (Mg^{2+})	26	8	Evian is richer; Volvic is lighter
Sodium (Na^{+})	6.5	9.5	Both are low in sodium, suitable for low-sodium diets
Potassium (K^{+})	1	5	Volvic is slightly richer in potassium
Bicarbonates (HCO_3^{-})	360	130	Evian is more alkaline
Sulfates (SO_4^{2-})	14	9	Low in both waters
Chlorides (Cl^{-})	10	10	Similar concentrations
Silica (SiO_2)	15	33	Volvic is very rich in silica, beneficial for skin and hair
Dry residue at 180 °C	309 mg/L	130 mg/L	Evian: “high mineralization”; Volvic: “low mineralization”

I.5. Minor Toxic Elements of Natural Origin

I.5.1. Arsenic

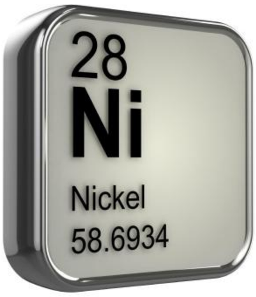
Arsenic is highly toxic; it is carcinogenic and can cause skin lesions, cardiovascular disorders, and pulmonary diseases. The maximum admissible concentration of arsenic in drinking water is set at 10 $\mu g \cdot L^{-1}$, a limit that is often exceeded in groundwater. Arsenic contamination affects all types of aquifers, with no single predominant lithology.



For example, in the Miocene aquifer of Aquitaine (composed of sandy limestones), arsenic concentrations exceed 100 $\mu g \cdot L^{-1}$. In the Upper Bathonian and Callovian limestone aquifer of Haut-Rhin, values can reach more than 6,000 $\mu g \cdot L^{-1}$, while in the crystalline basement aquifer (granites and gneisses) of the Puy-de-Dôme, concentrations exceed 130 $\mu g \cdot L^{-1}$.

I.5.2. Nickel

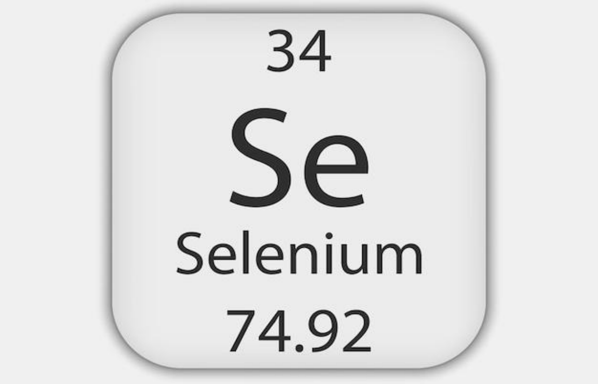
Nickel toxicity is mainly expressed through risks of asthma, as well as mutagenic and carcinogenic effects at high doses. According to the drinking water standard in force since 20 December 2001, the maximum admissible concentration of nickel in water is 20 $\mu g \cdot L^{-1}$.



The main natural source of nickel is pyrite, a mineral in which nickel can substitute for iron in the crystal structure $(Fe,Ni)S_2$. Variations in redox conditions in the environment can lead to the release of nickel into solution. This natural process can generate nickel concentrations exceeding 100 $\mu g \cdot L^{-1}$ in some groundwater bodies, as observed in the chalk aquifer of the Artois–Picardy Basin.

I.5.3. Selenium

Selenium is toxic and can cause skin, respiratory, dental, and/or neurological damage, as well as gastrointestinal disorders. The drinking water standard sets its maximum admissible concentration at 10 $\mu g \cdot L^{-1}$. Its main natural source comes from sulfur-bearing minerals in which sulfur is substituted by selenium, often in geological contexts rich in uranium; its dissolution is generally linked to variations in redox conditions.



Selenium anomalies have been observed in the Eocene and Oligocene aquifers of the Paris Basin, with Se concentrations exceeding 30 µg·L⁻¹, as well as in the hydrothermal springs of La Roche-Posay, where concentrations exceed 50 µg·L⁻¹.

I.5.4. Other Toxic and "Undesirable" Elements

Toxic elements such as antimony, cadmium, chromium, mercury, and lead are subject to strict drinking water standards, with maximum admissible concentrations ranging from 1 to 50 µg·L⁻¹ depending on the substance. These limits are rarely exceeded in cases of naturally occurring contamination in groundwater.

Although these heavy metals are highly toxic even at low doses—causing neurotoxic, carcinogenic, and renal effects—their low solubility under natural conditions generally limits the occurrence of significant anomalies. Their natural sources include sulfides and oxides present in sedimentary or crystalline rocks; however, their mobilization is uncommon in the absence of anthropogenic influences such as mining activities or industrial discharges.

Element	Drinking water standard (µg/L)
Antimony	5
Cadmium	5
Chromium	50 (total)
Mercury	1
Lead	10

Undesirable Elements

Undesirable elements such as aluminum, silver, barium, boron, copper, iron, manganese, fluoride, phosphorus, and zinc do not generally pose a major health risk at moderate concentrations, but they can significantly affect the organoleptic quality of water (taste, odor, color, turbidity). Their drinking water guideline values typically range from 50 µg·L⁻¹ to 2 mg·L⁻¹ and may be exceeded in some cases due to abundant natural sources in French aquifers.

These elements mainly originate from the dissolution of naturally occurring minerals:

- Clay minerals (Al, Fe, Mn),
- Oxides (Cu, Zn),

- Feldspars (B),
- Fluorides or apatites (F, P).

Their occurrence is not strictly controlled by lithology. When present in excess, they may cause turbidity (Fe, Mn), metallic taste (Cu, Zn), deposits, or corrosion in distribution systems. Appropriate treatments such as aeration, oxidation, and filtration are often required to restore acceptable water quality.

Guideline values and typical effects

Element	Guideline value	Typical effects / remarks
Aluminum (Al)	~200 $\mu g \cdot L^{-1}$	Turbidity, coloration
Iron (Fe)	200 $\mu g \cdot L^{-1}$	Reddish color, deposits
Manganese (Mn)	50 $\mu g \cdot L^{-1}$	Black deposits, taste
Copper (Cu)	2 $mg \cdot L^{-1}$	Metallic taste, corrosion
Zinc (Zn)	3 $mg \cdot L^{-1}$	Metallic taste
Fluoride (F^-)	1.5 $mg \cdot L^{-1}$	Dental effects at high levels
Boron (B)	1 $mg \cdot L^{-1}$	Taste issues at high levels
Barium (Ba)	1 $mg \cdot L^{-1}$	Rarely problematic naturally
Phosphorus (P)	No strict health limit	Aesthetic issues, eutrophication
Silver (Ag)	100 $\mu g \cdot L^{-1}$	Rare, mainly aesthetic concerns

Overall, while these elements are primarily an aesthetic and technical concern, regular monitoring and appropriate treatment are essential to ensure consumer acceptability and protect water distribution systems.

Element	Drinking water standard	Examples of natural exceedances
Aluminum	200 $\mu g \cdot L^{-1}$	Clay-rich formations, alluvial aquifers
Iron	200 $\mu g \cdot L^{-1}$	Iron oxides, sandstones; anoxic conditions > 1 $mg \cdot L^{-1}$
Manganese	50 $\mu g \cdot L^{-1}$	Reducing environments, crystalline basement > 100 $\mu g \cdot L^{-1}$
Copper	1 $mg \cdot L^{-1}$	Copper sulfide minerals, trace occurrences
Fluoride	1.5 $mg \cdot L^{-1}$	Fluorapatites, limestone formations
Zinc	5 $mg \cdot L^{-1}$	Sulfide minerals, low natural solubility

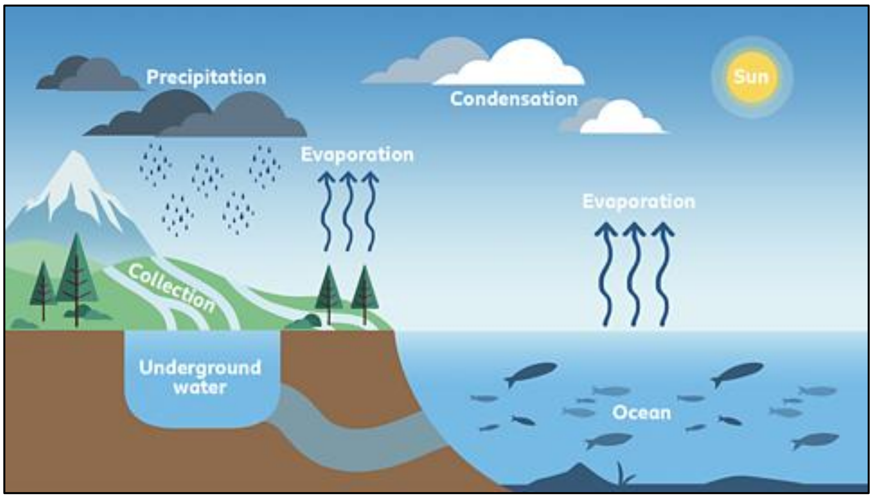
2. Water Cycle and Geosphere – Hydrosphere Interactions

Introduction

The water cycle, or hydrological cycle, refers to the full range of water transfers and transformations at, above, and below the Earth's surface. It forms the basis of geochemical exchanges between the planet's different compartments: atmosphere, hydrosphere, lithosphere, and biosphere.

I.2.1. Main Stages of the Hydrological Cycle

The main stages of the hydrological cycle are evaporation, transpiration, condensation, precipitation, runoff, infiltration. These stages interact in a complex manner, influencing both surface water and groundwater availability within a watershed.



1. Evaporation

Driven by solar energy and wind, water from seas and oceans evaporates into the atmosphere, leaving behind salts and impurities. The evaporated water contributes to cloud formation, which plays a crucial role in the water cycle and precipitation. Clouds, as condensates of water vapor, act not only as moisture reservoirs but also as regulators of the Earth’s radiative balance, thereby influencing the global climate. Variations in cloud formation and dynamics significantly impact the water and energy balance, highlighting the importance of their study in the context of climate change.

Evaporation can also occur from the land surface, a process known as evapotranspiration. This phenomenon transforms water from rivers, lakes, soils, animals, humans, and especially vegetation into water vapor, which then accumulates in clouds similarly to oceanic evaporation. Evapotranspiration is essential to the water cycle because it contributes to atmospheric humidity and influences precipitation and condensation processes. In particular, evapotranspiration plays a key role in transferring water to the atmosphere, thereby affecting climate, water availability, and ecosystem productivity. Increases in evapotranspiration can lead to significant changes in precipitation patterns and water availability under climate change, impacting agriculture and water resources. The effects of climate change on evapotranspiration and precipitation regimes require special attention, as they directly influence the availability of water resources.

2. Transpiration

Plants absorb water from the soil and release it into the atmosphere as water vapor, accounting for about 10% of precipitation. This process, known as plant transpiration, is also considered part of evapotranspiration. Transpiration plays a crucial role in the hydrological cycle by influencing the availability of water for other ecological and climatic processes.

3. Condensation

As water vapor rises into the colder layers of the atmosphere, it cools and transforms into droplets that form clouds, mist, or fog. The formation of these droplets also depends on the presence of aerosol particles, which act as cloud condensation nuclei, thereby influencing the life cycle of fog.

The chemical and physical properties of these particles, such as their size and concentration, play a crucial role in droplet activation and fog development. Studies have shown that aerosol particle concentration is a key parameter for accurately predicting the microphysical properties of fog and its vertical development. Moreover, numerical simulations reveal that interactions between microphysical and radiative processes are essential to understanding fog evolution throughout its life cycle. Measurement campaigns such as ParisFOG and ToulouseFOG have highlighted the critical role of aerosols in fog formation and dynamics. These findings emphasize the need to integrate precise observational data into predictive models to improve our understanding of fog phenomena.

4. Precipitation

Driven by winds, clouds move through the atmosphere. When weather conditions change and under the influence of gravity, clouds become heavy and fall to the ground as rain, hail, or snow. About 79% of precipitation falls over the oceans, while the remaining 21% falls on land, where it replenishes groundwater through infiltration or feeds rivers, lakes, and other surface water bodies through runoff. This process is essential for maintaining the hydrological balance of terrestrial and aquatic ecosystems. Rainwater that infiltrates the soil can remain underground for thousands of years before returning to the oceans. Slightly less than half of precipitation contributes to groundwater recharge, while the rest returns to the atmosphere through evaporation. This groundwater recharge is crucial for sustainable water resource management, especially in the context of climate change and evolving agricultural practices. Farmers must adapt their water management techniques to maximize groundwater recharge while minimizing the impact of climate variability on crops.

Water that does not infiltrate the soil flows along slopes as runoff, eventually reaching lakes and rivers. This water continues along river courses to the seas and oceans. All waters resulting from runoff- streams, rivers, lakes are collectively referred to as drainage networks. These watercourses play a vital role in the water cycle, facilitating the transport and redistribution of water resources across terrestrial landscapes. These hydrological processes are essential for maintaining ecosystem health and influence landscape dynamics, particularly in arid regions where water management is critical.

5. Runoff

A small proportion of precipitation (approximately 15%) remains on the soil or impermeable surfaces and flows directly into watercourses (rills, brooks, streams, rivers) before reaching the seas and oceans. This process is called runoff. It plays a crucial role in the water cycle and can lead to flooding, especially during heavy rainfall events.

6. Infiltration

About 25% of rainwater penetrates the subsurface, a process known as infiltration. As water infiltrates, it fills cavities and pores in rocks, forming a groundwater aquifer. Water stored in these aquifers may sometimes find a natural outlet, forming a spring. Surface water infiltration into aquifers is essential for maintaining water quality, but it can be compromised during intense rainfall events.

This closed cycle certainly maintains a constant total amount of water in the hydrosphere, but not in groundwater aquifers, which may take several decades to regenerate.

1.2.2. Water Residence in Natural Reservoirs

During its cycle, water passes through different natural reservoirs, where it remains for varying periods before continuing its journey to the seas and oceans. This period of stagnation is called the residence time of water, which varies depending on the type of reservoir.

- **Glaciers:** Glaciers play a crucial role in the water cycle because their residence time can reach several millions of years, thereby influencing surrounding hydrological systems.
- **Atmosphere:** About 8 days. The residence time of water in atmospheric and aquatic reservoirs is a key factor influencing their biogeochemical behavior and transport processes (Rueda et al., 2006).
- **Estuaries:** Residence time is intermediate, usually a few weeks to several months, depending on hydrodynamic conditions and freshwater inflows.

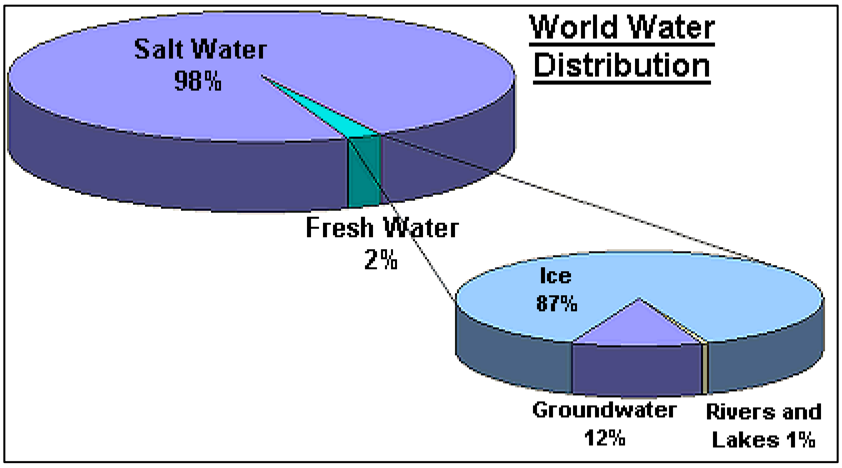
- **Lakes:** Residence time can vary considerably, influenced by water inputs, evaporation, and mixing processes.
- **Groundwater:** Residence times in aquifers vary widely, from a few days to several thousand years, highlighting their importance in water resource management
- **Rivers:** Water residence times in rivers typically range from a few days to a few weeks, depending on flow rates and watershed characteristics.
- **Oceans:** The average residence time is estimated at about 3,000 years, illustrating the scale of long-term hydrological processes.

These variations in residence time are essential for understanding mixing and transport processes within aquatic reservoirs.

1.2.3. Freshwater and Saltwater

The total volume of water on Earth is estimated at approximately 1.4 billion km³, a constant quantity for billions of years. Of this:

- 98% is saltwater, covering roughly two-thirds of the Earth's surface in oceans, seas, and ice sheets.
- 2% is freshwater, a critical and limited resource essential for life, ecosystems, and human societies, requiring careful management to prevent scarcity.



Freshwater is found in different reservoirs:

- 87% in glaciers and ice caps.
- 12% underground in groundwater aquifers, including deep confined layers. Only a small fraction of this groundwater is truly accessible for use, making sustainable management essential.

- 1% on the land surface in lakes, rivers, and ponds, highlighting the need for careful management of surface water resources.
- 0.04% in the atmosphere as clouds, rain, fog, or mist.

Although freshwater is present in much smaller quantities than saltwater, it is essential for life. Less than 1% of freshwater is readily accessible for human use, emphasizing the importance of preservation and sustainable management. Increasing pressures from urbanization and intensive agriculture require effective strategies to ensure the availability of freshwater for future generations.

1.2.4. Groundwater

Groundwater originates from the infiltration of rainwater into the soil. It forms two types of aquifers:

- Shallow aquifers (phreatic aquifers): located close to the soil surface.
- Confined aquifers: deeper underground.

This water is collected through wells or boreholes and then treated in water treatment plants to produce drinking water for human consumption.

1.2.5. The Domestic Water Cycle

In parallel with the endlessly renewed journey of water across the planet, water can be diverted into a shorter cycle, limited to human activities. Through this internal cycle, we can use tap water for drinking and domestic purposes, treat it after use, and return it to the natural environment.

To ensure proper water management, the domestic cycle includes several key steps:

- **Water capture:** It is essential to implement management strategies that preserve the quality of water resources while ensuring their availability for domestic and agricultural needs.
- **Water treatment:** This step is crucial to remove contaminants and make water potable, while addressing challenges related to its quality and taste.
- **Water storage:** Proper storage is necessary to prevent contamination and maintain water quality until its final use.
- **Water distribution:** Distribution must ensure traceability and meet growing consumer expectations regarding water quality and origin.

- **Collection after use:** Collecting wastewater is essential for recycling, contributing to integrated water cycle management.
- **Wastewater treatment:** Treating wastewater before returning it to the environment ensures safe reuse, preserves water resources, and reduces environmental impacts.
- **Return to nature:** Water should be returned thoughtfully, taking into account ecosystem needs and minimizing impacts on aquatic environments.

1.2.6. Sources of Drinking Water

- **Mineral water and spring water** come exclusively from groundwater.
- **Tap water** can originate from multiple sources, including surface water (rivers, lakes) and groundwater.

Approximately 62% of drinking water comes from groundwater, while the remaining 38% comes from surface water sources such as streams, rivers, and lakes. Effective water resource management must therefore include measures to ensure water quality, considering diffuse pollution and strict regulatory standards.

1.2.7. Geosphere–Hydrosphere Interactions

Chemical weathering of rocks refers to the set of reactive processes through which the primary minerals in rocks undergo transformation under the combined influence of water, atmospheric gases, and dissolved chemical agents. These interactions lead to the destabilization of the original mineral phases, their partial or complete dissolution, and the release of chemical elements as ions into solution. Simultaneously, new secondary minerals such as clays, oxides, hydroxides, or carbonates precipitate from the products of these reactions. Chemical weathering of silicates, particularly those rich in calcium and magnesium, plays a key role in the capture and storage of atmospheric CO_2. This natural process is fundamental to the carbon cycle, as it enables the formation of stable carbonates from greenhouse gases. Such transformations are essential for mitigating the effects of CO_2 emissions, thereby contributing to climate change mitigation and environmental sustainability. This phenomenon is a crucial mechanism in the exchanges between the geosphere and hydrosphere because it largely controls the chemical composition of natural waters and influences the mobility, redistribution, and speciation of elements in continental environments. At a global scale, chemical weathering plays a decisive role in the biogeochemical cycling of major and trace elements, including carbon and silicon, contributing over the long term to planetary climate regulation through the consumption of atmospheric carbon dioxide during silicate dissolution processes.

1.2.8. Changes in Water Quality During the Hydrological Cycle

Rainwater passes through soils and rocks before emerging at the surface. Rain forms by condensation of water vapor around solid particles present in the atmosphere. Initially, rainwater is very low in dissolved minerals; its mineralization is limited to the dissolution of airborne particles (mineral dust, aerosols, sea salts) and gases that can dissolve in water droplets (CO_2, various acids). The most significant chemical changes occur when water passes through the upper soil horizons. These changes depend on the nature of the terrain, climate, and the duration of water movement. Rainwater feeds shallow aquifers (phreatic aquifers) and sometimes deeper confined aquifers.

Water mineralization mainly results from water–rock interactions, enhanced by a partial CO_2 pressure in the soil 10–100 times higher than atmospheric levels, produced by the oxidation of organic matter (soil respiration) and diffusing to the external atmosphere. By dissolving CO_2 from the soil atmosphere, rainwater becomes slightly acidic, allowing it to react with soil minerals according to their solubility. In addition, water mineralization increases due to evaporation during infiltration into the soil. Other reactions and processes beyond simple mineral dissolution also modify water chemistry in the soil or deeper in the aquifer, including adsorption/desorption, ion exchange, and mixing of different water masses. The mineral content acquired by infiltrating water ultimately supplies plants with essential nutrients necessary for their growth.

1.2.9. Mechanisms of Chemical Composition Acquisition in Water

During its infiltration into the soil, water passes through organic or organo-mineral horizons and becomes enriched in dissolved CO_2. Dissolved CO_2 can provide H^+ ions through dissociation, enabling hydrolysis reactions of weatherable minerals. These hydrolysis reactions increase the dissolved load of natural waters by releasing the constituent elements of these minerals into solution, such as alkali metals (Na, K, …), alkaline earth metals (Mg, Ca, …), transition metals (Al, Fe, …), and metalloids (Si, P, S). Within the pH and redox potential ranges of the water stability domain, three groups of elements can be distinguished according to their charge:

- **Low charge (I and II):** These are surrounded by a hydration shell of water molecules (hydrated cations such as Na^+, K^+, Mg^{2+}, Ca^{2+}).
- **Charge +III:** These exist as cations under acidic pH, neutral molecules at neutral pH, and as anions under alkaline conditions. They have a pronounced acidic character

(e.g., Fe^{3+}, Al^{3+}), forming insoluble hydroxides at neutral pH and anions at alkaline pH.

- **Charge greater than +III:** These are present as neutral molecules (e.g., $Si(OH)_4$) or as oxyanions (e.g., PO_4^{3-}, SO_4^{2-}).

Example: Calcium aluminosilicate (anorthite) is a common, easily weatherable mineral in continental rocks. Its hydrolysis reaction can be written as:

(Here, the chemical equation would typically be included, showing anorthite reacting with H^+/H_2O *to release* Ca^{2+}*,* Al^{3+}*, and* $Si(OH)_4$ *into solution.)*

This process illustrates how soil–water interactions and mineral hydrolysis directly control the chemical composition of groundwater and surface waters.

$$Si_2Al_2O_8Ca + 8H^+ \longrightarrow 2Si(OH)_4 + 2Al^{3+} + Ca^{2+}$$

However, when the pH is neutral, aluminum becomes insoluble and precipitates as aluminum hydroxide, $Al(OH)_3$ (gibbsite), or as kaolinite, a very common mineral in temperate and tropical soils. Practically all the aluminum released by the reaction reprecipitates. As a result, the concentration of aluminum in water remains very low ($10^{-6} – 10^{-5}$ mol/L).

The dissolution of anorthite, coupled with the precipitation of kaolinite, leads to the release of **Ca^{2+}** into the solution.

The hydrolysis reaction of anorthite written with H^+ (acidic weathering) is thus:
(Here, the chemical equation would typically show anorthite reacting with H^+ *to produce* Ca^{2+}*,* Al^{3+}*, and* $Si(OH)_4$*, with* Al^{3+} *quickly precipitating as* $Al(OH)_3$ *or forming kaolinite.)*

This process demonstrates how mineral weathering and secondary mineral formation control the availability of cations in natural waters.

$$CaAl_2Si_2O_8 + 2\,H^+ + H_2O \longrightarrow Al_2Si_2O_5(OH)_4 + Ca^{2+}$$

The hydrolysis of other silicates is responsible for the presence of additional cations (Na^+, K^+, and Mg^{2+}) and dissolved silica in solution.

Dissociation of CO_2 and rock weathering as a CO_2 sink: The dissociation of dissolved CO_2 is the primary source of protons (H^+) and produces bicarbonate ions (HCO_3^-):

$$CO_2 + H_2O \longrightarrow H + HCO_3^-$$

As a result, the alkalinity of the solution and the buffering capacity of water with respect to pH increase. The weathering of minerals in continental rocks is therefore limited. In young soils, this limitation is controlled by the number of available protons, whereas in old soils it is governed by the quantity of weatherable minerals. In a young soil, the combination of these reactions can be expressed as:

$$Ca^{2+} + 2\,HCO_3^{-} \longrightarrow CaCO3 + CO_2 + H_2O$$

Thus, overall, the weathering of calcium silicates removes a molecule of CO_2 from the atmosphere and traps it in the form of calcium carbonate (limestone)**:**

$$CaAl_2Si_2O_8 + CO_2 + 2\,H_2O \longrightarrow Al_2Si_2O_5(OH)_4 + CaCO_3$$

The weathering of calcium silicates, accompanied by the formation of clay minerals in soils and calcite in sedimentary basins**,** represents the major CO_2 sink. The reaction can be simplified as follows:

$$CaO + CO_2 \longrightarrow CaCO_3$$

The process described above with Ca^{2+} also occurs with other alkali and alkaline earth cations**.** However, in sedimentary basins**,** Na^+ and K^+ typically reprecipitate as silicates, releasing the CO_2 back into the atmosphere, so the net CO_2 effect is zero. For Mg^{2+}**,** part of it precipitates as magnesium silicates (clay minerals), while another part forms dolomite, $CaMg(CO_3)_2$**.** It is this dolomite formation that also contributes to trapping atmospheric CO_2**.**

Main Types of Reactions

Chemical weathering reactions can be divided into several fundamental mechanisms, among which hydrolysis, redox reactions, and carbonation dominate depending on the local physicochemical conditions.

Hydrolysis involves the attack of water (H_2O) or H^+/OH^- ions on mineral bonds, transforming, for example, feldspars into kaolinite clays according to the simplified reaction:

$$2KAlSi_3O_8 + 2H^+ + 9H_2O \rightarrow Al_2Si_2O_5\,(OH)_4 + 2K^+ + 4H_4SiO_4.$$

Chemical weathering reactions can be divided into several fundamental mechanisms, among which hydrolysis, redox reactions, and carbonation dominate depending on local physicochemical conditions.

Hydrolysis involves the attack of water (H_2O) or H^+/OH^- ions on mineral bonds, transforming, for example, feldspars into kaolinite clays according to the simplified reaction. This transformation is influenced by factors such as temperature, pH, and the concentration of alkali ions, which modify the dissolution kinetics of feldspars and the rate at which ions are released into solution. The incongruent dissolution of feldspars, where alumina remains poorly soluble, also plays a crucial role in this process. primarily affects ferrous minerals, where Fe^{2+} is oxidized to Fe^{3+} by dissolved oxygen, promoting the formation of oxides such as goethite (FeOOH) or hematite (Fe_2O_3).

Carbonation results from the reaction of silicates with carbonic acid (H_2CO_3) derived from the dissolution of atmospheric CO_2 in water, producing secondary carbonates such as calcite ($CaCO_3$) from calcium plagioclase.

These processes are often coupled and modulated by factors such as pH, temperature, O_2/CO_2 partial pressure, and the presence of organic acids from the biosphere, enhancing their role in soil neoformation and the development of altered profiles. These chemical weathering mechanisms interact in complex ways, influencing soil dynamics and evolution over time, particularly in ferralitic soils where pedogenesis plays a key role.

Hydrolysis represents the dominant chemical weathering process, in which water and H^+/OH^- ions attack the Si–O–Al bonds of primary silicates such as feldspars, leading to their transformation into secondary clays (see image above). The simplified reaction of potassium feldspar illustrates this decomposition:

$$2KAlSi_3O_8 + 2H^+ + 9H2O \rightarrow Al_2Si_2O_5(OH)_4+2K^+ + 4H4SiO_4$$

This transformation is particularly influenced by the pH of the environment, where acidic conditions favor the formation of ordered, isotropic kaolinite, whereas more basic conditions lead to increased disorder and anisotropy.

This process is essential for the nutrient cycle and soil formation, highlighting the importance of feldspars in Earth’s geochemical processes, with the release of alkali ions and leached silicic acid. The diagram illustrates the molecular destabilization caused by CO_2-enriched acidic water, promoting the neoformation of stable kaolinite under acidic conditions.

Thus, feldspar hydrolysis can direct the formation of kaolinite, influenced by experimental conditions such as pH and CO_2 concentration.

1.2.10. Oxidation–Reduction

Oxidation–reduction (redox) reactions control the chemical speciation, mobility, and toxicity of many elements in natural waters (Fe, Mn, S, N, C, As…). Understanding these reactions is essential for assessing water quality and geochemical processes in aquifers, particularly regarding the redox potential (Eh).

Redox reactions strongly influence:

- the color of water,
- precipitation/dissolution of minerals,
- the presence of dissolved metals,
- microbial activity,
- Drinking water quality and the evolution of groundwater.

1. Basic Principles

1. Oxidation is a key process in redox reactions, where an electron donor loses electrons, causing changes in the chemical speciation of elements.

Oxidation involves:

- The loss of electrons and an increase in the oxidation state of the elements, which is crucial for understanding chemical transformations in aquifers.
- The formation of oxidized products, which can influence water quality and interactions between different chemical species in the aquifer.
- Often reactions with O_2, NO_3^-, or SO_4^{2-}, where oxygen, sulfates, and nitrates act as electron acceptors, controlling redox dynamics in aquifers.

Example: $Fe^{2+} \rightarrow Fe^{3+} + e^-$

2. Reduction, in contrast, involves the gain of electrons by an acceptor, leading to a decrease in the oxidation state of elements, which is also critical for geochemical processes in aquifers.

Reduction involves:

- The gain of electrons and a decrease in oxidation state, which can enhance metal solubility and influence water toxicity.
- Often occurs under anaerobic conditions, where microorganisms such as bacteria play a key role in transforming chemical species and affecting water quality.

Example: $NO_3^- + 2e^- \rightarrow NO_2^-$

2. Redox Couple

A redox couple is a pair of oxidized/reduced species. The dynamics of these redox couples are critical in regulating biogeochemical cycles, thereby influencing the health and quality of aquatic ecosystems. Understanding redox couples is essential for evaluating biogeochemical processes in aquatic ecosystems, including nitrification and denitrification.
A redox couple is a pair of oxidized and reduced species.

Important examples in natural waters:

Element	Redox Couple	Example / Role
Oxygen	O_2 / H_2O	Respiration, oxidation of metals
Iron	Fe^{3+} / Fe^{2+}	Controls water color
Manganese	MnO_2 / Mn^{2+}	Drinking water, filters
Sulfur	SO_4^{2-} / HS^-	Reducing zones, wetlands
Nitrogen	NO_3^- / NH_4^+	Pollution, nitrification/denitrification
Carbon	CO_2 / CH_4	Anaerobic zones, sediments

3. Redox Potential (Eh)

The redox potential, Eh, measures the tendency of a medium to oxidize or reduce chemical species. This potential is crucial for understanding redox reactions in various systems, ranging from food matrices to aquatic ecosystems.
In water geochemistry, a high Eh can promote oxidation processes, whereas low Eh conditions favor reduction reactions, both of which influence water quality and aquatic biodiversity. Strict control of redox potential is essential for the sustainable management of water resources, particularly in deep aquifers where Eh tends to be low.

- High Eh ⇒ Oxidizing environment (oxygenated surface waters);
- Low Eh ⇒ Reducing environment (deep aquifers, sediments).

Typical Values:

- Redox potentials generally range between -400 mV and +800 mV, depending on environmental conditions and ecosystem type.
- In groundwater, typical Eh values are between -200 mV and +300 mV, reflecting the frequently reducing conditions in these environments.
- In surface waters, typical Eh values range from +100 mV to +500 mV, indicating an oxidizing potential favorable to aquatic organisms.

- In soils, Eh values are around +200 mV to +600 mV, which can influence soil fertility and ecosystem health.

Environment	Eh (approx.)	Characteristic
Oxygenated surface water	+400 to +700 mV	Strongly oxidizing
Shallow groundwater	+200 to +300 mV	Oxidizing
Deep aquifer	0 to +100 mV	Weakly reducing
Stagnant water, sediments	-100 to -300 mV	Strongly reducing

4. Major Redox Processes in Natural Waters (Géosphere- Hydrosphere reactions) Oxidation of Iron and Formation of Hydroxides

Redox processes in natural waters play a crucial role in chemical self-purification and in controlling the dynamics of redox-sensitive elements. These processes are influenced by oxidizing agents such as oxygen (O_2), hydrogen peroxide (H_2O_2), and hydroxyl radicals (OH), which interact with transition metal compounds.

$$Fe^{2+} + \ O_2 + \ H_2O \rightarrow Fe\,(OH)_3\,(s) + 2H^+$$

Ferrous iron (Fe^{2+}, colorless/transparent) → Ferric iron (Fe^{3+}, red/orange).

Impact: river coloration, iron deposits, and natural water purification. These transformations have significant implications for water quality, affecting color, sediment formation, and natural purification processes. These processes are also influenced by the presence of manganese, which requires stronger oxidizing agents for removal during water treatment. Manganese removal is often achieved through chemical oxidation processes, using oxidizing agents such as air or more potent compounds. Chemical oxidation methods, essential for treating manganese, typically involve reactions with various oxidants depending on the specific water conditions.

$$Fe^{2+} + \frac{1}{4}\,O_2 + \frac{5}{2}\,H_2O \rightarrow Fe\,(OH)_3\,(s) + 2H^+$$

Ferrous iron (Fe^{2+}, colorless/transparent) → Ferric iron (Fe^{3+}, red/orange)
Impact: river coloration, iron deposits, and natural water purification.

Manganese oxidation: $Mn^{2+} + \frac{1}{2}\,O_2 + H_2O \rightarrow MnO_2\,(s) + 2H^+$

- Requires a higher Eh than Fe^{2+} oxidation.
- MnO_2 acts as a strong oxidizing agent in soils.
- Sulfur cycle

- Oxidation:

  $HS^- + 2\ O_2 \rightarrow SO_4^{2-}$

  The oxidation of bisulfide ions to sulfate represents a key step in the sulfur cycle, influencing the quality of natural waters and associated biological processes.

Reduction (sulfate reduction): $SO_4^{2-} + 8\ e^- + 10\ H^+ \rightarrow HS^- + 4\ H_2O$

Sulfate reduction, carried out by specific bacteria, plays an important role in the sulfur cycle and can affect the dynamics of elements in natural waters. Responsible for the “rotten egg” smell (H_2S) in anaerobic waters.

These sulfate-reduction processes are also linked to the formation of hydrogen sulfide, which can cause odor issues and corrosion problems in wastewater systems.

Metal reduction (Cr, U)

Example: Cr(VI) (toxic) → Cr(III) (less mobile)

The reduction of Cr(VI) to Cr(III) is an important redox process, often catalyzed by agents such as Fe(II) and oxidants like manganese oxides. This process can help immobilize chromium in soils and limit its environmental toxicity.

Uranium: U(VI) (soluble) → U(IV) (precipitates)

The reduction of uranium in lake sediments is often influenced by the presence of iron, which plays a key role in transforming uranium from a soluble to a precipitated form.

Redox conditions control both toxicity and mobility. Variations in redox potential and pH in contaminated soils significantly affect the solubility and speciation of contaminants, including arsenic.

5. Eh–pH Diagrams (Pourbaix Diagrams)

These diagrams are essential for understanding chemical interactions in aquatic environments and for predicting the behavior of contaminants under various conditions. Eh–pH diagrams show the stable forms of an element depending on: pH, redox potential, and chemical speciation (dissolved vs. precipitated forms).

Log S–pH diagrams can also be used instead of Eh–pH diagrams to better represent relationships between sulfide and carbonate contents in reducing water bodies. These approaches help optimize the management of trace elements in aquatic environments, taking into account redox variations and contaminant dynamics.

Examples: Fe^{2+} is stable in reducing and acidic conditions

$Fe(OH)_3$ is stable in oxidizing and neutral conditions

MnO_2 is stable at Eh values higher than $Fe(OH)_3$

These diagrams are essential for predicting the dominant form of an element in aquifers.

Environmental Importance: Understanding redox processes and their impact on contaminant solubility is crucial for water resource management and environmental protection.

Pollutant Mobility

Low Eh: metals are mobilized (Fe^{2+}, Mn^{2+}, As^{3+}, etc.)Low redox potential favors the mobility of metals, increasing the risk of groundwater contamination. Monitoring and managing redox conditions are therefore critical in aquatic systems.

High Eh: metals precipitate High redox potential leads to the precipitation of metals, reducing their mobility and environmental risk. Proper management of redox conditions helps prevent water contamination.

The redox couples ranking arrow illustrates the thermodynamic order of oxidation–reduction reactions in water geochemistry, ranging from reducing conditions (left, negative Eh) to oxidizing conditions (right, positive Eh), based on standard potentials adjusted by the Nernst equation.

- In aerated surface waters (Eh +400 to +700 mV), O_2/H_2O (+0.82 V, red) dominates, oxidizing Fe^{2+} and Mn^{2+} into precipitated oxides.
- In deep, reducing aquifers (Eh -100 to -300 mV), CO_2/CH_4 (-0.24 V, violet) and SO_4^{2-}/HS^- (-0.22 V, blue) prevail, releasing dissolved Fe^{2+} and trace elements such as As and U through oxide reduction.

These arrows help visualize the transitions between different redox states, facilitating the understanding of chemical processes that influence water quality in various aquatic environments. They also highlight how variations in redox potential can affect contaminant mobility, underscoring the importance of proactive water resource management. Redox processes are crucial for maintaining water quality and preventing contamination, especially in pollutant-sensitive areas.

Strong Oxidant **Strong Reductant**

$$\longleftarrow\!\!\longrightarrow$$

$$\mathbf{MnO_4^-/Mn^{2+} \mid O_2/H_2O \mid Fe^{3+}/Fe^{2+} \mid Cu^{2+}/Cu \mid Zn^{2+}/Zn}$$

On the left: increasingly strong oxidants

On the right: increasingly strong reductants

A reaction is possible if:

- The oxidant is on the left
- The reductant is on the right

Reductant → Oxidant
(right) (left)
Example: Is the reaction between Cu^{2+} and Zn possible?

Answer: Yes.

- **Zn** is a strong reductant (on the right)
- **Cu^{2+}** is an oxidant (on the left)

So, Zn can reduce Cu^{2+} to Cu, while Zn is oxidized to Zn^{2+}.

Reaction:
$Zn \rightarrow Zn^{2+} + 2e^-$
$Cu^{2+} + 2e^- \rightarrow Cu$
$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$

This follows the redox arrow rule.

Strong Oxidant	Strong reductant
$\longleftarrow$	$\longrightarrow$
Cu^{2+} / Cu	Zn^{2+} / Zn
E° = +0,34 V	E° = −0,76 V

<u>Standard potential</u> **(E °):** what it exactly is?

The standard potential (E °) measures the tendency of a redox couple to gain or accept electrons, under standard conditions: 25 °C, 1 bar, and unit activities (essentially zero ionic strength). It is measured relative to the standard hydrogen electrode (SHE), which is defined as (E ° = 0V).
It helps determine the spontaneity of redox reactions:

If (E°> 0), the reaction is thermodynamically favorable.

Example for arsenic:
AsO_4^{3-}/AsO_2^- at E° = +0.56 V (in basic medium)

A redox couple always links an oxidized form (Ox) and a reduced form (Red), such as: O_2/H_2O, E∘=+1,23 V

The half-cell reaction is always written as a reduction: $Ox + ne^- \rightleftharpoons Red$

$Red \rightleftharpoons Ox + ne^-$

Large positive (E°) → species is easily reduced → good oxidant

Small or negative (E°) → species is difficult to reduce → good reductant (in its reduced form)

Standard measurement conditions:

Temperature: 25 °C, Pressure: 1 bar, Concentration: 1 $mol \cdot L^{-1}$ for all dissolved species

How is E° measured? The potential is always measured relative to a reference: the Standard Hydrogen Electrode (SHE). By convention: $2\ H^+ + 2\ e^- \rightarrow H_2$, E° = 0,00 V
All other potentials are measured in comparison to this electrode.

Physical meaning of the standard potential:

A standard potential (E°) corresponds to the electrical energy per unit charge. The larger the (E°), the more the electrons "want" to move toward that species and the stronger its tendency to attract electrons. It's similar to a difference in height: electrons naturally "fall" from the lower potential to the higher potential.

