International Journal of Multidisciplinary Comprehensive Research

The chemical elements of plants: A review

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Article Info

ISSN (online): 2583-5289
Volume: 03
Issue: 04
July-August 2024
Received: 14-04-2024
Accepted: 19-05-2024
Page No: 06-11

Abstract
Plants contain many chemical elements, the accumulation of individual elements or groups of five to ten elements (such as CR, CO, MN, and Zn) in medicinal plants have been reviewed. The chemical features of medicinal plants act as an integral determinant of the characteristics of their species, pharmacological properties and enable their widespread use in medical practice. Where these elements are used in the synthesis of physiologically active substances and these elements are divided into large elements and small elements.

DOI: https://doi.org/10.54660/IJMCR.2024.3.4.06-11

Keywords: plant, element, macroelements, non-essential elements

1. Introduction
In ancient times, the first objective of man was to know the world and to understand natural phenomena. A great problem that those ancestors had was the study of food. At that time, the food was a magic and divine gift. They knew of the need that man had for food to live and, in the same way, animals. Man also knew that the life of the plants depended on their roots. Sometime later, it was thought that food was a gift from the land and her produce, from mother earth. As a consequence of this conception, it was believed that the food was something supernatural and was generally associated with the will of the gods. Before the discovery of the microscope, many scientists believed that man is formed from the sperm of chocolate or male seed and the blood of women. During 83 BC, the Greeks, mainly Theophrastus (371-286 BC) and Plutarch (46-125 BC), were particularly dedicated to the study of plants. However, only in the Christian 3rd century, Greeks and Romans became particularly dedicated to the study of both humans and plants. (GIESECKE & SIEDE, 2023, Irwin, 2020, TOUWAIDE 2022) [11, 15, 39].
Given the history of plants and the importance of chemistry in determining the composition of molecules, this chapter attempts to address the chemical composition of the elements of plants. To determine the composition of the mature, dry plant, samples of water-insoluble solids after lyophilization are usually analyzed. In most cases, whole plants or individual tissues were ground, dried and subjected to further mild extraction to remove readily available water, then soluble carbohydrates, organic acids and certain cations (K^+, Mg^{2+} and Ca^{2+}) were selectively extracted by weak solvents such as 80% ethanol over 4 h at 80°C, before final drying. The proximate cell wall products, cellulose, lignin and some protein, were historically determined by physical, chemical and spectroscopic methods for component analysis. These methods are still in use to provide information on cell wall chemistry of plants or cell suspension cultures. (Valkama *et al*. 2021, Yamamoto *et al*., 2021, Feng *et al*., 2022) [40, 43, 9].

2. Importance of Chemical Elements in Plants
Chemical elements are an integral part of the major classes of constituents of plants. They are widely distributed throughout the plant and provide mechanistic capabilities of physiological functions and reproduction. With few exceptions, the 93 natural elements have been found in flower plants. Some contribute major strength, bulk, and rigidity to plant architecture and are present in often decreasing concentration within and throughout the plant from the first internode to leaves, to reproductive and nonreproductive organs.

Many are essential for the completion of the life cycle of all flowering plants and for specialized parts or in specialized metabolic pathways of a few species. Some are multifunctional and may contribute structural and functional strength in different roles in major groups of plants. (Pengelly, 2020, Kirkby, 2023) [29, 21].

Advances in our ability to define the types and quantify the amounts of the atoms in plants have become possible in the last 20 years. Methods have been developed that are capable of defining and determining the concentration of most of the elements throughout different parts of selected plants at the part per billion level for most elements. Quantitative capabilities now are increasingly becoming possible for much smaller concentrations as we become more capable of measuring and collecting and analyzing data. This is especially and most capable with extra special sensitivity by utilizing the properties of specific isotopes and isotopic ratios of hydrogen, carbon, nitrogen, oxygen, and sulfur, and triply differentiating molybdenum, uranium, thorium, and lead, and quadruply differentiating specific rare earths during mass spectrometric measurements. (Fitzgerald *et al*., 2020, Wieczorek *et al*., 2022) [10, 42].

