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Review

Elucidating rhizosphere processes by mass spectrometry – A review

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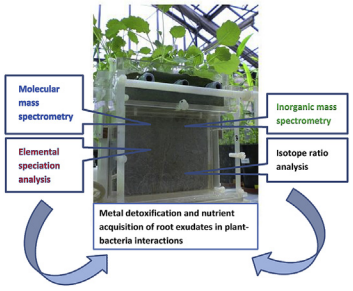
HIGHLIGHTS

- State-of-the-art mass spectrometry methods developed and applied in rhizosphere research are reviewed.
- Elemental and molecular mass spectrometry emphasizing different separation techniques (GC, LC or CE) are discussed.
- Case studies on metal detoxification and nutrient acquisition of root exudates in plant-bacteria interactions are discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

The presented review discusses state-of-the-art mass spectrometric methods, which have been developed and applied for investigation of chemical processes in the soil-root interface, the so-called rhizosphere. Rhizosphere soil's physical and chemical characteristics are to a great extent influenced by a complex mixture of compounds released from plant roots, i.e. root exudates, which have a high impact on nutrient and trace element dynamics in the soil-root interface as well as on microbial activities or soil

Abbrevation: APCI, atmospheric pressure chemical ionization; CE, capillary electrophoresis; CE-ESI-MS, capillary electrophoresis coupled to electron ionization mass spectrometry; CE-ICP-MS, capillary electrophoresis coupled with inductively coupled plasma mass spectrometry; CE-ICP-SFMS, capillary electrophoresis coupled to (double focusing) sector field mass spectrometry; CRM, certified reference material; DMA, 2′-deoxymugineic acid; ESI-MS, electrospray ionisation mass spectrometry; GC, gas chromatography; GC-APIC, gas chromatography coupled with atmospheric pressure chemical ionisation; GC-c-IRMS, gas chromatography combustion isotopic ratio mass spectrometry; GC-ICP-MS, gas chromatography coupled with inductively coupled plasma spectrometry; GC-ICP-TOF-MS, gas chromatography inductively coupled plasma time of flight mass spectrometry; HF-LPME, hollow fibre liquid-phase micro extraction; HILIC, hydrophilic interaction liquid chromatography; HPIC, high performance ion chromatography; HPLC, high performance liquid chromatography; HPLC-ICP-MS, high performance liquid chromatography coupled to inductively coupled plasma mass spectrometry; IC-ICP-MS, ion chromatography inductively coupled plasma mass spectrometry; IC-ICP-QMS, ion chromatography coupled to inductively coupled plasma quadrupole mass spectrometry; IC-ICP-SFMS, ion chromatography coupled to inductively coupled plasma sector field mass spectrometry; ICP, inductively coupled plasma; ICP-AES, inductively coupled plasma atomic emission spectrometry; ICP-DRC-MS, inductively coupled plasma mass spectrometer equipped with dynamic reaction cell; ICP-MS, inductively coupled plasma mass spectrometry; ICP-QMS, inductively coupled plasma quadrupole mass spectrometry; ICP-SFMS, inductively coupled plasma sector-field mass spectrometry; ICP-TOF-MS, inductively coupled plasma time of flight mass spectrometry; IRMS, Isotope ratio mass spectrometry; LC, liquid chromatography; LC-ESI-MS or LC-ESI-MS/MS, liquid chromatography coupled with electrospray ionization mass spectrometry; LC-ESI-Q-TOF-MS, Liquid chromatography-electrospray ionization-quadrupole-time of flight mass spectrometer; LC-ESI-TOF-MS, liquid chromatography coupled with ESI with time of flight MS; LC-ICPMS, liquid chromatography inductively coupled plasma mass spectrometry; LC/IRMS, liquid chromatography isotope ratio mass spectrometry; LOD, limit of detection; MS, mass spectrometry; MALDI-TOF/TOF-MS, matrix assisted laser desorption ionisation tandem time of flight mass spectrometry; MC-ICPMS, multicollector inductively coupled plasma mass spectrometry; Py-FIMS, pyrolysis-field ionization mass spectrometry; QMS, quadrupole mass spectrometry; RP-HPLC, reversed phase high performance liquid chromatography; RP-HPLC-ICP-DRC-MS, high performance liquid chromatography coupled to inductively coupled plasma dynamic reaction cell mass spectrometry; SEC, size exclusion chromatography; SFMS, (double-focusing) sector field mass spectrometry; TOF-MS, time of flight mass spectrometry; TOF-SIMS, time of flight secondary ion mass spectrometry; UHPLC-TOF-MS, ultra-high-performance liquid chromatography time-of-flight mass spectrometry.