What does ΔE° represent?

ΔE° is the driving force of a redox reaction. When two redox couples are combined, there is:

- an electron donor (reductant)
- an electron acceptor (oxidant)

Electrons spontaneously move from the lower potential to the higher potential.

$$\Delta E° = E°(\text{oxidant}) - E°(\text{reductant}$$

- If $\Delta E° > 0$ → the reaction is spontaneous
- If $\Delta E° < 0$ → the reaction is not possible

The driving force is related to the Gibbs free energy:

$$\Delta G° = - n\ F\ \Delta E°$$

n: number of electrons exchanged

F: Faraday constant, a fundamental physical constant in electrochemistry, representing the electric charge of one mole of electrons. Its exact value is $F = 96485.3321 C \cdot mol^{-1}$, and it helps predict natural speciation.

If $\Delta E° > 0 \rightarrow \Delta G° < 0$ → the reaction is spontaneous

Redox Zone Succession

Highly oxidizing (O_2/H_2O, NO_3^-/N_2): Redox zones evolve in a sequence that determines the availability of electron acceptors, thereby influencing contaminant mobility in aquifers. Reducing zones, where electron acceptors are limited, favor the reduction of nitrates and toxic metals, playing a key role in the natural purification of aquifers.

Fe^{3+}/Mn^{4+} precipitation, low metal mobility: Redox conditions affect metal speciation, notably promoting the precipitation of oxidized forms of iron and manganese, which reduces their mobility in the environment. This is typical of surface waters.

Moderately oxidizing (Fe^{3+}/Fe^{2+}): Under slightly reducing conditions, metals can be reduced, promoting the stabilization of contaminants in soils and waters. Variations in redox conditions can also influence the bioavailability of trace metals, affecting their behavior in aquatic ecosystems.

Transition with Aquifer Clogging by Oxides/Hydroxides; Shallow Waters

Redox potential variations in shallow aquifers can lead to clogging phenomena, affecting water resource management and drinking water quality. These transitions between redox zones are crucial for understanding long-term natural water purification processes.

Reducing conditions (SO_4^{2-}/HS^-, CO_2/CH_4): Reducing environments favor the dissolution of metals, which can cause contamination issues in groundwater and impact drinking water quality.

Release of Fe^{2+}, H_2S, trace metals, sediments, and anoxic aquifers: Managing redox conditions is therefore essential for preserving water quality and preventing contamination, particularly in deep aquifers where reduction processes dominate. These redox processes are also critical for aquifer management, as they influence contaminant dynamics and groundwater quality.

1.2.11. Carbonation

Carbonation is a key geochemical process involving the reaction of carbon dioxide (CO_2) originating from the atmosphere, biological activity, or hydrogeological sources with water and rock minerals, leading to the formation of carbonate ions and carbonate mineral phases. This mechanism plays a crucial role in the chemical weathering of silicate rocks, the dissolution-precipitation of carbonates, the regulation of pH in natural aquatic environments, and the global biogeochemical carbon cycle.

Carbonation is also influenced by redox conditions, which alter the solubility and speciation of carbonate ions in aquatic environments. The interaction between carbonation and redox processes is complex, affecting elemental dynamics and water quality across diverse aquatic systems. Understanding this interaction is essential for natural purification mechanisms and sustainable water resource management. Integrating carbonation processes into water management strategies is therefore critical for improving water quality and supporting aquatic ecosystems. Dissolved CO_2 converts into carbonic acid (H_2CO_3), which dissociates into bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions. These ions react with divalent cations (Ca^{2+}, Mg^{2+}) released from mineral weathering to precipitate calcite ($CaCO_3$) or dolomite. Through this process, carbonation buffers pH to moderately alkaline values (7–8.5), serves as a long-term geological CO_2 sink, and promotes soil formation and karst development.

This process perfectly illustrates the geosphere hydrosphere interfaces, with significant climatic implications (silicate CO_2 sequestration) and hydrological impacts (carbonate hardness of waters), which are essential for environmental modeling.

Step 1: Dissolution of CO_2 in Water

Gaseous CO_2 dissolves in water: $CO_2\ (g) \rightleftharpoons CO_2\ (aq)$

It then reacts with water to form carbonic acid: $CO_2\ (aq) + H_2O \rightleftharpoons H_2CO_3$

This reaction slightly lowers the pH, making the medium more acidic.

Next, carbonic acid dissociates into bicarbonate (HCO_3^-) and hydrogen ions (H^+), contributing to pH regulation in aquatic environments.

The dissociation of carbonic acid is essential for understanding pH variations in aquatic systems, thereby influencing carbonation processes and chemical interactions.

Step 2: Formation of Carbonate Species

Carbonic acid dissociates in two steps: $H_2CO_3 \rightleftharpoons HCO_3^- + H^+$

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$$

Bicarbonate (HCO_3^-) is the dominant species in natural waters (pH 6–9).

Carbonate (CO_3^{2-}) becomes more abundant in basic waters.

Step 3: Carbonation of Minerals (Formation of Carbonates)

Carbonate ions react with dissolved cations to form solid carbonates. The formation of solid carbonates, such as calcite and dolomite, depends on the concentrations of divalent cations and the pH conditions, thereby influencing the geochemical dynamics of aquatic systems.

Example: Calcium carbonation: $Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3(s)$

This process of carbonation is intrinsically linked to pH variations, which control the solubility and precipitation of carbonates in aquatic environments.

Magnesium Carbonation**:** $Mg^{2+} + CO_3^{2-} \rightarrow MgCO_3(s) \rightarrow$ formation of magnesite. Understanding magnesium carbonation is essential for optimizing carbon dioxide sequestration processes and improving water quality.

Silicate Carbonation (Chemical Weathering): Silicates (e.g., feldspars) undergo alteration under the influence of CO_2: $CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2$

Carbonation of silicates, such as wollastonite (a calcium silicate, $CaSiO_3$), is influenced by temperature and pressure conditions, affecting the efficiency of CO_2 sequestration in aquatic environments. This process consumes CO_2, playing a major role in climate regulation over millions of years. Carbonation is also affected by redox conditions, which modify the solubility of cations and anions in aquatic systems, thereby impacting element dynamics and water quality.

Reverse Carbonation: Carbonate Dissolution

When there is an excess of CO_2, even slightly acidic, water can dissolve carbonates: $CaCO_3(s) + CO_2 + H_2O \rightarrow Ca^{2+} + 2\ HCO_3^- \rightarrow$ Formation of calcium bicarbonate waters (e.g., Evian, Vichy…).

Importance of Carbonation in Aquatic Geochemistry**:** Carbonation plays a key role in regulating pH and element dynamics in aquatic environments, thus influencing water quality and associated biological processes. Carbonation is also a crucial process for CO_2 sequestration, contributing to the long-term capture of CO_2 in aquatic environments. It is therefore a fundamental process for CO_2 sequestration, affecting both water chemistry and global biogeochemical cycles.

pH Control**:**The carbonate system ($CO_2/HCO_3^-/CO_3^{2-}$) is the main natural buffer in waters. This system is crucial for pH regulation, maintaining conditions favorable for aquatic life and ecosystem health. Managing carbonation processes and redox conditions is essential to optimize water quality and support CO_2 sequestration in aquatic environments.

Determination of Hydrochemical Facies**:** Hard water = high carbonation of Ca and Mg. Water hardness, influenced by calcium and magnesium concentrations, plays a crucial role in water chemistry and potability. Soft water = low carbonation. Understanding the differences between hard and soft waters is essential for water resource management and optimizing drinking water treatment.

Formation/Dissolution of Carbonate Rocks**:** The formation and dissolution of carbonate rocks are key geochemical processes that influence water quality and the carbon cycle in aquatic ecosystems. Examples include travertines, stalactites, and calcite in karst environments. Travertines, often associated with karstic springs, play an important role in aquatic ecosystems by affecting the dynamics of carbonate deposits and water quality.

CO_2 Transport and Storage: Mineral carbonation = method of CO_2 sequestration. Mineral carbonation is a promising method for CO_2 sequestration, allowing the transformation of carbon dioxide into stable carbonates and thereby reducing its impact on climate change.

*Influence on Rock Weathering***:** Mineral carbonation also contributes to the alteration of silicate rocks, affecting biogeochemical cycles and water quality in aquatic environments. Silicates are altered by acidic carbonation. This carbonation process is also essential for pH regulation and element dynamics in aquatic systems, thereby influencing water quality. A thorough understanding of these processes is crucial for developing effective strategies for water resource management and the preservation of aquatic ecosystems.

3. Fundamental Physico-Chemical Parameters of Natural Waters

Understanding the physico-chemical parameters of natural waters is essential for assessing their quality and their impact on aquatic ecosystems. Redox and carbonation processes interact in complex ways, influencing the dynamics of elements and water quality in various aquatic environments, which is crucial for water resource management.

1.3.1. Physical Characteristics

1. Temperature (T): Temperature plays an important role in the solubility of salts and gases and consequently affects conductivity. It varies according to the ambient temperature, seasonal changes, geological nature, and the depth of the water level relative to the ground surface. The World Health Organization (WHO) guidelines set 12°C as the reference temperature for water intended for human consumption, with 25°C as the maximum allowable temperature.

2. pH: The pH of water is a measure of its acidity or alkalinity. In natural waters, pH is related to the geology of the area it passes through. In most natural waters, pH depends on the calco-carbonic equilibrium: $Ca(HCO3)2 \leftrightarrow CaCO3 + CO2 + H2O$

Generally, pH values of natural waters range between 6 and 8.5.

3. Conductivity: Conductivity measures the ability of water to conduct electrical current between two metal electrodes with a 1 cm^2 surface area, spaced 1 cm apart. Measuring conductivity allows a quick, though approximate, assessment of water mineralization and its evolution over time (see Table bellow).

4. Redox Potential (Eh) is a fundamental parameter for studying water chemistry, as it indicates whether the environment is oxidizing or reducing. It reflects the capacity of an aquatic system to gain or lose electrons during chemical reactions.

- A high Eh indicates an oxidizing environment, favorable for the formation of oxidized mineral species (e.g., nitrates, sulfates, ferric iron).
- A low Eh indicates a reducing environment, conducive to the presence of reduced species such as ammonium, sulfides, or ferrous iron.

Measuring the redox potential allows prediction of the stability and chemical form of dissolved elements (metals, nitrogen, sulfur, carbon, etc.) and helps estimate the direction of natural reactions that may occur in water or sediments. This parameter, closely linked to pH, along with it, serves as a key indicator of the oxidation state of an aquatic environment and plays a crucial role in interpreting biogeochemical processes.

5. Turbidity: is an indicator of water clarity and reflects the presence of suspended particles that scatter or absorb light. These particles may be mineral (clays, silts, metal oxides) or organic (humic matter, plant debris, plankton, microorganisms, colloids, etc.).Turbidity not only affects the visual aspect of water but is also a key parameter for evaluating physico-chemical water quality, as high turbidity can influence sedimentation processes, aquatic photosynthesis, and the effectiveness of water treatment.

Turbidity is measured using a nephelometer, which determines the amount of light scattered by particles, and is usually expressed in NTU (Nephelometric Turbidity Unit) or FTU (Formazin Turbidity Unit), both derived from a formazine standard solution. According to WHO recommendations, turbidity in water intended for human consumption should not exceed 5 NTU, although values below 1 NTU are often targeted for better aesthetic acceptability and more effective disinfection.

6. Relationship between Mineralization and Electrical Conductivity

Electrical conductivity (EC) is a direct indicator of the degree of mineralization of water, that is, the total amount of dissolved ions (both cations and anions). The higher the concentration of mineral salts (chlorides, sulfates, bicarbonates, sodium, calcium, etc.), the higher the conductivity. This index allows for a quick assessment of water's chemical quality and can help guide its potential uses (drinking water, agricultural, or industrial).

The general correspondence between conductivity values and the degree of mineralization is given in the table below:

Electrical Conductivity (µS/cm)	**Degree of Mineralization**
0 – 100	Very low
100 – 200	Low
200 – 333	Medium
333 – 666	Medium-high
666 – 1000	High-medium
> 1000	High

This classification is indicative because the exact relationship between conductivity and mineralization also depends on the nature of the dissolved ions and the water temperature, which affects ion mobility.

1.2.2. Chemical Characteristics of Natural Waters

1. Total Solids (Total Mineralization)

Total solids represent the total amount of solid matter contained in water after complete evaporation at a specified temperature (usually 105 °C). It reflects the overall mineralization of the aquatic environment.

- When measured on an unfiltered sample, it includes both dissolved and suspended matter (total solids).
- In a filtered sample, it only includes dissolved matter, called TDS (Total Dissolved Solids).

According to WHO drinking water standards, the recommended total solids content is below 1000 mg/L; exceeding this value may cause salty taste and pipe scaling. Waters with values above 1500 mg/L are generally considered brackish and often unsuitable for consumption without specific treatment.

2. Total Hardness

Total hardness of water reflects its content of divalent cations, primarily calcium (Ca^{2+}) and magnesium (Mg^{2+}), derived from the dissolution of the geological formations the water passes through. This parameter thus depends on the geology of the watershed:

- Limestone or dolomitic terrains typically provide hard to very hard water, rich in carbonates and sulfates.
- Granite, crystalline, or schist terrains usually yield soft water, low in minerals.

Two main forms of hardness are distinguished:

- **Temporary hardness (carbonate hardness):** Related to the presence of calcium and magnesium bicarbonates, removable by boiling.
- **Permanent hardness (non-carbonate hardness):** Due to sulfates, chlorides, or nitrates of Ca and Mg, not removable by heating .

Total hardness (TH) can be calculated using Todd's relation (1980):

$$TH = 2.497[Ca^{2+}] + 4.117[Mg^{2+}]$$

Where calcium and magnesium concentrations are expressed in meq/L.

In French degrees (°F), hardness can be approximated as:

$$TH = 2.5[Ca^{2+}] + 4.1[Mg^{2+}]$$

With 1 °F = 10 mg/L of $CaCO_3$.

Classification of water according to total hardness is given below :

TH (mg/L $CaCO_3$)	**Water Type**
< 75	Soft
75 – 150	Moderately hard
150 – 300	Hard
> 300	Very hard

Waters with hardness above 30 °F often pose a risk of scaling in water supply systems and heating installations. This phenomenon is usually evaluated using the Langelier Saturation Index, which estimates the potential for calcium carbonate ($CaCO_3$) precipitation.

3. Total Alkalinity (TAC)

Total alkalinity (TAC) measures the buffering capacity of water, that is, its ability to neutralize acids. It corresponds to the sum of dissolved weak bases, primarily hydroxides (OH^-), carbonates (CO_3^{2-}), and bicarbonates (HCO_3^-), minus the concentration of hydronium ions (H_3O^+).

The relationship proposed by Rodier et al. (2009) can be expressed as:

$$TAC = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H_3O^+]$$

In most natural waters, with a pH ranging between 7.6 and 8.3, alkalinity is primarily due to bicarbonates. Therefore, TAC provides valuable information about the carbonate system and the chemical stability of the water with respect to corrosion or calcium carbonate precipitation.

Chapter II: Geochemical Processes in Aquatic Environments

Introduction

Geochemical processes in aquatic environments encompass all chemical, physical, and biological reactions that control the composition of water, sediments, and exchanges with rocks. They determine the mobility of elements, water quality, and the evolution of aquatic ecosystems.

In surface and groundwater, the major processes include:

- Water–rock interactions (weathering, dissolution, precipitation).
- Redox reactions controlling the oxidation state of elements.
- Acid–base reactions and the carbonate system (pH, alkalinity, CO_2).
- Sorption processes (adsorption–desorption) on minerals and organic matter.

1. Speciation, Dissolution, Precipitation, Ion Exchange

Introduction

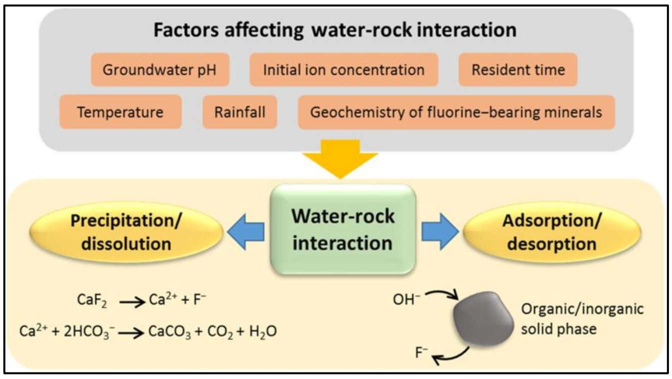
In water geochemistry, the behavior of dissolved substances is controlled by several key processes: speciation, dissolution, precipitation, and ion exchange.

Speciation describes the different chemical forms an element can take in water, which determines its mobility and reactivity. Dissolution is the process by which minerals enter water as dissolved ions. In contrast, precipitation occurs when dissolved ions combine to form solid minerals. Ion exchange involves the swapping of ions between water and mineral surfaces, influencing water composition.

Together, these processes regulate water chemistry in natural systems such as rivers, groundwater, and soils.

II.1.1. Water–rock interactions (weathering, speciation, dissolution, precipitation)

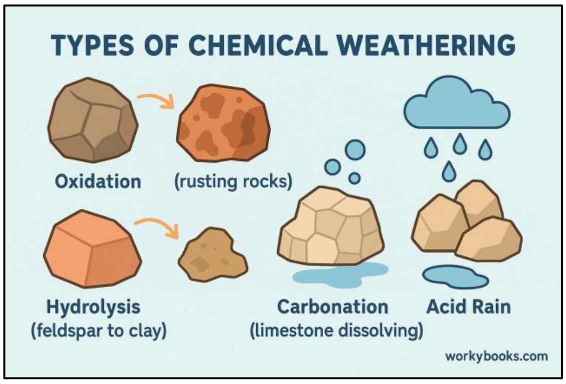
Water–rock interactions refer to the set of processes through which water alters the chemical composition of rocks and acquires its mineral content, via reactions such as weathering, dissolution, and precipitation.



These exchanges control the quality of both groundwater and surface water by releasing major ions (Ca^{2+}, Mg^{2+}, HCO_3^-, SO_4^{2-}) and forming secondary minerals like clays. These interactions are particularly influenced by local geological factors, including rock composition and the specific hydrogeological conditions of each region.

II.1.2. Mechanisms of chemical weathering Chemical weathering refers to the breakdown of rock minerals through chemical reactions induced by water, dissolved CO_2, oxygen, or microorganisms, altering their composition without physical transport of matter. It includes hydrolysis, dissolution, oxidation, and hydration. Water, often enriched with dissolved CO_2 (forming carbonic acid H_2CO_3), acts as the primary weathering agent in humid climates. The main reactions include:

- **Hydrolysis:** Decomposition of silicates (feldspars → clays + soluble ions, e.g., $KAlSi_3O_8 + H^+ + H_2O \rightarrow K^+ + HAlSi_3O_8$). This process is influenced by factors such as CO_2 concentration, which affects the ion equilibrium in solution and the dissolution rate of feldspars.
- **Hydration:** Incorporation of water into minerals (Fe oxides → swelling and disaggregation). Hydration of iron oxides can also induce mineralogical transformations, affecting soil and rock stability in wet areas.
- **Oxidation:** Transformation of sulfides or Fe^{2+} into insoluble oxides. Sulfide oxidation is crucial for forming minerals like boehmite and kaolinite, influencing soil dynamics and surrounding ecosystems.
- **Decarbonation / Carbonate dissolution:** ($CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$ soluble). Decarbonation is a key chemical weathering process, as it releases calcium and contributes to soil acidification, thereby influencing nutrient bioavailability.



These processes are dependent on climate (accelerated in tropical regions), temperature, and the mineralogical composition of the rocks.

II.1.3. Speciation in Aquatic Environments: Speciation in aquatic environments refers to the distribution of an element's chemical forms (such as arsenic) among dissolved ions, complexes, precipitates, or adsorbed species. This distribution is controlled by pH, ionic strength, redox potential (pe or Eh), and the presence of ligands. Speciation determines solubility, mobility, toxicity, and bioavailability of elements in natural waters such as rivers, lakes, and groundwater.

In water, a metal like copper can exist in several forms: free Cu^{2+} ions (toxic), $Cu(HCO_3)^+$, $Cu(CO_3)_2^{2-}$, or organic complexes with dissolved organic matter (DOM). Understanding these forms is crucial to assess the environmental risks associated with contamination—for example, copper contamination in aquatic ecosystems. Copper speciation directly affects its toxicity and bioavailability to aquatic organisms, making its study essential for managing contaminated ecosystems.

- **Acidic pH (<6):** Free hydrated ions dominate, resulting in high bioavailability. Copper speciation is strongly influenced by dissolved organic matter, which can form complexes with the metal, reducing its bioavailability and toxicity to species like *Daphnia magna* (a small freshwater planktonic crustacean, 1.5–5 mm, often called a water flea, subclass Phyllopoda).
- **Neutral to alkaline pH (>7):** Stable carbonate and organic complexes form, lowering toxicity. Copper speciation shifts toward less bioavailable forms, reducing toxicity to aquatic organisms. This highlights the importance of considering the composition of dissolved organic matter when evaluating copper risks in aquatic ecosystems.
- **Reducing Eh:** Fe^{3+} is reduced to soluble Fe^{2+}.
- **Oxidizing Eh:** Fe/Mn oxides form, trapping trace metals via adsorption.

Variations in pH therefore influence copper speciation, determining its toxicity to aquatic organisms. Moreover, organic and mineral colloids transport 20–80% of trace metals in dissolved form, moderating copper bioavailability. These speciation factors are essential for understanding how copper interacts with aquatic organisms and how its bioavailability changes under different environmental conditions.

II.1.4. Dissolution and Precipitation: Dissolution and precipitation are key geochemical processes that control the solubility of minerals in groundwater, particularly during chemical weathering and speciation.

Dissolution releases soluble elements into water (e.g., limestone → karst caves; evaporites → high salinity), while precipitation forms new minerals when the solution reaches saturation (e.g., calcite in stalactites). These dissolution/precipitation reactions govern the distribution of elements between dissolved and solid phases. Depending on the solution composition, a mineral may either dissolve or precipitate.

These processes are essential for understanding geochemical cycles and the evolution of aquatic environments, influencing the formation of geological structures such as caves and mineral deposits. Complex interactions between dissolution and precipitation are especially visible in karst systems, where rapid saturation can continue to favor dissolution even under apparently saturated conditions. This dynamic highlights the importance of studying physicochemical processes in porous formations to predict environmental impacts associated with mineral dissolution.

The reactions depend on the element's concentration, the concentration of other ions in solution (with hydroxides and thus pH playing a major role for heavy metals), the solid phase, and temperature. Recent studies show that dissolution can continue even in saturated media, highlighting complex physicochemical processes in karst systems. These interactions influence the dynamics of dissolved and solid elements, impacting the environment.

- **Congruent dissolution:** Complete dissolution leaving cavities (karst).
- **Incongruent dissolution:** Formation of insoluble residues (clay soils).

The solubility of many minerals is also directly related to pH (e.g., Fe, Mn, Cu) and the redox potential (Eh) of the environment. The dissolution of a mineral in water can be written as:

$$AB(s) \rightarrow A^{+}(aq) + B^{-}(aq) \qquad (1.4)$$

Exemples: L' halite ($NaCl(s)$) → $Na^{+}(aq) + Cl^{-}(aq)$

Calcite ($CaCO_3(s)$) → $Ca^{2+}(aq) + CO_3^{2-}(aq)$

The solubility constant (K_s) of a mineral is expressed from the dissolution equation:

$$KS = [A^+(aq)] \times [B^-(aq)]$$

where $[A^+]$ and $[B^-]$ are the molar concentrations (mol/L). This constant depends only on temperature and can be found in tables. Understanding the solubility constant allows us to assess how variations in temperature and pressure affect dissolution and precipitation processes in different geological environments. Changes in temperature and pressure not only alter mineral solubility but also the chemical reactions occurring in porous formations, which can significantly influence fluid dynamics and rock permeability. These changes can also affect contaminant migration, making the understanding of dissolution and precipitation processes crucial for water resource management and environmental protection.

Examples of Solubility Constants:

- Halite ($NaCl(s)$): $K_s = [Na^+(aq)] \times [Cl^-(aq)]$
- Dolomite ($CaMgCO_3(s)$): $K_s = [Ca^{2+}(aq)] \times [CO_3^{2-}(aq)]$

The solubility (s) of a mineral is the maximum amount of the solid that can dissolve in one liter of solution. Solubility increases with temperature. Knowing the solubility allows calculation of K_s, and vice versa. For example, the solubility of calcite is influenced by thermodynamic factors such as temperature, which affects K_s values at different temperatures. Understanding the temperature–solubility relationship of calcite is particularly important for geochemical modeling, as it influences precipitation and dissolution processes. Determining solubility constants like that of calcite is essential for modeling geochemical processes in aquatic systems. Thermodynamic relationships allow better understanding of environmental impacts from temperature variations on mineral solubility and help predict mineral behavior in diverse environments, including karst formations and aquatic systems.

II.1.5. Precipitation: Precipitation refers to the process by which a dissolved species transitions to a solid state, representing the inverse and complementary process to dissolution. It is governed by the solubility equilibrium of a given mineral:

$$\text{Minéral (s)} \rightleftharpoons \text{Ions dissous } (K_{sp} = \prod a_i^{\nu_i})$$

This equilibrium is influenced by factors such as temperature, pressure, and the chemical composition of the solution. Precipitation is crucial in many fields, including environmental chemistry and materials science, where understanding precipitation mechanisms are essential.

II.1.6. Thermodynamic and Kinetic Conditions of Precipitation

The transition to the solid state depends on the saturation index (SI) and the prior presence of the mineral. Understanding these conditions is essential for predicting the behavior of geological systems during precipitation, particularly in contexts such as the injection of acidic gases. Precipitation is also influenced by the dynamics of chemical reactions, for example during CO_2 and associated gas injections into geological reservoirs. These interactions can significantly alter the physical properties of rocks, affecting their porosity and permeability.

1. **Mineral absent (or not precipitated previously):**

$$SI = \log \frac{IAP}{K_{sp}} > SI_{\text{critique}} \ (> 1 + \Delta SI_{\text{nucléation}})$$

- **Critical supersaturation threshold:** Required to overcome the nucleation energy barrier (formation of the first crystals).
- **Example – Calcite:** (SI= 1.2–1.5) (depending on temperature and impurities).

This threshold is crucial for understanding the conditions under which calcium carbonate

precipitation occurs efficiently. Controlling supersaturation allows optimization of crystal formation and improves precipitation yields. Manipulating supersaturation conditions, particularly at appropriate pH levels, can significantly influence precipitation rates and the quality of the crystals formed.

2. **Mineral already present (existing crystals):**

$$SI > 1 \ (\log IAP > \log K_{sp})$$

Crystal growth occurs on existing nuclei without the nucleation barrier.

Faster and thermodynamically favorable.

<u>Diagram of Precipitation Conditions</u>

- Precipitation depends on the saturation index (SI) and the presence of the mineral.

Geochemical Applications:

- ✓ Aquifères calcaires : SI_calcite >1 → entartrage conduites (pH↑, CO_2↓).
- ✓ Sédiments : SI_gypsum > SI_critique → précipitation anhydrite.
- ✓ Remédiation : SI_$Pb(OH)_2$ >1 → immobilisation Pb^{2+}.

<u>Kinetic factors</u>**:** temperature, crystal specific surface area, inhibitors (e.g., phosphates block calcite formation). PHREEQC modeling integrates SI with nucleation/growth kinetics to predict precipitation behavior.

II.1.7. Adsorption–Desorption: Definition and Mechanisms: Dissolved substances in water can attach to soil components or suspended particles and later be released; these processes are called adsorption and desorption. These mechanisms play a crucial role in controlling the concentrations of metals and other trace elements in natural waters.

Adsorption refers to the accumulation of chemical species at the surface of a solid, at the interface between the aqueous phase and particles, without forming a crystalline lattice or three-dimensional structure.

Two main types of interactions can occur:

1. **Physical adsorption (physisorption):**
    - Related to electrostatic interactions or Van der Waals forces.
    - Generally reversible, with low binding energy.
2. **Chemical adsorption (chemisorption):**
    - Involves chemical bonds, often covalent in nature.
    - More specific and stronger, sometimes irreversible.

In natural environments, both types of adsorption coexist, and their relative importance depends on the physicochemical characteristics of the water and the nature of the solid surfaces.

Hydrogeochemical Consequences

These interactions enrich water in divalent cations (hardness), alkalinity, and trace metals, influencing conductivity and pH. In limestone aquifers, they promote moderate mineralization (200–1000 µS/cm), whereas in granitic aquifers, they result in soft water (<100 µS/cm). They also explain the risks of scaling ($CaCO_3$ precipitation) or corrosion.

2. Role of Minerals and Organic Matter

Introduction

The chemical composition of water, before any anthropogenic influence, is controlled by its environmental setting (atmosphere, biosphere, soils, and rocks). Following the water cyclefrom the atmosphere to continental waters and eventually the oceans the concentrations of major and trace elements, as well as the overall chemical composition of water, change significantly.

Atmospheric precipitation is typically low in major elements (from µg/L to mg/L) and primarily composed of sodium (Na^+), chloride (Cl^-), and sulfate (SO_4^{2-}) ions, whereas rivers and aquifers are more concentrated (10 to 10^2 mg/L), containing mostly calcium (Ca^{2+}), magnesium (Mg^{2+}), and bicarbonate (HCO_3^-) ions.

River waters, once discharged into the oceans, see their concentrations increase due to evaporation. The dissolved salt content of seawater reaches 35 g/L, with a chloride–sodium composition (87% NaCl), because the least soluble minerals, such as carbonates, precipitate out. The more soluble minerals, such as NaCl, remain in solution.

II.2.1. Factors and Controlling Processes

The natural composition of precipitation is influenced by coast-to-interior gradients, caused by the decrease in chloride of oceanic origin and the relative increase in ions from continental sources (e.g., calcium), as well as by altitudinal gradients, corresponding to increased precipitation (dilution effect) and decreased continental dust. Except for calcium, the concentrations of most ions decrease from the coast to the interior, but their ratio relative to ocean-derived chloride increases.

These rainwaters feed rivers, and their element concentrations are further concentrated by evapotranspiration. In the absence of evaporitic rocks containing salts, riverine chloride originates from precipitation. Rainwater can also acquire additional elements as it passes through the forest canopy, leaching dry-deposited elements from leaves and exchanging ions with foliage. These “throughfall” waters can have concentrations 3–10 times higher than rainfall, especially for potassium, sulfate, and chloride.

Rainwater and throughfall then percolate through soils, becoming enriched in carbonic acid (H_2CO_3), a weak natural acid formed by the mineralization/oxidation of organic matter. These acidic, CO_2-rich soil solutions participate in the hydrolysis and dissolution of rock minerals, releasing cations, silica (SiO_2), and dissolved inorganic carbon (DIC) into rivers and aquifers. These weathering processes control the chemical composition of continental waters and contribute to the consumption of atmospheric CO_2.

	SiO_2	**Ca**	**Mg**	**Na**	**K**	**Cl**	**SO_4**	**DIC**	**DOC**
Atmospheric Precipitations	0.3	0.31	0.26	1.46	0.135	2.6	1.37	0.20	1.93
Rivers and Streams	10.4	13.5	3.6	7.4	1.35	9.6	8.7	10.2	5.37
Oceans	4.24	400	1336	11500	390	19775	2784	25.1	0.94

In waters draining silicate rocks, bicarbonates (HCO_3^-) originate entirely from atmospheric CO_2, whereas in waters draining carbonate rocks, only about half come from atmospheric CO_2, the other half coming from carbonates in the minerals. The percentage of HCO_3^- derived from atmospheric CO_2 therefore varies between 50 and 100% depending on the rock type: 67% for all continents as well as the Amazon basin, 57% for the Garonne River (where carbonates are more abundant), and 77% for the Congo River (where silicates are more abundant).

The weathering of rocks releases elements into solution in rivers and forms secondary minerals in soils, notably clays, iron oxides, and aluminum oxides. The type and intensity of weathering depend on rainfall, drainage, and temperature. The warmer and wetter the climate, the more advanced and intense the weathering, with soils evolving from clay formation to iron and aluminum oxide formation.

For granitic rocks, these different weathering types can be characterized from the composition of runoff waters by calculating the molar ratio (RE) between cations and silica. This ratio corresponds to the molar ratio between silica and alumina of the secondary minerals formed in the soils.

Finally, organic compounds are primarily supplied under natural conditions by the mineralization of organic matter, which releases dissolved organic carbon (DOC), particulate organic carbon (POC), organic nitrogen, and nitrate into waters, as well as by plankton production. The DOC flux is directly proportional to the intensity of drainage and the organic carbon stock in the soils.

Nitrogen and phosphorus concentrations in natural waters remain low (from µg/L to mg/L). Forest fires can also release organic compounds whose molecular composition differs significantly from that of soils or peatlands.

The composition of DOC varies according to its source and the nature of the processes that released it into the waters. Vegetation type (deciduous or coniferous forest, tundra, steppes, savannas, grasslands), the age of soil organic matter, and its degree of decomposition play an important role in the composition of DOC and POC in waters.

II.2.2.Natural Changes in Water Composition After acquiring their geochemical signature, the composition of river waters can be altered during their downstream transfer by various natural chemical, physical, and biological processes. These include the degassing of CO_2 at the water/atmosphere interface, phytoplankton production, diatom formation, exchanges with riparian vegetation and aquatic macrophytes, interactions with groundwater, inputs from tributaries with different geochemical and biological signatures, and interactions between dissolved elements, suspended matter, and/or bottom sediments. Other processes include the precipitation or dissolution of minerals, interactions with river biofilms, and the breakdown of leaf litter in aquatic environments.

Water chemistry is strongly modified over time during flood events due to varying contributions from different water reservoirs and flow pathways, such as rainfall, surface runoff, subsurface flow (soils), and groundwater. During these events, chemical and physical erosion processes are highly active.

Finally, nowadays, various anthropogenic impacts such as diffuse contamination from atmospheric fallout, agricultural inputs, and point-source urban and industrial pollutiondisrupt these natural balances and processes, leading to significant alterations in the natural chemical compositions of rainwater, rivers, groundwater, and oceans.

3. Stability Diagrams (Eh-pH) and Equilibrium

Introduction

II.3.1. Definition

Potential-pH diagrams are specific to a given element. They display all the species containing that element for different oxidation states and pH values. These different species can be interconnected through redox, acid-base, complexation, or precipitation reactions.

Potential-pH diagrams, also called Pourbaix diagrams after the Belgian electrochemist who developed them in 1938, are graphical tools used to study redox reactions in aqueous solutions.

An Eh-pH or Pourbaix diagram represents the stability domains of the different chemical species of a given element as a function of:

- **Eh**: the redox potential of the solution (in volts, V),
- **pH**: the acidity or basicity of the solution.

These diagrams are graphical representations of the thermodynamic predominance of different chemical species—dissolved ions, solid precipitates, or gases—of a given element.

They show:

- The regions where water is stable;
- The oxidized and reduced forms of the elements;
- The conditions under which precipitation or dissolution reactions may occur.

Such diagrams are essential for predicting chemical speciation, corrosion, oxidation, and the precipitation of elements in water.

2. Basic Principles
3. Horizontal axis (pH): ranges from 0 to 14.
4. Vertical axis (Eh): measured in volts (V), generally from –1 to +1.5 V.
5. Main zones:
   - Stable water: between O_2/H_2O and H_2/H_2O.
   - Oxidation**:** elements exist in their oxidized forms.
   - Reduction: elements exist in their reduced forms.
6. Boundary lines: correspond to redox reactions or dissolution/precipitation equilibria.

The zones are defined by boundaries derived from the Nernst equation, which relates the measured redox potential (E) of an oxidant/reductant pair to the standard potential (E^0) and to the actual conditions of the aqueous environment (concentrations, temperature, pH).

$$E = E^0 + \frac{0.059}{n}\log\frac{[\text{oxydé}]}{[\text{réduit}]} - 0.059 \cdot m \cdot \text{pH}$$

They predict the dominant stable form of an element under given Eh–pH conditions (e.g., $Fe(OH)_3(s)$ vs. Fe^{2+}).

Where:
E^0: Standard potential (V, from thermodynamic tables). This is the potential of a redox couple measured under standard conditions:

- Concentration = 1 mol/L
- Gas pressure = 1 atm
- Temperature = 25 °C (298 K)
- Activity of pure solids and liquids = 1

These values are already known and tabulated in standard potential tables.

For example, in a redox couples table:

- Ag^+/Ag : $E^0 \approx +0.80$ V
- Cu^{2+}/Cu : $E^0 \approx +0.34$ V
- Fe^{3+}/Fe^{2+} : $E^0 \approx +0.77$ V
- Zn^{2+}/Zn : $E^0 \approx -0.76$ V
- H^+/H_2 (standard hydrogen electrode) : $E^0 = 0$ V (by convention)

$$R = 8.314 \text{ J/mol·K}$$

Here’s the translation into English with proper scientific phrasing:

- $R = 8.314$ J·mol^{-1}·K^{-1} : Ideal gas constant
- T : Temperature (K)
- n : Number of electrons exchanged
- $F = 96485$ C·mol^{-1} : Faraday constant
- Q : Reaction quotient $\frac{[\text{oxidized}]}{[\text{reduced}]}$

These parameters are typically used in the Nernst equation to calculate the redox potential of an electrochemical reaction.

II.3.2.Plotting the Potential-pH Diagram

A/ Presentation

Plotting Conventions

Typically, the concentrations of dissolved species at the boundaries are fixed, along with the temperature (and the pressure for gases). Three conventions can be used for the concentrations of species in solution:

1. **Simple convention**: At the boundary between the predominance domains of two dissolved species, their concentrations are equal to the plotting concentration Ctra. *Example*: For iodine, at the I_2/I^- boundary: $[I_2] = [I^-] = \text{Ctra}$.
2. **Species convention**: At the boundary between the predominance domains of two dissolved species, their concentrations are equal, and their sum equals the plotting concentration (Ctra). *Example*: For iodine, at the I_2/I^- boundary: $[I_2] = [I^-] = \frac{\text{Ctra}}{2}$
3. **Atomic convention**: At the boundary between the predominance domains of two dissolved species, the "atomic concentrations" are equal, and the total atomic concentration equals the plotting concentration (Ctra). *Example*: For iodine, at the I_2/I^- boundary: ($2[I_2] = [I^-] = \text{Ctra}/2$).

Note: The choice of plotting convention has very little effect on the overall shape of the E-pH diagram. It is also assumed that the solution is ideal: activities are considered equal to the concentrations of species in solution.

B/ Steps for Plotting

The plotting of boundaries in the diagram is based on the Nernst equation and the equilibria between the different species.

Inventory the species to be placed on the diagram, specifying their phase. *Example for zinc*: Zn(s), Zn^{2+}(aq), $Zn(OH)_2$(s), and $[Zn(OH)_4]^{2-}$(aq).

Note: If a hydroxide is considered, the corresponding oxide is not included, and vice versa. For example, here we consider $Zn(OH)_2$(s) but not ZnO(s).

Classify the species according to their oxidation number, from lowest to highest, and for a given oxidation state, from the most acidic to the most basic species, left to right. *Example for zinc*:

o.n	Species to consider		
+II	Zn^{2+}	$Zn(OH)_2$	$[Zn(OH)_4]^{2-}$
	Zn		

We can now determine the equations for the boundaries. To do this, we consider the equation linking the species on either side of the boundary. Additionally, we use the simple plotting convention: $C_{tra} = 10^{-2}$ mol/L, at 298 K.

Example with zinc:
Boundary Zn^{2+}/Zn: Zn^{2+} (aq) + 2 e^- → Zn(s)

The Nernst equation gives: $E = E\ (Zn^{2+}/Zn) + \frac{RT}{2F}\ 2F\ \ln \frac{[Zn2+]}{C} = E°(Zn^{2+}/Zn) + \frac{RT}{2F}\ \ln \frac{Ctra}{2F}$ (1)

This expression is independent of pH, so this boundary is horizontal. **Note:** The potential at the boundary differs from the standard potential of the couple; it is the Nernst potential.