3. Essential Macroelements

The role and behavior of the elements are also considered, establishing a connection between known properties, both physical and chemical, and the functions and behavior of the element in plants. Each of these elements belongs to a group, which connects the common behaviors of a determined group of elements and contributes to predetermine their behavior in the biological process. The last section is dedicated to the definition of stoichiometry, a very useful concept when considering ion exchangers, nutrient balance in soil, and ion absorption. The definition of stoichiometry is related to the composition and balance of elements in plants. Relations with elements, aspect ratios, nutrient balance, the Law of Minimum, and Liebig's Law are also considered. Other modifications to Liebig's Law are included, and a relationship between biochemical processes and the elements involved in the process is established. (Nardi *et al*., 2021, Khan *et al*. 2021, Ali *et al*. 2020) [26, 18, 3].

The essential elements, their functions, and proven values as such are considered. A brief summary of the discovery, isotopes, and reboils of each element are also included. The role and behavior of the elements are also considered, establishing a connection between known properties, both physical and chemical, and the functions and behavior of the element in plants. Each of these elements belongs to a group, which connects the common behaviors of a determined group of elements and contributes to predetermine their behavior in the biological process. The last section is dedicated to the definition of stoichiometry, a very useful concept when considering ion exchangers, nutrient balance in soil, and ion absorption. (Feng *et al*. 2021, Nardi *et al*., 2021) [8, 26].

3.1. Nitrogen

Nitrogen is a component of many of the most important plant materials. It is present in proteins, amino acids, nucleic acids, chlorophyll, vitamins, hormones, and alkaloids. The amount of nitrogen in harvested produce of field crops varies between 0.01% in true seed of corn to 2.5% in young foliage on a dry weight basis. By weight, it constitutes only about 0.5% of the whole plant but it is the main functioning element that regulates the development of the plant. Within the cell, nitrogen is mainly present in the protoplasm and is the key element of the structure and function of enzymes which perform biosynthesis. The nitrogen use efficiency depends on nitrogen signals perceived by plants, indicating that increases in nitrogen levels sustain inflammation and subsequently prompt a mechanism for high nitrogen use efficiency. The leaf area, height, and biomass values of the Clusia fluminensis submitted to treatments with 60% NH4+-N as a source of nitrogen and 40% NO3--N as a source of nitrogen are higher than those of the control. (Fathi, 2022, Ahmad *et al*.2022) [7, 1].

Nitrogen, the assimilation of nitrogen, and nitrate reductase (NR) gene expression were studied in the cells of a green microalga, Scenedesmus sp. under the effect of short-term and long-term exposures to various concentrations of nitrogen sources. Studies performed in a long-term culture indicated that fresh weight, total protein, chlorophyll a, and carotenoids increased with urea, amino acids, or nitrate when the biological index was at the maximum level. However, the fastest rates of fresh weight, growth, and carotenoid content were obtained when the nitrate nitrogen covered 100% of the plant requirements, and the optimal condition for the nitrate reductase activity was when the nitrate covered 50% or 100% of the nitrogen plant requirements. Nitrate is the main form of nitrogen available to plants, and in most nitrate assimilation studies, nitrate has been treated as the sole or overwhelmingly preferred source of nitrogen by plants. (Chen *et al*., 2020, Vidal *et al*. 2020) [5, 41].

3.2. Phosphorus

Phosphorus is a major nutrient and energy carrier in living cells. Combined with sugars and nitrogen compounds, energy-rich nucleotides such as adenosine triphosphate are formed in the reactions of photosynthesis and oxidative phosphorylation. Organic phosphorus compounds are used as part of DNA and RNA, as structural components of some proteins, coenzymes, and transfer substances. In plants, a great majority of phosphorus accumulates within cells. Phosphorus is mainly an internal factor of plants, limiting desirable water-use efficiency, growth, seed and fruit production, and fruit quality (reducing sugar content and hence reducing flavor). The most common states of P in soil that are of importance for plant nutrition are the inorganic P classes—orthophosphate (HPO4–, H2PO4–) and the organic P classes—substances containing ester, anhydride linkage, ester-linked sugars possessing P, and cyclic acid anhydrides found in nucleic acids. (Elser & Haygarth, 2020, Bird & Eskin, 2021) [6, 4].