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physico-chemical characteristics. Chemical characterization as well as accurate quantification of the compounds present in the rhizosphere is a major prerequisite for a better understanding of rhizosphere processes and requires the development and application of advanced sampling procedures in combination with highly selective and sensitive analytical techniques. During the last years, targeted and non-targeted mass spectrometry-based methods have emerged and their combination with specific separation methods for various elements and compounds of a wide polarity range have been successfully applied in several studies. With this review we critically discuss the work that has been conducted within the last decade in the context of rhizosphere research and elemental or molecular mass spectrometry emphasizing different separation techniques as GC, LC and CE. Moreover, selected applications such as metal detoxification or nutrient acquisition will be discussed regarding the mass spectrometric techniques applied in studies of root exudates in plant-bacteria interactions. Additionally, a more recent isotope probing technique as novel mass spectrometry based application is highlighted.

Contents

1. Introduction

Plant root exudates comprise an enormous range of low and high molecular weight compounds that are released into the close environment of soil, the so-called rhizosphere [1]. The rhizosphere, as described first by Lorenz Hiltner in 1904, is the “soil influenced by roots” [2] representing the highly dynamic interface between soils and roots as well as between roots and soil microbes, invertebrates, and root systems of competitors [3]. The rhizosphere itself is different from bulk soil due to a range of biological, biochemical, chemical and physical processes that occur as a consequence of root growth, water and nutrient uptake, respiration, rhizo-deposition and enhanced microbial activities [4].

Plant root exudates consist of a complex mixture of hundreds of different compounds [5] which can be categorized according to their molecular mass [6] along to their solubility in water. The water-soluble fraction comprises low molecular weight carbohydrates, amino acids, organic acid anions, inorganic ions (*e.g.* HCO_3^-, OH^-, H^+), gaseous molecules (CO_2, H_2) and various secondary metabolites (*i.e.* natural compounds). On the other hand the more hydrophobic fraction is largely composed of polymeric carbohydrates, enzymes, plant mucilages or mucigel [7]. Amongst low molecular weight root exudates organic acids represent the most abundant fraction playing a crucial role involved in different processes, thus they are of great interest for detailed investigation.

A large range of low molecular weight exudates are pivotal for nutrient acquisition [8] based on chelation and/or ligand exchange by organic acids (citrate, malate and oxalate) [9–11]. It is well known that organic acids [12–14], as well as amino acids and phenolic surfactants [8] are involved in iron and phosphorous acquisition. Vitamins [15] and sugars [16] are considered as promoters of plant and microbial growth, while, *e.g.* detoxification of aluminium is attributed only to organic acids [17] and phenolic compounds [16]. Furthermore, several complex interactions with soil microorganisms mediated by root exudates are taking place in the rhizosphere, as illustrated in Fig. 1 [18]. Roots produce chemical signals that attract or repel bacteria and fungi via the secretion of flavonoids, strigolactones or antimicrobials, phytotoxins, nematicidal and insecticidal compounds [18].

Even though plant root exudates and the biological processes triggered within the rhizosphere have a crucial role in plant development, there is still a lack of information about their characterization and function [19]. Comprehensive chemical characterization as well as quantification of exudates present in the soil root interface is to a great extent an analytical challenge due to their localized deposition as well as the low concentration in the soil solution and the associated difficulties of proper sampling of exudates and/or rhizosphere soil and soil solution. In the recent years the development of mass spectrometric techniques contributed significantly to an increased understanding of the rhizosphere. The method portfolio offered by mass spectrometry (MS) combined with diverse separation methods for volatile and polar compounds