Boundary $Zn(OH)_2/Zn^{2+}$: Zn^{2+} (aq) + 2 OH^- (aq) → $Zn(OH)_2$(s)

There is no electron exchange between these species, so the boundary is vertical. The pH at the boundary can be calculated using the equilibrium constant of the reaction:

3. $$Ks = \frac{[Zn2+][OH\ ]2}{(c)3} = \frac{[Zn2+]Ke2}{[H3O+]2}\ C° \quad (2)$$

$$pHs = pKe - \frac{1}{2}\ (\ pKs + \log \frac{Ctra}{C°}\ ) = \ 6{,}5 \quad (3)$$

Boundary $Zn(OH)_2/Zn$:

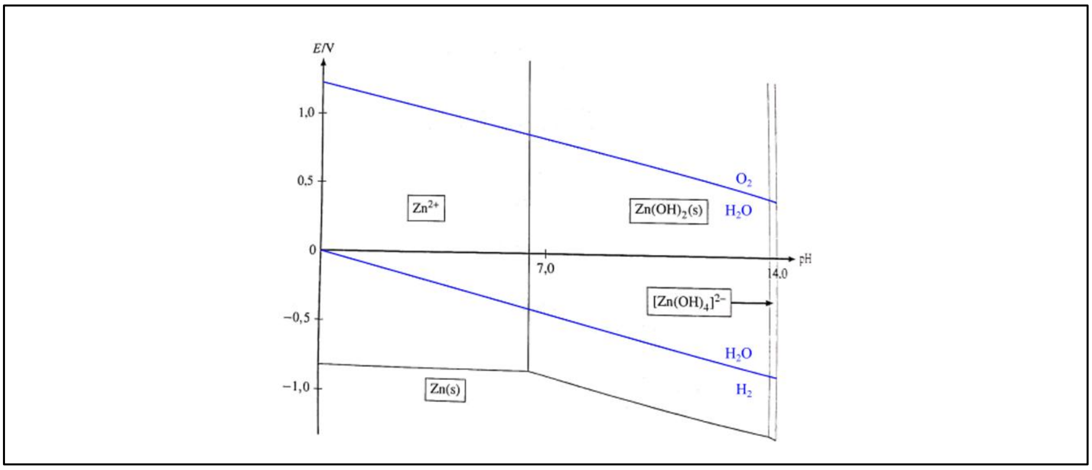
$Zn(OH)_2$(s) + 2 e^- → Zn(s) + 2 OH^- (aq), which can be rewritten in acidic medium as:

$Zn(OH)_{2(s)} + 2H^+_{(aq)} + 2e = Zn_{(s)} + 2H_2O$

The Nernst equation gives: $E = E\ (Zn(OH)_2/Zn) + \frac{RT}{2F} \ln[H^+]^2 = E°(Zn(OH)_2/Zn) - 006\ pH$

The boundary is thus a straight line with slope -0.06 and intercept equal to the apparent potential $E°(Zn(OH)_2\ /Zn)$.

Finally, we superimpose the E–pH diagram of water (showing H_2, H_2O, and O_2 species) onto the zinc diagram.



II.3.3. Use of Eh–pH diagrams

Eh–pH diagrams are powerful tools to predict thermodynamically favored reactions.

A. Disproportionation:

Using Eh–pH diagrams, disproportionation reactions can be easily observed, particularly the pH at which a species undergoes disproportionation.

Example: Figure shows the Eh–pH diagram of chlorine at 298 K, with (Ctra = 0.1) mol/L (Source: Sciences-en-ligne). In this example, Cl_2 disproportionates at pH values above 2.2. Beyond this point, the Cl_2 stability domain disappears and is replaced by the domains of HClO and Cl^- species.

B. Predicting the stability of a species:

Using the zinc Pourbaix diagram, we observe that the stability domains of metallic zinc Zn(s) and water are disjoint. This means they react together: zinc is oxidized to Zn^{2+}(aq), $Zn(OH)_2$(s), or $[Zn(OH)_4]^{2-}$(aq), depending on the solution pH. In addition, the predominance domains of these species partially overlap with that of water.

II.3.4. Geochemically Adapted Forms

1. Without H^+ (horizontal Eh–pH):

$$E = E^0 + \frac{0.059}{n}\log\frac{[\mathrm{Fe}^{3+}]}{[\mathrm{Fe}^{2+}]}$$

2. With H^+ (slope −59 mV/pH):

$$E = E^0 + \frac{0.059}{n}\log\frac{[\mathrm{ox}]}{[\mathrm{red}]} - 0.059 \cdot m \cdot \mathrm{pH}$$

Example: $\mathrm{Fe(OH)_2} + 2\mathrm{H}^+ + 2e^- \rightleftharpoons \mathrm{Fe}^{2+} + 2\mathrm{H_2O}$

$$E = -0.15 - 0.059\text{pH} + 0.0295\log[\text{Fe}^{2+}]$$

II.3.5. Applications of Eh–pH Diagrams

Diagram boundaries:

- $Q = 1 \rightarrow E = E^0$ (50/50 oxidized/reduced).
- [ox] ≫ [red] → E ↑ (oxidizing zone).
- pH ↑uparrow → E ↓ downarrow) (slope −59 mV/pH per H^+).

Concrete example (Fe^{3+}/Fe^{2+} at pH 7, $[Fe^{3+}]/[Fe^{2+}] = 10^4$):

$$E = 0.77 + \frac{0.059}{1}\log 10^4 = 0.77 + 0.236 = +1.01\ \text{V}$$

Standard conditions (25°C): Simplified factor: $\frac{0.059}{n}$, n = 1 → 59 Mv/decade, n = 2 → 29.5 mV /decade

Natural waters: pH 6–9 → correction −0.35 to −0.53 V for H^+-involved couples

Represented Elements

- **Dissolved species:** Fe^{2+}, Fe^{3+}, HCO_3^-, SO_4^{2-}
- **Solids:** $Fe(OH)_3(s)$, $CaCO_3(s)$, oxides
- **Gases:** O_2, H_2, CO_2, H_2S

Water Stability Domain

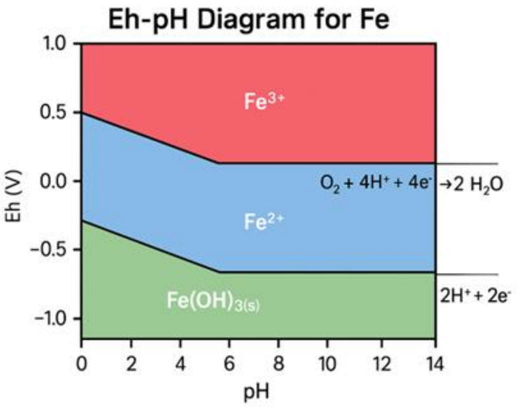
- **O_2/H_2O:** (E = 1.23 - 0.059 pH) (upper limit)
- **H^+/H_2:** (E = -0.059 pH) (lower limit)

II.3.6. Reading an Eh–pH Diagram

- Each zone corresponds to the dominant form of an element.

Example for iron:

- **Fe^{2+}:** stable in reducing, acidic conditions
- **Fe^{3+}:** stable in oxidizing conditions
- **$Fe(OH)_3(s)$:** precipitates within specific pH and Eh ranges
- **Forbidden zones** (outside water stability) indicate decomposition of water into H_2 or O_2.



Red–Ox Zones (Eh–pH Diagram for Iron)

- **Red zone:** Fe^{3+} (oxidized)
- **Blue zone:** Fe^{2+} (reduced)
- **Green zone:** $Fe(OH)_3$(s) (precipitate)
- **Upper and lower lines:** water stability limits (O_2/H_2O and H_2/H_2O)

Interpretation

- At neutral pH (=7) and Eh ~0.2–0.4 V → Fe^{2+} is stable under reducing conditions
- If Eh increases (>0.5 V) → Fe^{3+} dominates or $Fe(OH)_3$ precipitates
- If pH increases (>7–8) → $Fe(OH)_3$(s) becomes predominant; less Fe^{3+} remains soluble

Applications in Aquatic Geochemistry

- Predict chemical speciation of metals and major elements
- Analyze corrosion or metal protection
- Evaluate mobility of pollutants (As, Cr, Mn, Fe…)
- Plan water treatment strategies (precipitation, oxidation, reduction)

Applied examples using the Nernst equation: Fe^{2+}/Fe^{3+}, Cu^{2+}/Cu

1. Fe^{3+}/Fe^{2+} Couple (Natural Waters, pH 7)

Reaction (without H^+, horizontal Eh–pH):

$$\mathrm{Fe}^{3+} + e^- \rightleftharpoons \mathrm{Fe}^{2+} \quad E^0 = +0.77\ \mathrm{V}$$

Nernst equation: $$E = 0.77 + 0.059\log\frac{[\mathrm{Fe}^{3+}]}{[\mathrm{Fe}^{2+}]}$$

Typical Aquifer Conditions:

Condition	Fe^{3+}/Fe^{2+} Ratio	Calculated E (V)	Interpretation
Fe^{2+} dominant (reducing)	10^{-4}	0.77 - 0.236 = +0.53	Anaerobic sediments
1:1 Equilibrium	1	+0.77	Transition
Fe^{3+} dominant (oxidizing)	10^4	0.77 + 0.236 = +1.01	Oxygenated waters

Natural pH = 7: $Fe(OH)_3(s)$ is stable for Eh > +0.2 V → colloidal turbidity.

Couple Cu^{2+}/Cu (trace metals, pH 7)

Reaction (solid metal): $Cu^{2+} + 2e^- \rightleftharpoons Cu(s)\ E^0 = +0.34\ V$

Nernst Equation:

$$E = 0.34 + \frac{0.059}{2}\log[Cu^{2+}] = 0.34 + 0.0295\log[Cu^{2+}]$$

Typical pollution conditions:

$[Cu^{2+}]$ (M)	Calculated E (V)	Stability	Context
10^{-12} (clean water)	0.34 − 0.354 = −0.014	Cu(s) stable	Not relevant for aquatic systems
10^{-6} (polluted water)	0.34 − 0.177 = +0.163	Cu^{2+} dominant	Adsorption on Fe oxides
10^{-3} (high pollution)	0.34 + 0.089 = +0.429	Cu^{2+} dominant	Aquatic toxicity

Complexes involving H^+ (slope 45°)

$Fe(OH)_2(s)/Fe^{2+}$ couple: $Fe(OH)_2 + 2H^+ + 2e^- \rightleftharpoons Fe^{2+} + 2H_2O$

Nernst equation: $E = -0.15 - 0.059pH + 0.0295\log[Fe^{2+}]$

pH 7, $[Fe^{2+}]=10^{-6}$: E = -0.15 - 0.413 - 0.177 = - 0.74 V (reducing conditions).

Practical geochemical applications:

- Predicting the redox state of iron in natural waters.
- Identifying the conditions where Fe^{2+} is stable versus precipitation of $Fe(OH)_2(s)$.
- Assessing reducing environments in sediments or groundwater.
- Guiding water treatment strategies involving iron oxidation or removal.

Redox Couple	Typical E at pH 7	Eh-pH Zone	Aquatic Consequence
Fe^{3+}/Fe^{2+}	+0.4 to +0.8 V	Oxidizing	$Fe(OH)_3(s)$ → turbidity
Cu^{2+}/Cu	+0.2 V	Oxidizing	Free Cu^{2+} → fish toxicity
NO_3^-/NH_4^+	+0.3 V	Reducing	Sediment denitrification

Result: Fe^{2+} is dominant, Cu^{2+} is adsorbed.

Rule: In natural waters with Eh between +100 and +400 mV → oxidized couples dominate (Fe^{3+}, NO_3^-, SO_4^{2-}).

PHREEQC example:

```
SOLUTION 1
    pH 7
    Eh 0.3
    Fe(2) 1e-5
    Fe(3) 1e-9
    Cu 1e-6

SELECTED_OUTPUT 1
    -Eh
    -pH
    -molalities Fe(2) Fe(3) Cu(2)
```

Eh-pH Stability Diagram: Iron (Fe) and Copper (Cu) Systems

- The red dashed line represents the O_2/H_2O stability boundary.
- The blue dashed line represents the H^+/H_2 stability boundary.
- Brown lines correspond to $Fe(OH)_3(s)/Fe^{3+}$, Fe^{3+}/Fe^{2+}, and $Fe(OH)_2/Fe^{2+}$ equilibria.
- Green lines correspond to $Cu(OH)_2/Cu^{2+}$, Cu^{2+}/Cu^+, and Cu^{2+}/Cu equilibria.
- The black star indicates the position of natural water conditions (Eh ~0.3 V, pH ~7).
- Species labels: Fe^{3+} (aq), Fe^{2+} (aq), $Fe(OH)_3(s)$, Cu^{2+} (aq), Cu^+, Cu (s)

This diagram shows the stability fields of different iron and copper species depending on pH and redox potential (Eh). Natural waters generally fall within the zone where Fe^{2+} and Cu^{2+} species are stable.

Eh-pH Stability Diagram: Iron (Fe) and Copper (Cu) Systems in Aquatic Environments

This diagram overlays the thermodynamic stability domains of the $Fe^{3+}/Fe^{2+}/Fe(OH)_3$ system (orange) and the Cu^{2+}/Cu system (green) in aquatic environments:

Key Interpretation (25°C, [Me]_tot = 10^{-6} M)

Starred Point ★ represents typical natural waters (pH 7, Eh +0.3 V):

- Fe: Stable $Fe(OH)_3(s)$ zone → colloidal turbidity from iron oxides.
- Cu: Dominant $Cu^{2+}(aq)$ zone → adsorption onto Fe/Mn oxides, potential toxicity.

Main boundaries plotted:

$Fe(OH)_3(s)$ / Fe^{3+}: Vertical line (solubility at pH 7)

Fe^{3+} / Fe^{2+}: Horizontal line at approximately +0.45 V ($[Fe^{3+}]/[Fe^{2+}] = 10^4$)

$Fe(OH)_2$ / Fe^{2+}: 45° slope with -59 mV/pH (involving H^+)

Cu^{2+} / Cu: Horizontal line at approximately +0.16 V ($[Cu^{2+}] = 10^{-6}$ M)

Water stability limits: O_2/H_2O (upper) and H^+/H_2 (lower)

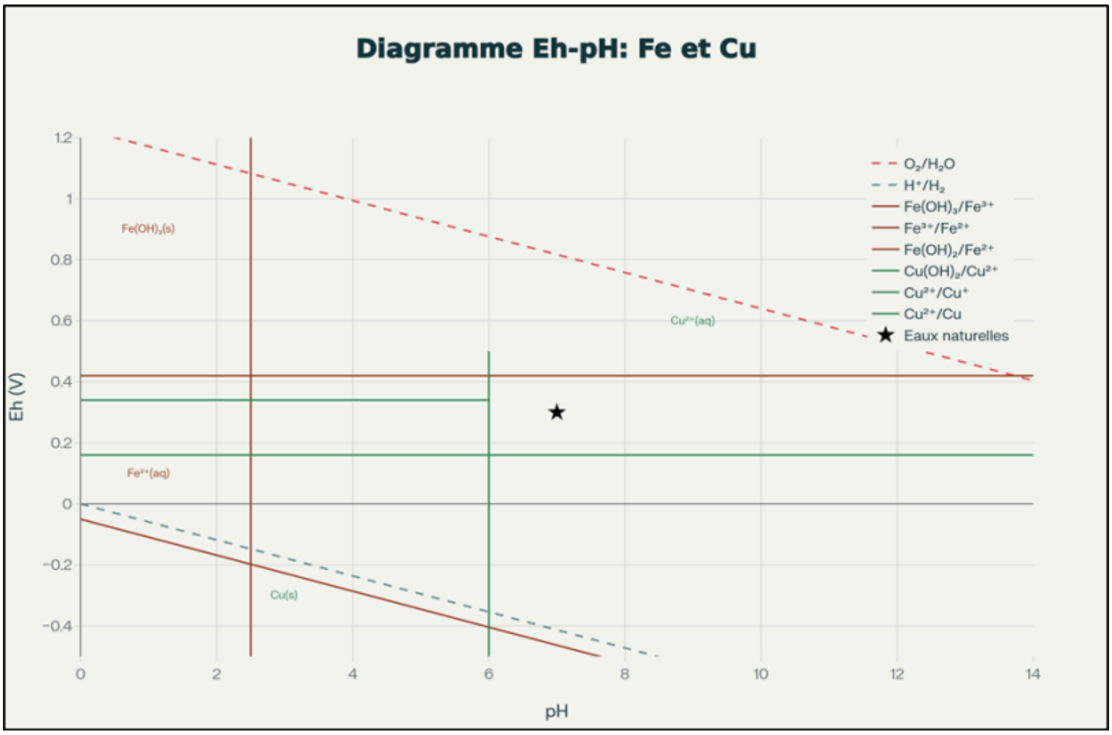
Immediate Geochemical Applications

Zone	Stable Fe	Stable Cu	Aquatic Context
Oxidizing, pH 7	$Fe(OH)_3(s)$	$Cu^{2+}(aq)$	Oxygenated aquifers, turbidity
Reducing, pH 7	$Fe^{2+}(aq)$	$Cu^{2+}(aq)$	Anaerobic sediments
Acidic, pH 4	$Fe^{3+}(aq)$	$Cu^{2+}(aq)$	Acid mine drainage

Practical use: Locate real water samples on the diagram to predict chemical speciation and metal mobility.

On an Eh–pH diagram, a real water sample is positioned using its pH and redox potential, allowing direct reading of stability domains to predict element speciation and mobility. For example, for a typical natural water around pH ≈ 7 and Eh ≈ +0.3 V (star on the diagram), iron falls within the $Fe(OH)_3(s)$ oxyhydroxide domain, meaning it is mostly in solid form, relatively immobile, and capable of trapping other metals through adsorption. Copper, on the other hand, lies in the $Cu^{2+}(aq)$ domain, meaning it is dissolved and potentially mobile and bioavailable. Therefore, even if iron itself does not migrate, it indirectly controls copper behavior: Cu can be immobilized by adsorption onto ferric phases or, conversely, released if conditions become more reducing (Eh decreases), causing dissolution of iron oxyhydroxides and co-mobilization of associated metals.

Eh–pH Stability Diagram: Iron (Fe) and Copper (Cu) Systems in Aquatic Environments



Chapter III: Water Pollution – Origins and Types

Introduction

Pollution of surface, groundwater, and coastal waters results from complex interactions between human activities and natural processes, altering the chemical, biological, and physical composition of aquatic environments. This phenomenon threatens the quality of drinking water resources, aquatic biodiversity, and geochemical balances.

This chapter aims to identify the main sources of water pollution and classify its types, in connection with the processes of pollutant transfer and transformation in aquatic systems. A tabular summary will facilitate analysis for educational applications in hydrogeochemistry.

1. Natural and Anthropogenic Sources

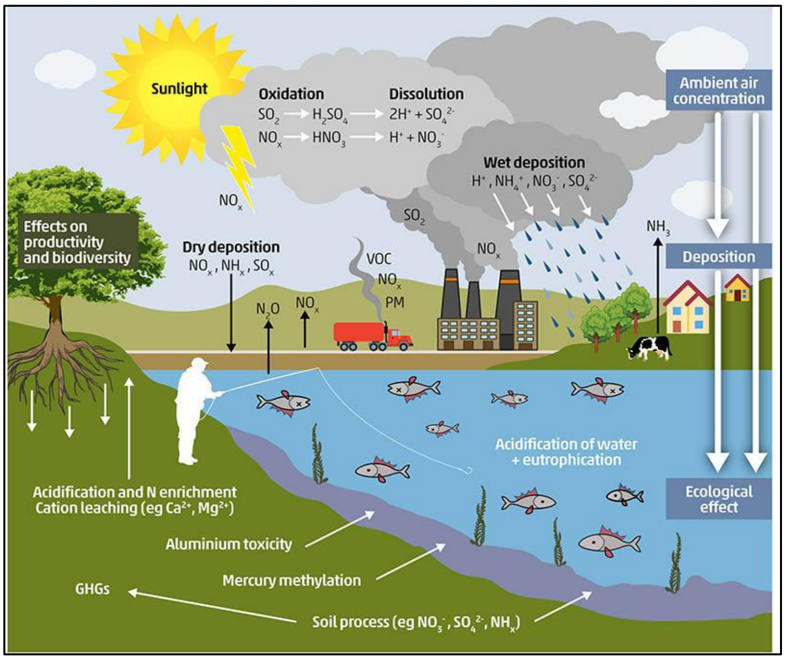
Introduction

The origins of water pollution can be divided into two main categories: anthropogenic (related to human activities) and natural (geogenic), with varying contributions depending on hydrogeochemical contexts. The geochemical processes influencing water quality are complex and can vary significantly across regions, particularly due to human activities and local geological characteristics. Understanding these processes is essential for establishing water quality standards and for the sustainable management of water resources. Effective water quality management requires accurate assessment of both organic and inorganic pollutants in aquatic systems.Anthropogenic sources dominate in densely populated or industrialized areas and include point and diffuse discharges. Industrial and urban effluents contribute significantly to aquatic pollution, requiring suitable assessment methods to understand their impact on water quality.

III.1.1.Anthropogenic sources of water pollution

1. Urban and domestic pollution: Untreated wastewater (organic matter, nutrients, pathogens) and stormwater runoff loaded with urban pollutants (hydrocarbons, metals) are major anthropogenic contributors. This type of pollution primarily arises from domestic and municipal wastewater discharges, including effluents from street washing, urban irrigation, and stormwater. Household waste accumulated in uncontrolled or noncompliant landfills produces leachates containing organic, inorganic, and microbial contaminants that can migrate into groundwater.

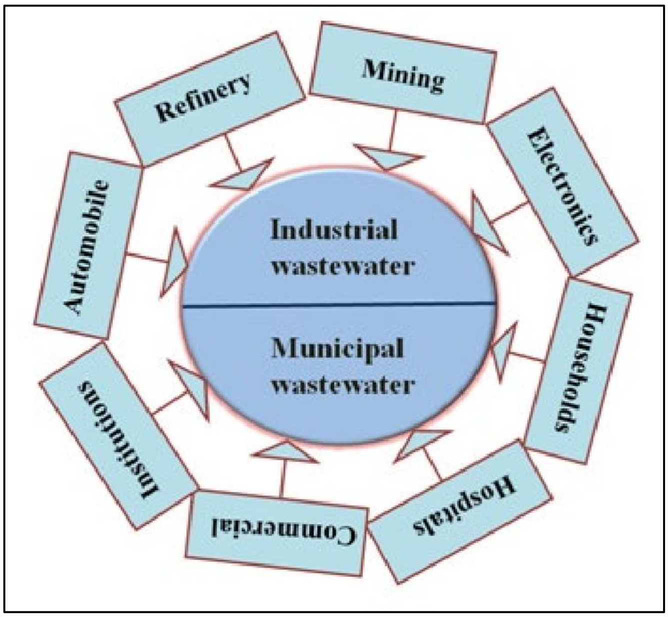
Proper water resource management must consider the impacts of wastewater discharges on water quality, particularly regarding trace elements and microbial contaminants.



Domestic wastewater is typically rich in organic matter, measured by biochemical oxygen demand (BOD_5) and chemical oxygen demand (COD), as well as nitrogenous (NH_4^+, NO_3^-) and phosphorus (PO_4^{3-}) compounds. These substances can interact with soil and aquifer minerals, resulting in sorption, precipitation, or complexation processes. Ammonium ions (NH_4^+) can be oxidized to nitrites (NO_2^-) and then nitrates (NO_3^-) through nitrification, affecting the chemical quality of the aquifer and its dissolved oxygen content. Phosphates may precipitate with cations such as Ca^{2+}, Fe^{3+}, or Al^{3+}, reducing their bioavailability but contributing to eutrophication in receiving waters.

Wastewater also contains significant loads of fecal microorganisms and pathogens, which can persist in aquifers depending on hydrogeological conditions, temperature, and water chemistry. Therefore, groundwater contamination by domestic discharges and landfill leachates represents a complex interaction of organic, inorganic, and microbial pollutants, governed by geochemical and microbiological processes that determine the mobility, transformation, and toxicity of contaminants.

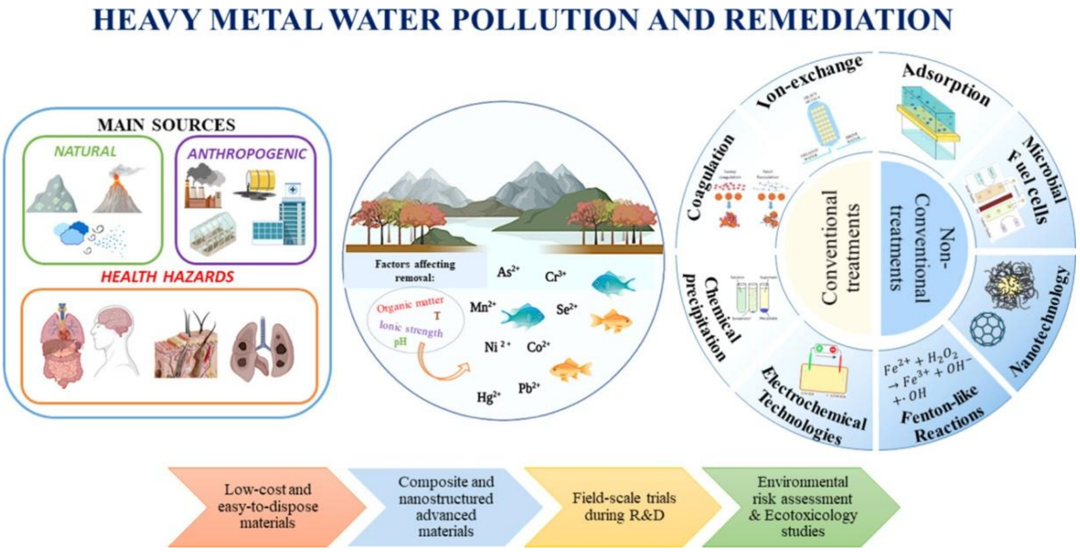
2. Industrial pollution: Industrial effluents often contain toxic substances such as heavy metals (Pb, Cd, Hg), solvents, acids, hydrocarbons, accidental spills, or thermal discharges. Industrial effluents, frequently rich in heavy metals such as lead (Pb) and cadmium (Cd), contribute to the deterioration of groundwater quality; increasing contamination risks. Poorly regulated industrial activities require careful management to prevent water contamination, particularly by heavy metals and other chemical pollutants.



This type of pollution primarily arises from industrial, thermal, and chemical discharges and is characterized by a wide variety of contaminants depending on the type of industrial activity.

3. Heavy metals: due to their toxicity, present a major challenge for water resource management, requiring appropriate treatment and regulatory strategies Organic matter and fats, mainly from the agro-food industry, can accumulate in groundwater, compromising its quality and safety for human and agricultural use.

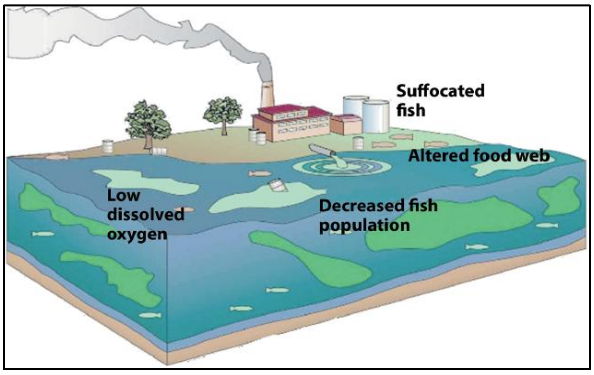
Hydrocarbons originating from refineries and petroleum processing: Hydrocarbons, particularly those from refineries, can contaminate groundwater and degrade water quality, requiring strict preventive measures.



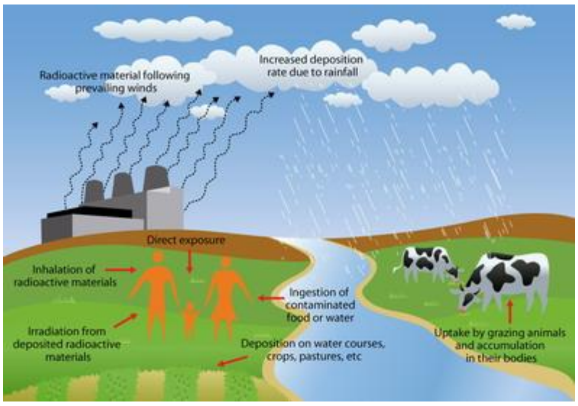
Heavy metals and trace elements released during metallurgical processes and surface treatments: Industrial processes, especially those related to metallurgy, are major sources of groundwater pollution, often resulting in high concentrations of heavy metals such as lead and cadmium. Rigorous management of these effluents is essential to protect groundwater quality and prevent associated health risks.

4. Acids, bases, and various chemicals from the chemical industry: Continuous monitoring of industrial effluents is crucial to minimize impacts on water resources, particularly concerning heavy metals and other chemical contaminants.

5. Thermal waters discharged from power plant cooling circuits, which can induce thermal and chemical disturbances in aquatic ecosystems: Thermal discharges can also affect aquatic biodiversity by altering the living conditions of organisms, leading to significant ecological imbalances.

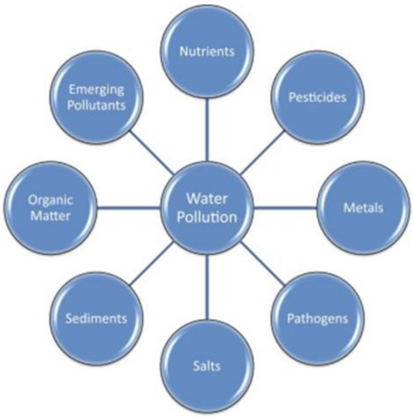


6. Radioactive materials from nuclear power plants, which can persistently contaminate aquatic environments: The management of radioactive discharges requires strict protocols to evaluate their impact on water quality, taking into account the specific characteristics of aquatic ecosystems.



These effluents can interact with soils and groundwater through geochemical processes such as sorption, precipitation, complexation, or redox reactions, modulating the mobility and toxicity of pollutants in the aquifer.

7. Agricultural sources: Leaching of fertilizers (nitrates, phosphates), pesticides, and livestock effluents (ammoniacal nitrogen, antibiotics) can lead to eutrophication and groundwater contamination. This pollution is characterized by its spatial and temporal extent, chronic nature, and impact over large agricultural areas. It is mainly linked to intensive use of chemical fertilizers, pesticides, and agrochemicals. The transfer of these substances to groundwater occurs either through diffuse infiltration across the soil profile or via point discharges into soaks pits, sinkholes, or drains, with irrigation practices accelerating the process. Intensive agricultural practices, particularly fertilizer and pesticide use, exacerbate groundwater pollution by promoting nitrate and phosphate leaching. This contamination poses significant risks to human health and the environment, requiring appropriate sustainable management strategies.



These agricultural products lead to high concentrations of nitrates (NO_3^-), resulting from mineralization and nitrification of organic and ammoniacal nitrogen, as well as trace metals (Zn, Cu, Pb…), whose mobility and bioavailability in the aquifer are controlled by geochemical processes such as sorption on clay minerals, complexation with dissolved organic matter, and precipitation with metal oxides and hydroxides. These interactions determine the persistence, toxicity, and spatial distribution of contaminants in groundwater. Groundwater contamination by nitrates and pesticides is a growing problem, especially in intensive agricultural zones, requiring careful monitoring of agricultural practices.

8. Other sources: Transport (oil spills), landfills (leachates), hydraulic fracturing. Additional sources of groundwater pollution include transport-related activities, such as oil spills and accidental hydrocarbon discharges, as well as landfills producing leachates rich in organic and inorganic contaminants. Hydraulic fracturing also contributes to contamination through injection of chemical fluids into geological formations, which can migrate into aquifers. These pollutants interact with soils and groundwater through geochemical processes such as sorption onto clay particles, precipitation of salts and metals, redox reactions, and complexation with dissolved organic matter, which modulate their mobility, persistence, and toxicity in the aquifer.

A classification of inorganic species found in groundwater is presented in Table 3.3. The concentration categories serve only as a general guide. In some groundwater systems, concentration ranges may be exceeded. The major elements in Table 3.3 primarily occur in ionic form and commonly refer to the main ions (Na^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}). The total concentration of these six major ions typically represents more than 90% of the total dissolved solids, whether the water is diluted or has salinity higher than seawater. Variations in the ionic composition of groundwater are often influenced by geological and anthropogenic factors, notably nitrate inputs from agricultural and industrial activities.

The concentrations of these major, minor, and trace inorganic constituents in groundwater are controlled by the availability of these elements in the soils and subsurface through which the water flows, by geochemical constraints such as solubility and adsorption, by the rates (kinetics) of geochemical processes, and by the sequence of contact the water has had with different minerals along its path. It has become increasingly common for the concentrations of dissolved inorganic constituents to be influenced by human activities. In some cases, anthropogenic contributions can lead to the presence of elements listed as minor or trace, appearing as contaminants at concentration levels exceeding the ranges indicated in the table.

These variations highlight the importance of integrated water resource management that takes into account both natural and human influences on groundwater quality. They underscore the need for a holistic approach to water resource management, integrating geochemical variability and the impacts of human activities on groundwater quality.

III.1.2.Natural Origins of Contamination in Hydrogeochemistry

Although water pollution is often associated with human activities, some sources of contamination originate naturally from geological and climatic phenomena. These natural sources, though less frequent, play a crucial role in the quality of surface and groundwater and can affect ecosystem health and water potability.

It is therefore essential to study these natural sources to better understand their impact on water chemistry and the associated contamination risks. Analyzing the interactions between natural and anthropogenic contaminants is fundamental for assessing water quality and public health. Integrating this knowledge will help develop more effective and sustainable water management strategies that consider the diverse sources of contamination.

1. Erosion and Sedimentation

Soil erosion and sedimentation naturally move solid particles such as clay and silt. Over time, these particles may accumulate trace metals or other substances. When remobilized, for example after a flood or a change in hydrological regime, they can release these elements into the water. This phenomenon is observed in some rivers where ancient sediments naturally concentrate arsenic or iron, locally altering the water chemistry. The chemical speciation (dissolved or solid form) of metals then depends on the pH and redox potential of the water, influencing their mobility and toxicity. Studies have shown that the mobility of arsenic in aquatic systems is strongly influenced by redox potential and pH, as well as by interactions with sediments. These factors must be considered to properly assess the risks associated with natural water contamination, particularly in areas prone to significant hydrological variations.

2. Extreme Climatic Events

Droughts and floods concentrate or redistribute elements naturally present in the water. For example, during a drought, the reduction in water volume increases the concentration of dissolved salts and alkaline compounds, while a flood may cause the dilution or, conversely, the release of pollutants contained in soils and sediments. These variations can be either short-term (after an extreme event) or chronic (continuous erosion), affecting the total mineralization, alkalinity, and ionic composition of the water. These events can also lead to significant changes in water quality, making it essential to evaluate their impact on water resources. Extreme climatic events, such as floods, can also promote the remobilization of trace metals, such as arsenic, thereby increasing the risk of water contamination. Understanding these dynamics is crucial for anticipating changes in water quality in the context of climate change. These phenomena underscore the importance of proactive water resource management, especially in light of the expected increase in the frequency and intensity of extreme climatic events.

3. Ecological and Health Consequences

Even without human activity, these processes can have significant impacts: the release of dissolved metals or salts can influence aquatic biodiversity, disrupt food chains, and, in some cases, make water unsafe for consumption. Therefore, it is essential to integrate these geological and climatic factors into water resource assessments and contamination risk management. An integrated approach that combines monitoring of climatic events and analysis of natural contamination sources is necessary to ensure drinking water safety. Special attention should be given to the interaction between extreme climatic events and natural contaminants, as this can significantly influence water quality and public health. Such an approach will help better anticipate future challenges related to water management and public health preservation in the face of environmental changes.

2. Major Pollutants: Nitrates, phosphates, heavy metals, micropollutants

Introduction

Water pollution is the degradation of water quality due to the introduction of chemical, physical, or biological substances that are harmful to the environment and human health. In the context of bioclimatology, studying water pollution helps to understand the interactions between climate, aquatic ecosystems, and human activities.

III.2.1.Classification of Water Pollution

The scientific literature proposes several approaches to classify water pollution. The following types are generally distinguished:

1. Chemical Pollution

This refers to the introduction of chemical substances into water that disrupts its natural composition and quality.

2. Inorganic Pollutants:

Heavy Metals: The most common heavy metals in natural waters include lead (Pb), mercury (Hg), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), and zinc (Zn). Their sources can be natural, through the weathering of parent rocks, or anthropogenic, related to industrial waste, metallurgical activities, and agricultural practices.

These elements are particularly concerning due to their toxicity at low concentrations, non-biodegradability, and bioaccumulation in soils and living tissues.

In surface and groundwater, their mobility and chemical availability depend on geochemical processes such as sorption onto clay particles and organic matter, precipitation with metal oxides and hydroxides, complexation with natural ligands, and redox reactions. These interactions determine the spatial distribution, persistence, and toxic potential of metals in aquatic ecosystems.

Nutrients: Essential nutrients such as nitrogen (N) and phosphorus (P) are central to aquatic ecosystem productivity, but an excess in natural waters constitutes a major pollutant.

- **Nitrogen (N):** It occurs in various chemical forms: ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-), and organic nitrogen. These forms result from geochemical processes such as organic matter mineralization, nitrification ($NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$), and denitrification ($NO_3^- \rightarrow N_2$), which regulate nitrogen mobility and transformation in surface and groundwater.
- **Phosphorus (P):** Found as inorganic (PO_4^{3-}) or organic phosphates. Its mobility is limited by adsorption onto clay minerals and precipitation with Ca^{2+}, Fe^{3+}, or Al^{3+}, but it can accumulate in sediments and contribute to eutrophication. The main sources of these nutrients are agricultural fertilizers, domestic wastewater, and agricultural leachates, which can infiltrate soils and contaminate both groundwater and surface water. Understanding their geochemical cycle is essential for evaluating ecological impacts and managing water quality.

3. Salts and Other Ions: Natural waters contain various major ions such as calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), chloride (Cl^-), bicarbonate (HCO_3^-), and sulfate (SO_4^{2-}). These ions originate from both natural processes (rock weathering, mineral dissolution) and anthropogenic sources (industrial effluents, wastewater, road salting). Their concentration and composition influence total mineralization, alkalinity, and water hardness, as well as the mobility of chemical pollutants and heavy metals. Geochemical interactions such as precipitation, sorption, and complexation regulate the distribution and bioavailability of these ions in surface and groundwater.

4. Organic Pollutants:

- **Hydrocarbons:** Oils and petroleum products, mainly from industrial spills and transportation, which can disturb aquatic flora and fauna.

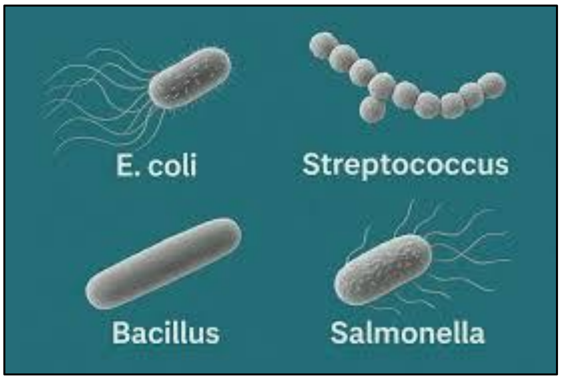
- **Pesticides and Herbicides:** Used in agriculture, these compounds exhibit acute and chronic toxicity to aquatic organisms and can accumulate in sediments.
- **Pharmaceuticals and Micropollutants:** Drug residues, hormones, and other chemicals act as endocrine disruptors and can affect surface and groundwater quality even at very low concentrations.

5. Microbiological Pollution

Microbiological pollution corresponds to the presence of pathogenic microorganisms in water (bacteria, viruses, protozoa), capable of spreading through water and causing numerous waterborne diseases. The main sources include septic tanks, landfills, wastewater spreading, and livestock activities.

Examples:

- *Escherichia coli*, *Salmonella* → contamination from domestic wastewater.
- *Vibrio cholerae* → cholera outbreaks in tropical areas.



Origin: Untreated urban effluents, sewage leaks, and agricultural runoff.

6. Physical Pollution

Physical modifications of water affecting its use or aquatic life.
The main physical pollutants are heat, suspended solids (TSS), and radioactivity.

III.2.2. Main Types of Water Pollution

1. Sedimentary Pollution: This involves an excess of suspended particles originating from natural erosion or human activities (industry, wastewater treatment plants). These particles increase turbidity and cause sedimentation in watercourses, affecting light penetration and the transport of adsorbed pollutants. Physical contaminants are often referred to as "sediments" and "suspended solids." They consist of insoluble solid matter in water. While they can carry adsorbed chemical substances (chemicals adhering to the surface of solids), this category of water pollution concerns primarily the impacts of the solids themselves. Sediments in water include sand, silt, and other soil types entering watercourses through runoff, often from rainfall. Suspended solids represent a broader category that can also include all debris transported in water bodies, from microplastics to discarded items, plant and animal debris, microorganisms, and soil particles. Physical contamination reduces water clarity, blocks light for aquatic plants and animals, can clog fish gills, reduce stream flow, fill shallow water bodies, block drainage pipes, and restrict water flow in dams and culverts. It degrades habitats for fish and aquatic invertebrates and can also impede exchanges between surface water and groundwater.

2. Thermal Pollution: This occurs when warm water is discharged from thermal or nuclear power plants or from natural sources. Temperature increases reduce the solubility of dissolved oxygen, promote algae growth, and disrupt aquatic ecosystems.