Large amounts of P are usually absorbed from soil and accumulated in plant parts before the critical growth stages (e.g., increasing grain number stages in rice and maize). However, during the harvest phase, plant P is remobilized and translocated to seeds, or edible parts, and stem microdomains, and this may exceed the P in roots. Phosphorus in plants is often remobilized within the parentheses and translocated to the parentheses in pea and Arabidopsis. As with the remobilization of nutrients incorporated into seeds, the P absorbed by pea plants was located on one branch, whereas only low levels were detected elsewhere. Consequently, the overall dynamic patterns of the subcellular and ultrastructural changes during the redistribution of remobilized P in leaves mirrors the changes across the entire leaf area. Phosphorus losses occur during leaf P remobilization and translocation of the parenthesis decreases the overall P use efficiency of the plants. (Lambers, 2022, Tian *et al*., 2021) [22, 38].

3.3. Potassium

K (potassium) is an element of great importance to plants and is the third element in terms of the quantity absorbed. It enters the composition of chlorophyll, performs osmotic functions, and activates many enzymes. The aerosol leaves a plant where it is transported by the xylem, called saturating sap because of the high concentration of KCl. The leaves have a higher concentration of K than Ca and Mg. Maintaining a good potassium status helps plants strengthen cellular structures and resist stress caused by drought, pathogens, pests, salinity, and low temperatures. (Sardans & Peñuelas, 2021, Johnson *et al*. 2022) [32, 16].

The elements fulfill diverse functions in the dynamic life of plants. Many of them are found in large quantities in the dry matter of plants, generally associated with their essential activity. K (potassium) is an element of great importance to plants and is the third element in terms of the quantity absorbed. It is present, in general, in relatively large amounts in the ground (K excess). For this reason, it is less frequently added to the cultivation area. Its availability depends on the ability of the clay portion of the soil to fix K+ and possibly provide it to plants. Its removal is dependent on the species, part of the plant, and crop productivity. The plant's potassium status is higher than that of Ca and Mg. This concentration can be explained by several reasons. The properties of K in soils regulate the amount of K absorbed by plants as a function of K reserves, where crops can help regulate potassium concentration in animals, both of which require it for various organic compounds. Besides being a constituent of chlorophyll, K develops specific functions in the metabolisms of plants. The stochastic moment of the enriched K-free channel in the ventral membrane controls the opening and closure of light of the stammer. In plants, K passes from the soil to the root surface and then to the root inside. The entry of K from the soil to the cortex into the root is an active process. Once inside the cortex cells, K passes via a membrane and a symporter transport tool, which, as a K+ proton channel, exchanges the entry of K for the exit of a proton. After that, K passively spreads into the plant through the xylem. When potassium is not enough, it affects the assimilatory, digestive, and respiratory functions. The plant grows stunted and the tissues become more susceptible to biotic and abiotic stress. In cases of phloem injury, the K concentration of the plant becomes toxic, especially in the apex tissue cells where K accumulates. (Pandey & Mahiwal, 2020, Sardans & Peñuelas, 2021, Soumare *et al*., 2023, Johnson *et al*. 2022) [27, 32, 16, 34].

4. Essential Microelements

Essential microelements (those required in quantities of 1–100 mg per kg of plant tissue) have only been demonstrated for a small number of plant species. The soil solution contains the elements likely to be present in the largest concentration, as either or both parent compounds or ions; these are present at concentrations greater than 10-5 equivalents/litre. The semi-metal micronutrients (Fe, Cu, Zn, and Mn) required by vascular plants are almost all present in the soil as ions—not as compounds-and are thus ions when they are taken up by the plants. For several of these elements, in conditions of soil pH, water content, and aeration that govern the bioavailability of their ions, the concentration of these ions can drop quite rapidly within the root zone due to the activities of the roots and soil microorganisms. Boron is an exception to the above. In the soil solution, boron is present in five forms, principally the boron-rich molecules BO3- and B4O5 (OH) 4, which are both negatively charged ions. Among them, they make up at least half the boron present and in some soil types 90 per cent or more. (Kicińska *et al*. 2022, Khan *et al*. 2021, Ali *et al*. 2020) [20, 19, 3].

The elements essential in a typical situation are needed by plants because they fill structural or functional roles in certain essential organic molecules. These vital functions have rarely been demonstrated, or are not universally accepted. The element indicated by the symbol is based on elemental analysis and is given in full, even though its English name also begins with the same letter. Barium, bromine, iodine, molybdenum, and silicon are sometimes mentioned in the microelement context but other examples might be found. Experiments have demonstrated that arsenic, chlorine, and some or all of the rare earth elements are needed by a terrestrial crop under certain circumstances. A wide variety of elements can play a beneficial role in some plant tissue, but this does not make these elements essential. In this review, only those elements essential for – and taken up by – some plant species are considered. (Ajeesh *et al*. 2020, Huang *et al*., 2020) [2, 14].

4.1. Iron

Iron is essential for the respiration of all plants, and its functional role is the transfer of electrons in chlorophyll, cytochrome, and Fe-protein. Indeed, chlorophyll synthesis and respiration in plants continue with less iron. Iron regulates many metabolic pathways of living cells, such as tricarboxylic acid, citric acid, and the biosynthesis of lipoic acid. It also serves as a structural component of DNA in a living cell. Iron is absorbed from the rhizosphere in the form of ferric ion but is converted into ferrous ion and absorbed by the root. Translocation of iron from root to shoots through xylem is limited, and its distribution in coated and non-coated parts is low. The main physiological problems in plants related to iron are iron absorption and the stability of iron in the presence of oxygen. However, in the xylem, iron utilized as an enzyme is easy to induce the generation of active oxygen. (Riaz & Guerinot, 2021, Murgia *et al*. 2022) [30, 25].

Since the start of studies on plant nutrition, iron deficiency has been of major interest. Typical symptoms of iron (Fe) deficiency begin with a decrease in the dry weight of various above-ground plant parts. Subsequent bleaching of the young leaves is closely associated with low chlorophyll concentration and inactivation of photosynthesis. Iron does not move easily from roots to the shoot. In other words, Fe preferentially accumulates in the root tissues. Many plants grown under high or low levels of Fe show anoxic conditions when filled with nutrient solution without aeration. The solubility of Fe is low in the rhizosphere, in which a rhizosphere indicator called the resin ratio of the root iron biologisia appears. (Zhang *et al*. 2024, Tamuk *et al*. 2024) [45, 37].

4.2. Zinc

Zinc is an essential trace element for plants and animals. Zinc needs an intermediate level of plant-available zinc in soils, and wheat is known for having a high Zn requirement in contrast to other cereals for proper growth. Zinc deficiency is one of the major malnutrition problems in the world. Zinc utilization in the plant is highly regulated. Competition and regulation across the membrane deliver a spatiotemporal regulation of zinc and various ions in plants are imported. Downstream, the plasma membrane usually has uptake transporters that bring the ions into the cell. There is evidence for both non-selective and more selective cation channels transporting Zn into the plant cell. In particular, the role of HMA2, an ortholog to the mammalian Zn export transporter ZnT, is involved in more selective Zn transport processes regulating shoot and leaf Zn contents. Calcineurin B-like protein 1 (CBL1) might regulate the HMA2 transporter in Arabidopsis thaliana. In Brassica napus, there is evidence for a role of heavy metal P-type ATPases encoding the HMA2 transporter in Zn hyperaccumulation. (Gondal *et al*. 2021, Kaur *et al*., 2023) [12, 17].

In the plant, multiple mechanisms regulate the zinc distribution from root to shoot, which has been nicely reviewed in 2016 by Wirth *et al*. Apart from Zn uptake, there are also reports on transport processes where a plant lacks an intra- or extracellular zinc transport functionality. Deficiency and hyperaccumulation mechanisms for zinc need to be carefully balanced to maximize Zn content in the edible plant part. Although the underlying mechanisms are conserved, their regulation seems to differ. Zn distribution and accumulation in edible plant parts are likely to be important for the human diet. There is evidence for a link between Ca deficiency and Zn bioavailability in plants, which is important for human health. Auxin homeostasis determines proper zinc distribution independent of shoot boron accumulation, which is independent of shoot zinc accumulation, and the fight for Zn uptake between the heavy metal ions cadmium and zinc needs to be balanced. (Stanton *et al*., 2022, Hamzah *et al*. 2022) [36, 13].

4.3. Copper

The symbol of copper is Cu, and the atomic number is 29. The deficiency of this element happens rarely in plants growing on soils with a high content of this element, while in soils with an oxidized layer where the copper content decreases considerably, the growth of the plants that need a high level of copper is significantly restricted. The characteristic which the elemental metal of copper has is the atomic system. This metal guarantees that the electrons can move through the system isolated, generating a very peculiar activity that lodges its name exactly, and is the characteristic that satisfies the high capacity of heat and electric conductivity of copper. The important chemical characteristic of copper is possibly its capacity to present cupric and cuprous ions, capable of acting as cathodes whereas the metal acts as an anode, protecting structurally another body. (Rong *et al*. 2021, Zhao *et al*. 2020) [31, 46].