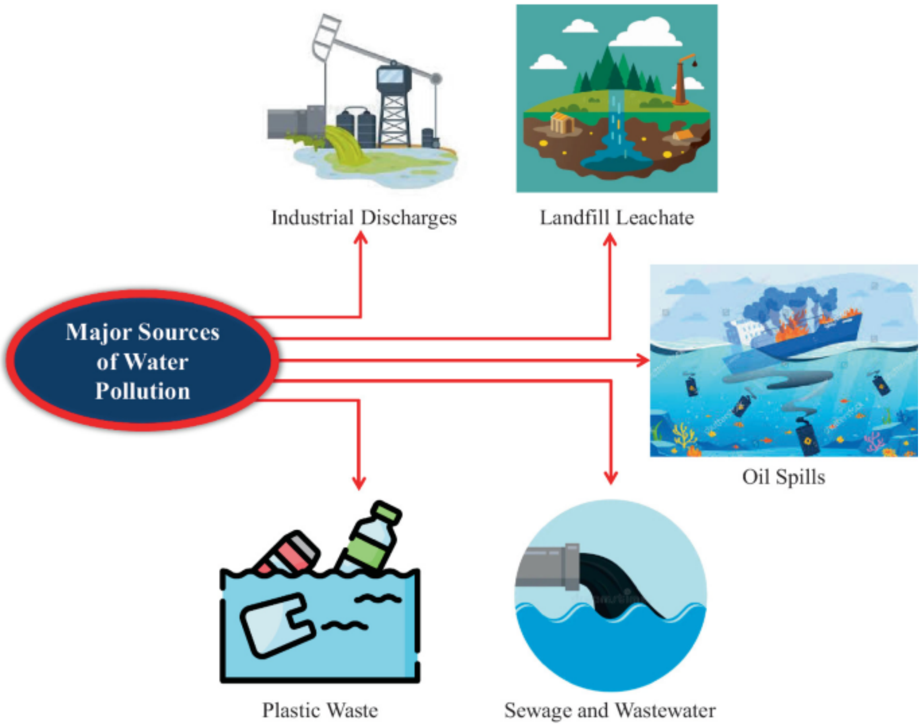
3. Radioactive Pollution: The release of radionuclides from nuclear power plants, reprocessing activities, hospital wastewater, or certain rocks (such as radon from granites) can have long-term impacts on human health and the environment.

4. Emerging Contaminants: Emerging contaminants include a range of recently detected chemical compounds or those found at very low concentrations in natural waters, often unregulated. They include:

- **Pharmaceutical residues:** medications, antibiotics, hormones, which may act as endocrine disruptors.
- **Cosmetics and detergents:** UV filters, fragrances, surfactants, which can interfere with aquatic biological cycles.
- **Nanoparticles and microplastics:** originating from industrial products and plastics, which can bioaccumulate in organisms and present ecological and chemical toxicity.
- **Industrial compounds:** flame retardants, plasticizers, and other emerging pollutants that may accumulate in sediments and organisms.

These substances are transported by urban, agricultural, and industrial effluents and pose ecotoxicological and geochemical risks due to their persistence, bioaccumulation, and interactions with other contaminants in surface and groundwater.

III.2.3. Pollutant Transfer Modes



1. Point-source Pollution: Pollution is considered point-source when the source is identifiable and limited to a small area (less than a few km²). Examples: soils contaminated by local dust emissions or aquifers polluted by hydrocarbon leaks from storage tanks.

2. Diffuse Pollution: Diffuse pollution results from multiple pollutant inputs over large areas and long periods. Examples: industrial zones releasing various atmospheric pollutants, agricultural activities dispersing nitrates and pesticides, vehicle emissions. Pollutant transfer depends on the chemical and physical properties of the substances, the characteristics of the environment (soil type, microbial activity), as well as climate and timing of application.

3. Temporary or Accidental Pollution: This occurs due to exceptional releases of pollutants, often following an industrial or traffic accident.

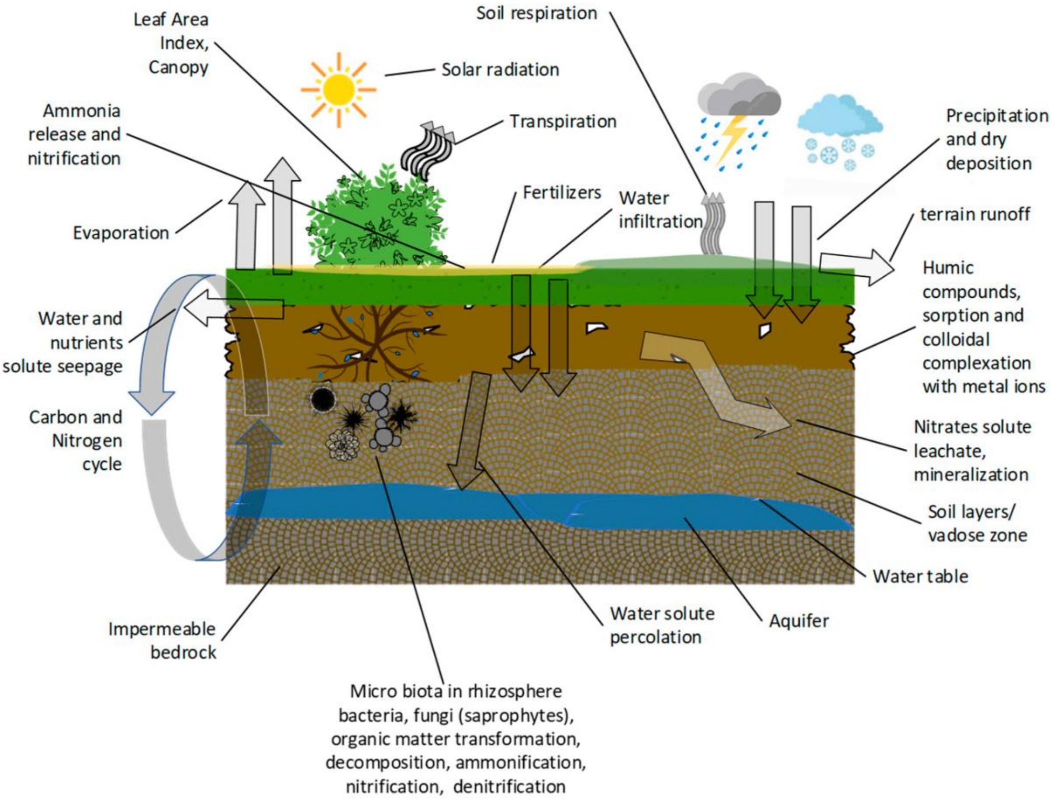
4. Chronic Pollution: Chronic pollution is continuous and results from repeated emissions or highly persistent pollutants. It is often insidious and less visible but can be particularly damaging.

Examples: agricultural nitrate contamination or aquifers polluted by persistent hydrocarbons.

III.2.4. Pollutant Transfer Mechanisms in Water

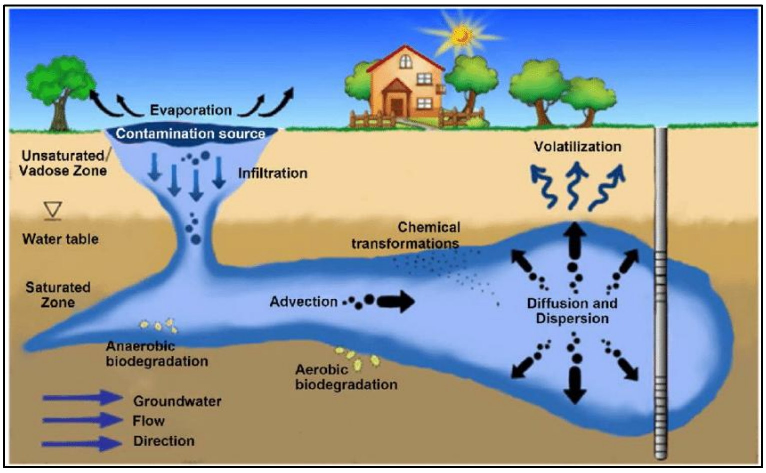
Pollutants present in natural environments undergo various transfer mechanisms that control their mobility, persistence, bioavailability, and impact on surface and groundwater. These mechanisms result from the interaction of physical, chemical, and biological processes and are influenced by hydrogeological, geochemical, and climatic conditions.

1. Transfer in the Soil and Unsaturated Zone In the vadose (unsaturated) zone, pollutants undergo several processes that control their migration to groundwater and their interaction with soils. These processes include adsorption, biological degradation, and chemical reactions, which can influence the speed and extent of groundwater contamination. These mechanisms are crucial for understanding how contaminants spread and concentrate in aquifers, thus affecting groundwater quality.



- **Infiltration and percolation**: Vertical movement of dissolved pollutants with water towards the water table.
- **Leaching**: The removal of soluble elements (nitrates, pesticides) to deeper soil horizons.
- **Adsorption / desorption**: Pollutants are bound to soil particles (clays, organic matter) and may be remobilized back into solution.
- **Molecular diffusion**: Migration of pollutants according to a concentration gradient.
- **Filtration**: Mechanical retention of suspended particles by soil and rock.

2. Transfer to and in Groundwater In aquifers, pollutants primarily move through the following mechanisms:



- **Advection**: Transport with the natural flow of the groundwater.
- **Hydrodynamic dispersion**: Spreading of the pollution plume depending on the heterogeneity of the aquifer.
- **Soil-water exchanges**: Chemical interactions between the water and the geological matrix (dissolution, precipitation, adsorption).

3. Transfer in Surface Waters Rivers, lakes, and streams receive pollutants through:

- **Runoff**: Transport from agricultural and urban soils.
- **Erosion and particulate transport**: Movement of pollutants adsorbed to sediments.
- **Mixing and dilution**: Redistribution of pollutants in the water column.

4. Air-Water and Air-Soil Transfers

- **Atmospheric deposition**: Pollutants from the atmosphere (metals, nitrates, sulfates) fall onto soils and waters.
- **Volatilization**: Passage of volatile organic pollutants from water or soil into the atmosphere.

5. Physical Transfers

- **Volatilization**: Passage of organic substances to the gaseous state into the atmosphere, reducing their concentration in soil or water.

- **Dispersion**: Mixing and spreading of pollutants in porous media; includes mechanical dispersion (dependent on grain size and soil heterogeneity) and molecular diffusion (migration based on a concentration gradient).
- **Filtration**: Removal of suspended particles through mechanical processes or adsorption by soils and rocks.
- **Dilution**: Mixing with groundwater or surface water, reducing the concentration and toxicity of pollutants.

6. Chemical Transfers These mechanisms modify the chemical form of pollutants and their interactions with environments:

- **Dissolution-Precipitation**: Solubilization or precipitation of substances depending on saturation, pH, temperature, and the chemical composition of water and soil.
- **Adsorption/Desorption**: Pollutants bind to solid surfaces (clays, organic matter) through physical bonds (Van der Waals forces, ion exchange) or chemical bonds (covalent bonds on reactive sites).
- **Redox reactions**: Modify the chemical state of elements (Fe, Mn, As, N) and influence their mobility and toxicity.

7. Biological Transfers Biological processes play a role in the transformation and elimination of pollutants:

- **Biodegradation and mineralization**: Transformation of organic compounds into simpler or inorganic forms by microorganisms, under aerobic or anaerobic conditions.
- **Bioaccumulation and biomagnification**: Accumulation and amplification of pollutants along trophic chains.

These processes are modulated by geochemical parameters: redox potential, pH, availability of electron acceptors/donors, mineral composition, and microbial activity. The metabolic products can be less or sometimes equally toxic, influencing the final quality of the water.

III.2.5. Water Pollution Indicators

In water geochemistry and pollution studies, pollution indicators are used to assess the chemical composition, ecological quality, and anthropogenic impact on water resources. They provide information about the mobility, bioavailability, and toxicity of pollutants and serve as a basis for modeling the fate of contaminants. These indicators play a crucial role in managing aquatic ecosystems by improving understanding of contaminants' effects on biodiversity and ecosystem functions. Studies show that using multi-substance indicators can enhance our comprehension of chemical exposure gradients and their impacts on aquatic communities. Systematic application of these indicators also helps detect pollution sources and evaluate risks associated with contaminants in aquatic ecosystems.

1. Physico-chemical Indicators

Physico-chemical indicators reflect chemical and physical alterations in water. They are essential for assessing water quality, detecting environmental changes, and guiding appropriate management actions. Indicators such as pH and biochemical oxygen demand provide key information to understand the impact of human activities on aquatic ecosystems. This data is vital for developing sustainable management strategies, as it helps identify the most significant anthropogenic pressures on aquatic environments. Regular monitoring of these indicators is necessary to ensure the health of aquatic ecosystems and effectively address growing environmental challenges.

pH: Indicates the acidity or alkalinity of water, influencing chemical speciation (e.g., heavy metals), pollutant toxicity, metal solubility, nutrient bioavailability, and microbial activity. pH interacts with other physico-chemical parameters such as dissolved oxygen and processes like precipitation/adsorption. Continuous monitoring is essential for effective water resource management. Low pH (acidic water) tends to release more toxic metals (e.g., Al, Fe), while high pH (alkaline water) may promote more toxic ammonia forms harmful to aquatic organisms. pH affects many physico-chemical equilibria that influence microorganism growth. The practical pH scale ranges from 0 (very acidic) to 14 (very alkaline), with 7 being neutral at 25°C.
Algerian standards: Surface water: generally pH 5.5–9, Drinking water: pH 6.5–8.5

Electrical Conductivity: Indicates the amount of dissolved salts in water and helps detect pollution. Conductivity also relates to the geological layers or presence of undesirable minerals. Mineral salts in solution are good conductors; organic compounds are poor conductors. The main unit is microsiemens per centimeter (µS/cm). High conductivity may indicate salinization (saltwater intrusion, evaporites) or anthropogenic influence (agricultural/industrial effluents). Conductivity is a key indicator for assessing water quality and detecting human impact. *Algerian drinking water standard*: approximately 2800 µS/cm (relatively permissive but serves as a guideline).

Temperature: Influences gas solubility (e.g., O_2), reaction kinetics, and microbial activity. Higher temperatures generally reduce oxygen solubility and may promote eutrophication. Many standards (including Algerian) recommend a maximum temperature of about 25°C for service or surface waters.

Turbidity and Suspended Solids: Indicators of sedimentation and erosion, potentially transporting adsorbed pollutants. Turbidity results from suspended particles such as clays, silts, and organic matter, which reduce water clarity and affect pollutant diffusion and adsorption processes. Sources include erosion, industrial discharges, and runoff. *Algerian drinking water standard for turbidity:* ≤ 5 NTU (Nephelometric Turbidity Units).

Suspended Solids (SS): Include all insoluble solid substances suspended in water: mineral particles (clay, sand, silt) and organic matter (plankton, debris). They affect turbidity, river sedimentation, and contaminant transport dynamics. Concentrations depend on soil type, season, rainfall, anthropogenic discharges, and biological activity.

Dissolved Oxygen (DO): Reflects water's capacity to support aquatic life and controls redox reactions (Eh). DO is a key biological water quality indicator and a measure of self-purification: high DO usually indicates good ecological status, while low DO may indicate high organic load or eutrophication. O_2 solubility depends on atmospheric pressure, temperature, and salinity. Well-aerated water is typically saturated with oxygen; water rich in biodegradable organic matter is oxygen-poor.

- High DO values generally indicate good ecological condition.
- Low DO values may indicate high organic pollution, eutrophication, or contamination, negatively affecting aquatic fauna.

Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD_5): Assess total and biodegradable organic load in water.

- COD represents the amount of oxygen required to chemically oxidize organic and inorganic matter in water.
- BOD_5 measures the oxygen consumed by microorganisms to biologically decompose biodegradable organic matter over 5 days. High COD or BOD_5 values indicate a significant organic load (from domestic or industrial effluents), often correlated with organic pollution.

  In Algerian studies, threshold values for BOD_5 and COD are approximately 7 mg/L O_2 and

30 mg/L O_2, respectively, used to evaluate natural waters and pollution levels. Units: mg O_2/L.

2. Specific Chemical Indicators

Nutrients: Nitrates (NO_3^-), Nitrites (NO_2^-), Ammonium (NH_4^+), Phosphates (PO_4^{3-}), excess linked to agricultural activities and wastewater. Excessive nutrients, particularly nitrates, contribute to the degradation of groundwater and surface water quality, causing significant environmental problems. Eutrophication, caused by the excess of these nutrients, can lead to harmful algal blooms and a decrease in dissolved oxygen in coastal waters. These changes can have severe consequences on marine biodiversity and the health of coastal ecosystems, exacerbating hypoxia effects. Studies show that eutrophication is a key factor contributing to the increase of hypoxic zones in coastal waters, severely impacting marine life.

Nitrates (NO_3^-): Final oxidized form of nitrogen after nitration (transformation of NO_2^- into NO_3^-).
Sources: Application of nitrogen fertilizers (both chemical and organic).
Natural nitrogen cycle, through organic matter decomposition or fixation by certain plants.
Limits: WHO: 50 mg/L for drinking water. European Directive: guide level 25 mg/L, maximum concentration 50 mg/L.

Nitrites (NO_2^-): Less oxidized and intermediate form of nitrogen, toxic for drinking water.
Should be assessed together with nitrates: WHO guideline value: 3 mg/L for NO_2^-.

Ammonium (NH_4^+): Reduced form of nitrogen, highly toxic.
Indicative of incomplete organic matter degradation and domestic pollution (human waste).

Phosphates (PO_4^{3-}): Phosphorus can exist in several oxidized forms: meta (HPO_3), pyro ($H_4P_2O_7$), ortho (H_3PO_4). In natural waters (pH 7–8), the dominant orthophosphates are: $H_2PO_4^-$ and HPO_4^{2-}.

Heavy Metals (Pb, Cd, Hg, As, Cr): Indicate industrial or geochemical contamination. Heavy metals are persistent pollutants that can accumulate in the food chain and pose serious risks to human health and ecosystems. Their measurement is essential in water geochemistry.

Pollutant	Effects / Source	Algerian Drinking Water Standard
Arsenic (As)	Carcinogenic, toxic at low doses	0.05 mg/L (50 µg/L)
Cadmium (Cd)	Toxic for kidneys / bones	0.01 mg/L (10 µg/L)
Chromium (Cr)	Toxic in certain forms	0.05 mg/L

Mercury (Hg)	Powerful neurotoxin	0.001 mg/L
Lead (Pb)	Neurotoxic, especially for children	0.055 mg/L
Manganese (Mn)	Neurological effects at high doses	0.5 mg/L
Iron (Fe)	Can alter taste, cause corrosion	0.3 mg/L
Zinc (Zn)	Essential, but toxic at high doses	5 mg/L
Copper (Cu)	Toxic at high doses	1.5 mg/L

These thresholds are drawn from Algerian standards for drinking water and allow for the assessment of water quality according to national requirements for human health.

3. Organic Compounds: Hydrocarbons, Solvents, Pesticides Representing Anthropogenic Organic Pollution

Organic compounds are a major class of anthropogenic pollutants in surface and groundwater. They mainly come from:

Hydrocarbons: Petroleum hydrocarbon discharges, industrial leaks, accidental spills.
Organic Solvents: Derived from the chemical industry, paints, adhesives, and cleaning processes.
Pesticides: Herbicides, insecticides, and fungicides used in intensive agriculture.

Impacts on Aquatic Environments

- **Direct Toxicity**: Certain polycyclic aromatic hydrocarbons (PAHs) and chlorinated solvents are carcinogenic or mutagenic.
- **Persistence**: Many organic compounds are resistant to biodegradation, which leads to their accumulation in sediments and the food chain.
- **Indirect Eutrophication**: Some nitrogen- or phosphate-based pesticides can contribute to excess nutrients in surface waters.
- **Geochemical Alteration**: These compounds can interact with soils and sediments, adsorb onto organic matter or clays, and influence the mobility of metals and other pollutants.

Standards and Limits: Algerian standards for drinking water:

Total hydrocarbons: ≤ 0.1 mg/L

Total pesticides: ≤ 0.5 µg/L
Specific solvents: Limits set based on toxicity (e.g., trichloroethylene ≤ 0.01 mg/L).
International references: WHO and EU set very low limits for pesticides and PAHs due to their chronic toxicity.
Mineral Salts and Chlorides: Reflect salinization, saline intrusion, or urban influence.

4. Biological and Microbiological Indicators

Indicator Bacteria: Indicator bacteria are microorganisms used to assess microbiological contamination in water, particularly from fecal matter or domestic and agricultural effluents. While they don't always cause disease directly, their presence signals a potential health risk and the possible presence of pathogens. E. coli and fecal coliforms mark contamination from domestic or agricultural wastewater.

Main Types:

- **Total Coliforms**: A group of Gram-negative bacteria found in the environment (soil, vegetation) and in the intestines of animals and humans. Their detection indicates general water contamination and poor environmental hygiene.
- **Fecal Coliforms (E. coli)**: Specific to human and animal feces. They are preferred indicators of recent fecal pollution and a potential risk of waterborne diseases.
- **Enterococci**: More resistant to extreme environmental conditions than E. coli. Used to confirm fecal contamination in surface and groundwater.

Role in Geochemistry and Water Pollution

- **Early Detection**: Their presence signals untreated wastewater discharge or infiltration into aquifers.
- **Water Quality Monitoring**: Used in national and international standards to assess drinking water, bathing waters, and treated effluents.
- **Health Risk Assessment**: They help predict the likelihood of pathogen presence.
- **Interactions with Chemical Pollutants**: Some bacteria can aid in the biodegradation of organic pollutants, influencing geochemical processes.

Algerian and International Standards

Indicator Bacteria	Drinking Water (Algeria / WHO)	Swimming/Surface Water
Total Coliforms	0 CFU/100 mL	< 100 CFU/100 mL
Fecal Coliforms (E. coli)	0 CFU/100 mL	< 200 CFU/100 mL
Enterococci	0 CFU/100 mL	< 200 CFU/100 mL

CFU: Colony Forming Unit

Detection Methods

Culture Methods: Selective media (e.g., Endo, MacConkey, Violet Red Bile).

Rapid Methods: Enzymatic detection (β-galactosidase, β-glucuronidase), PCR for specific identification.

5. Aquatic Bioindicators: are living organisms whose presence, abundance, or diversity reflect the ecological quality of water. They help evaluate the impact of chemical, physical, or biological pollution on aquatic ecosystems and complement physical-chemical and microbiological analyses.

Main Types of Bioindicators:

1. **Aquatic Macroinvertebrates**: Include aquatic insects (ephemeroptera, plecoptera, trichoptera), mollusks, crustaceans, and worms. They are highly sensitive to changes in dissolved oxygen, pH, nutrients, metals, and pesticides. Rich and diverse communities indicate good ecological health, while communities dominated by a few tolerant species signal pollution or degradation.
2. **Algae and Phytobenthos**: Includes diatoms, cyanobacteria, and other microalgae. They are sensitive to nutrients (N, P), pH, and chemical contaminants. Their composition and diversity are used to calculate ecological quality indices (e.g., Diatom Index, IPS).
3. **Fish**: The species diversity, abundance, and health of populations indicate long-term water quality. Certain species are highly sensitive to heavy metals, pesticides, or physical disturbances, serving as bioindicators of chronic pollution.

Role in Geochemistry and Water Pollution

- *Ecological Assessment:* Integration of the combined effects of chemical and biological pollution.
- *Long-term Impact Monitoring*: Unlike instantaneous physical-chemical parameters, bioindicators reflect the historical pollution.
- *Complement to Chemical Analyses:* The presence or absence of certain species can confirm the geochemical effects of specific pollutants.

Examples of Ecological Indices:

- *Global Biological Index (IBG):* Based on the diversity and abundance of macroinvertebrates.
- *Diatom Index IPS:* Reflects ecological quality based on the species composition of diatoms.
- *Fish Index:* Assesses fish population health and diversity.

Standards and Thresholds: Bioindicators do not have strict threshold values like chemical parameters, but their monitoring is codified by standardized ecological monitoring protocols (e.g., European standards, WFD directives, and national Algerian protocols for river monitoring).

5. Geochemical Biomarkers Geochemical biomarkers are molecules, enzymes, or pigments produced by microorganisms in response to exposure to pollutants. They are used to detect and quantify the biological impact of chemical contaminants, complementing physico-chemical and biological analyses.

Main Types of Biomarkers

- **Specific Enzymes**: Examples include dehalogenases, laccases, and peroxidases. These indicate microbial activity and the capacity to degrade persistent organic compounds (hydrocarbons, solvents, pesticides).
- **Pigments and Proteins**:
  - Photosynthetic pigments from algae or cyanobacteria (chlorophylls, carotenoids) reflect trophic quality and exposure to contaminants.
  - Stress proteins (e.g., heat-shock proteins, metallothioneins) signal oxidative stress caused by heavy metals or other pollutants.
- **Secondary Metabolites**: Produced during pollutant biodegradation and often specific to certain chemical compounds, they allow tracking of in situ degradation and biotransformation of contaminants.

Role in Geochemistry and Water Pollution

- **Early Pollution Detection**: Biomarkers reveal biological effects before visible changes occur in flora or fauna.
- **Assessment of Pollutant Bioavailability**: Unlike total concentrations measured chemically, biomarkers indicate the biologically active fraction of contaminants.
- **Indicators of Natural Degradation**: Certain enzymes and metabolites provide information on the self-purification of contaminated waters.

Applications

- Monitoring metal contamination via metallothioneins in algae and invertebrates.
- Tracking persistent organic pollution through detection of specific degradation enzymes in sediments.
- Analyzing pigments and chlorophylls to evaluate eutrophication and phytoplankton responses to nutrients and pesticides.

Standards and Interpretation: Biomarkers do not have strict regulatory threshold values, but their relative variations compared to a reference site or baseline conditions allow the detection and quantification of anthropogenic pressures on aquatic environments. They are used in integrated monitoring protocols combining chemical, physico-chemical, and biological analyses.

BOD_5/COD Ratio: The **COD/BOD_5 ratio** is a key indicator of effluent biodegradability and its potential impact on water quality. It reflects the capacity of organic matter to be degraded or oxidized by microorganisms during biological wastewater treatment.

- ➔ COD/BOD_5 < 3 → easily biodegradable organic matter; low potential impact on water. Conventional biological processes (activated sludge, lagooning) are sufficient.
- ➔ $3 \leq COD/BOD_5 \leq 5$ → moderately biodegradable organic matter; moderate potential risk to dissolved oxygen in receiving waters. Often requires adaptation of retention time, reactor volume, or pre-treatment to enhance biodegradability. Intensive biological processes: activated sludge with recirculation, membrane bioreactors, prolonged contact time.
- ➔ COD/BOD_5 > 5 → Poorly or non-biodegradable organic matter; high likelihood of disruption. May require physico-chemical or combined treatment before biological treatment, as bacteria alone will struggle to reduce the organic load. Combined processes: chemical pre-treatment (ozonation, Fenton) followed by biological treatment.

Role in Geochemistry and Water Pollution

- Characterizes effluent type (domestic, industrial, agricultural) and organic pollution potential.
- Guides the design and selection of biological wastewater treatment processes.
- Predicts impacts on aquatic environments, including dissolved oxygen consumption, microbial growth, and eutrophication risk.

Standards and References: Algerian standards recommend maintaining BOD_5 of treated effluents ≤ 30 mg/L, depending on water destination (rivers, industrial discharge, irrigation).

The COD/BOD_5 ratio is also used in international standards (WHO, EU) to assess wastewater treatment efficiency and biodegradable organic load.

Water Quality Indices (WQI, IQA): The Water Quality Index (WQI) is a multi-parameter synthesis used for an overall evaluation of water quality. The WQI was developed by Horton in 1965 and has since been widely used to determine the state of water quality. Its calculation is based on the weighted arithmetic method developed by Bowen in 1972, which defines water quality into five categories, as shown in the table.

Nine important parameters (pH, Dissolved Oxygen, EC, Temperature, SO_4^{2-}, BOD_5, PO_4^{3-}, $N\text{-}NH_4$, and $N\text{-}NO_3$) have been selected to calculate the Water Quality Index (WQI). This index is a technique for classifying water quality based on a comparison of water quality parameters with international or national standards, as applied in this study. The WQI summarizes large amounts of data on water quality into simple terms (Excellent, Good, Poor, Very Poor, etc.). In this study, the WQI is applied to estimate the influence of both natural and anthropogenic factors based on several key parameters of surface water chemistry.

The index is calculated using the weighted arithmetic method. In this approach, a numerical value called the relative weight (Wi), specific to each physico-chemical parameter, is calculated (Tab. 1) using the following formula:

$$\boldsymbol{Wi = \frac{K}{Si}}$$

Where: k is a proportionality constant and can also be calculated using the following equation:

$$\boldsymbol{K = \frac{1}{\sum_{i=1}^{n} \left(\frac{1}{Si}\right)}}$$

n: number of parameters

Si: maximum value of the standard norm for surface water (Water Quality Standards) for each parameter in mg/l, except for pH, temperature (T°C), and electrical conductivity. Then, a quality evaluation scale (Qi) is calculated for each parameter by dividing the concentration by the standard norm for that parameter and multiplying the result by 100, as shown in the following formula:

Where: $$\boldsymbol{Qi = \left(\frac{Ci}{Si}\right) \times 100}$$

Qi: quality evaluation scale for each parameter.
Ci: the concentration of each parameter in mg/l.

Finally, the overall water quality index is calculated using the following equation:

$$\boldsymbol{IQE = \sum_{i=1}^{n} Qi \times Wi \Big/ \sum_{i=1}^{n} Wi}$$

Five quality classes can be identified based on the values of the Water Quality Index (WQI) (Tab.).

Tab. Classification and possible use of water according to the WQI.

IQE Class	Water Type	Possible Use
0–25	Excellent Quality	Drinking, irrigation, industry
25–50	Good Quality	Drinking, irrigation, industry
50–75	Poor Quality	Irrigation, industry
75–100	Very Poor Quality	Irrigation
>100	Non-Potable Water	Requires appropriate treatment before use

Chemical speciation: is a fundamental concept in water geochemistry and in the assessment of water pollution. It involves determining the exact chemical form in which an element (metal or nutrient) exists in water, as this form directly influences its mobility, bioavailability, and toxicity. This includes the analysis of dissolved, complexed, or adsorbed forms of metals and nutrients to predict their mobility and toxicity. (See Chap. ?)

Saturation géochimique : Elle décrit l'état d'équilibre entre l'eau et un minéral dissous. Elle est généralement évaluée à l'aide d'indices comme l'Indice de Saturation (IS) est mesurée par des indices qui reflètent les interactions entre l'eau, les roches et les minéraux, notamment à travers l'indice de saturation (SI) qui indique la sensibilité aux fluctuations de pH. L'indice de saturation est donc un paramètre clé pour évaluer les réactions hydro-géochimiques dans divers contextes environnementaux. L'indice de saturation permet ainsi de mieux comprendre les conditions de dissolution et de précipitation des matériaux dans l'eau, influençant la gestion des ressources en eau.

$$SI = \log(\left(\frac{IAP}{Ksp}\right)$$

where:

IAP (Ion Activity Product): the product of the activities of the ions in solution that make up the mineral, for example, for calcite ($CaCO_3$):

$$\mathrm{IAP} = [\mathrm{Ca}^{2+}] \cdot [\ \mathrm{CO_3}^{2-}]$$

Les concentrations doivent être exprimées en activités, pas seulement en molarité, donc il faut tenir compte des coefficients d'activité (gamma) γ.

Ksp *(Produit de solubilité)* : constante de solubilité du minéral à la température considérée.

SI (Indice de Saturation)	Signification
SI < 0	Eau sous-saturée → tendance à dissoudre le minéral
SI = 0	Eau en équilibre → ni précipitation, ni dissolution
SI > 0	Eau sur-saturée → tendance à précipiter le minéral

Example: Calculation of the Saturation Index (SI) for Calcite

Measured data in a water sample:

Paramètre	Valeur
$[Ca^{2+}]$	2,5 mmol/L
$[HCO_3^-]$	3,0 mmol/L
Température	25 °C

Constant: Solubility product of calcite: $Ksp=10^{-8,48}=3,31\times10^{-9}$ (mol^2/L^2) à 25 °C

Step 1: Convert concentrations to mol/L

$[Ca^{2+}]$ = 2,5 mmol/L = $2,5\times10^{-3}$ mol/L $[HCO_3^-]$ = 3,0 mmol/L = $3,0\times10^{-3}$ mol/L

Note: For calcite, the active form is carbonating CO_3^{2-}, not bicarbonate HCO_3^- directly. We need to calculate $[CO_3^{2-}]$ from the pH and bicarbonate concentration.

Step 2: Calculate carbonate concentration CO_3^{2-}

The relationship between bicarbonate and carbonate depends on pH:

$$[CO_3^{2-}] = \frac{[HCO_3^-]\cdot 10^{pH-pKa2}}{1+10^{pH-pKa2}}$$

- For the carbonate system, pKa2 ≈ 10,33 à 25 °C
- Suppose the pH of the water = 7.5

$$[CO_3^{2-}] = \frac{[3.\ 10^{-3}]\cdot 10^{7,5-10,33}}{1+10^{7,5-10,33}} = \frac{[3.\ 10^{-3}]\cdot 10^{-2,83}}{1+10^{-2,83}} = 10^{-2,83} \approx 1,48\times10^{-3}$$

$$[CO_3^{2-}] = \frac{[3.\ 10^{-3}]\cdot 1,48.10^{-3}}{1+1,48\ .10^{-3}} = \frac{4,44\cdot10^{-6}}{1,00148} = 4,43\times10^{-6}\ \text{mol/L}$$

The calcite is slightly supersaturated, so precipitation is possible.

Step 3: Calculate the Ionic Activity Product (IAP)

$$IAP = [Ca^{2+}]\cdot[\ CO_3^{2-}]$$

$$IAP = (2,5\times10^{-3})\cdot(4,43\times10^{-6}) \approx 1,11\times10^{-8}\ mol^2/L^2$$

Step 4: Calculate the saturation index (SI)

$$SI = \log\left(\frac{1{,}11\times10^{-8}}{3{,}31\times10^{-9}}\right) = \log(3{,}35) \approx 0{,}525$$

Étape 5 : Interprétation

- SI = +0,525 → sur-saturé par rapport à la calcite
- L'eau a donc tendance à précipiter du $CaCO_3$.
- Ce phénomène peut expliquer la formation de dépôts calcaires dans les conduites ou les sédiments d'une rivière.

Example: Saturation Index for Iron (Fe) as $Fe(OH)_3(s)$

Measured data in a water sample:

Parameter	Value
Total $[Fe^{3+}]$	0.10 mmol/L
pH	7.0
Eh	+0.3 V (oxidizing)
Temperature	25 °C
Solubility product of $Fe(OH)_3(s)$ (Ksp)	10^{-38} (mol^3/L^3)

Step 1: Check the dominant form of Fe

The speciation of iron strongly depends on pH and Eh:

- At pH 7 and Eh +0.3 V, the Eh–pH diagram shows that Fe^{3+} predominantly precipitates as $Fe(OH)_3(s)$.
- The ferrous iron Fe^{2+} is very minor under these oxidizing conditions.

Step 2: Calculate the Ion Activity Product (IAP)

For $Fe(OH)_3(s)$, the ion activity product is defined as:

$$\mathbf{IAP = [Fe^{3+}] \times [OH^-]^3}$$

- Le pH = 7 → $[H^+] = 10^{-7}$ mol/L
- $[OH^-] = \frac{Kw}{[H+]} = 10^{-14}/10^{-7} = 10^{-7}$ mol/L
  - $IAP = (0{,}10\times10^{-3})\cdot(10^{-7})^3 = 1{,}0\times10^{-4}\cdot10^{-21} = 1{,}0\times10^{-25}$ mol^4/L^4

(The Ksp for $Fe(OH)_3$ is in mol^3/L^3, but the powers are adjusted according to the balanced chemical equation: $Fe^{3+} + 3\,OH^- \rightleftharpoons Fe(OH)_3(s)$)

Step 3: Calculate the Saturation Index (SI)

$$I = \log(\left(\frac{IAP}{Ksp}\right) = \log\left(\frac{1\times10^{-25}}{10^{-38}}\right) = \log 10^{-13} = 13$$

Interpretation

SI = +13, highly supersaturated

Iron will therefore precipitate massively as $Fe(OH)_3(s)$.

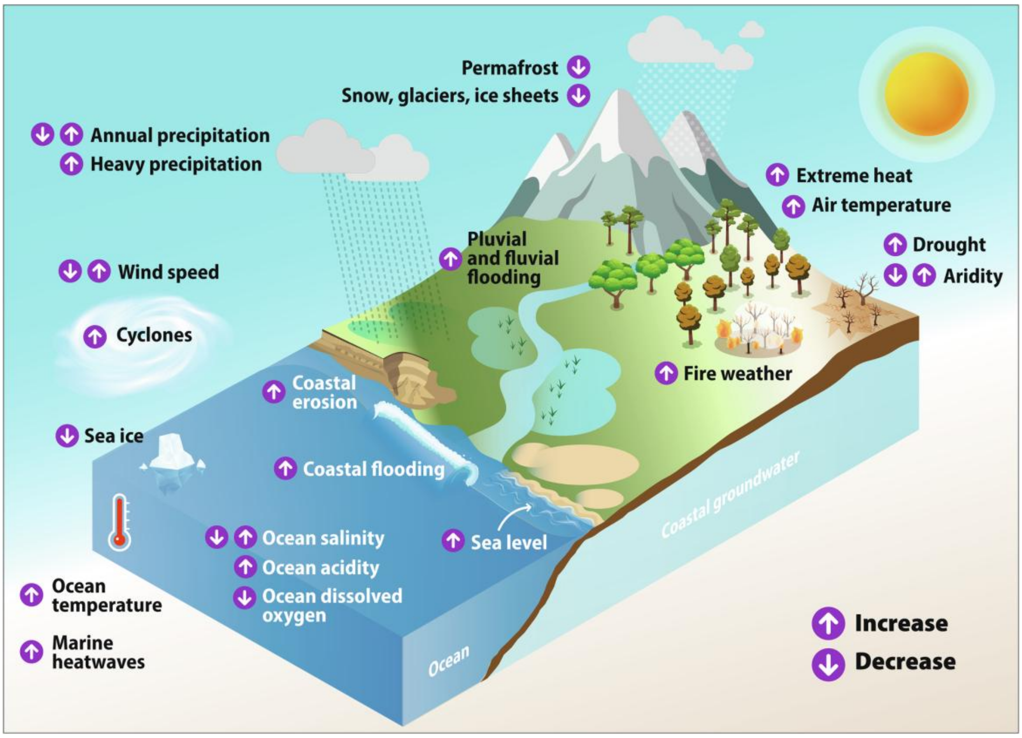
This explains the formation of iron deposits in waters rich in Fe^{3+}, such as in wells or oxidizing rivers.

- Unlike calcite, redox speciation is crucial for iron: Fe^{2+} remains soluble in reducing environments, while Fe^{3+} precipitates in oxidizing environments.
- The saturation index helps predict the precipitation or dissolution of metals in natural waters.
- Precipitation of $Fe(OH)_3$ can adsorb other metals, reducing their mobility (e.g., Cu, Pb, Zn).

3. Impacts des changements climatiques sur la pollution des eaux

Introduction

Climate change causes significant alterations in hydrological patterns, temperature, and water chemistry, which can exacerbate pollution and affect the quality of aquatic environments. These changes influence the mobility, concentration, and toxicity of pollutants while modifying biochemical reactions and water stratification, potentially disrupting the functioning of aquatic ecosystems.



III.3.1. Hydrological Effects

Intense rainfall and floods increase runoff, pollutant transport, and soil erosion, resulting in massive inputs of nutrients, metals, and suspended solids into rivers and lakes. These events can alter aquatic habitats and degrade water quality. Acid rain or acid snow reaching rivers and lakes can lower pH. Aquatic organisms generally cannot tolerate pH below 5. In severe cases, “dead” lakes may form, where most plankton, fish, amphibians, and invertebrates are absent. While acid rain was a more significant problem in the past, it can still occur today in regions burning high-sulfur coal, particularly in Asia and parts of Russia. Increased runoff transports agricultural pollutants such as nitrates, phosphates, and pesticides into rivers, lakes, and groundwater. Overflow of sanitation systems can also result in the direct discharge of wastewater into aquatic environments. For example, following extreme rainfall events, increased concentrations of *E. coli* and other pathogens are often observed in rivers.

Prolonged droughts reduce water volumes, concentrating pollutants, lowering dissolved oxygen, and increasing stress on aquatic organisms, which heightens ecosystem vulnerability.

III.3.2. Geochemical Interactions

Climate change also alters chemical processes in water. Variations in pH and temperature can change the speciation of metals and nutrients, affecting their bioavailability and toxicity. For example, iron and manganese may transition between soluble and solid forms depending on oxidizing or reducing conditions. Some heavy metals can bind to particles and sediments, altering their mobility and accumulation in sediments or aquatic organisms.