Copper is a constituent of the structure of the systems of plants capable of accepting cations with the same load and hydrated of similar size, like a cupric ion Cu^{++} of hydrated radius 0.445 nm being absorbed in the root zone. Acting as a cofactor, this element takes part in several enzymatic reactions. Among the enzymes present in plants in very small quantities are the superoxide dismutase that uses the superoxide ion and the water molecule, and the ascorbate oxidase which acts in the ascorbic acid oxidation. Copper also intervenes in the substitution of oxygen in the cytochrome c oxidase process. Copper is translocated in significant proportions as a major component of the extracellular oxidase tyrosinase and of the plastocyanin involved in the photosynthesis in the chloroplasts. Due to the large consumption of oxygen, cereals submitted to short treatments with $CuSO_4$ present reduced germination levels, and the others show biochemical harmful effects. In grapevine in deficiency, the culture also presents vegetal vigor reduction, accompanied by a decrease in the berry sugar accumulation. (Mir *et al*., 2021, Zandi *et al*., 2020, Shabbir *et al*. 2020) [24, 44, 33].

5. Non-Essential Elements and Their Functions

Non-essential Elements

To date, non-essential elements such as silicon (Si), sodium (Na), cobalt (Co), bromine (Br), and cadmium (Cd) have been recognized to play roles in a few or more functions. Many studies delve into obtaining detailed behavior of these non-essential elements using different techniques. However, the results are insufficient for us to explain the roles of the non-essential elements. Furthermore, some elements in this group also have beneficial effects and could be beneficial elements. Proper studies of these non-essential beneficial elements are needed. (Souri *et al*. 2021, Pavlovic *et al*. 2021) [35, 28].

Silicon exists extensively in the earth's crust. Si has several effects in plants depending on the species, form, and concentration of its medium. Surprisingly, Si is not essential for the growth of many plants. For instance, Si is not essential for rapeseed plants. However, Si exerts beneficial or functionally beneficial effects on most plants. The concentration of Si in plant roots is rather stable under different experimental conditions, and Si performs its beneficial influence in combination with other elements. Research shows that Si is related to metal accumulation, which is the main reason Si is taken up into plants. In recent years, Si has become one of the main topics in plant studies. In addition, the largest difference between organic and chemical fertilizers is diatomite, which is the main form of a natural source of Si. Consequently, the effects of Si on plants attracted the attention of experts. In the present review, we will describe our understanding of Si in detail. (Souri *et al*. 2021, Pavlovic *et al*. 2021, Mandlik *et al*. 2020) [35, 28, 23].

6. Conclusion and Future Research Directions

Plants consist of non-metallic elements that are not the focus of many studies. However, they are critically important in their uptake and thus to the provision of human health. We have reviewed literature studies that discuss the nutritional requirements and the detection and determination of the non-metallic elements of plants, including elements such as H, C, O, N, P, S, F, Cl, and Br. The combinations of detection instrumental techniques are also discussed in this perspective such as chemical composition (CC), chemical analysis (CA), X-ray spectrometry (XRF), X-ray fluorescence (XRF-G, XRF-W), Fourier-transform infrared adsorption, Σ-XRS, tube X-ray fluorescence, X-ray photoelectron spectroscopy (XPS, XPS-C, XPS-CV), electron microprobe, ion chromatography (IC), inductively coupled plasma-optical emission spectroscopy, inductively coupled plasma-mass spectroscopy (ICP-MS, ICP-MS-SIM, ICP-MS), inductively coupled plasma-atomic emission spectroscopy, inductively coupled plasma-mass spectrometer, isotope ratio mass spectrometry, and nano-DESI-MS.

Future research purposes could be focused on the elements that are unknown to both the detection instrumental techniques and to the other focus factors. In addition to this, other purposes could involve the discovery of new instrumental techniques that could be used as a comparison for data quality, reliability, and the determination of the elements for plants. These focuses should involve more research studies, especially for the elements fluorine and bromine, and also in other doses, e.g., median lethal dose (LD50). This is because only one instrumental technique is the mostly commonly used as the detection and determination factor, which is mainly the ICP/OES technique.

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