III.3.3. Ecological and Health Consequences

The combination of floods, droughts, and chemical variations can lead to the mortality of sensitive species, algal blooms, and disruptions of trophic chains. Changes in the speciation and concentration of pollutants, including heavy metals, nutrients, and micropollutants, may compromise drinking water quality and increase health risks.

III.3.4. Rising Temperature and Biological Effects

Higher temperatures promote eutrophication, increasing the proliferation of algae and cyanobacteria. Certain cyanobacteria produce toxins that pose health risks for drinking water and recreational activities. Reduced dissolved oxygen can lead to the accumulation of organic compounds and reduced metals such as iron and manganese. Temperature changes also alter chemical reaction rates, causing some pollutants to persist longer in water.

III.3.5. Acidification and Changes in Chemical Speciation

More acidic waters promote the release of heavy metals adsorbed onto sediments, including lead, cadmium, and arsenic. Nutrient mobility, particularly nitrogen and phosphorus, is altered, which can impact algal growth and increase toxicity. Acidic rivers often show higher metal accumulation in the water column.

III.3.6. Erosion, Sedimentation, and Particulate Pollution

Intense rainfall and snowmelt transport nutrient- and pollutant-rich sediments to water bodies. Sediments can adsorb and store pollutants, which are later released depending on chemical conditions such as pH and temperature. After heavy rainfall, lakes may exhibit elevated phosphorus concentrations, which can trigger algal blooms.

III.3.7. Combined Effects on Pollution and Ecological Health

Climatic Effect	Impact on Water	Ecological and Health Consequences
Intense Rainfall	Runoff + Flooding	Transport of nutrients, pesticides, pathogens
Droughts	Concentration of pollutants	Increased toxicity, stress for aquatic fauna
High Temperature	Algal blooms	Eutrophication, toxin production
Acidification	Release of heavy metals	Accumulation in the food chain
Erosion/Sedimentation	Transport of polluting particles	Habitat alteration, algal blooms

These effects can be cumulative: drought followed by flooding can result in an extreme peak of point-source pollution. Climate change is an aggravating factor for water pollution. It affects the quantity, concentration, and mobility of pollutants, complicating the management of water resources. Understanding these interactions is crucial for:

- Developing sustainable water management strategies.
- Adapting treatment and monitoring systems for water quality.
- Preventing ecological and health risks associated with emerging pollutants.

Chapter IV: Diagnostic and evaluation tools

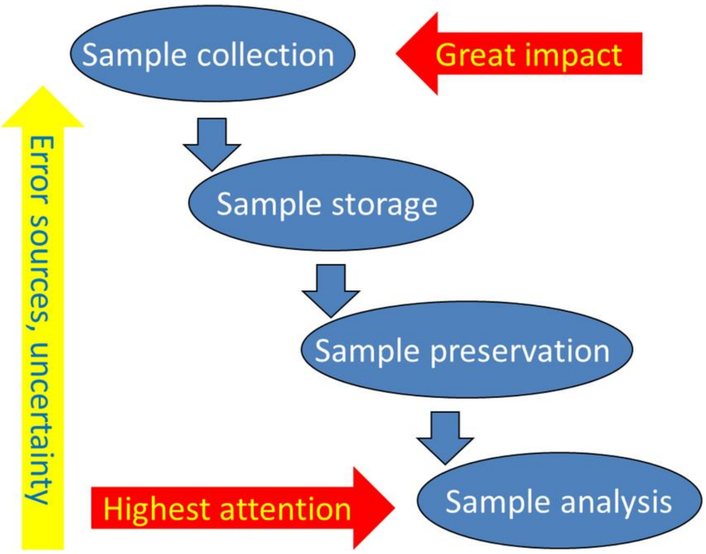
Introduction

Diagnostic and evaluation tools in water geochemistry and water pollution rely on the analysis of physicochemical parameters, the implementation of rigorous sampling and analysis validation methods, as well as the use of modeling software such as DIAGRAMMES & PHREEQC, etc. These tools enable the assessment of water quality, saturation states, geochemical equilibria, and contamination risks. When applied to water pollution studies, particularly using PHREEQC, these approaches facilitate the analysis of ionic speciation, mineral equilibria, and pollutant transfer mechanisms to aquifers. They thus provide essential support for the monitoring and management of water resources, especially in the Algerian context, where some aquifers are affected by nitrates, heavy metals, and other pollutants.

1. Sampling and Analysis: In Situ and Laboratory

IV.1.1. Sampling and Analysis (In Situ/Laboratory)

No rigorous geochemical study can rely on poor-quality or unreliable chemical data. Therefore, acquiring reliable data is essential, both in terms of strategy (sampling frequency, spatial density, and representativeness in a river or aquifer) and the reliability of the analytical measurements. The sampling strategy should be defined and integrated from the very first stages of a geochemical or water pollution study.



A/ Planned Sampling Strategy from the Outset (Geostatistics and Chronostatistics)

It is important that the sampling strategy be well thought out before any fieldwork begins.

Economic Aspects: The budget allocated for analytical tasks, field mission costs, etc., must be considered.

Spatial Density: Ensuring that the spatial density of sampling points is sufficient is essential, with enough closely spaced sample pairs to measure the range (refer to geostatistics lectures), even if the range is small. Also, attention must be paid to the temporal representativeness of the samples.

Position of Sampling Points in Time and Space:

Hydrology: Ensure representativeness. Pay attention to river confluences.

- The chemistry of water can vary significantly during floods. Chemical export calculations cannot rely on just one randomly collected sample during such an event, especially since solid exports often concentrate within a short time frame.
- For long-term monitoring of river water chemistry, time intervals should be compatible with the expected range, meaning they should be much smaller. This can be determined through a chronostatistical study.

Study Area (Hydrogeology):

A plan with a minimum spatial sampling density must be designed from the start. It should cover the entire area with enough density so that each point is located at a distance from the nearest sampling points that is much smaller than the range (see geostatistics). If necessary, revisit the field to sample in areas with low density or to increase the frequency of acquisition. This is crucial when creating risk or sensitivity maps of the environment related to chemical risks.

When studying the mechanisms responsible for water quality, a broad range of samples should be taken. Quick measurements with a conductivity meter should be performed. Two nearby points in space or time showing the same electrical conductivity are likely to be similar in all other physico-chemical parameters. Sampling both would be redundant.

IV.1.2. Measurement of Instantaneous Parameters in the Field

Several parameters must be measured in the field immediately:

Temperature: The temperature of a sample will change after sampling, and the information will be lost. It should, therefore, be measured quickly after the sample is collected.

Parameters such as pH, Eh (actually rH), chlorophyll content, dissolved oxygen, or CO2 must be measured on-site.

Electrical Conductivity: While it can wait until the sample reaches the laboratory, it is useful for better managing the sampling strategy (as mentioned earlier) and can be used as an on-site measurement in the same way.

When the partial pressure of CO_2 in the sample is significantly different from that of the air, a rebalancing process occurs rapidly**.** Therefore, the pH/rH pair should be measured as quickly as possible, and care should be taken not to agitate the solution, even during sampling or when transporting the sample to the measuring bottle. It is important to note the direction of pH (and rH) change.

Generally, an increase in pH should not be interpreted as an electrode issue ("unstable stabilization"), but as an indication of CO_2 loss from water that was initially rich in this gas. A decrease in pH, on the other hand, suggests that the water was very poor in CO_2 and is now being charged with CO_2 from the atmosphere. It is essential to measure both rH/pH pairs simultaneously as they allow for distinguishing the redox couple active in the solution.

Note: If pH and rH measurements cannot be made on-site, they can be performed in the laboratory. In that case, care must be taken to fill the bottle underwater; it should be completely filled, meaning no air bubbles are trapped, and sealed underwater. However, the pH measurement will still be slightly different from what would have been obtained on-site.

IV.1.3. Sample Conditioning

There is no single method of sample conditioning that can be applied universally for all types of analysis. Depending on the parameters being studied, different conditioning methods and containers are used.

Choice of Containers: Materials, Closures, and Washing of Bottles The most commonly used containers are glass, polyethylene, and Teflon.

Glass Bottles:

Advantages: Glass containers have very tight closures, making them suitable for storing samples intended for isotopic measurements. They also have excellent resistance to evaporation through the walls.

Disadvantages: The weight of glass bottles makes transport cumbersome, and the risk of breakage during transport cannot be ignored. Over time, glass can degrade and release chemical elements into the solution, which is problematic. Long-term storage in glass is not recommended, especially for low-mineralized waters.

Polyethylene Bottles:

Advantages: These bottles are lighter and shatter-resistant. Their closures are less airtight, but there are bottles with double closures that are very effective. Polyethylene releases very few soluble elements, so the chemical composition of the stored solutions remains largely unaltered.

Disadvantages: The material's porosity causes a slight evaporation. Solutions intended for stable water isotopic measurements should not be stored for long in polyethylene bottles.

Teflon Bottles:

Teflon bottles are best suited for studying trace elements. These bottles must be carefully washed with acid and rinsed thoroughly. If rinsing is necessary during sampling, the best water to use for rinsing would be the water to be sampled.

B. Conditioning Solutions

There is no universal method for conditioning samples. The conditioning method varies depending on the parameters of interest. Typically, when studying a large number of parameters, it is necessary to separate the collected sample into several aliquots, each conditioned differently. This increases the number of containers, weight, work, and preparation.

No Conditioning Required: For most major elements (except nitrates), solutions may not need to be conditioned. Exceptions include waters in rapid dynamic reaction due to recent and significant changes in state. Example: In hydrology studies, runoff waters are altering the surface horizons they erode. Initially, they are poorly mineralized and therefore under-saturated with respect to many minerals, often in complete imbalance with the atmosphere and the minerals they transport. In this case, it is essential to filter on-site as quickly as possible and then perform micro-filtration.

Poisoning:

For parameters that can be rapidly influenced by biological activity, it may be useful or even essential to poison the solutions to prevent the action of microorganisms. This is the case for various forms of nitrogen or organic carbon. The most commonly used poisons are mercuric chloride, which is incompatible with some organic carbon measurement devices, and sodium azide (NaN_3).

Filtration: Filtration is often very useful as it removes solid phases that could later interact with the solution, as well as germs that could attack organic or nitrogenous compounds. It is shown that a filtered bottle (even microfiltered) stored in cool conditions and away from light can maintain its nitrate content for more than a day without altering the values. This demonstrates the importance of filtering immediately after obtaining the sample, using ash-free paper.

Freezing: Freezing is a drastic method for halting biological activity. This conservation method should only be used with caution, as it significantly affects the chemical composition of major elements. Various minerals precipitate during the freezing process. These minerals will not be dissolved when thawed, and the chemical composition of the solution will be greatly altered. This process resembles evaporation or dehydration because, during freezing, the water that freezes is almost devoid of dissolved elements, which migrate and concentrate in the remaining liquid water. Furthermore, the modification of solubility constants with temperature exacerbates the alteration of water characteristics.

Storage Away from Light and Cool Conditions: Regardless of the chosen conditioning technique, it is beneficial to store samples away from light and in cool conditions. Photosynthetic activity related to exposure to light can modify nitrate content and chemical oxygen demand (COD).

Particular Precautions for Isotopes (18O, 2H, 13C, etc.): For stable water isotopes, the key point is to limit the evaporation of solutions. This can be done by:

- Ensuring the quality of the closure (a double-threaded cap tightly screwed onto a rigid container, e.g., glass).
- Storing all bottles together in a hermetically sealed plastic bag.
- Poisoning solutions for carbon and nitrogen isotopes to prevent biological activity.

IV.1.4. Verification of the Consistency of Chemical Data

When the analysis results arrive from the laboratory, they cannot be used until they undergo certain tests to ensure their quality and reliability. The verification process mainly concerns three aspects. These same principles are particularly useful because, when necessary, they make it possible to “correct” the analyses or to “complete missing data.”

I. Verification of the Ionic Balance

Solutions are electrically neutral; therefore, the sum of positive charges must equal the sum of negative charges. The different situations encountered can generally be classified into three typical cases.

a. The ionic balance error is significant; it exceeds 10–15%.

Such analyses may present problems. However, they should not necessarily be discarded. The situation needs to be examined more closely. The imbalance may be due to an incomplete list of analyzed parameters (especially major elements). It may be useful to analyze the COD (Chemical Oxygen Demand), as the imbalance could be caused by an organic ionic compound. Another option is to request a comprehensive screening of the periodic table, even with low analytical precision, simply to identify the missing element(s). The imbalance may also be related to poor analytical accuracy for all or some of the measured elements. Other verification techniques cannot be used to smooth the data or correct the ionic imbalance if it is too large. In such cases, unfortunately, it is better to refrain from using the analysis results.

b. The ionic balance error is small; it ranges between 3% and 10%.
The data are of good quality and should then be tested using the other consistency criteria.

The ionic balance error is zero; in practice, it is less than 1%.
WARNING! In this case, the analysis results have probably been manipulated, or more precisely, adjusted. It is then necessary to obtain the raw data and verify the consistency of the data yourself.

Verification of the Consistency Between Major Element Composition and Electrical Conductivity

When the electrical conductivity is high, indicating a high level of water mineralization, the composition shown by the analysis should reflect high concentrations of ionic elements. If this is not the case, there is an inconsistency. Specifically, the electrical conductivity can be calculated from the chemical composition using three or four proposed methods. The measured electrical conductivity is then compared to the range of these four estimates. An inconsistency exists if the measured value falls outside this range.

In general, the measurement of conductivity, whether performed in the laboratory or in the field, is considered reliable. Therefore, any suspected error is usually attributed to the analysis of the major ionic compounds.

Approximate Formulas: This empirical equation, often used in agronomy and soil science to quickly estimate the total ion concentration (meq/L) from the electrical conductivity (EC) in dS/m, comes from classical studies on the characterization of saline soils and irrigation waters, such as those conducted by the U.S. Salinity Laboratory.

Cations ou Anions (méq/l) = CE (dS/m)*10 .

This expression is a standard empirical approximation used in soil science and hydrogeology to quickly estimate the total ionic concentration of a solution from its electrical conductivity (EC).

Principle of the Relation: Electrical conductivity measures a solution's ability to conduct electric current, a property directly related to the presence of dissolved ions. In relatively dilute solutions, the movement of ions is proportional to their concentration. The basic equation is written as above.

Conditions of Validity

- **Measurement range:** The relation is optimal between 0.1 and 5 dS/m. Below 0.1 dS/m, the relationship becomes unstable. Above 5 dS/m, ion interactions and the formation of ion pairs reduce ionic mobility, making the relation non-linear.
- **Chemical composition:** This rule assumes that the solution is composed mainly of common ions (calcium, magnesium, sodium, chlorides, sulfates, bicarbonates).

This formula is mainly used as a quality control check for laboratory water analyses. If the sum of the measured cations or anions deviates by more than 10–20% from the value calculated using EC × 10, it suggests either a measurement error or the presence of ions not included in the standard analysis.

Conversion of Concentrations (mg/L → meq/L)

Proper geochemical comparison requires the use of milliequivalents per liter (meq/L), as they represent the ionic charge.

$$meq/L \ = \frac{mg/L}{Poids\ moléculaire} \times valence$$

This conversion is essential for: Ionic balance calculations,

Assessing the consistency between electrical conductivity (EC) and dissolved ions.

Theoretical Estimation of Conductivity from Ions

Electrical conductivity can be estimated from the sum of individual ionic contributions:

$$CE_{\text{calculée}} = \sum (Ci \times \lambda i)$$

where: Ci = ionic concentration (meq/L)

λ_i = specific molar ionic conductivity

This method is more accurate but is rarely used in routine teaching practice.

Verification of Consistency Between pH and Alkalinity

Checking the consistency between pH and alkalinity in water samples rarely reveals unexpected results.

However, two main situations can be distinguished:

a) Alkalinity is measured directly, and a major discrepancy is observed. In most cases, this leads to the rejection of the analytical results. The origin of the problem should be investigated, and in all cases, the full set of analyses should be repeated.

b) Alkalinity is calculated from the analysis of major ions and electrical neutrality.
More specifically, inconsistency in a complete analysis can be identified as follows:

➢ If **alkalinity < 0**, then, pH < -log10 (-alcalinity) + epsilon ε is due to the activity coefficient of H^+ (hydrogen ion).
➢ If **alkalinity > 0**, then, pH < 14-log10, Otherwise, there is inconsistency between pH and alkalinity.

Automatic Correction of Analyses

The main automatic correction actions are as follows:

a) Estimate alkalinity by electrical balance when it has not been measured.

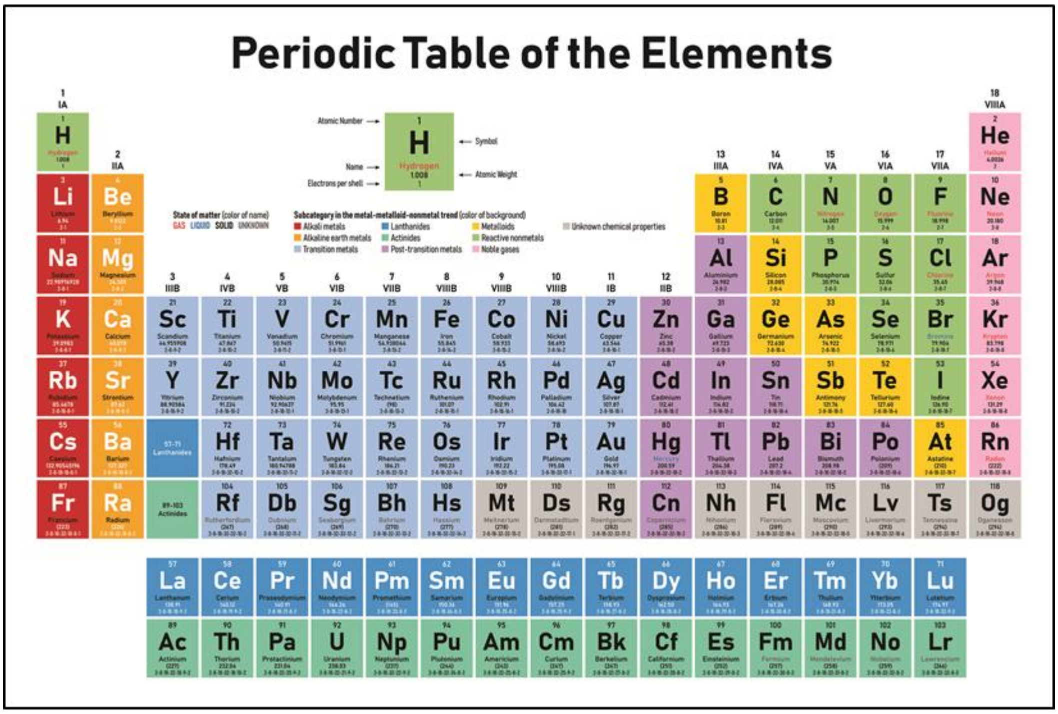
b) Correct the electrical balance error using electrical conductivity (EC) when it is available.

- ➔ *If EC is consistent with the chemical composition, the charge balance correction will be applied to all ionic species—both anions and cations—in proportion to their concentrations.*
- ➔ *If EC is not consistent with the chemical composition, the charge balance error will be assigned either to the anions or to the cations according to the EC/charge balance inconsistency pattern, and the correction will be applied proportionally to the adjusted parameters.*

IV.1.4. Basic Concepts: Elements, Atoms and Chemical Bonding; Fundamentals of Chemistry

1. Mendeleev's Periodic Table

Many chemists in the 19th century attempted to classify chemical elements, often without much success. Dmitri Ivanovich Mendeleev (1834–1907) proposed the most convincing classification, now known as the Periodic Table of the Elements. This classification is still used today, and we are going to (re)discover it.



Each box corresponds to one element: H for hydrogen, He for helium, and so on.

What is the principle behind this classification?

In Mendeleev’s original table, the elements were arranged in order of increasing atomic mass, and the elements in each column had similar chemical properties. In the modern periodic table, the elements are arranged in order of increasing atomic number. To satisfy these conditions, Mendeleev intentionally left some gaps in his table. In a stroke of genius, he predicted that each empty space corresponded to an element that had not yet been discovered. He was right: over time, the gaps were filled as new elements were discovered. These elements are made up of atoms, the basic units of matter. An atom consists of a central nucleus made of protons (positively charged) and neutrons (no charge), surrounded by electrons (negatively charged) that move around the nucleus.

Almost all the mass of the atom is concentrated in the nucleus, since electrons have a negligible mass. Therefore, the atomic mass of an atom is essentially determined by the mass of its nucleus. The simplified structure of an atom helps illustrate these ideas. Mendeleev’s table makes it possible to highlight and understand many physical principles.

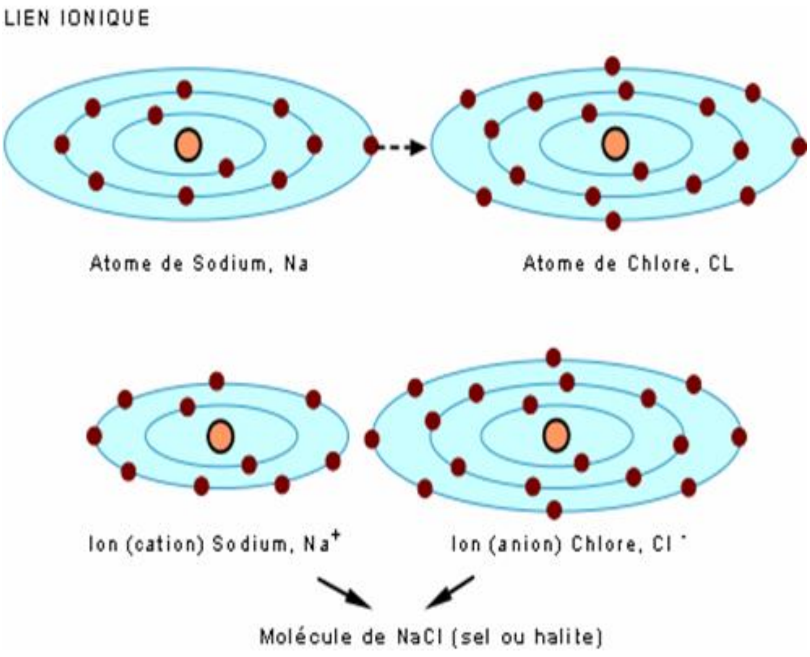
Atomic Number: The number shown at the top of each column corresponds to the atomic number of the element concerned; that is, the number of protons in its nucleus. Since atoms are electrically neutral, this is also the number of electrons in the atom (electrons carry a negative charge, while protons carry a positive charge). Therefore, the elements are arranged in order of increasing atomic number, which makes sense, since most of an atom’s mass is located in its nucleus.

Electronic Structure: If we observe the table, each column is labeled with Roman numerals, from I to VIII. This actually represents the number of electrons in the outer shell of the element. Since elements in the same column have similar chemical properties, we can conclude that the number of electrons in the outer shell of an atom is responsible for its chemical properties. In addition, the row of the table indicates which electron shell we are referring to. The shells have specific names: the first shell is called K, the second L, the third M, and so on in alphabetical order.

Chemical Bonding If we move up one level in the organization of matter, we find molecules, which are formed from groups of atoms bonded together by two main types of bonds: ionic bonds and covalent bonds.

→ **Ionic Bond**: An ionic bond is formed through the transfer of one or more electrons from one atom to another.

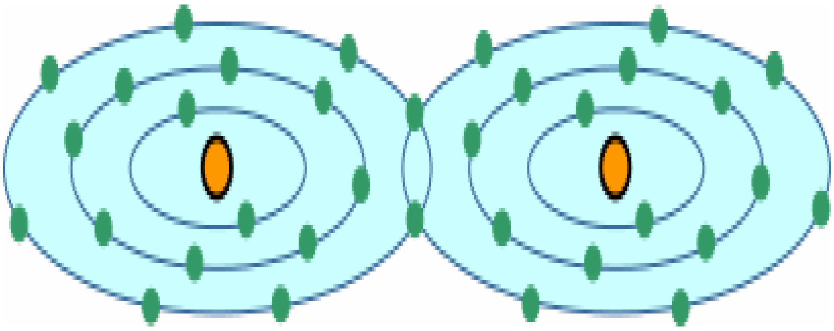
For example, in sodium chloride (NaCl, common salt), one electron is transferred from sodium (Na) to chlorine (Cl). This transfer produces a stable compound, sodium chloride (NaCl), in which the atoms exist in their ionic forms (Na^+ and Cl^- ions).



→ **Covalent Bond** A covalent bond is formed when atoms share electrons.

This is the case, for example, with hydrogen gas (H_2), oxygen gas (O_2), and chlorine gas (Cl_2).

LIEN COVALENT



Molécule de Chlore (Cl_2)

Molarity of a Solution: The molarity of a solution is the concentration of a given substance expressed in moles of solute per liter of solution.

Example calculation: Calculate the molarity of an aqueous solution containing 585 mg of NaCl per liter of water. (Na: atomic mass = 23 g/mol; Cl: atomic mass = 35.5 g/mol)

The mass concentration of the NaCl solution is 585 mg/L (or 0.585 g/L).
The molar mass of NaCl is 58.5 g/mol (23 + 35.5).
The molar concentration is therefore: 0.585 ÷ 58.5 = 0.01 mol/L = **10 mM**.

Question: What is the difference between molarity and molality?

Molarity (M) is the number of moles of solute per liter of solution (mol/L). It depends on the total volume of the solution and therefore varies with temperature (since volume changes with temperature).

Molality (m) is the number of moles of solute per kilogram of solvent (mol/kg). It depends on mass, not volume, and therefore does not change with temperature.

In short: Molarity → based on volume of solution, Molality → based on mass of solvent

Answer: Molarity is the concentration expressed in moles per liter of solution. A solution that contains one mole per liter is called a molar solution.

Molality is the concentration expressed in moles per kilogram of water. A solution that contains one mole per kilogram of water is called a molal solution.

2. Water Quality Data Processing

Introduction

Water quality data processing in hydrogeochemistry and in the context of water pollution involves collecting, analyzing, interpreting, and utilizing information on the chemical composition of natural or contaminated waters. The main steps and methods used are as follows:

1. Sample Collection

Field sampling: Groundwater, surface water, wastewater, etc.

Preservation: Use of appropriate containers and addition of preservatives (acids, cooling, etc.). See (Chapter I).

2. Analysis of Physico-Chemical Parameters

In situ measurements: Temperature, pH, electrical conductivity, dissolved oxygen, redox potential (see Chapter 1).

Laboratory analyses:

- *Major ions*: Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}, HCO_3^-.
- *Trace elements and heavy metals*: Pb, Cd, Zn, As, etc.
- *Specific pollutants*: Nitrates, phosphates, pesticides, hydrocarbons, etc.

3. Data Processing and Validation

Data quality control: Ionic balance, electrical conductivity consistency, compliance with standards, etc.

Validation: Detection of outliers and possible corrections.

4. Statistical Analysis and Interpretation

Descriptive statistics: Means, medians, standard deviations.

Multivariate analyses: PCA (Principal Component Analysis), hierarchical clustering, correlations.

Geochemical diagrams: Piper, Stiff, Schoeller, PHREEQC to interpret water origin and geochemical processes.

5. Assessment of Water Pollution

Comparison with standards: WHO, EU, and national guidelines.

Water quality indices: WQI (Water Quality Index), etc.

Pollution assessment: Identification of sources (natural or anthropogenic) and evaluation of risks to human health and the environment.

IV.2.1.Objectives and Challenges of Water Quality Data Processing

1. Objectives

- *Ensure data reliability*: Verify the accuracy, consistency, and completeness of analytical results.
- *Assess water quality status*: Determine whether water is suitable for drinking, irrigation, industry, or ecosystem sustainability.
- *Identify geochemical processes*: Understand water–rock interactions, mineral dissolution/precipitation, ion exchange, redox reactions, etc.
- *Detect and quantify pollution*: Identify contamination sources and evaluate their intensity.
- *Support decision-making*: Provide scientific evidence for environmental management, remediation strategies, and policy development.
- *Monitor temporal and spatial trends*: Track changes in water quality over time and across different locations.

2. Challenges (Issues at Stake)

- *Data quality and uncertainty*: Analytical errors, sampling bias, and incomplete datasets.
- *Complexity of hydrogeochemical systems*: Multiple interacting physical, chemical, and biological processes.
- *Distinguishing natural vs. anthropogenic sources*: Differentiating geogenic contributions from human-induced pollution.
- *Regulatory compliance:* Meeting national and international water quality standards.
- *Environmental and health risks:* Protecting ecosystems and public health from contamination.
- *Data management:* Handling large datasets and ensuring proper storage, processing, and interpretation.

IV.2.2. Data Preparation, Organization, and Validation

Preparation, organization, and validation of data are essential steps to ensure the reliability and usefulness of water quality analyses. These steps include:

1. Data Preparation

Collection and centralization: Gather all data from field measurements and laboratory analyses.

Standardization: Ensure uniform units (mg/L, meq/L, °C, pH, etc.), consistent parameter names, and sampling dates.

Removal of duplicates and obvious errors: Check for inconsistent or missing values.

2. Data Organization

Database structuring: Organize data by site, date, water type, or measured parameter.
Coding and classification: Assign consistent codes to stations, samples, and parameters.
Documentation: Maintain records of sampling methods, analytical procedures, and storage conditions.

3.Data Validation

Quality control: Verify ionic balance, consistency with electrical conductivity, and compliance with analytical standards.
Outlier detection: Identify and justify atypical results.
Possible corrections: Apply necessary adjustments (e.g., charge balance correction, estimated alkalinity).
Final verification: Ensure the database is complete, consistent, and ready for statistical analysis and geochemical interpretation.

These steps ensure that conclusions drawn from water quality data are accurate, reliable, and scientifically sound.

IV.2.3. Statistical Processing of Water Quality Data

1. Descriptive Statistics

Descriptive statistics constitute the first step in water quality data analysis. They allow characterization of the distribution and variability of measured parameters:

- **Central tendency:** Mean and median.
- **Range of variation:** Minimum and maximum values.
- **Heterogeneity:** Standard deviation and coefficient of variation.

These indicators provide an initial overview of spatial and temporal variations in chemical and physico-chemical parameters of water.

2 Multivariate Statistical Analyses

2.1 Principal Component Analysis (PCA)

PCA is used to reduce the dimensionality of datasets and identify the dominant parameters controlling water chemistry. It helps distinguish natural processes (rock weathering, mineral dissolution) from anthropogenic influences (agriculture, urban discharges).

2.2 Cluster Analysis (CA)

Hierarchical classification methods group samples into homogeneous classes, facilitating the identification of areas with similar hydrochemical characteristics.

2.3 Statistical Correlations

Correlation matrices highlight relationships between chemical parameters and can provide insights into pollutant sources and transfer mechanisms.

IV.2.4. Geochemical Processing of Data

4.1 Hydrochemical Diagrams

Hydrochemical diagrams are essential tools for visualizing and interpreting water composition:

- **Piper diagram:** Identification of hydrochemical facies.
- **Schoeller-Berkaloff diagram:** Comparison of ionic profiles.
- **Gibbs diagram:** Identification of dominant controlling mechanisms (lithological control, evaporation, precipitation).
- **Equilibrium diagrams:** Analysis of chemical species relationships.

4.2 Chemical Speciation

Chemical speciation determines the forms in which elements are present in water: free ions, complexes, or precipitated species. It is strongly influenced by pH, redox potential, temperature, and salinity. Speciation is particularly important for heavy metals because it controls their mobility, bioavailability, and toxicity.

4.3 Saturation Indices

Saturation indices evaluate the equilibrium state between water and mineral phases. They provide information on dissolution or precipitation processes for minerals such as calcite, gypsum, and halite.

IV.2. 5. Water Quality and Pollution Indices

5.1. Global Water Quality Indices:

Indices such as WQI synthesize multiple parameters into a single value, facilitating communication of results to decision-makers and water managers (refer to chapter III).

5.2 Pollution Indices

Geoaccumulation Index (Igeo): Assesses the intensity of metal contamination by comparing measured concentrations with geochemical background levels, using a correction factor of 1.5 to account for natural variability (Müller, 1979).

$$I\text{geox} = log2\frac{Cn}{1{,}5\ Bgx}$$

In both indices $\mathbf{C_n}$ is the measured concentration of the metal **"n"**, within the sediment or size fraction. $\mathbf{B_n}$ represents the background concentration of the metal **"n"**, found either in the literature, or measured in texturally-equivalent uncontaminated sediments or size fractions. The factor 1.5 is introduced into the expression, to account for variations in background values due to lithogenic effects. The index of geoaccumulation consists of seven grades, or classes: from unpolluted ($\mathbf{I_{geo}} < 1$); very low and low polluted ($1 < \mathbf{I_{geo}} < 3$); moderately polluted ($3 < \mathbf{I_{geo}} < 4$); highly polluted ($4 < \mathbf{I_{geo}} < 5$); to very highly polluted ($5 < \mathbf{I_{geo}} < 6$). The highest-grade (6) indicates a 100-fold enrichment, above the background data. The $\mathbf{I_{geo}}$ was used originally for metal concentrations in the < 2 µm fractions, together with background global standard shale values. However, several researchers have extended the above expression, to metal concentrations in < 63 µm fraction and to regional background values. In Table 12.3 are shown the I_{geo} values for several metals, using the < 63 µm fraction and the background shale average data. The values for Oria, Deba, and Pasaia estuaries (Gipuzkoa, N Spain) have been calculated taking into account data from the study of Arambarri *et al.* (2003), together with the average shale data shown in Table 12.1. The superficial sediments of these localities provided high $\mathbf{I_{geo}}$ values, especially for zinc, lead and copper. These values are comparable to others found in polluted areas (Salomons and Förstner, 1984; Ruiz, 2001). Results obtained from international intercomparison exercises recommend the use of a two-tiered normalisation approach, including wet sieving (< 63 µm); this is followed by an additional geochemical co-factor normalization.

IV.2.6. Spatio-Temporal Analysis of Data: Spatio-temporal analysis helps understand how water quality evolves over time and space:

- Seasonal variations linked to hydrological regimes.
- Impacts of human activities.
- Effects of climate change.

Integration of data into a Geographic Information System (GIS) allows detailed mapping of risk zones and supports monitoring and management decisions.

IV.2.7. Environmental Interpretation and Management

The final interpretation phase aims to:

- Identify pollution sources (natural or anthropogenic).
- Assess impacts on ecosystems and human health.
- Formulate recommendations for the management, protection, and remediation of water resources.

3. Introduction to Simulation Software: Diagrams & PHREEQC for Geochemical Modeling

Introduction

Simulation software is an essential tool for interpreting and predicting water chemistry. It allows visualization, modeling, and analysis of hydrochemical processes.

- **Hydrochemical Diagrams:** Tools such as Piper, Stiff, Schoeller, and Gibbs diagrams help visualize water composition, identify hydrochemical facies, and infer dominant geochemical processes.
- **PHREEQC Software:** PHREEQC is a widely used geochemical modeling program that enables:
    - Calculation of chemical speciation and saturation indices.
    - Simulation of mineral dissolution and precipitation.
    - Modeling of redox reactions and contaminant mobility.
    - Prediction of water–rock interactions under varying environmental conditions.

These tools provide a quantitative and visual framework for understanding the geochemistry of natural and polluted waters, supporting both research and environmental management.

IV.3.1. DIAGRAMMES Software

The software “DIAGRAMMES” (developed by the University of Avignon) is the standard tool in hydrogeochemistry for visualizing water analyses through Piper, Schoeller, Stiff, and Wilcox diagrams directly from Excel files. It automatically validates the ionic charge or balance and calculates the theoretical conductivity to check analytical consistency. This makes it an essential tool for interpreting water facies and understanding the origins of mineralization.

1. Importance of Graphical Representations in Water Geochemistry

In water geochemistry, chemical analyses produce a large set of numerical data that can be difficult to interpret directly. Simply reading ionic concentrations does not always allow a clear identification of water origins or the geochemical processes controlling their composition.

Graphical representations, known as hydrochemical diagrams, are therefore a fundamental tool that allows:

- Visual synthesis of analytical data
- Classification of waters into hydrochemical facies
- Identification of dominant geochemical processes (rock dissolution, ion exchange, water mixing, salinization, pollution)
- Spatial and temporal comparison of water quality

In this context, the use of specialized software is essential to ensure the reliability and efficiency of data processing. The DIAGRAMMES and PHREEQC software are among the most widely used tools for this purpose.

2. General Overview of the DIAGRAMMES Software

2.1. Origin and Objectives

The DIAGRAMMES software was developed by Roland Simler, a hydrogeologist at the Hydrogeology Laboratory of the University of Avignon. It was designed to meet the needs of researchers, engineers, and students working on the classification and geochemical interpretation of natural and polluted waters. Its main objective is to facilitate the graphical representation of water chemical analyses based on major elements by automating the creation of classical hydrochemical diagrams.

2.2. Advantages of the DIAGRAMMES Software

The DIAGRAMMES software offers several advantages:

- Simplicity and ease of use
- Intuitive interface
- Automatic conversion of concentrations (mg/L → meq/L)
- Compatibility with Excel and text files
- A tool suitable for both teaching and research

3. Types of Hydrochemical Diagrams Available in the DIAGRAMMES Software

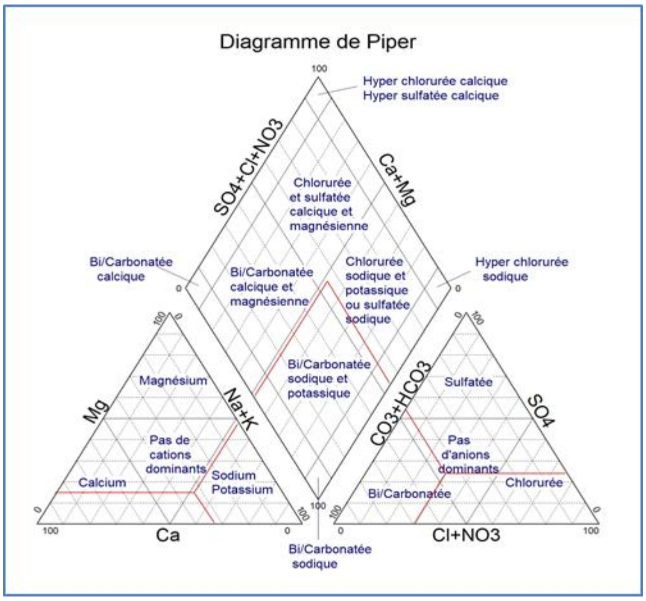
3.1. Piper Diagram

The Piper diagram is one of the most widely used tools in hydrogeology. It consists of two triangles (cations and anions) and a central diamond.

- The two triangles represent the relative proportion (%) of different cations (cationic facies) and anions (anionic facies) in the analyzed water.
- The central diamond synthesizes the overall water facies.

Figure No. X shows:

- **Top of the diamond:** Calcium–sulfate facies (e.g., gypsum) or calcium–chloride or magnesium–chloride facies
- **Base of the diamond:** Sodium–bicarbonate facies
- **Right tip of the diamond:** Sodium–chloride facies
- **Left tip of the diamond:** Calcium–bicarbonate or magnesium–bicarbonate facies



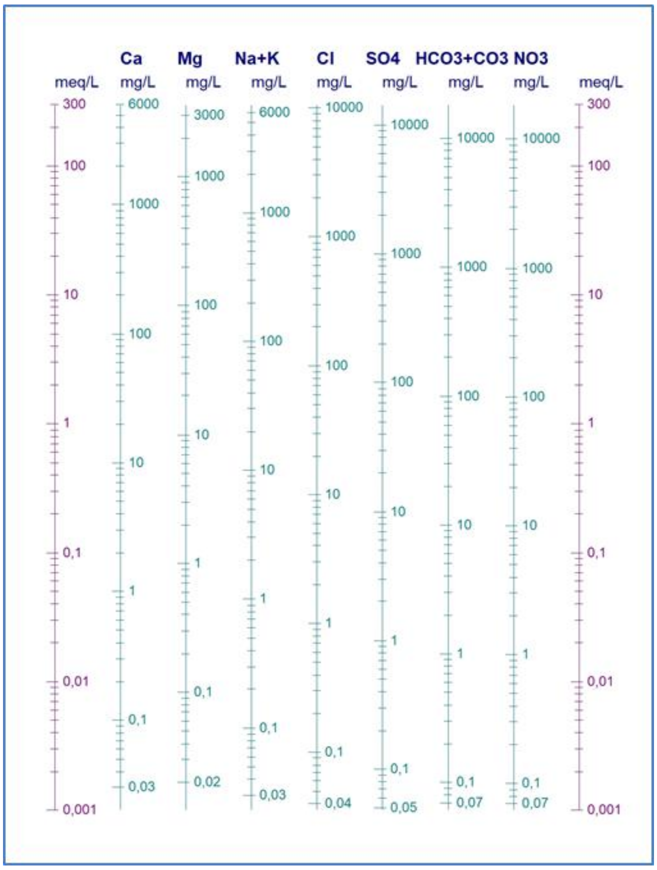
Usefulness of the Piper Diagram

1. **Hydrochemical Classification of Waters**
   - Allows quick classification of waters according to their chemical type, e.g., Ca-HCO_3, Mg-HCO_3, Na-Cl, Na-SO_4, etc.
   - **Advantage:** Multiple samples can be easily compared, highlighting the dominant types of surface or groundwater.
2. **Visualization of Ionic Composition**
   - Immediately shows whether the water is calcium-, magnesium-, sodium-, or bicarbonate-dominated, or rich in chlorides/sulfates.
3. **Detection of Geochemical Trends**
   - Helps identify hydrochemical processes:
     - Rock dissolution (limestones, dolomites, evaporites)
     - Cation exchange in soils or aquifers
     - Influence of human activities (industrial, agricultural, urban pollution)
   - **Example:** A shift of points toward the Na-Cl facies in the central diamond may indicate salinization or anthropogenic contamination.
4. **Comparison and Temporal Monitoring**
   - Enables comparison of multiple samples over time or space:
     - Different wells or surface water sources, even soil samples.
     - Seasonal evolution of water composition.
   - Useful for monitoring the impact of pollution or agricultural practices.
5. **Preparation for Complementary Analyses**
   - Serves as a basis for:
     - Dendrograms / Hierarchical classification → grouping similar samples
     - Binary graphs → presence/absence of ions
     - Durov diagram → detection of anomalies or geochemical processes
6. **Educational Advantage**
   - The Piper diagram synthesizes complex data visually, making it an effective teaching tool.

3.2. Schoeller and Stiff Diagrams

The Schoeller diagram is a graphical representation based on a series of vertical axes, each scaled logarithmically and corresponding to a specific ion or group of ions.

The concentrations (in mg/L) are plotted on the axes, and the points are connected by straight lines. The resulting shape of the graph allows visualization of the water's hydrochemical facies**.**



Reading and Interpretation

The Schoeller–Berkaloff diagram allows detailed and comparative hydrochemical analysis:

1. **Identification of Chemical Facies**
    - High lines in **Ca^{2+}** and **HCO_3^-** indicate a calcium–bicarbonate facies.
    - Dominance of **$Na^+ + K^+$** and **Cl^-** indicates a sodium–chloride facies.
    - High **SO_4^{2-}** values characterize waters influenced by evaporite formations.
2. **Comparison Between Samples**
    - Parallel lines suggest a common origin or similar processes.
    - Crossing lines indicate chemical evolution, water mixing, or anthropogenic inputs.
3. **Geochemical Evolution**
    - A gradual increase in concentrations across multiple samples indicates mineral enrichment.

    - A targeted change in a specific ion reveals a dominant process (dissolution, ion exchange, pollution).

Advantages of the Schoeller–Berkaloff Diagram

- Simultaneous comparison of multiple samples
- Quantitative analysis of concentration differences
- Rapid detection of chemical anomalies
- Effective tool for time series and hydrogeological transects

Role in Hydrochemical Analysis

The Schoeller–Berkaloff diagram is generally used:

- After quality control (ionic balance, consistency between EC and ions)
- Before or in complement to the Piper diagram
- In combination with the Stiff diagram to provide:
    - Individual representation (Stiff diagram)
    - Quantitative comparison (Schoeller–Berkaloff diagram)

It is thus a key tool for interpreting chemical evolution in waters and understanding dominant hydrogeochemical processes.

Typical Applications

- Study of spatial variability in groundwater
- Analysis of temporal changes in water quality
- Identification of areas with anthropogenic influence
- Comparison between natural and polluted waters

3.3. Stiff Diagram: provides a concise graphical representation of each water sample, allowing rapid comparison of chemical facies. It is a widely used hydrogeochemical tool to visually summarize the ionic composition of a water sample, whether from groundwater, surface water, or polluted sources**.** Each sample is represented by a characteristic polygon, whose shape, size, and symmetry directly reflect the nature and proportion of the major dissolved ions.

Construction Principle

The diagram is based on the representation of major ion concentrations expressed in milliequivalents per liter (meq/L):

- **Cations:** Ca^{2+}, Mg^{2+}, $Na^+ + K^+$ (plotted on the left)

- **Anions:** $HCO_3^- + CO_3^{2-}$, SO_4^{2-}, Cl^- (plotted on the right)

Each ion is plotted horizontally relative to a central vertical axis. The points are then connected to form a polygon, which can be symmetric or asymmetric depending on the sample.

Reading and Interpretation

The Stiff diagram allows immediate hydrochemical interpretation:

1. **Identification of Chemical Facies**
    - Polygon dominated by Ca–HCO_3: recently recharged waters circulating through carbonate rocks.
    - Polygon dominated by Na–Cl: saline waters, evaporation effects, or marine intrusion.
    - Polygon dominated by Ca–SO_4: influence of evaporitic formations (gypsum, anhydrite).
2. **Comparison Between Samples**
    - Polygons with similar shapes indicate waters of the same origin or undergoing comparable geochemical processes.
    - Different shapes suggest chemical evolution, mixing, or anthropogenic influences.
3. **Spatial or Temporal Evolution**
    - Comparison of diagrams along a hydrogeological transect visualizes changes in facies.
    - Changes in polygon size reflect increases or decreases in total mineralization.

Advantages of the Stiff Diagram

- Individual and concise representation of each sample
- Rapid visual comparison of multiple samples
- Intuitive identification of chemical facies
- Highly suitable for hydrochemical mapping (overlaying diagrams on a map)

Role in Hydrochemical Analysis

The Stiff diagram is generally used after:

- Checking the ionic balance
- Ensuring consistency between EC and major ions

And before or in complement to:

- Piper diagram (classification)

- Schoeller diagram (quantitative comparison)

It thus serves as a powerful intermediate tool, bridging raw chemical analysis and hydrogeochemical interpretation.

3.4. Durov and Chadha Diagrams

These diagrams are used for more advanced hydrochemical interpretation, enabling:

- Identification of ion exchange processes
- Detection of water mixing
- Recognition of salinization or anthropogenic pollution processes

Durov Diagram is a hydrochemical analysis tool that combines water classification with the interpretation of geochemical processes responsible for water evolution. It is an extension of the Piper diagram, providing a dynamic view of hydrochemical transformations such as mineral dissolution, ion exchange, water mixing, or anthropogenic inputs.

This diagram is particularly suitable for studies of water pollution, geochemical evolution, and aquifer system diagnostics.

Construction Principle: The Durov diagram consists of four main components:

1. **Cation triangle:** Ca^{2+} – Mg^{2+} – Na^{+} + K^{+}
2. **Anion triangle:** HCO_3^{-} + CO_3^{2-} – SO_4^{2-} – Cl^{-}
3. **Central square projection** resulting from the combination of the two triangles
4. **Two additional axes** representing:
    - **pH**

- **Mineralization** (TDS or electrical conductivity)

Ion concentrations are expressed in percentage milliequivalents (%).

Reading and Interpretation: The central square is divided into nine zones corresponding to different water types and dominant processes:

- **Calcium–bicarbonate field** → Recent recharge waters, carbonate dissolution
- **Sodium–bicarbonate field** → Ca^{2+} ↔ Na^+ ion exchange
- **Sodium–chloride field** → Marine intrusion, evaporation, or saline pollution
- **Calcium–sulfate field** → Gypsum or anhydrite dissolution
- **Intermediate zones** → Water mixing, facies transitions

Including pH and TDS allows interpretation of the chemical evolution of water along its hydrogeological flow path.

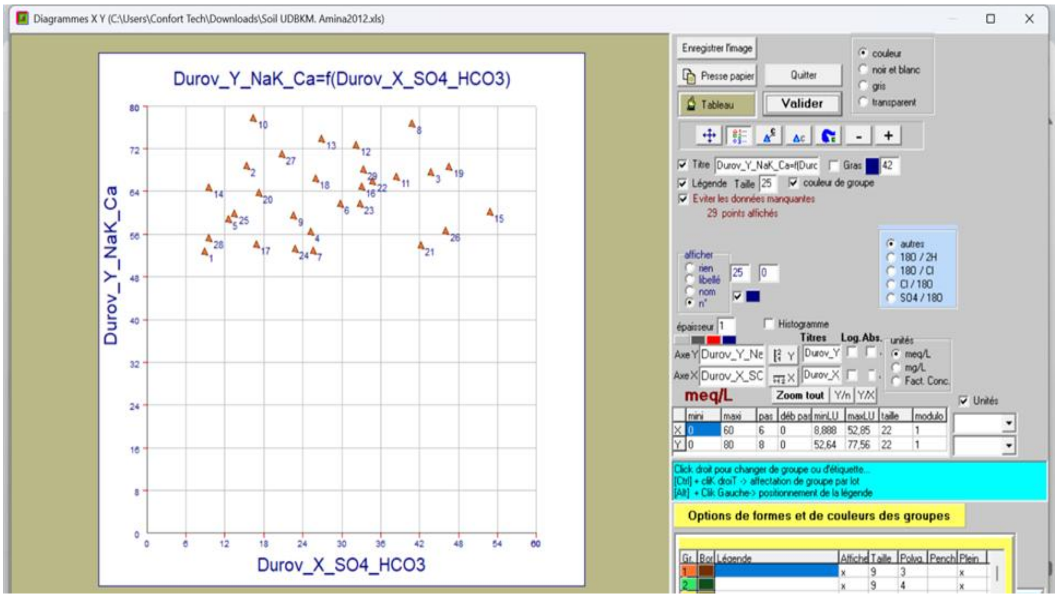
Specific Contributions of the Durov Diagram: Compared to other diagrams:

Links chemical composition with geochemical processes
Facilitates identification of: Ion exchange, Water mixing, Anthropogenic pollution, Progressive salinization
Advantages : Interpretation of hydrochemical processes**,** Integration of pH and mineralization**;** Highly relevant for pollution studies and aquifer evolution analysis
Limitations : More complex to read than Stiff or Schoeller diagrams**,** Less suitable for large numbers of samples**,** Strongly dependent on the analytical quality of the data

Role in Hydrochemical Analysis
The Durov diagram is generally used:

- After quality control (ionic balance, EC–ions consistency)
- In complement to the Piper diagram
- Together with Stiff and Schoeller–Berkaloff diagrams for a comprehensive interpretation

It thus serves as an advanced synthesis tool, bridging chemical classification and geochemical interpretation.



● couleur
○ noir et blanc
○ gris
○ transparent

☑ Titre Durov_Y_NaK_Ca=f(Durc ☐ Gras 42
☑ Légende Taille 25 ☑ couleur de groupe
☑ Eviter les données manquantes
29 points affichés

afficher
○ rien
○ libellé
○ nom
● n°
25 0
☑

● autres
○ 180 / 2H
○ 180 / Cl
○ Cl / 180
○ SO4 / 180

épaisseur 1 ☐ Histogramme

Titres Log. Abs.
Axe Y Durov_Y_Ne Durov_Y ☐ ☐
Axe X Durov_X_SC Durov_X ☐ ☐

unités
● meq/L
○ mg/L
○ Fact. Conc.

meq/L

☑ Unités

	mini	maxi	pas	déb pas	minLU	maxLU	taille	modulo
X	0	60	6	0	8,888	52,85	22	1
Y	0	80	8	0	52,64	77,56	22	1

Click droit pour changer de groupe ou d'étiquette...
[Ctrl] + cliK droiT -> affectation de groupe par lot
[Alt] + Clik Gauche-> positionnement de la légende

Gr.	Bor	Légende	Affiche	Taille	Polyg.	Pench	Plein
1			x	9	3		x
2			x	9	4		x

This Durov diagram, generated by the DIAGRAMMES software, classifies water samples based on cations (Ca^{2+}, Mg^{2+}, $Na^{+}+K^{+}$ in %) and anions (Cl^{-}, SO_4^{2-}, HCO_3^{-} in %) expressed in meq/L, revealing mixed hydrochemical facies.

- **Cation zone:** Ca–Mg dominance (right side) → typical calcium–magnesium waters resulting from the weathering of carbonate rocks (limestones/dolomites).
- **Anion zone:** HCO_3–Cl–SO_4 (lower left) → indicates recent recharge with slight evaporation; no marine influence (Cl not dominant).
- **Clustering:** Homogeneous group suggests a common origin (single aquifer), with probable EC between 800–1500 µS/cm.

Typical Applications

- Studies of groundwater pollution
- Analysis of hydrochemical evolution along flow paths
- Diagnosis of salinization processes
- Identification of mixing zones and ion exchange

3.5. Chadha Diagram

The Chadha diagram is a graphical hydrochemical tool that allows simplified classification of natural waters while highlighting the dominant geochemical processes controlling ionic composition. It is a rectangular plot derived from the Piper diagram, designed for quick interpretation of chemical data and identification of mechanisms such as ion exchange, water mixing, salinization, and anthropogenic inputs**.** Within the DIAGRAMMES software, the

Chadha diagram is valued for its clarity, pedagogical readability, and efficiency in comparative studies involving multiple samples.

Construction Principle: The Chadha diagram is based on ionic difference calculations expressed in milliequivalents per liter (meq/L):

- **Horizontal axis (X – cations):** $(Ca^{2+} + Mg^{2+}) - (Na^{+} + K^{+})$
- **Vertical axis (Y – anions):** $(HCO_3^{-} + CO_3^{2-}) - (Cl^{-} + SO_4^{2-})$

These two parameters are plotted on a rectangular diagram divided into four quadrants, each representing a characteristic hydrochemical type.

Reading and Interpretation

The Chadha diagram distinguishes four main quadrants, corresponding to water facies and dominant processes:

1. **Quadrant I: Ca–Mg / HCO_3**
    - Calcium–magnesium bicarbonate waters
    - Recent recharge waters
    - Carbonate dissolution (calcite, dolomite)
2. **Quadrant II: Na–K / HCO_3**
    - Sodium–bicarbonate waters
    - Ion exchange ($Ca^{2+} \leftrightarrow Na^{+}$)
    - Progressive hydrochemical evolution in the aquifer
3. **Quadrant III: Na–K / Cl–SO_4**
    - Sodium–chloride and sodium–sulfate waters
    - Marine intrusion
    - Salinization via evaporation
    - Anthropogenic saline pollution (urban, agricultural, industrial)
4. **Quadrant IV: Ca–Mg / Cl–SO_4**
    - Calcium–chloride and calcium–sulfate waters
    - Gypsum and anhydrite dissolution
    - Influence of evaporitic formations

Points near the axes often indicate: Water mixing, Hydrochemical transitions, Evolving systems

Specific Contributions of the Chadha Diagram

Compared to traditional triangular diagrams:

- Provides direct and rapid reading of chemical facies
- Clearly highlights:
    - Ion exchange
    - Salinization processes
    - Water mixing
    - Anthropogenic inputs
- Particularly suitable for comparison of multiple samples

Within DIAGRAMMES software, the Chadha diagram is often used as a complementary synthesis tool alongside Piper and Durov diagrams.

Advantages

- Simple and clear representation
- Rapid interpretation of chemical facies
- Effective identification of salinization processes
- Well-suited for regional and comparative studies

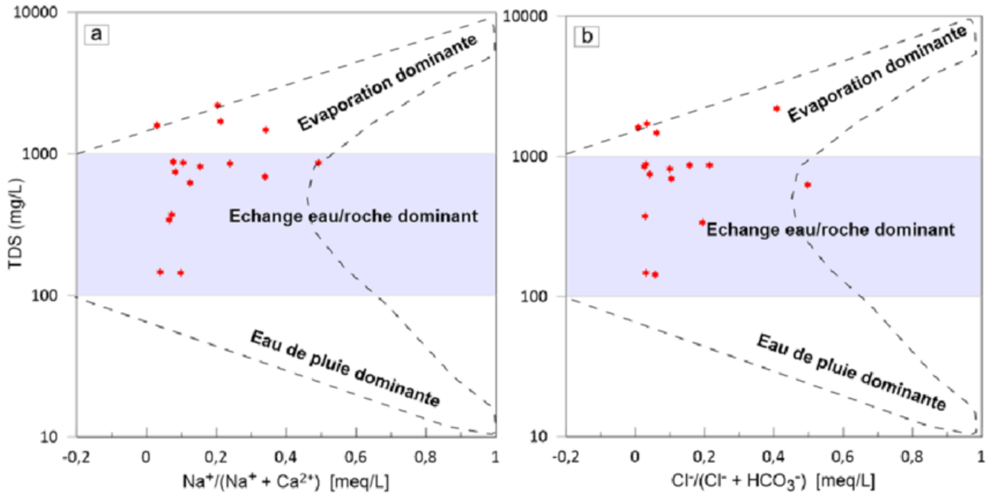
Role in Hydrochemical Analysis

The Chadha diagram is used after analytical quality control (ionic balance, EC–ions consistency) as a synthetic classification tool, complementing:

- Piper diagram (detailed classification)
- Durov diagram (advanced interpretation)
- Stiff and Schoeller–Berkaloff diagrams

It is thus a powerful pedagogical and analytical tool, linking hydrochemical classification to the interpretation of dominant processes, particularly in studies of water pollution and aquifer evolution.

3.6.Gibbs Diagram

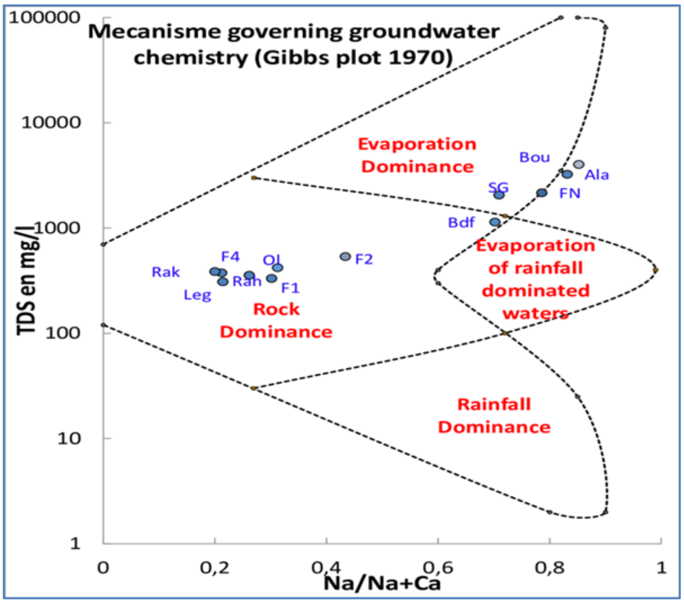


Gibbs Diagram showing the main processes controlling groundwater mineralization:

a) **TDS vs Na^+ / (Na^+ + Ca^{2+}) diagram**, used to identify the influence of rock weathering, evaporation, and precipitation on cation composition.

b) **TDS vs Cl^- / (Cl^- + HCO_3^-) diagram**, used to evaluate the relative contribution of evaporation, rock interaction, and atmospheric inputs on anion composition.

These diagrams help distinguish whether groundwater chemistry is primarily controlled by precipitation dominance, rock dominance, or evaporation dominance.



IV.3.2. Input Data and Quality Control

2.1. Required Parameters: The software primarily uses major ions:

Cations: Ca^{2+}, Mg^{2+}, Na^+, K^+

Anions: HCO_3^-, CO_3^{2-}, SO_4^{2-}, Cl^-

Data are generally expressed in mg/L.

2.2. Analytical Consistency Check

Before using the software, it is essential to verify:

- Ionic balance (electrical balance error)
- Consistency between electrical conductivity and the sum of dissolved ions
- Reliability of field measurements (pH, EC, temperature)

2.3. Practical Steps

1. Import data into Diagrammes
2. Automatic conversion to meq/L
3. Select the diagram type (Piper, Schoeller, etc.)
4. Generate the graphical plot
5. Analyze the hydrochemical facies

2.4. Interpretation

In this example, the dominance of Na^+ and Cl^- ions indicates a sodium–chloride facies**,** which may reflect:

- Marine influence
- Salinization
- Anthropogenic pollution

Diagrammes is an essential tool in water geochemistry**.** It provides a clear and reliable graphical representation of chemical analyses, facilitating both hydrochemical classification and interpretation of geochemical processes**.** Its use is particularly well suited for university teaching and applied studies in hydrogeology and water pollution assessment**.**

3.7. Riverside and Wilcox Diagrams

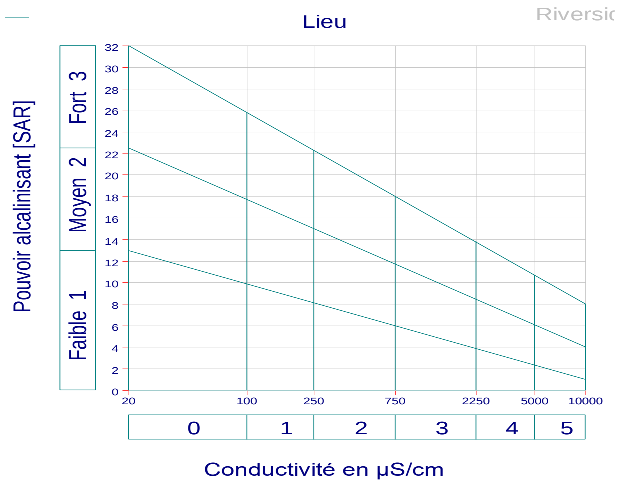
This classification, widely used for irrigation water assessment, was proposed by the Riverside Laboratory (Richard, 1954)**.** It is based on salinity and the risk of alkalinization of waters intended for irrigation.

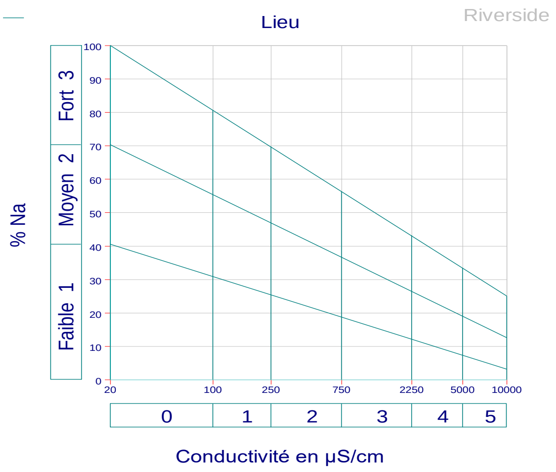
The method considers:

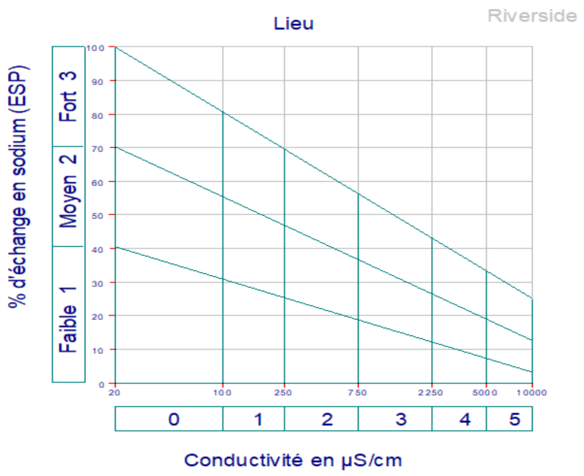
- **Electrical Conductivity (EC):** usually expressed in µS/cm or mS/cm, reflecting the water’s salinity**.**

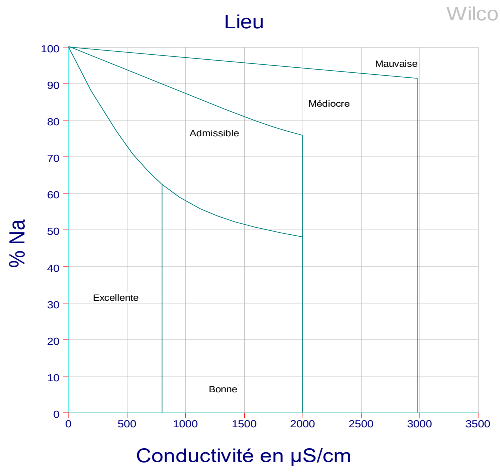
- **Sodium Adsorption Ratio (SAR):** indicating the risk of sodium accumulation and potential soil alkalinization.

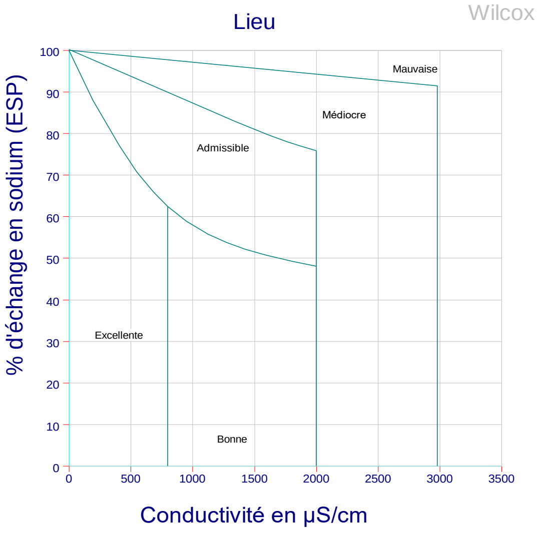
These diagrams help determine water suitability for irrigation, balancing both salinity hazard and sodium hazard, which are critical for maintaining soil structure and crop productivity.











Water Classification for Irrigation Use (U.S. Salinity Laboratory Classification – USSL)

Several classification systems have been proposed to assess water suitability for irrigation. Most of these are based on two key factors: salinity, represented by Electrical Conductivity (EC**)**, and the Sodium Adsorption Ratio (SAR)**.**

Classification of Irrigation Water Based on Electrical Conductivity

Irrigation waters can be classified according to their electrical conductivity at 25°C**,** as shown in the table below:

Class EC at 25°C (µS/cm)	Water Type / Salinity	Possible Use
< 250	Fresh water	Suitable for drinking and unrestricted irrigation
250 – 750	Slightly mineralized	Irrigation with low risk
750 – 2,000	Moderately mineralized	Irrigation with caution
2,000 – 3,000	Highly mineralized	Limited irrigation; not suitable for drinking
> 3,000	Very saline	Not recommended for irrigation or consumption

This classification helps farmers, engineers, and water managers evaluate the potential risks of salinity in irrigation practices. Here’s an academic English translation of your text, keeping it precise and suitable for a Master’s level course in Bioclimatology or Soil & Water Science:

Water Classification According to Richards’ Method

The Richards classification was proposed by Lorenzo A. Richards at the USDA Riverside, California, in 1954. It is widely used and provides a simple and practical way to characterize irrigation water. However, it cannot directly estimate the risk of soil salinization or sodicity**.**

Sodium Adsorption Ratio (SAR)

The Sodium Adsorption Ratio (SAR)**,** introduced by Richards (1954), is calculated as:

$$SAR = \frac{\mathrm{Na}+}{\sqrt{(Ca2 + Mg2+)}/2}$$

where the concentrations are expressed in mmol/L. The SAR evaluates the potential alkalinization risk of soils when irrigated with a given water. According to SAR, waters are classified from S1 to S4 based on increasing sodicity risk (all ions expressed in meq/L).

Exchangeable Sodium Percentage (ESP)

The salinization and sodicity risks of soils are typically assessed using Electrical Conductivity (EC) and SAR. The US Salinity Laboratory at Riverside emphasized the Exchangeable Sodium Percentage (ESP) as a key parameter. Since measuring ESP directly is difficult, SAR was introduced as an indirect estimator of ESP (Suarez, 1981). ESP is defined as:

$$ESP = 100 \times \frac{(\mathrm{Na}^{+})\mathrm{Echangeable}}{\mathrm{CEC}}$$

Where (Na+exchangeable) is the amount of exchangeable sodium and CEC is the cation exchange capacity. Direct measurement of ESP can be challenging, especially in saline soils, due to difficulties in separating dissolved salts from exchangeable ions. Consequently, SAR is often used as a proxy for ESP.

The USSL proposed a statistical correlation between SAR and ESP**:**

$$ESP = \frac{0.01475 \times \mathrm{SAR} - 0.0126}{1 + (0.01475 \times SAR - 0.0126)}$$

While measured ESP generally aligns with estimated ESP, discrepancies exist depending on soil type. For example, Durant (1958) observed in Algeria that errors exceeded 100% in 40% of cases and sometimes reached 200%. In Australian red soils, the relation was found to be:

$$\mathrm{ESP} = 1\,.95 \times \mathrm{SAR} + 1.84 \; (R\,2 = 0\,,82.\; N = 138).$$

These results indicate that the relationship is largely empirical and region-specific. According to Richards (1954), a soil is considered sodic when ESP exceeds 15%, though studies suggest structural degradation can occur at ESP values between 5–6% (McIntyre, 1979; Sumner, 1993; Shainberg, 1984; Shainberg & Singer, 1990).

Limitations of SAR

The SAR assumes calcium and magnesium have the same effect, while potassium is neglected. However, studies by Quirk & Schofield (1955) demonstrated that:

- Magnesium behaves differently from calcium, having an intermediate effect between calcium and sodium.
- Threshold concentrations for Mg are about three times higher than for Ca, indicating that Mg is more dispersive and affects soil structure differently.

- These effects were confirmed for common clays such as smectites, kaolinites, illites, and vermiculites.
- Replacement of Ca by Mg reduces structural stability of aggregates.
- Higher exchangeable Mg decreases hydraulic conductivity in vertisols.

The dispersion of clays is influenced not only by sodium but also by magnesium, showing specific ionic effects. Experiments with mono- and divalent chloride solutions (Na, K, Ca, Mg) show that the threshold concentration for permeability reduction decreases in the order: $Na^+ > K^+ > Mg^{2+} > Ca^{2+}$.

Studies of Na-K-Ca-Mg poly-electrolyte solutions also show potassium has an intermediate effect between Na and Mg. Additionally, in mixed $NaCl$-$CaCl_2$ solutions, the threshold concentrations for divalent ions were similar to those in homogeneous divalent solutions, while ESP remained highly variable. Threshold concentrations do not correspond to a fixed ionic strength value.

Table 2: Threshold concentrations for homo-ionic solutions (Quirk and Schofield, 1955)

Salts	Threshold Concentration (mol/L)	pH	Ionic Strength I (mol/L)
NaCl	2.5×10^{-1}	5.2	2.5×10^{-1}
KCl	6.7×10^{-2}	5.4	6.7×10^{-2}
$MgCl_2$	1×10^{-3}	5.4	3×10^{-3}
$CaCl_2$	3×10^{-4}	5.4	9×10^{-4}

The key concept is thus the calcium concentration threshold, which is much simpler to understand than SAR. For different values of the ESP (Exchangeable Sodium Percentage), the hydraulic conductivity varies, and to avoid reaching the critical threshold at which it drops significantly, it is sufficient to maintain the calcium concentration above a constant value of 2.5×10^{-4} mol/L, regardless of the sodium concentration.

According to Barbiéro et al. (2004b), the SAR concept introduced by Richards (1954) presents two main problems:

a) The assessment of sodicity risk using SAR was established empirically based primarily on data from North America, where irrigation waters typically evolve under saline conditions due to evaporation. In general, these waters exhibit negative residual carbonate alkalinity (RA_calcite = Carbonate Alkalinity − Ca < 0), and the sodicity risk is practically zero in this case. However, sodicity risk is present in areas where irrigation waters have positive residual carbonate alkalinity (RA_calcite > 0), such as in the Niger region. Therefore, in such cases, using the SAR concept underestimates the actual sodicity risk, as observed for irrigation water in the Niger Valley in Mali and in Niger.

b) The assessment of sodicity risk using SAR provides a static view of the problem and does not account for changes in water chemistry due to concentration after evaporation. This is illustrated in Figure 3, where the evolution of SAR and electrical conductivity (EC) of three types of water during a pan evaporation experiment are plotted. The data were collected by Vallès (1987) in Tunisia, Gonzalez Barrios (1992) in Mexico, and Barbiéro (1995) in Niger. All three irrigation waters present the same sodicity risk to the soil, but they evolve in three different ways. Consequently, this experiment highlights the limitations of the SAR and EC concepts.

Table I.2: Classification of Irrigation Water Based on SAR (Richards, 1954)

SAR Class	SAR Range (meq/L)	Sodium Hazard	Implications for Irrigation
S1	0 – 10	Low	Safe for irrigation, minimal risk of soil sodicity
S2	10 – 18	Medium	Moderate sodicity risk; may require management practices
S3	18 – 26	High	High sodicity risk; careful management required to avoid soil structure degradation
S4	> 26	Very High	Very high sodicity risk; not suitable for most crops without treatment or amendments

This classification evaluates the alkalinization risk of soils from irrigation water by using the Sodium Adsorption Ratio (SAR), with higher SAR values indicating a greater likelihood of sodic soils.

IV.3.2. Phase Diagrams in Water Geochemistry

In water geochemistry, unary, binary, and ternary diagrams are essential tools for visualizing phase equilibria (solid–liquid–gas) and chemical compositions in aqueous systems. They help understand how water interacts with different salts and how these interactions influence crystallization, dissolution, and the chemical evolution of groundwater and seawater under varying temperature and pressure conditions.

1. Unary Diagrams (Single Component)

- **Principle**: These diagrams represent a single component, usually pure water (H_2O), showing its phases (solid, liquid, gas) as a function of temperature and pressure.
- **Educational Use**: They allow identification of conditions under which water freezes, boils, or remains liquid.

- **Example**: Water phase diagram showing the coexistence of solid, liquid, and vapor phases.

2. *Binary Diagrams (Two Components)*

- **Principle**: They represent two components, for example H_2O + NaCl, with composition (mole fraction) on the x-axis and temperature on the y-axis. These diagrams show regions where solid and liquid phases coexist and where salts crystallize.
- **Educational Use**: Useful for understanding fractional crystallization, brine formation, and eutectic points (composition and temperature where a solid–liquid mixture is stable).
- **Example**: H_2O–NaCl diagram showing the temperature at which halite precipitates during evaporation.

3. *Ternary Diagrams (Three Components)*

- **Principle**: These diagrams represent three components, e.g., H_2O–NaCl–Na_2SO_4, in an equilateral triangle where each vertex represents 100% of one component. Triliner coordinates indicate the exact composition of the mixture.
- **Educational Use**: They allow modeling of complex aqueous systems, visualizing precipitation zones for different salts, and determining isotherms (lines of constant temperature).
- **Key Examples**:
  - Solubility curves: define the limits of salt dissolution.
  - Ternary eutectic points: conditions where three solid phases and one liquid phase coexist.

4. *Applications in Water Geochemistry*

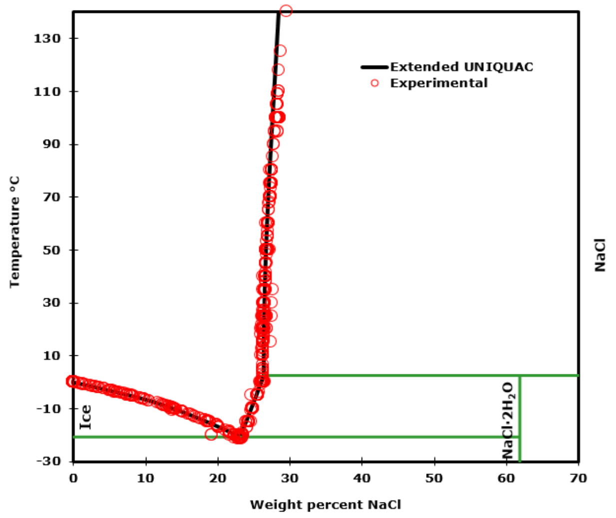
- **Groundwater**: Understanding mineral dissolution (e.g., gypsum, halite) and formation of salt deposits.
- **Oceanography**: Studying marine salt crystallization during evaporation or freezing.
- **Geothermal Studies**: Modeling interactions between hydrothermal fluids and rocks.

Unary, binary, and ternary diagrams are powerful graphical tools for clearly representing the thermodynamics of aqueous systems. They simplify the understanding of complex relationships between chemical components, temperature, and phase behavior, and are indispensable for interpreting and predicting the chemical evolution of natural and industrial waters.

xamples:

- Phase diagrams for binary salt solutions

The sodium chloride – water system



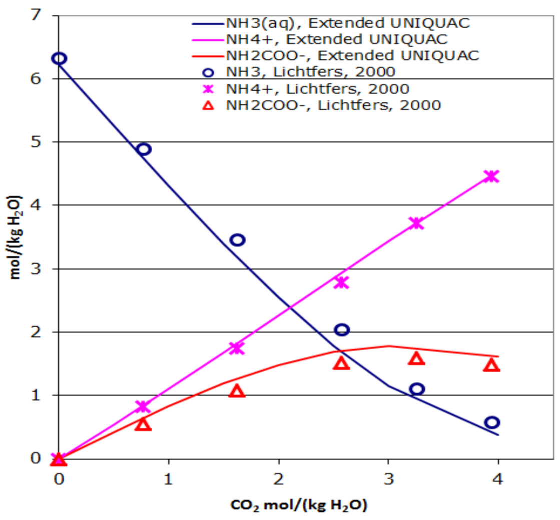
In the sodium chloride – water system, one eutectic point and one peritectic point is found. These points are shown in the phase diagram to the right.

The eutectic point is at -21°C.The peritectic point is at 0.1°C.

The eutectic point is the cryohydratic point, where ice and $NaCl \cdot 2H_2O$ (hydrohalite) both are in equilibrium with the same saturated solution. This point is at the lowest temperature where a liquid sodium chloride solution can exist.

The peritectic point at 0.1 °C marks the transition between hydrohalite and anhydrous sodium chloride as the stable solid phase in equilibrium with a saturated sodium chloride solution. If heated, solid hydrohalite will at this temperature be transformed into anhydrous sodium chloride (NaCl) and a saturated solution of sodium chloride.

- **Phase diagrams for ternary salt solutions:**



The carbon dioxide – ammonia – water system

The phase behavior and the thermal properties of this system is important because of its potential use for removing carbon dioxide from flue gas in post combustion carbon capture processes. One such process is the chilled ammonia process (Eli Gal, Ultra cleaning combustion gas including the removal of CO2, United States Patent US7641717B2.

In the chilled ammonia process, a slurry consisting of a liquid in equilibrium with solid ammonium bicarbonate (NH4HCO3) is produced in an absorber. The slurry releases CO2 at a relatively high pressure after being heated in a desorber. The liquid is cooled and led back to the absorber for a new cycle.

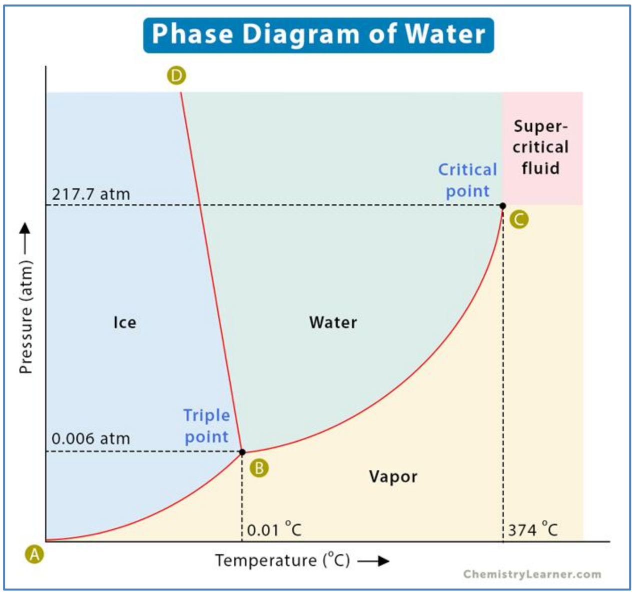
The CO_2, NH_3, H_2O system was modeled with the Extended UNIQUAC model. (Thomsen K and Rasmussen P, "Modeling of Vapor-liquid-solid equilibrium in gas-aqueous electrolyte systems", Chemical Engineering Science, 54(1999)1787-1802. An upgraded version of this model valid to higher temperatures and more accurate was published by Victor Darde, Willy J.M. van Well, Erling H. Stenby, Kaj Thomsen, "Modeling of carbon dioxide absorption by aqueous ammonia solutions using the Extended UNIQUAC model", Ind. Eng. Chem. Res., 49(2010), pp 12663–12674 (24), https://doi.org/10.1021/ie1009519.

The figures show the experimentally measured and the calculated speciation in a 6.226 molal NH_3 solution at 40°C. The amount of carbamate formed is indicated in the figure to the left with red triangles (experimental) and a red line (calculated with the Extended UNIQUAC model).

The amounts of NH_3, NH_4^+, and NH_2COO^- are shown in the figure to the left, the amounts of CO_2, CO_3^{2-}, and HCO_3^- in the same solution are shown to the right. The experimental data were measured by Ute Lichtfers and published in her PhD Dissertation, University of Kaiserslautern, Germany, 2000. The lines were calculated with the Extended UNIQUAC model. There is a good agreement between the experimental data and the corresponding calculated values. It is seen that the amount of carbamate apparently goes through a maximum at approximately 3 mol CO_2 per kg water. This maximum occurs at a pH about 9 and at a loading of 0.5 mol CO_2 per mol NH_3.

- Unary Diagrams example:

A phase diagram is a graphical way of representing a substance's pressure-volume relationship and identifying its various phases. This relationship is essential because it can predict in which direction phase transformation occurs as we proceed along a constant pressure or temperature line. A water phase diagram indicates what happens to water as it undergoes various phase change processes, as shown below.



IV.3.3. Introduction to Simulation Software: PHREEQC for Geochemical Modeling

PHREEQC is an aqueous geochemical modeling software developed by the U.S. Geological Survey USGS, widely used to simulate chemical equilibrium, ion speciation, mineral solubility, redox reactions, ion exchange, adsorption, and certain aspects of reactive transport in natural waters and solid–water–gas systems. it allows scientists, engineers, and researchers to simulate complex chemical processes such as mineral dissolution and precipitation, ion exchange, adsorption, redox reactions, and gas–water interactions.

The main objectives of PHREEQC are:

- ➔ To predict the chemical evolution of groundwater, surface water, and other aqueous systems.
- ➔ To simulate geochemical reactions under varying conditions of temperature, pressure, and water composition.
- ➔ To evaluate the effects of environmental changes, pollution, or remediation strategies on water chemistry.

What is PHREEQC used for?

- ➔ Calculation of solution speciation (dissolved forms, ionic complexes, organic complexes, etc.) based on raw chemical analysis.) and saturation indices with respect to minerals.
- ➔ Simulation of equilibrium between solution, minerals, and gases (saturation, precipitation/dissolution, saturation indices).

- ➔ Modeling of simple processes: water mixing, evaporation, titration, acid water neutralization, surface reactions (cation exchange, adsorption), and kinetic processes of mineral dissolution/formation.

2. Operating Principle

The software solves a system of equations based on:

- ➔ The law of mass action for chemical reactions (aqueous, solid, and gaseous phases) [water.usgs].
- ➔ Mass and charge balance laws, as well as activity coefficient models (e.g., Debye–Hückel, SIT, Pitzer) for concentrated solutions [geochemical-consulting+1].

Calculations are performed using input files (text scripts) that describe the water composition, minerals, gases, kinetic reactions, and conditions such as temperature (T), pressure (P), pH, and redox potential (Eh) [bordeaux-inp+1].

3. Databases and Syntax

PHREEQC relies on thermodynamic databases (e.g., *phreeqc.dat*, *minteq.v4*, *llnl.dat*) containing equilibrium constants and activity coefficient parameters [geochemical-consulting+1].

Its syntax is based on key blocks, such as:

- Solution: to define water composition
- Equilibrium phases: for minerals at equilibrium
- Gas-Phase: for gases
- Kinetics: for kinetic reactions
- Transport: for reactive transport [bordeaux-inp+1]

4. Relevance in Water Geochemistry

In water geochemistry, PHREEQC is used to:

- Interpret the chemical composition of groundwater and surface water
- Predict the mobility of pollutants (metals, nitrates, etc.) depending on pH, Eh, and present minerals
- Design treatment scenarios (precipitation, adsorption, reagent injection) [formations.univ-grenoble-alpes+1]

Basic Structure of the Software

- PHREEQC operates from a text-based input file, organized into keyword blocks such as SOLUTION, EQUILIBRIUM_PHASES, REACTION, SELECTED_OUTPUT, etc.
- The graphical interface (PHREEQC for Windows or PHREEQCI) provides tabs for Input, Output, Database, and sometimes Errors or Grid/Chart, making it easier to read results and modify databases.

PHREEQC uses a combination of thermodynamic databases, reaction modeling, and numerical solvers to provide accurate predictions of aqueous speciation, saturation indices, and chemical equilibria. It is particularly useful for hydrogeologists, environmental engineers, and researchers studying water–rock interactions, contamination processes, and geochemical cycles.

The software can handle both batch reactions (closed systems) and transport modeling (flowing systems), making it versatile for laboratory simulations, field data interpretation, and predictive studies. Its integration with data formats like Excel and text files further facilitates data analysis and visualization of geochemical results. In short, PHREEQC is an indispensable tool in modern hydrogeochemistry, enabling rigorous analysis and simulation of water chemistry under natural and anthropogenic influences. Here is a very simple tutorial for a first PHREEQC simulation: calculating water speciation (pH, ionic speciation, mineral saturation) from a given chemical composition.

1. Install PHREEQC (basic version)

Download the USGS version of PHREEQC (.exe for Windows or Linux binary) from the USGS website. Install it, then open the interface (or use a text editor to write the input file).

2. Objective of the first simulation

We will simulate a simple water, e.g., groundwater:

Initial pH = 7
Temperature = 25 °C
Composition: Na^+, Cl^-, Ca^{2+}, Mg^{2+}, HCO_3^-

The software will calculate:

Speciation (dissolved species: Na^+, $NaCl^0$, $CaCO_3^0$, etc.)
Final pH after equilibrium with atmospheric CO_2

Saturation indices (SI) for minerals such as calcite, dolomite

3. Example PHREEQC script (beginner)

Create a text file, e.g., `example1.pqi`, with the following content:

```
# Example 1: Speciation of a simple water
SOLUTION 1
    temp      25
    pH        7
    units     mg/L
    Na        100
    Cl        150
    Ca        50
    Mg        20
    Alkalinity 200 as HCO3

EQUILIBRIUM_PHASES 1
    CO2(g)     -3.5  10    # pCO2 ≈ 10^-3.5 atm (air)
    Calcite    0     0     # Calcite at equilibrium

SELECTED_OUTPUT
    -reset false
    -pH
    -pe
    -alkalinity
    -totals Na Cl Ca Mg
    -saturation_indices Calcite Dolomite

USER_PUNCH
    -headings pH SI_Calcite SI_Dolomite
    -start
    10 punch -la("H+")
    20 punch SI("Calcite")
    30 punch SI("Dolomite")

END
```

4. Quick explanation of the blocks

SOLUTION 1: defines the water composition (in mg/L here).

EQUILIBRIUM_PHASES 1:

`CO2(g) -3.5 10`	sets the partial pressure of atmospheric CO_2 (~$10^{-3.5}$ atm).
`Calcite 0 0`	allows calcite to reach equilibrium with the solution.

SELECTED_OUTPUT: chooses which quantities to display in the output file (pH, alkalinity, total concentrations, SI).

USER_PUNCH: creates a custom output line showing pH and saturation indices.

5. Running the simulation

1. Place `example1.pqi` in the PHREEQC folder.
2. In the interface, load the file or run it via command line:
    - **Windows**: `phreeqc.exe example1.pqi`

    - **Linux**: `phreeqc example1.pqi`
3. PHREEQC generates an output file (e.g., `phreeqc.out`) that can be opened with a text editor.

6. What you should see

In the output file, you will find:

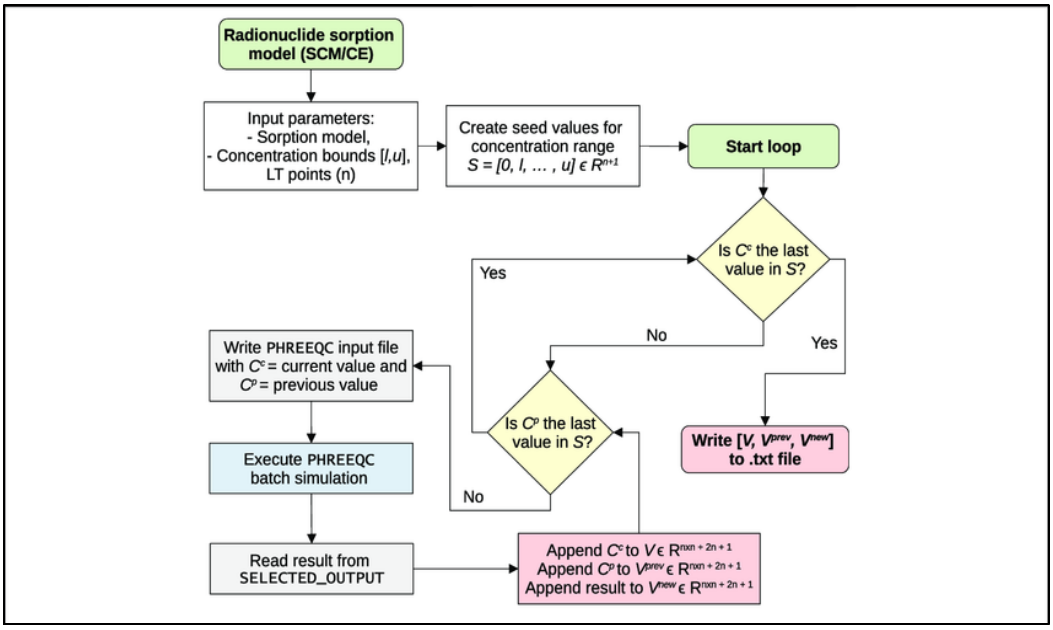
- The final pH after equilibrium with CO_2
- Total concentrations of Na, Cl, Ca, Mg
- Saturation indices for calcite and dolomite (SI > 0 = supersaturated, SI < 0 = undersaturated)

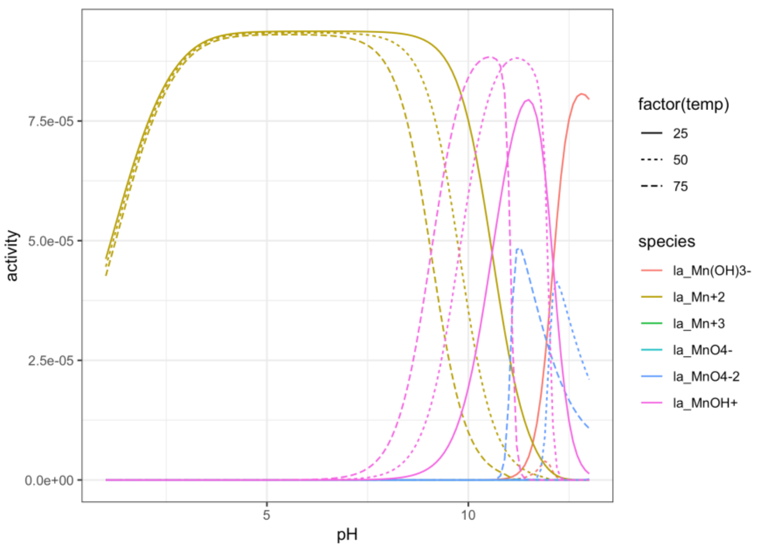
7. Next steps (Tutorial Step 2)

Once this first simulation is successful, you can try:

- Mixing two waters (MIX block)
- Titration (adding acid or base, REACTION block)
- Kinetic reactions (mineral dissolution/precipitation, KINETICS block)

Great! Here's a simple diagram illustrating the workflow for your first PHREEQC simulation:





Workflow Description:

- Define Water Composition → Input the concentrations of Na^+, Cl^-, Ca^{2+}, Mg^{2+}, HCO_3^- in the SOLUTION block.
- Set Mineral & Gas Equilibria → Specify minerals (Calcite) and gases (CO_2) in EQUILIBRIUM_PHASES.
- Select Output Parameters → Decide what to monitor (pH, SI, totals) in SELECTED_OUTPUT.
- Optional Custom Output → Use USER_PUNCH to create a tailored output table.
- Run Simulation → Execute the script in PHREEQC.
- Analyze Results → Check final pH, ion speciation, and saturation indices in the output file.

Chapter V: Case Studies

1. Diffuse pollution in an agricultural watershed
2. Urban and industrial contamination of aquifers
3. Effects of drought on pollutant concentrations

Introduction

In this chapter, we focus on the first of three practical case studies, while the second and third cases are proposed as exercises for students to apply their knowledge and test their analytical skills. Chapter V presents examples illustrating the complex interactions between human activities, natural processes, and water quality, highlighting how different sources of contamination, hydrogeochemical processes, and environmental conditions influence the chemical composition of surface and groundwater.

The first case study, which is discussed here, addresses diffuse pollution in agricultural watersheds, where fertilizers, pesticides, and soil erosion contribute to widespread nutrient and chemical loading. This example serves to guide students in understanding the principles of hydrogeochemical assessment and water quality analysis.

The second case examines urban and industrial contamination of aquifers, focusing on point-source pollutants, heavy metals, and organic contaminants resulting from industrial discharges and urban runoff. The third case investigates the effects of drought on pollutant concentrations, showing how reduced water flow, increased evaporation, and lower dilution capacity can exacerbate the levels of dissolved ions and pollutants in both surface and groundwater systems. These two cases are intended as student exercises to reinforce learning and encourage the practical application of hydrogeochemical methods.

Together, the three case studies demonstrate the practical use of hydrogeochemical analysis, water quality assessment, and modeling tools for understanding, monitoring, and managing water resources under various anthropogenic and natural pressures.

1. Diffuse pollution in an agricultural watershed

Abstract

The Songnen Plain in Northeast China is a global hotspot for soda saline-alkalization. This region suffers from severe water security challenges that limit agricultural productivity. Our assessment reveals severe irrigation hazards in the local saline-alkaline water. These waters show prevalent alkaline conditions with pH values ranging from 8.04 to 9.50. The dominant water type is NaHCO$_3$, withextreme sodicity levels. Importantly, 63.3% of water samples were classified as C4S4 (EC>2,250 µS cm^{-1}, SAR>26), indicating extreme hazard. These samples exceeded sodium hazard thresholds by 2.3-4.8 times. Hydrochemical analysis identified silicate weathering, cation exchange, and evaporative concentration as key processes driving water quality deterioration. Importantly, rice-crab co-culture systems, particularly with juvenile crabs, effectibvely transform these constraints into opportunities for sustainable agriculture. The juvenile crab system achieved comprehensive improvements, reducing SAR by 41.25%, alkalinity by 1.21 mmol/L., and sodicity (%Na$^+$=58.05), while increasing rice yields by 10.61% and total economic output by 84.51% compared to rice monoculture. A key finding was the consistent association between crab activity and concurrent RSC increases with sodium leaching, providing a new perspective on interpreting water quality indices in integrated systems. Our findings establish rice-juvenile crab co-culture as an effective nature-based solution that simultaneously addressed water security and agricultural productivity in soda saline-alkaline regions.

Key words

Saline-alkaline water, Rice-crab co-culture, Hydrochemical assessment, Songnen Plain, Sustainable agriculture

1. Introduction

The Songnen Plain, situated in northeastern China (121°21′-128°18′ E, 43°36′-49°26′ N), is a significant agricultural region that faces challenges due to saline-alkaline conditions, which adversely affect crop productiivity. This region—one of the world's three major chernozem regions— is a critical national base for grain production and animal husbandry[1]. However, this area has become a global hotspot for soda saline-alkalization. This is constrained by soil parent material, hydrological conditions, and unsustainable anthropogenic activities (e.g., overgrazing, irrigation without drainage). The majority of the region exhibits slight to moderate salinity levels, particularly in its central-western plains[2]. Despite implementing comprehensive remediation strategies-including hydraulic engineering, soil amendments, and cultivation of salt-tolerant crops-soil re-salinization remains a significant challenge [3].

Rice cultivation in the Songnen Plain has emerged as an effective strategy for ameliorating saline-alkaline soil. It also enhances grain yield and sequesters organic carbon[4]. Field investigations revealed that integrated rice-crab co-culture systems increased crab yields by 20-40 kg/mu. This is equivalent to 500 kg/mu of annual excrement deposition. These systems also boosted economic returns by over 50% compared to monoculture rice systems. The rice-crab integrated co-culture system not only reduces soil salinity-alkalinity but also expands arable land. Furthermore, it enhances ecological resilience and restructures soil microbial communities through organic matter enrichment from aquaculture residues[5]. Nevertheless, the agricultural utilization of saline-alkaline water is severely limited by its complex hydrochemistry, This is characterized by elevated pH, alkalinity, salinity, and ionic imbalances.

Previous water quality assessments in this region primarily focused on pH, salinity, alkalinity, and major ion concentrations. Soda saline-alkaline waters typically exhibit high Na^+ and HCO_3^-/CO_3^{2-} concentrations, as well as elevated pH[1]. Silicate weathering has been identified as the dominant source of Ca^{2+} and Mg^{2+} exceeding standards[6]. Excessive salinity and sodium adsorption ratio (SAR) exacerbate soil alkalinization, impairing crop productivity. Zhang et al.[7] classified surface waters into four categories based on USDA irrigation criteria, emphasizing sodium regulation. While existing studies have extensively analyzed hydrochemical compositions, systematic evaluations of irrigation suitability for saline-alkaline water remain inadequate. Furthermore, China's recent initiatives to develop saline-alkaline lands have accelerated integrated agri-aquaculture integration utilization, such as rice-crab co-culture system. However, empirical data quantifying their benefits and constraints—particularly how aquaculture modulates pH, alkalinity, ionic loads, and irrigation water quality—are critically lacking.

This study addresses these gaps through a dual approach: (1) collecting saline-alkaline water samples from four representative zones to characterize current hydrochemical conditions, and (2) conducting comparative analyses between rice-crab co-culture and rice monoculture systems to quantify aquaculture-mediated water quality improvements. Specifically, we characterizes the hydrochemical signatures of saline-alkaline waters via multivariate statistics and geochemical modeling, develops tailored irrigation suitability indices to the Songnen Plain, and holistically evaluates the rice-crab co-culture system's efficacy in salinity mitigating alongside productivity. This integrated framework providing actionable strategies for sustainable saline-alkaline water use and soil conservation.

2. Materials and Methods

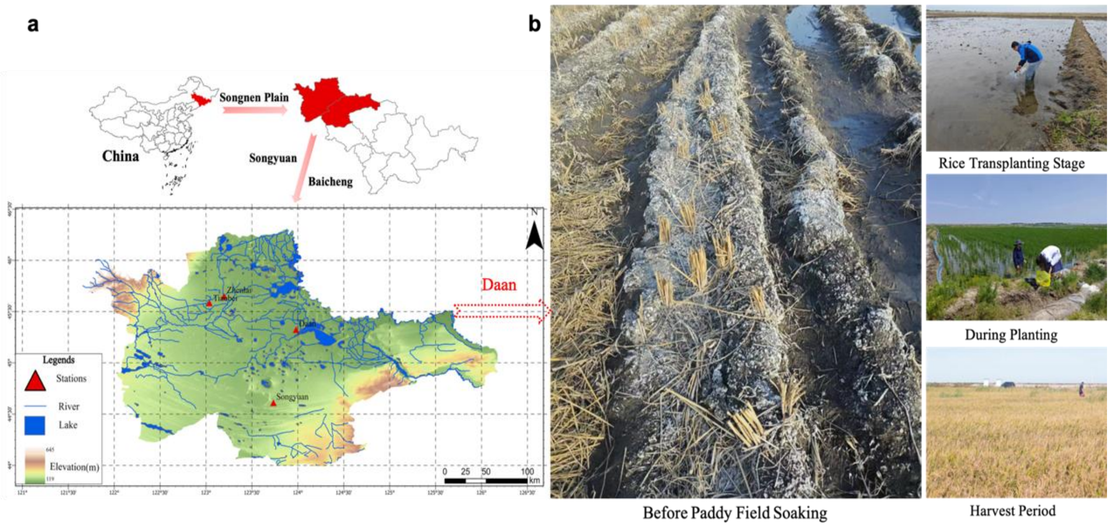
2.1 Study Area

The study area spans western Songnen Plain in Jilin Province, China, encompassing Zhenlai County(Baicheng), Da'an City(Baicheng), Taobei District (Baicheng), and Ulan Aodu Township (Songyuan) (Fig. 1: Remote sensing locator map). This temperate continental monsoon climate zone experiences arid to semi-arid conditions, with a mean annual temperature of 5°C and precipitation of 400-500 mm (predominantly summer rainfall). The region exhibits strong evaporation (1,200-1,600 mm/year), yielding an evaporation-to-precipitation ratio of (3-4):1. The flat topography (elevation: 120-200 m) features extensive wetlands, depressions, and interconnected lakes ("paozi" in local terminology)To capture representative saline-alkaline water conditions, we collected 30 surface water samples (depth: 0.2 m below water surface) from integrated agri-aquaculture integration utilization demonstration sites in Baicheng and Songyuan during Spring 2023. Samples were categorized by source/usage: source water (SW), aquaculture water (ASW), paddy field water (FW), and drainage alkali channel water (FSW). The ASW samples represent water from aquaculture ponds with prior cultivation history, providing a baseline of historically influenced water quality. SW serves as the incoming background water, FW represents the core crop cultivation area, and FSW characterizes the final agricultural effluent. To further evaluate the impacts of aquaculture on salinity-alkalinity water dynamics, additional sampling campaigns were conducted at the Da'an demonstration site in Baicheng during the rice transplanting (May), mid-growth (August), and harvesting (September) stages in 2024. Saline-alkaline water samples were taken from three treatments, including rice monoculture, rice juvenile crab co-culture, and rice adult crab co-culture system, with concurrent yield measurements of rice and Chinese mitten crab (*Eriocheir sinensis*).

Fig. 1. Sampling locations and experimental design. a) Geographical distribution of the demonstration sites within the surveyed regions; b) Schematic diagram of the field sampling design for a typical integrated fishery and agriculture demonstration zone

2.2 Sample Collection and Analysis

Prior to sampling, 500 mL polyethylene bottles were triple-rinsed with deionized water, They were then followed by three successive rinses with ambient water. In-situ measurements of



pH and salinity were obtained using calibrated portable meters (YSS ProDSS, YSI incorporated, American). Samples were immediately sealed, labeled, and transported to the laboratory under 4°C refrigeration. Cations (K^+, Na^+, Ca^{2+}, Mg^{2+}) were quantified via atomic absorption spectrometry (GBC SavantAA, GBC instruments, Australia) following Chinese National Standard GB11904. Anions, including sulfate (SO_4^{2-}), were measured using barium chromate spectrophotometry (HJ342). Chloride (Cl^-) was measured by $AgNO_3$ titration (GB11896). Carbonate species (CO_3^{2-}/HCO_3^-) were determined by dual-indicator titration (SL83). Total dissolved solids (TDS) were determined gravimetrically at 105°C through evaporation residue method.

2.3 Water Quality Assessment

(1) Ionic Balance Validation

Ion balance was used to verify the reliability of the water analysis data. The formula is as follows:

$$E\ (\%) = (\sum nc \ / \sum na) * 100$$

where E is the relative error, and nc and na represent the milliequivalent concentrations of cations and anions, respectively.

Assuming no experimental errors, the total milliequivalent concentration of anions in the water should be very close to that of cations. Theoretically, the ratio of the total milliequivalent concentration of all cations to that of all anions should be within 90%-110%. If the value of E exceeds this range, the water analysis data is considered unreliable and requires re-collection and re-measurement.

(2) Irrigation Suitability Indices

Sodium Adsorption Ratio (SAR)

SAR reflects the potential of sodium to cause soil dispersion and reduce soil permeability and is an important indicator for evaluating the suitability of water for agricultural irrigation[8]. The SAR is calculated as follows:

$$SAR = Na^+/\sqrt{[（Ca^{2+}+Mg^{2+}）/2]}$$

Sodium Percentage ($\%Na^+$)

Since the interaction of Na^+ with soil can reduce soil permeability, calculating the percentage of Na^+ is also a common method for assessing the suitability of water for agricultural irrigation[9]. The $\%Na^+$ is calculated as follows:

$$\%Na^{+}=[（Na^{+}+K^{+}）/（Ca^{2+}+Mg^{2+}+Na^{+}+K^{+}）]\times 100$$

Residual Sodium Carbonate (RSC)

When the concentration of carbonate in agricultural irrigation water is higher than that of alkaline earth metals, excess carbonate will combine with Na^{+} to form $NaHCO_3$, affecting soil structure. Therefore, the relationship between the content of carbonate and alkaline earth metals can be calculated to assess the suitability of agricultural irrigation water. The concentration of excess carbonate is called residual sodium carbonate (RSC), which is an indicator reflecting the alkaline hazard of irrigation water[8]. The RSC is calculated as follows:

$$RSC=（CO_3^{2-}+HCO_3^{-}）-（Ca^{2+}+Mg^{2+}）$$

Magnesium Hazard (MH)

Szaboles and Darab proposed magnesium hazard to assess the suitability of agricultural irrigation water. Under normal circumstances, exchangeable Na^{+} in irrigated soil can cause high levels of Mg^{2+}. When the Mg^{2+} content in irrigation water reaches a certain level, magnesium alkalization may occur in the soil, affecting soil structure and producing toxic effects on crops[10]. The MH is calculated as follows:

$$MH=[（Mg^{2+}/（Ca^{2+}+Mg^{2+}）]\times 100$$

Permeability Index (PI)

PI is used to measure the permeability of the soil medium[10]. The permeability index (PI) is a key indicator used to evaluate the suitability of irrigation water, reflecting the influence of calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), and bicarbonate (HCO_3^{-}) ion concentrations on soil permeability and drainage capacity. Lower PI values usually indicate better irrigation water quality, as they suggest that the soil structure remains conducive to water movement, which is essential for healthy crop growth. Groundwater with a PI value greater than 75% is classified as Class III, indicating that it may not be suitable for irrigation, while lower PI values indicate better suitability (MDPI). The PI is calculated as follows:

$$PI=Na^{+}+\sqrt{}HCO_3^{-}/（Ca^{2+}+Mg^{2+}+Na^{+}）\times 100$$

where all ion concentrations are expressed in milliequivalents per liter.

2.4 Statistical Analysis

The homogeneity of variances was first assessed using Levene's test. When variances were homogeneous, standard ANOVA was applied. This was followed by Tukey's Honestly

Significant Difference (HSD) post-hoc test for multiple comparisons. In cases of heterogeneous variances, Welch ANOVA and Brown–Forsythe ANOVA were used as robust corrections. For these cases, the Games–Howell method was employed for post-hoc comparisons. The significance level was set at $P < 0.05$ for all tests. All statistical analyses were performed using SPSS version 23.0 (SPSS, USA).

For geospatial and geochemical analysis, the Copernicus Digital Elevation Model (Copernicus DEM) with a spatial resolution of 30 m was used as the data source. ArcGIS Pro software was employed for terrain visualization and analysis. It was used to generate distribution maps of terrain slope and elevation. Rivers, lakes, and sampling demonstration sites were labeled in the maps (Fig. 1a). Descriptive statistics (Mean and standard deviation) were also calculated using SPSS. Origin 2022 was utilized to create Piper diagrams, Gibbs diagrams, ionic ratio plots, and ionic concentration boxplots. Theese were used for water chemistry interpretation. The US Soil Salinity Laboratory (USSL) diagram was adopted to evaluate the suitability of the study area for saline-alkaline water for irrigation reuse.

3. Results

3.1 Hydrochemical Characteristics of Saline-Alkaline Water Types

Descriptive statistics of four saline-alkaline water types (Aquaculture Water, ASW, n=8; Paddy Field Water, FW, n=10; Source Water, SW, n=8; Drainage Canal Water, FSW, n=4) are summarized in Table 1 and Table S1. All parameter except pH and alkalinity (mmol/L) are reported in mg/L, with cation-anion balance error <10% confirming data reliability. Key findings include: ASW samples exhibited moderate alkalinity (pH 8.04–9.10, mean 8.74) and high salinity (TDS 1007.10–3999.31 mg/L), with mean alkalinity (11.98 mmol/L) significantly exceeding SW samples (6.72 mmol/L). FSW samples demonstrated extreme alkalinity (pH 9.02–9.50) and the highest alkalinity (18.54 mmol/L), measuring 2.76, 2.28, and 1.55 times higher than SW, FW, and ASW samples, respectively. FW samples displayed the greatest alkalinity variability (1.53–24.56 mmol/L). All water types exceeded the pH 8.5 threshold for optimal crop irrigation.

Table 1 Mean values and significance levels of hydrochemical parameters accoss different saline-alkaline types.

Index	ASW	SW	FW	FSW
TDS（mg/L）	2089.82^{ab}	659.7^{b}	1719.4^{ab}	3358.5^{a}
pH	8.74^{ab}	7.98^{c}	8.55^{b}	9.19^{a}

Na^{+}（mg/L）	616.08^{ab}	104.95^{c}	415.06^{b}	1012.14^{a}
K^{+}（mg/L）	3.70^{b}	3.65^{b}	11.85^{a}	14.49^{a}
Ca^{2+}（mg/L）	16.70	45.57	38.82	25.73
Mg^{2+}（mg/L）	20.75^{b}	16.52^{b}	51.92^{a}	45.73^{a}
Cl^{-}（mg/L）	475.43^{ab}	30.66^{b}	160.87^{b}	873.93^{a}
SO_4^{2-}（mg/L）	228.21	48.87	545.68	257.20
CO_3^{2-}（mg/L）	123.01^{ab}	21.33^{c}	54.20^{bc}	148.60^{a}
HCO_3^{-}（mg/L）	605.93^{ab}	388.26^{b}	440.45^{b}	980.06^{a}

Note: a, b, c indicate significant differences among the grouos based on statistical analysis, with different letters representing statiscally significant differences at a specified significance level.

During the sampling period in Spring 2023, although aquaculture activties for crab had not commenced, it is essential to acknowlegde that such practices had been conducted in previous years.. Consequently, the ASW samples collected during this time still reflect the hydrochemical conditions of saline-alkaline water influenced by past aquaculture. This historical context is crucial for understanding baseline conditions and the potential improvements that aquaculture could offer to saline-alkaline water quality. Furthermore, while soil return salt and alkaline were detected, this doesn't not diminish the positive effects observed from active co-culture. The significant economic benefits derived from aquaculture underscore its role in enhancing the management of saline-alkaline lands, demonstrating that the advantages of aquaculture extend beyond immediate water quality improvements to broader agricultural and economic outcomes.

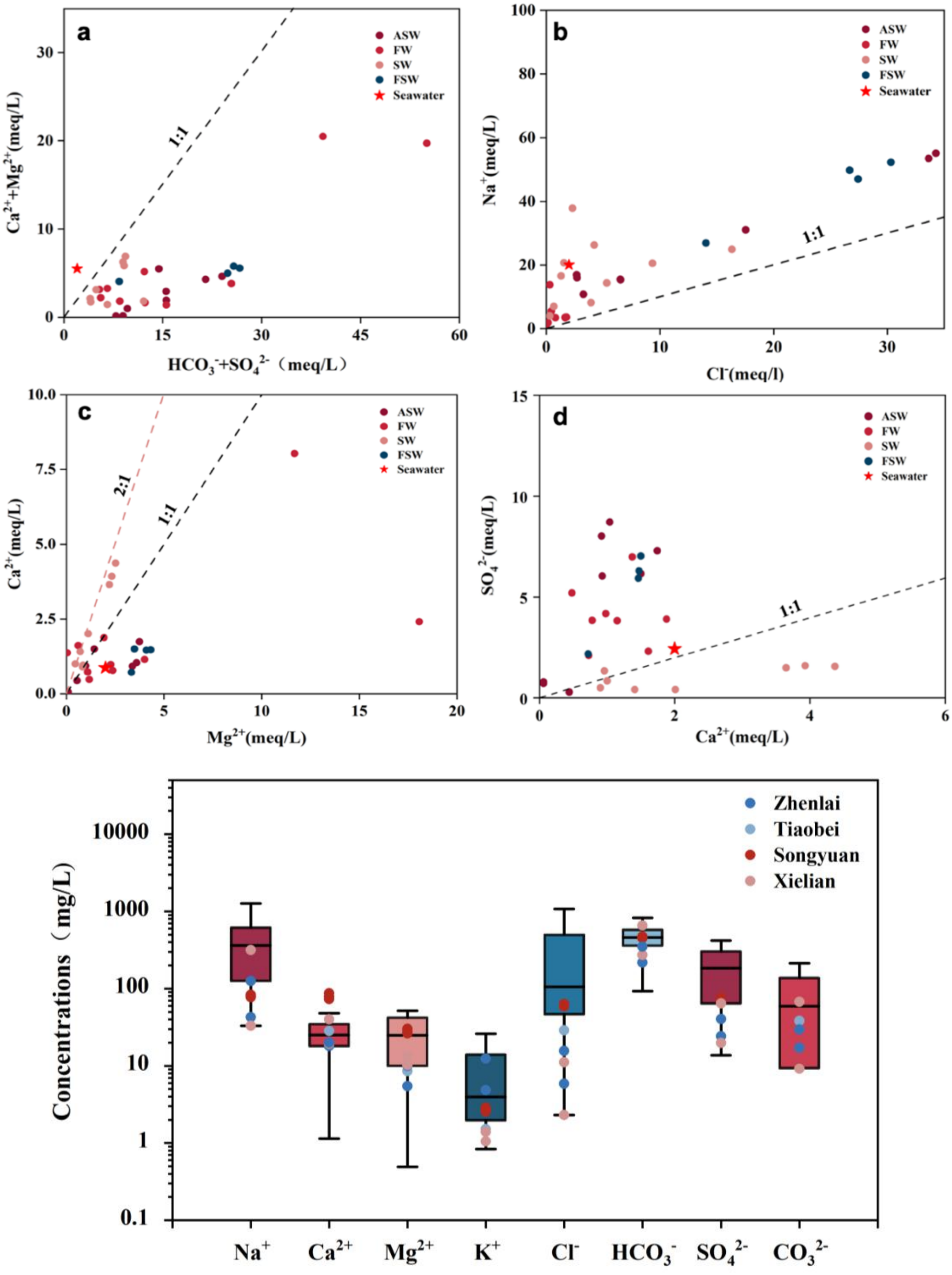


Fig 2. Boxplot comparison of major ion mass concentrations in saline-alkaline water, regional water sources, and seawater.

Ionic Composition displayed that HCO_3^- and Cl^- were dominant anions. Na^+ was the dominant cation across all types. HCO_3^- showed relative stability in ASW (CV=29.62%) and SW (CV=39.19%), while Na^+ varied least in FSW (CV=26.36%). SO_4^{2-} exhibited extreme fluctuation in FW (CV=139.69%). Prior to cultivation initiation, FW samples showed elevated SO_4^{2-} release, ASW promoted Cl^- release, and FSW experienced marked increases in Na^+, Cl^-, and alkalinity. To elucidate the distribution patterns of major ions in saline-water water sources and their environmental correlations, this study conducted a comparative analysis of concentration distributions for Na^+, Ca^{2+}, Mg^{2+}, K^+, Cl^-, HCO_3^-, SO_4^{2-}, and CO_3^{2-} across different saline-alkaline water types using boxplots (Fig. 2). Cl^- had universally high median concentrations (150.13 mg/L). HCO_3^- showed remarkable stability (median 458.11 mg/L). SO_4^{2-} and CO_3^{2-} exhibited high variability (medians 183.93 mg/L and 59.38 mg/L). SW ion concentrations (except HCO_3^- and Ca^{2+}) consistently fell below saline-alkaline water medians, with Na^+ and Cl^- near minimum thresholds (Fig. 2).

Fig.3 Ions scatter diagrams under different saline-alkaline water types. a [Ca^++Mg^{2+}] versus [HCO_3^-+ SO_4^{2-}]. b [Na^+] versus [Cl^-]. c [Ca^{2+}] versus [Mg^{2+}]. d [SO_4^{2-}] versus [Ca^{2+}].

To elucidate hydrochemical characteristics and potential weathering sources across saline-alkaline water types, we analyzed scatterplots of [Ca^{2+}+Mg^{2+}] vs [HCO_3^-+SO_4^{2-}], [Na^+] vs [Cl^-], [Ca^{2+}] vs [Mg^{2+}], and [SO_4^{2-}] vs [Ca^{2+}] were analyzed. Reference lines in Fig. 3a-b,d represent 1:1 equilibrium line, while Fig. 3c includes 1:1 and 2:1 equilibrium line. Artificial seawater (salinity 1.5) was prepared following Zhu Shuping's ionic formulation with eight major ions. Scatterplot analyses revealed dominance of reverse ion exchange, carbonate/sulfate dissolution, and silicate weathering, with supplementary Na^+ from silicate weathering and cation exchange (Na^+/Cl^- ratio = 2.3 ± 0.4, $p<0.01$) (Fig. 3b). Mg^{2+} exceeded Ca^{2+} due to preferential Mg release and evaporative enrichment (Fig. 3c). Gypsum dissolution and silicate weathering primarily controlled Ca-SO_4 relationships (Fig. 3d).

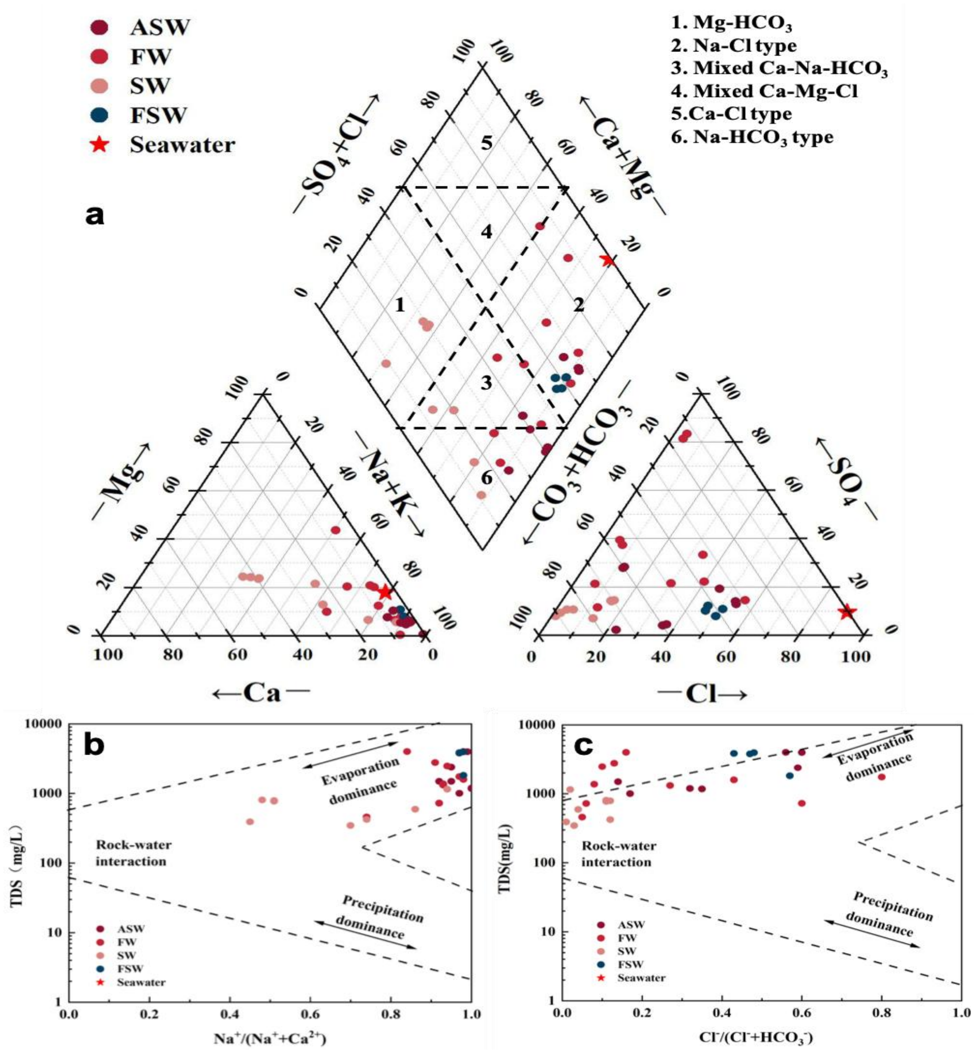


Fig. Piper diagrams of saline-alkaline water in the study area, b and c the Gibbs diagram for major processing saline-alkaline water chemistry

To examine the hydrochemical characteristics composition differences among various saline-alkaline water types (ASW, SW, FW, FSW, and Seawater 1.5), a Piper trilinear diagram was used (Fig. 4a). $NaHCO_3$ was the dominant water type (60% of samples). SW samples plotted in Zone 1 (leaching influence), while some FW, ASW, and all FSW samples plotted in Zone 2 (anthropogenic influence). ASW and artificial seawater clustered in high-$Cl^-/SO_4^{2-}/Ca^{2+}/Mg^{2+}$ regions. Water type evolution followed: SW (HCO_3^--Na-Ca) → FW (HCO_3^--SO_4^{2-}-Cl-Na) → ASW (HCO_3^--Cl-Na) → FSW (Na-Cl). Anthropogenic chloride enrichment (e.g., KCl fertilizers, disinfectants) drove final NaCl-type formation in populated areas. Gibbs ratio analysis (Fig. 4b-c) identified evaporation-crystallization ($Na^+/[Na^+ + Ca^{2+}]=0.45\text{-}1$) and rock weathering ($Cl^-/[HCO_3^- + Cl^-] = 0.01\text{-}0.99$) as dominant controls, with FSW showing intense evaporation signatures.

3.2 Irrigation Suitability Assessment

Using the US salinity Laboratory (USSL) diagram (Fig. 5), we evaluated the sodium adsorption ratio (SAR) and salinity of five water types: aquaculture saline-alkaline water (ASW), source water (SW), field saline-alkaline water (FW), flowing saline-alkaline water (FSW), and artificial seawater (1.5). Only Zhenlai SW samples (C2S1: EC=412-587 μS/cm, SAR=3.2-5.1) were suitable for most soils. Artificial seawater (1.5) and Songyuan/Daan SW samples (C3S1: EC=896-1345 μS/cm) required salt-tolerant crops with enhanced drainage. Critically, 63.3% of the spring 2023 samples fell into the C4S4 class (EC>2250 μS/cm, SAR>26), exceeding sodium hazard thresholds by 2.3-4.8-fold. This prevalence of extreme-hazard water in spring alone underscores the pervasive and serious nature of salinity and sodicity challenges in the region. Our data provide a conservative yet robust quantification of the baseline hazard level, against which the efficacy of management interventions (such as rice-crab co-culture) can be measured, and upon which future studies can build to explore intra-annual variability.

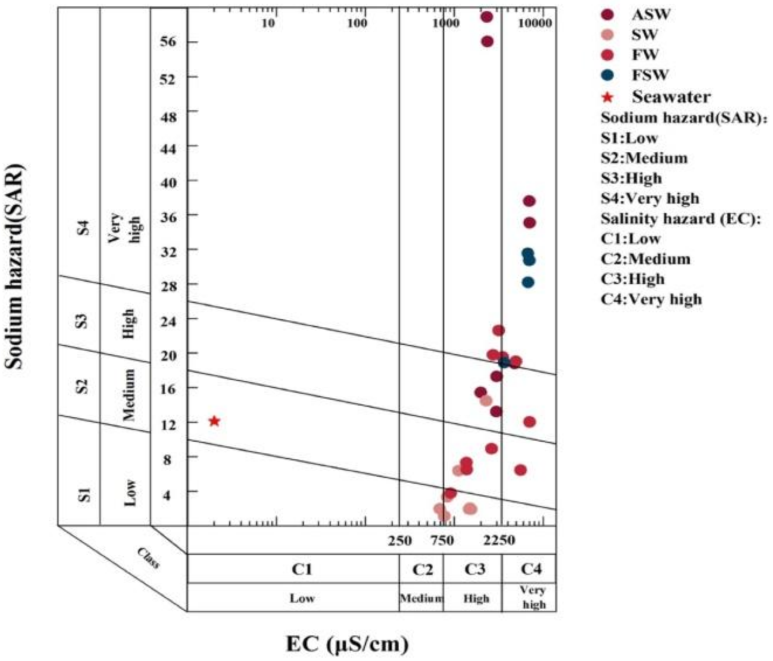


Fig.5 USSL classification of saline-alkaline water

To further explore the agricultural irrigation suitability of different saline-alkaline water, this study analyzed five indicators: SAR, permeability index (PI), sodium percentage (%Na^+), residual sodium carbonate (RSC), and magnesium hazard (MH) for aquaculture water (ASW), paddy field water (FW), drainage alkali channel water (FSW), and source water (SW)(Table 2). ASW samples performed poorly across all indices (SAR: 50.0% extreme hazard; PI, %Na^+, and RSC: 100.0% unsuitable; MH: 87.5% high risk). FSW samples demonstrated catastrophic unsuitability (75–100% hazard rates). FW samples showed contradictory characteristics in SAR and %Na^+ (50% suitability and 90% unsuitable, respectively), while other indicators were generally poor. SW samples presented partial viability (SAR/%Na^+: 87.5%/50% suitable) but limitations in PI (62.5% unsuitable) and MH (100% moderate risk).

Table 2 Evaluation results for groundwater irrigation suitability

Index	Criteria	Hazard description	ASW	FW	FSW	SW
			%	%	%	%
SAR	≤10	Low-sodium water, suitable	0.0	50.0	0.0	87.5
	10-18	Medium-sodium water, fairly suitable	37.5	10.0	0.0	12.5
	18-26	High-sodium water, less suitable	12.5	40.0	25.0	0.0
	>26	Extremely high sodium water, unsuitable	50.0	0.0	75.0	0.0

	≤25	Good water quality, suitable for irrigation	0.0	0.0	0.0	0.0
PI	25-75	Medium water quality, marginally suitable for irrigation	0.0	20.0	0.0	37.5
	≥75	Poor water quality, unsuitable for irrigation	100.0	80.0	100.0	62.5
	≤20	Excellent water quality	0.0	0.0	0.0	0.0
	20-40	Suitable water quality	0.0	0.0	0.0	50.0
Na%	40-60	Restricted water quality	0.0	10.0	0.0	12.5
	60-80	Unsuitable	0.0	50.0	0.0	25.0
	>80	Extremely unsuitable	100.0	40.0	100.0	12.5
	≤1.25	Suitable for irrigation	0.0	40.0	0.0	25.0
RSC	1.25-2.50	Marginally suitable for irrigation	0.0	0.0	0.0	37.5
	>2.5	Unsuitable for irrigation	100.0	60.0	100.0	37.5
	≤30%	Suitable for irrigation	0.0	20.0	0.0	0.0
MH	30-50%	Moderate risk	12.5	0.0	0.0	100.0
	>50%	High risk	87.5	80.0	100.0	0.0

3.3 Impact of Rice-Crab Co-culture on Saline-alkaline Water

To validate the effects of rice-crab co-culture systems on saline-alkaline water chemistry, we analyzed alkalinity, pH, and total ion content (TIC) across cultivation phases (Fig. 6). During rice transplanting, Paddy monoculture (Paddy) had peak alkalinity (4.91 mmol/L), while Rice-Juvenile Crab co-culture (Paddy-JC) showed the lowest (3.37 mmol/L). During mid-planting phase, Rice-Adult Crab (Paddy-AC) reached maximum alkalinity (5.68 mmol/L), surpassing Paddy by 27.3%. At the harvesting stage, Paddy maintained the highest alkalinity (5.90 mmol/L), while Paddy-JC demonstrated optimal mitigation (20.5% lower than Paddy). pH and Total Ion Content (TIC) trends mirrored alkalinity, with Paddy consistently showing elevated values except during mid-planting. Paddy-JC consistently showed the lowest values at key stages (TIC: 0.27 vs 2.14 mg/L in Paddy at harvest; pH: 7.61 vs 7.6). The reduction in pH and alkalinity is agronomically significant because it mitigates the stress on crops sensitive to high pH, which can impair nutrient uptake and reduce yields.

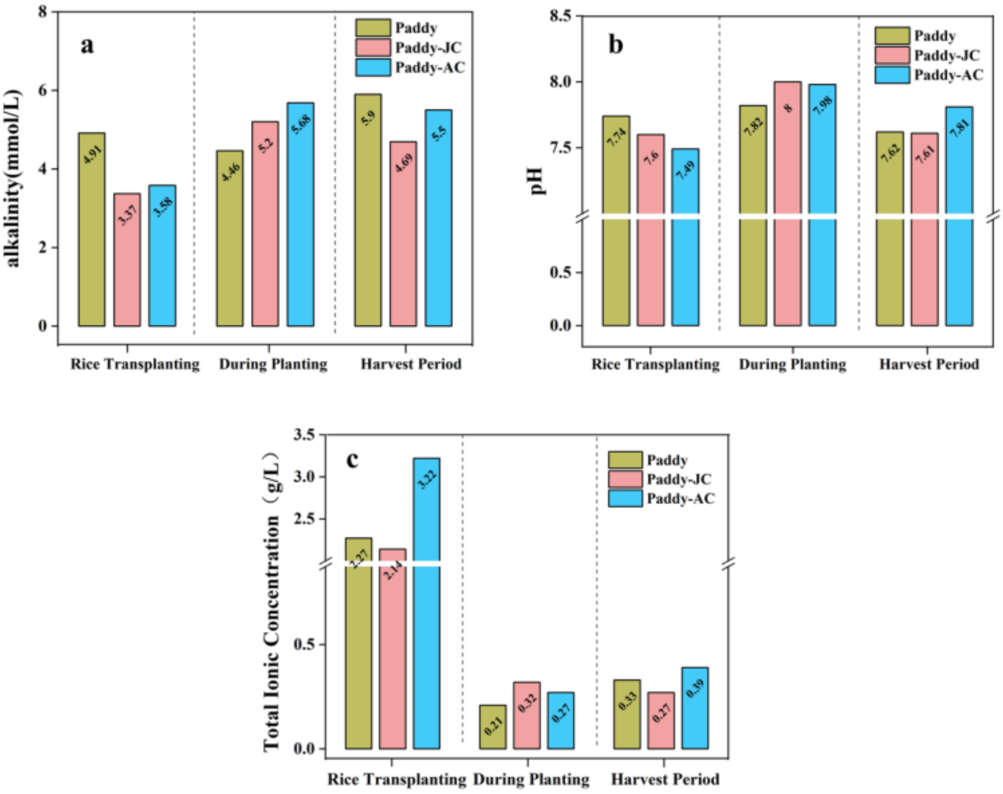


Fig.6 Changes in saline-alkaline water properties of alkalinity, pH, and Total ionic concentration under different growth stages and improvement modes.

To investigate the impacts of Paddy-JC and Paddy-AC co-culture systems on soil physicochemical properties, we analyzed SAR, PI, %Na^+, RSC, and MH across treatments (Fig. 7). At transplanting, Paddy had significantly higher SAR (17.53) than Paddy-JC (9.03) and Paddy-AC (15.82). At harvest, Paddy-AC SAR (4.02) remained lower than Paddy (5.77) but slightly higher than Paddy-JC (3.39). Paddy showed reduced permeability (PI=88.04) vs. Paddy-JC (68.46) and Paddy-AC (79.10) at transplanting, this degradation worsened in monoculture by harvest (PI=99.56), while co-culture maintained better permeability. Paddy-JC reduced %Na^+ by 22.9% (63.63 vs. Paddy’s 82.57) at transplanting and achieved optimal balance (58.05, 20.2% lower than Paddy) at harvest. Paddy-AC demonstrated superior RSC control (1.28, 68.2% lower than Paddy). Elevated MH in Paddy-AC (51.37 vs. Paddy-JC’s 22.49) correlated with juvenile crab growth. An elevated MH can disrupt the soil's calcium-magnesium balance, leading to poor soil structure and potentially toxic effects on plant root systems. Moreover, rice-crab co-culture increased rice yields by 8.73–10.61% and total economic output by 68.16–84.51% compared to rice monoculture (Table 3).

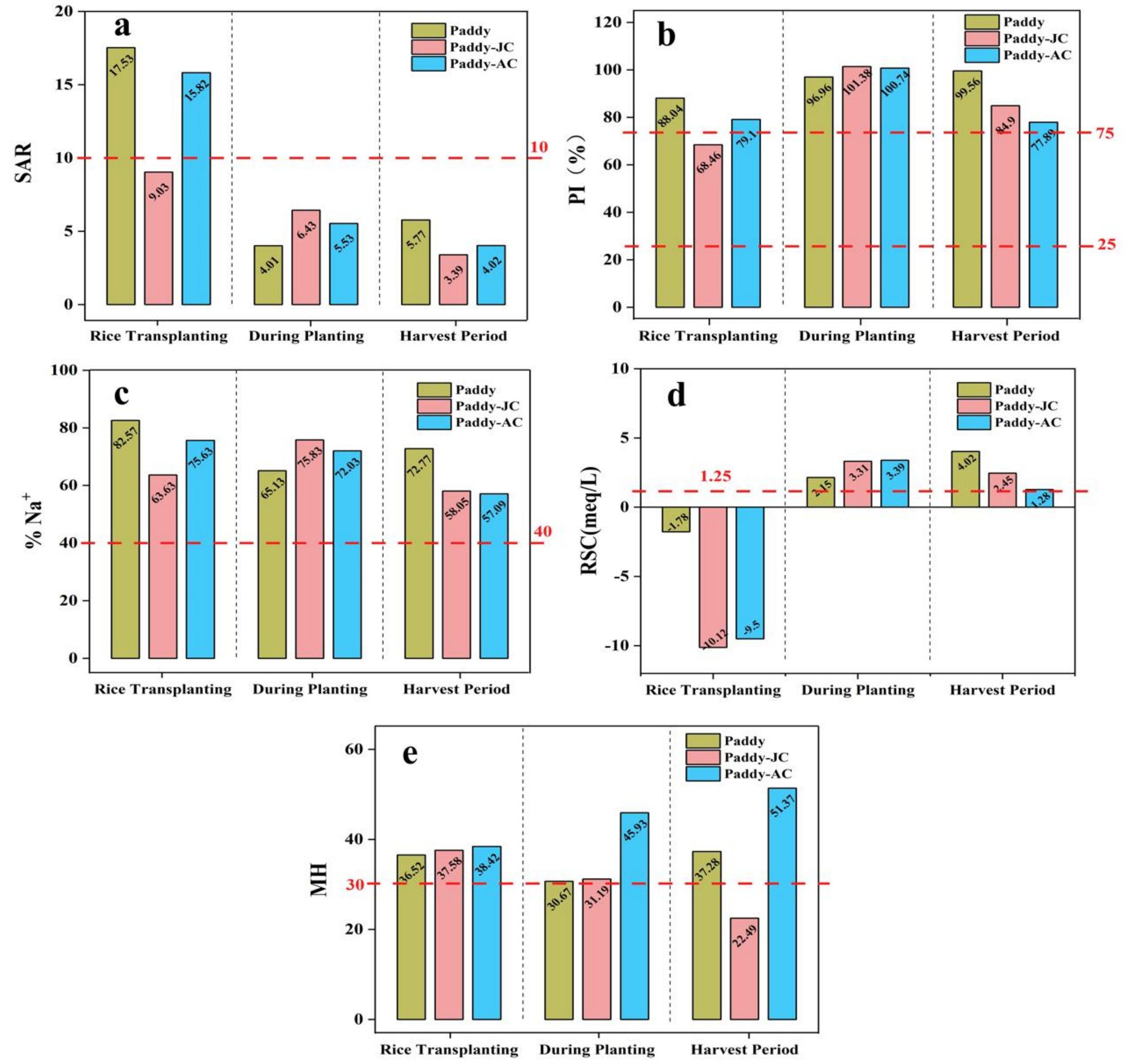


Fig.7 Changes in saline-alkaline water properties of SAR, PI, %Na, RSC, and MH under different growth stages and improvement modes.

Table 3 Effects of integrated rice-crab co-culture on rice yield and *Eriocheir sinensis* biomass output.

Yield	Rice production (kg/mu)	Rice total economic (RMB)	Crab production (kg/mu)	Crab total economic (RMB)
Paddy	424	1272	0	0
Paddy-JC	469	1407	23.5	940
Paddy-AC	461	1383	18.9	756

4. Discussion

4.1 Drivers of Saline-Alkaline Hydrochemistry and Irrigation Hazards

Our hydrochemical analysis reveals a complex interplay of natural geochemical processes governing water quality in the Songnen Plain. The prevalence of $NaHCO_3$ water types (Fig. 4a) and elevated Na^+/Cl^- ratios (Fig. 3b) strongly support silicate weathering and cation exchange as primary ion sources[11], a regime intensified by evaporative concentration (Fig. 4b-c, FSW extremes). This hydrochemical signature is characteristic of soda saline-alkaline environments globally, consistent with recent characterizations in other endorheic basins[1,11-13]. Furthermore, the observed enrichment of Mg^{2+} over Ca^{2+}(Fig. 3c) aligns with the findings of Bian et al.[1], which underscores the role of evaporative concentration in the region. The evolution towards Na-Cl type in drainage water (FSW) (Fig. 4a), coupled with anomalous Cl^- enrichment (Fig. 4), clearly implicates significant anthropogenic chloride inputs—such as from KCl fertilizers and disinfectants[14-15]—that are overriding natural weathering controls.

The predominance of C4S4 water classification in our foundational spring 2023 (Fig. 5) coupled with widespread unsuitability across irrigation indices (Table 2), confirms the prevalence of extreme sodicity and salinity risks. Elevated SAR values (>26) indicate that irrigation with this water will promote soil particle dispersion, severely reducing water infiltration and soil aeration, which can physically constrain root development and exacerbate water stress in crops. This finding aligns with Bian et al.'s[1] but contrasts with earlier reports of milder conditions[6], underscoring the severity of the region challenge. These water quality constraints pose direct threats to ecosystem health: high SAR degrades soil structure and reduces permeability, while extreme salinity and alkalinity disrupt microbial communities (e.g., favoring *Halomonadaceae*) and impair C/N/P metabolic functions[16], The serious irrigation hazards documented in our spring baseline provide a compelling rationale for future research to quantify the potential intensification of these risks during drier "resurgence phases." Consequently, the direct agricultural use of most local water sources is ecologically unsustainable and necessitates prior remediation.

Despite the direct irrigation risks of spring aquaculture water (ASW) and drainage channel water (FSW), field investigations have found that farmers still reuse them. Although several studies have pointed out that such water types can enhance soil bacterial diversity, increase soil carbon reserves and fertility, regulate soil pH, improve soil structure, and reduce soil salinization and alkalinization[17-19], but the persistent risks during saline-alkaline recurrence periods (such as evaporation concentration in the dry season) (fluctuation trends in Fig. 6) warn that sustainable management must be achieved through rice-crab symbiosis systems.

4.2 Co-culture System Performance and Plausible linkages

The rice-crab co-culture system, particularly the Paddy-JC treatment, demonstrates a consisten correlative association with the mitigation of key saline-alkaline constraints. The superior reduction in water alkalinity, pH, TIC (Fig. 6), SAR, %Na^+, and RSC (Fig. 7) in Paddy-JC, particularly during critical growth stages (transplanting, harvest), highlights its efficacy. While specific mechanistic drivers were not directly measured in this study, the observed improvements are consistent with known ecological processes reported in previous research. This improvement likely stems from multiple ecological mechanisms, including nutrient coupling, ionic regulation, and soil structuring through biological activity.

The correlative reductions in sodium-related indices (SAR, %Na^+) and improvements in soil permeability (PI) align with the established concept that the presence of benthic organisms like crabs can influence soil physical properties through activities such as bioturbation[20]. Similarly, the nutrient data and yield increases (Table 3) are consistent with the documented role of animal excreta in providing bioavailable nutrients[21-24]. The modulation of the ionic environment (e.g., TIC and RSC) was particularly insightful. Compared with previous studies[25-26], the observed increase in RSC from negative values to a low positive value in the co-culture system is a critical finding. A positive RSC typically indicates an alkaline hazard, which can raise soil pH and induce crop micronutrient deficiencies. However, the shift from a strongly negative baseline in our study suggests a more complex biogeochemical transformation. Crab bioturbation and respiration enhance the dissolution of soil minerals, such as carbonates (e.g., $CaCO_3$). The dissolution process consumes H^+ and releases Ca^{2+}, HCO_3^-, and CO_3^{2-} ions into the water, which would concurrently increase the RSC and water's alkalinity-buffering capacity. This newly released Ca^{2+} could then participate in ion exchange, displacing Na^+ from soil colloids, which aligns with the observed reductions in SAR and %Na^+. Thus, the RSC increase may not be a simple deterioration but rather a sign of an activated geochemical cycle where the release of calcium, even as it elevates RSC, simultaneously facilitates the mobilization and leaching of sodium, leading to an overall improvement in soil structure and sodicity.

It is noteworthy that Paddy-JC was associated with more favorable outcomes in over 60% of the measured ecological indices compared to Paddy-AC (Fig. 6 and Fig. 7). This correlative pattern strongly suggests that juvenile crabs induce different or more pronounced system feedbacks. The higher surface-area-to-volume ratio and potentially greater mass-specific metabolic and activity rates of juvenile crabs lead to more intense bioturbation and a greater relative excretory load per unit biomass. This heightened biological activity would intensify mineral dissolution and ion exchange processes, explaining the stronger ameliorative effects observed in Paddy-JC.

4.3 Research Value, Implications and Future Research Directions

This study provides robust, correlative evidence from a real-world agricultural setting, positioning rice-crab co-culture as a highly promising nature-based strategy for saline-alkaline land restoration in the Songnen Plain. By capturing the system's performance under practical field conditions, our findings establish a critical baseline and a compelling reference for its efficacy, particularly for the rice-juvenile crab (Paddy-JC) system in mitigating complex environmental stressors. The consistent trends observed—simultaneous mitigation of water and soil hazards alongside enhancements in productivity and economic returns—deliver a powerful and holistic validation that aligns with global goals for sustainable intensification on marginal lands.

The observational nature of this research, which reflects the inherent complexities of large-scale agricultural studies, is a key source of its ecological relevance. While this approach places constraints on traditional statistical replication for establishing definitive causality, it successfully documents the integrated system's performance in a manner that highly controlled experiments cannot [27-28]. Therefore, this work should be regarded not as a terminal finding, but as a vital and robust real-world assessment that provides both a springboard for future mechanistic investigations and a valid reference for practical application. The strong correlations we report, most notably the novel geochemical interpretation of the RSC shift, generate concrete, testable hypotheses for the research community.

Guided by these clear trends and hypotheses, future research is to build effectively upon this work. The immediate priorities include: (1) Controlled experiments to quantify crab bioturbation and excretion impacts on carbonate dissolution and ion exchange; (2) Replicated trials to statistically validate the causal relationships suggested by our correlative patterns; and (3) Investigations into the role of the soil microbiome in mediating these processes[29]. The validation of these proposed mechanisms will solidify the theoretical foundation for a sustainable restoration strategy for which our study provides a robust empirical benchmark. Ultimately, this research pathway will enable the precise optimization of management practices, ensuring that the full potential of this integrated agroecosystem can be realized for sustainable landscape restoration.

5. Conclusions

This study establishes the ecological unsustainability of direct irrigation with saline-alkaline waters from the Songnen Plain, where hydrochemical evolution—driven by evaporation and anthropogenic inputs—creates severe sodicity and salinity hazards (C4S4 classification in 63.3% of samples). In contrast, the rice-juvenile crab co-culture system (Paddy-JC) demonstrates a strong correlative link with multifaceted amelioration of these constraints. This system was consistently associated with reduced water alkalinity, pH, and TIC, alongside significant enhancements in soil health, as evidenced by a 41.2% decrease in SAR and a 20.2% reduction in %Na^+ at harvest.

A key insight of this research is the reinterpretation of a critical water quality parameter. The increase in RSC from negative to a low positive value under co-culture is not viewed as a simple deterioration, but as a potential signature of an activated, beneficial geochemical cycle. We propose that this shift marks crab-driven carbonate dissolution, a process that releases calcium to displace exchangeable sodium—thus providing a unified explanation for the concurrent rise in RSC and decline in sodium-related indices. The superior performance of juvenile crabs is hypothetically linked to their heightened metabolic and bioturbation activity, which may intensify this mechanism.

Consequently, the rice-juvenile crab co-culture system emerges not merely as a palliative measure, but as a potentially transformative agroecological strategy that actively redirects local biogeochemical cycles to restore degraded land. Its implementation, supported by the future research outlined, presents a globally relevant model for achieving simultaneous ecological restoration and economic prosperity in saline-alkaline environments.

References

1. Bian, J., Nie, S.Y., Wang, R., Wan, H.L. & Liu, C.H. Hydrochemical characteristics and quality assessment of groundwater for irrigation use in central and eastern Songnen Plain, Northeast China. *Environ. Monit. Assess.* **382**, 1-16 (2018). https://doi.org/10.1007/s10661-018-6774-4

2. Gao, R.Z., Li, X.J., Zuo, L.J., Zou, B. & Wang, B. Unveiling soil salinity patterns in soda saline-alkali regions using Sentinel-2 and SDGSAT-1 thermal infrared data. *Remote Sens. Environ.* **322**, 114708 (2025). https://doi.org/10.1016/j.rse.2025.114708

3. Fu, J.H., Liu, Y.W., Liu, X.C., Guo, M.F. & Gao, J.Z. Screening of saline-alkali tolerant microorganisms and their promoting effects on rice growth under saline-alkali stress. *J. Clean. Prod.* **481**, 144176 (2024). https://doi.org/10.1016/j.jclepro.2024.144176

4. Xu, S.Q., Na, M., Huang, Y.J., Zhang, J. & Zhou, J.H. Changes in microbial carbon cycling functions along rice cultivation chronosequences in saline-alkali soils. *Soil Biol. Biochem.* **202**, 109699 (2025). https://doi.org/10.1016/j.soilbio.2024.109699
5. Sun, Z., Yao, Z.L., Gao, P.C., Zhou, K. & Li, Y. Effects of fishery utilization on the physiochemical index and microbial community composition in saline-alkaline water. *ACS Omega* **9**, 18872-18881 (2024). https://doi.org/10.1021/acsomega.3c08437
6. Yan, J.H., Chen, J.S. & Zhang, W.Q. Study on the groundwater quality and its influencing factor in Songyuan City, Northeast China, using integrated hydrogeochemical method. *Sci. Total Environ.* **773**(15), 144958 (2021). https://doi.org/10.1016/j.scitotenv.2021.144958
7. Zhang, B., Song, X.F., Zhang, Y.H., Han, D.M. & Tang, C.Y. Hydrochemical characteristics and water quality assessment of surface water and groundwater in Songnen plain, Northeast China. *Water Res.* **46**(8), 2737-2748 (2012). https://doi.org/10.1016/j.watres.2012.02.033
8. Liu, B.S., Huang, L.H., Jiang, X.T., Huang, G.Z. & Yang, G. Quantitative evaluation and mechanism analysis of soil chemical factors affecting rice yield in saline-sodic paddy fields. *Sci. Total Environ.* **929**, 172584 (2024). https://doi.org/10.1016/j.scitotenv.2024.172584
9. Singh, A.K., Tewary, B.K. & Sinha, A. Hydrochemistry and quality assessment of groundwater in part of Noida metropolitan city, Uttar Pradesh. *J. Geol. Soc. India* **78**, 523-540 (2011). https://doi.org/10.1007/s12594-011-0124-2.
10. Arslan, H., Colak, M.G. The assessment of groundwater quality through the water quality and nitrate pollution indexes in northern Türkiye. *Environ. Monit. Assess.* **195,** 1257 (2023). https://doi.org/10.1007/s10661-023-11854-x.
11. Ismail, A.H., Shareef, M.A., Hassan, G., Alatar, F.M. Hydrochemistry and water quality of shallow groundwater in the Tikrit area of Salah AI Din Province, Iraq. *Appl. Water Sci*. **13**, 197 (2023). https://doi.org/10.1007/s13201-023-02008-y.
12. Sun, X.X., Wu, J.T., Jiang, L.J., Yao, J.N., & Chen, X.Y. Nutrient limitation and saline-alkaline stress primarily drive community and function shifts in protists inhabiting saline-sodic soils. *Agr. Ecosyst. Environ.* **396**, 110009 (2026) https://doi.org/10.1016/j.agee.2025.110009

13. E, J.F., Yang, S.Q., Zhang, W.F., Chen, X., Gu, Q.Y. Design and evaluation of abiological vertical shaft-subsurface ditch system for alkali spot improvement. *Agr. Water Manage.* **317**, 109625. (2025) https://doi.org/10.1016/j.agwat.2025.109625

14. Li, P.Y., Tian, R. & Liu, R. Solute geochemistry and multivariate analysis of water quality in the guohua phosphorite mine, Guizhou Province, China. *Expos. Health* **11**, 81-94 (2019). https://doi.org/10.1007/s12403-018-0277-y.

15. Sharma, A.R., Bordoloi, R., Paul, A., Gyanendra, Y. & Tripathi, O.P. Water quality and geochemical facie of high-altitude lakes in Tawang, Eastern Himalaya, India. *Environ. Sci. Pollut. R.* **31**, 24492-24511 (2024). https://doi.org/10.1007/s11356-024-32712-4.

16. Luo, S.Y., Yuan, J.B., Song, Y.Y., Ren, J.S. & Qi, J. Elevated salinity decreases microbial communities complexity and carbon, nitrogen and phosphorus metabolism in the Songnen Plain wetlands of China. *Water Res.* **276**, 123285 (2025). https://doi.org/10.1016/j.watres.2025.123285

17. Chen, L.J., Feng, Q., Li, C.S., Wei, Y.P. & Zhao, Y. Impacts of aquaculture wastewater irrigation on soil microbial functional diversity and community structure in arid regions. *Sci. Rep-UK.* **7**, 11193 (2017). https://doi.org/10.1038/s41598-017-11678-z.

18. Xu, M.J., Sun, C.W., Du, Z.L. & Zhu, X.D. Impacts of aquaculture on the area and soil carbon stocks of mangrove: A machine learning study in China. *Sci. Total Environ.* **859**, 160173 (2023). https://doi.org/10.1016/j.scitotenv.2022.160173

19. Zhang, S.X., Rasool, G., Wang, S., Zhang, Y.W. & Guo, X.P. Biochar and Chlorella increase rice yield by improving saline-alkali soil physicochemical properties and regulating bacteria under aquaculture wastewater irrigation. *Chemosphere* **340**, 139850 (2023). https://doi.org/10.1016/j.chemosphere.2023.139850

20. Bashir, M.A., Liu, J., Geng, Y.C., Wang, H.Y. & Pan J.T. Co-culture of rice and aquatic animals: An integrated system to achieve production and environmental sustainability. *J. Clean. Prod.* **249**, 119310 (2020). https://doi.org/10.1016/j.jclepro.2019.119310

21. Chakraborty, S.C. & Chakraborty, S. Effect of dietary protein level on excretion of ammonia in Indian major carp, Labeo rohita, fingerlings. *Aquacult. Nutr.* **4**, 47-51 (1998). https://doi.org/10.1046/j.1365-2095.1998.00049.x

22. Guo, L., Zhao, L.F., Ye, J.L., Ji, Z.J. & Tang, J.J. Using aquatic animals as partners to increase yield and maintain soil nitrogen in the paddy ecosystems. *eLife* **11**, e73869 (2022). https://doi.org/10.7554/eLife.73869.

23. Gu, B., Zhang, X., Lam, S.K., Yu, Y.L. & van Grinsven, H.J.M. Cost-effective mitigation of nitrogen pollution from global croplands. *Nature*, 613, 77-84 (2023). https://doi.org/10.1038/s41586-022-05481-8

24. Zou, Z., Chu, K., Wang, M., Guo, S. Carbon footprint assessment and economic benefits of rice-fish/poultry co-culture in China. *J. Clean. Prod.* **527**, 146651 (2025). https://doi.org/https://doi.org/10.1016/j.jclepro.2025.146651.

25. Ghaznavi, S., Yazdani, S., Rafiee, H., Saleh, I. & Jalilian, A. Sustainable synergies of rice–fish–duck symbiosis: a life cycle assessment in Guilan province of Iran. *Results Eng.* **28**, 107226 (2025) https://doi.org/10.1016/j.rineng.2025.107226.

26. He, Y.L., Fu, B., Fang, C., Zhang, N.N. & Zheng, M.P. Decoding the gut-microbiota-muscle nexus: multi-omics integration reveals mTOR driven flesh modulation in rice-fish co-cultured common carp (*Cyprinus carpio*). *Aquaculture* **612**, 743090 (2026). https://doi.org/10.1016/j.aquaculture.2025.743090.

27. Soga, M. & Gaston, K.J. Extinction of experience among ecologists. Trends Ecol. Evol. 40, 212-215 (2025). https://doi.org/10.1016/j.tree.2024.12.010

28. Zhao, Y.G., Wang, S.J., Li, Y., Liu, J.& Zhuo, Y.Q. Long-term performance of flue gas desulfurization gypsum in a large-scale application in a saline-alkali wasteland in northwest China. Agriculture, Ecosystems and Environment. *Agr. Ecosyst. Environ.* **261**, 115-124 (2018). https://doi.org/10.1016/j.agee.2018.01.009

29. Hartmann, M. & Six, J. Soil structure and microbiome functions in agroecosystems. *Nat. Rev. Earth & Environ.* **4**, 4-18 (2023). https://doi.org/10.1038/s43017-022-00366-w

30. Adjagodo, A., Tchibozo, M. A. D., Kelome, N. C., & Lawani, R. (2016). Flux des polluants liés aux activités anthropiques, risques sur les ressources en eau de surface et la chaine trophique à travers le monde : synthèse bibliographique. *International Journal of Biological and Chemical Sciences, 10*(3), 1459–1472. https://doi.org/10.4314/IJBCS.V10I3.43

31. Adiaffi, B., Marlin, C., Oga, Y., Pichon, R., & Biemi, J. (2013). Approche semi-quantitative de la minéralisation des aquifères schisteux en zone équatoriale de transition : Cas de la région Sikensi-Agboville (Côte d'Ivoire). *International Journal of Biological and Chemical Sciences, 6*(5), 2228–2240. https://doi.org/10.4314/IJBCS.V6I5.29

32. Alric, B., Geffard, O., Chandesris, A., Ferréol, M., François, A., Perceval, O., Piffady, J., Villeneuve, B., & Chaumot, A. (2019). Multisubstance indicators based on caged *Gammarus* bioaccumulation reveal the influence of chemical contamination on stream

macroinvertebrate abundances across France. *Environmental Science & Technology, 53*(10), 5906–5915. https://doi.org/10.1021/ACS.EST.9B01271

33. Archambault-Guézou, J., & Lefèvre, R. (1979). Biogenic and non-biogenic carbonates of calcium and magnesium: New studies by secondary ion imaging. 248–251. https://doi.org/10.1007/978-3-642-61871-0_73
34. Barth, J.-G. (2020). Limestone and calcium in plants. 112, 29–78. https://doi.org/10.18756/EDN.112.29
35. Barbier, J. (2006). Echanges de cations et sorption dans les eaux de nappes aquifères en socle cristallin, Massif central, France. *Houille Blanche-Revue Internationale De L'Eau, 3*, 71–75. https://doi.org/10.1051/LHB:200603011
36. Barbier, J. (2007). Devenir des eaux de pluie : géochimie des chlorures dans les eaux souterraines en milieu cristallin (Massif central, France). 12(1), 3–11. https://doi.org/10.1051/ASEES/20071201003
37. Barbier, J. (2008). Géochimie des eaux souterraines en milieu cristallin : incidence des apports organiques sur les paramètres chimiques majeurs. 13(1), 3–15. https://doi.org/10.1051/ASEES/20081301003
38. Barbier, J. (2012). Incidence des apports en azote sur les cations échangeables dans l'eau des sources: La question des métaux lourds. *European Journal of Water Quality*, *43*(2), 149–166. https://doi.org/10.1051/WQUAL/2013013
39. Bekkoussa, B., Jourde, H., Batiot-Guilhe, C., Meddi, M., Khaldi, A., & Azzaz, H. (2013). Origin of salinity and major elements in groundwater from the Ghriss plain, northwest Algeria. *Hydrological Sciences Journal*, *58*(5), 1111–1127. https://doi.org/10.1080/02626667.2013.800639
40. Belkhiri, L., & Boudoukha, A. (2013). Hydrogéochimie des eaux souterraines.
41. Behra, P., & Sigg, L. (1999). Chimie des eaux naturelles. *Revue Suisse de Chimie, 11*, 111–116.
42. Benhamida, S. A., Nezli, I. E., & Kechiched, R. (2017). Sources of chemistry of the Albian water under arid conditions. Application to the western regions of the Algerian Sahara. *Energy Procedia, 119*, 446–452. https://doi.org/10.1016/J.EGYPRO.2017.07.047
43. Bideau, L. L. (1996). Mécanismes de dénitrification de la nappe de l'oxfordien supérieur au droit du site de Beuxes (Vienne).
44. Blum, A., Chery, L., Barbier, J., Baudry, D., & Petelet-Giraud, E. (2003). Le fonds géochimique naturel des eaux souterraines. État des connaissances et méthodologie. *Houille Blanche-Revue Internationale De L'Eau, 2*, 120–124. https://doi.org/10.1051/LHB/2003039

45. Bonnard, R., & Lafont, M. (2003). Notions d'hydro-écologie et de qualité biologique.
46. Caballero, Y., Chazot, S., Citeau, J.-M., Dörfliger, N., Fleury, P., Ladouche, B., Martin, E., Maton, L., Neppel, L., & Pinault, J.-L. (2011). Vulnérabilité des ressources en eau au changement global en zone méditerranéenne - Le projet Vulcain. Compte-rendu de fin de projet.
47. Chapelle, F. H., & Knobel, L. L. (1985). Stable carbon isotopes of HCO3 in the Aquia aquifer, Maryland: Evidence for an isotopically heavy source of CO2. *Ground Water, 23*(5), 592–599. https://doi.org/10.1111/J.1745-6584.1985.TB01507.X
48. Chapman, D. (1996). *Water quality assessments: A guide to the use of biota, sediments and water in environmental monitoring* (2nd ed.). CRC Press.
49. Compétence. (2019). https://doi.org/10.1163/9789004419520_004
50. Corvisier, J. (2006). Implementation of nucleation, maturation, and growth phenomena of secondary solid phases in a reactive transport model in porous geological media: Development of the Archimède calculation code. *Geochimica et Cosmochimica Acta, 70*(5), 1234–1248.
51. Daughton, C. G., & Ternes, T. A. (1999). Pharmaceuticals and personal care products in the environment: Agents of subtle change? *Environmental Health Perspectives, 107*(Suppl 6), 907–938.
52. Delwiche, C. C. (1975). The geobiology of calcium. *Communications in Soil Science and Plant Analysis, 6*(3), 207–218. https://doi.org/10.1080/00103627509366562
53. Devidal, S., Rivard-Sirois, C., Pouet, M.-F., & Thomas, O. (2007). Solutions curatives pour la restauration de lacs présentant des signes d'eutrophisation.
54. Falantin, C. (2017). Influence du soufre sur la complexation de cations métalliques par la matière organique dissoute : du milieu naturel au modèle.
55. Forano, C., Amato, P., Baray, J.-L., & Joly, M. (2023). Chemical and biological signatures of water and fluxes from clouds to rivers at the watershed level in a natural context. https://doi.org/10.5194/egusphere-egu23-6760
56. Forestier, L. L. (2018). Réactivité et mobilité des contaminants métalliques dans les argiles et les sols : apport de la minéralogie environnementale.
57. Freeze, R. A., & Cherry, J. A. (1979). *Groundwater*. Prentice Hall.
58. Gat, J. R. (1980). The relationship between surface and subsurface waters: Water quality aspects in areas of low precipitation. *Hydrological Sciences Journal, 25*(3), 257–267. https://doi.org/10.1080/02626668009491933
59. Ghebouli, M. S., & Elhocine, M. B. (2008). Origine de la salinite des eaux souterraines des hautes plaines setifiennes (nord-est algérien). *Sciences & Technologie, 28*, 37–46.

60. Gossiaux, A. (2019). Effets des changements environnementaux sur le fonctionnement des ruisseaux de tête de bassin versant.
61. Guillaud, J. F. (1992). Les rejets urbains en mer. *Hydroécologie Appliquée, 4*(2), 159–172. https://doi.org/10.1051/HYDRO:1992213
62. Hydrological and geological controls for the joint evolution of dissolved oxygen and iron in crystalline rocks. (2022). https://doi.org/10.1002/essoar.10512568.1
63. Hui, Q. (2012). Application of saturation index to research of water-rock interaction and its sensitivity analysis. *Journal of Water Resources and Water Engineering, 23*(2), 45–52.
64. Ji, T.-T., Han, G., Li, X., Wan, L., & Jin, Z. (2024). Contrasting behavior of K isotopes in modern and fossil groundwater: Implications for K cycle and subsurface weathering. *Earth and Planetary Science Letters.* https://doi.org/10.1016/j.epsl.2023.118526
65. Kannel, P. R., et al. (2007). Pollution of water resources by heavy metals.
66. Land, L. S. (1995). The role of saline formation water in crustal cycling. *Aquatic Geochemistry, 1*(2), 137–145. https://doi.org/10.1007/BF00702887
67. Lefebvre, S. (2003). Interface eau-sédiments des cours d'eau en région agricole : rôle dans les cycles biogéochimiques.
68. Lacroix, G. (2008). From food webs to functioning of lake ecosystems: Toward an integration of heterogeneity and complexity.
69. Milanolo, S. (2016). A conceptual model of the inorganic carbon transport within a karst massif. 43–57. https://doi.org/10.1007/978-3-319-29308-0_4
70. Menegasse, L. N. (2003). Hidroquímica das águas subterrâneas do médio Jequitinhonha, Minas Gerais, Brazil. 3. https://doi.org/10.5380/HG.V3I0.2636
71. Menesguen, A., & Dion, P. (2007). Rôle du phosphore dans l'eutrophisation littorale. 33, 17–35.
72. Meybeck, M. (1986). Composition chimique des ruisseaux non pollués en France. *Chemical composition of headwater streams in France, 39*(1), 3–77. https://doi.org/10.3406/SGEOL.1986.1719
73. Milanolo, S. (2016). A conceptual model of the inorganic carbon transport within a karst massif. 43–57. https://doi.org/10.1007/978-3-319-29308-0_4
74. Moore, J. N., & Luoma, S. N. (1990). Hazardous wastes from large-scale metal extraction. A case study. *Environmental Science & Technology, 24*(9), 1278–1285. https://doi.org/10.1021/ES00079A001