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Review

The role of root exuded low molecular weight organic anions in facilitating petroleum hydrocarbon degradation: Current knowledge and future directions

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HIGHLIGHTS

- Rhizoremediation is a novel technology for remediating contaminated surface soils.
- Root exudates' interaction with microbes likely drives effective rhizoremediation.
- Carboxylates can provide microbial nutrients and/or enhance PHC bioavailability.
- The role of carboxylates in rhizoremediation requires further investigation.

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ABSTRACT

Rhizoremediation is a bioremediation technique whereby enhanced microbial degradation of organic contaminants occurs within the plant root zone (rhizosphere). It is considered an effective and affordable 'green technology' for remediating soils contaminated with petroleum hydrocarbons (PHCs). This paper critically reviews the potential role of root exuded compounds in rhizoremediation, with emphasis on commonly exuded low molecular weight aliphatic organic acid anions (carboxylates). The extent to which remediation is achieved shows wide disparity among plant species. Therefore, plant selection is crucial for the advancement and widespread adoption of this technology. Root exudation is speculated to be one of the predominant factors leading to microbial changes in the rhizosphere and thus the potential driver behind enhanced petroleum biodegradation. Carboxylates can form a significant component of the root exudate mixture and are hypothesised to enhance petroleum biodegradation by: *i*) providing an easily degradable energy source; *ii*) increasing phosphorus supply; and/or *iii*) enhancing the contaminant bioavailability. These differing hypotheses, which are not mutually exclusive, require further investigation to progress our understanding of plant–microbe interactions with the aim to improve plant species selection and the efficacy of rhizoremediation.

Contents

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1. Introduction

Increasing industrialisation and associated oil exploration has resulted in vast quantities of petroleum contaminants being released into the environment. Accidental spills from the petroleum industry are one of the leading causes of soil and groundwater pollution (Holliger et al., 1997). Soils contaminated by petrochemicals can rapidly lose their function and stability, with severe contamination events leading to considerable environmental deterioration and/or loss of natural and agricultural productivity.

Traditional remediation techniques involving physical (washing, excavation) and/or chemical treatments are expensive and can be environmentally destructive (Kuiper et al., 2004). For example, chemical treatment technologies such as flushing the soil with strong oxidisers or surfactants can exceed costs as high as US$300 yard^{-3} soil (US EPA, 2006). There is, therefore, a growing need to develop 'green technologies' that reduce both financial and environmental costs.

Rhizoremediation, whereby enhanced microbial degradation of contaminants occurs within the plant root zone (rhizosphere), is one such 'green technology' with great potential for mitigating the effects of organic pollutants in surface soils (Pilon-Smits, 2005). Much research in this area has aimed to compare the differing abilities amongst plant species or families to remediate petroleum hydrocarbons. A major reason for the differences in the ability of plant species to stimulate microbial biodegradation is likely due to the compounds exuded by plant roots. Carboxylic acid anions (carboxylates) comprise a significant proportion of exuded compounds and whilst their involvement in rhizoremediation as a component of the exudate mixture is often broadly alluded to, the exact mechanism remains poorly understood (Germida et al., 2002; Joner and Leyval, 2003; Macek et al., 2000; Sun et al., 2010). This needs to be addressed if we are to improve the efficiency and efficacy of rhizoremediation.

This review commences with an outline of our current understanding of bioremediation and rhizoremediation, with emphasis on how root exudation is believed to drive these processes. We survey current theories in regard to the functional role of carboxylates and their hypothesised links to the enhancement of hydrocarbon degradation in the rhizosphere. We also discuss current knowledge gaps and limitations that surround the function of carboxylates in rhizoremediation, with the ultimate goal of guiding work toward more efficient and effective selection and breeding of potential rhizoremediation plant species.

2. Bioremediation

The major oil spills that occurred during and after the 1970s, such as the *Exxon Valdez* and *Amoco Cadiz* tanker accidents, prompted research into the use of microorganisms to breakdown organic contaminants; a process known as bioremediation (Atlas and Cerniglia, 1995; Chapelle, 1999). Bioremediation is an effective and affordable clean-up strategy to remove organic contaminants from the environment, particularly those derived from the petroleum industry (Erickson et al., 1992). The concept utilises the natural metabolic capabilities of microbiological agents (chiefly, bacteria and fungi) to ultimately transform organic contaminants into carbon dioxide, water and cell biomass (Atlas, 1995). The success of bioremediation is actuated by the ability of soil microorganisms to gain access to the contaminant/s of interest (bioavailability) and also by the parameters which affect their growth and reproduction, such as nutrient availability, temperature, soil pH and habitat availability (Head and Swannell, 1999; Vidali, 2001). By understanding and ultimately manipulating these factors, the effectiveness of bioremediation may be vastly improved.

2.1. Microbial degradation of petroleum hydrocarbons (PHCs)

Microorganisms have been present on Earth for more than 3.5 billion years and are ubiquitous throughout an array of environments, so it is not surprising that they have evolved diverse degradative pathways capable of breaking down an equally diverse set of environmental chemicals (Westall, 2005). Typically, the microbial functional community in both terrestrial and marine environments changes following a petroleum spill due to an increase in the relative abundance of indigenous hydrocarbon degrading organisms (Chaudhry et al., 2005; Hamamura et al., 2006; Mikkonen et al., 2011). For instance, the concentration (cells mL^{-1}) of hydrocarbon degraders in a contaminated marine environment increased from as low as 1–10% of the microbial community to as high as 40% following the *Exxon Valdez* tanker accident of 1989 (Atlas and Hazen, 2011). Organic contaminants can provide microorganisms with a carbon source and provide the electrons required in respiration (Germida et al., 2002). Whilst some microbes are capable of completely mineralising organic contaminants, most individual species are not equipped with all the appropriate enzymes, and thus degradation is primarily achieved via a consortium of microbes with diverse enzyme systems (Chaudhry et al., 2005; Macek et al., 2000; Yateem et al., 2007).

2.2. Parameters affecting petrochemical degradation

There are a variety of parameters which may dictate the extent and rate to which petroleum hydrocarbons are biodegraded in the soil. Those parameters that are responsible for maintaining and/or increasing soil microbial activity and abundance and therefore affecting hydrocarbon biodegradation, are presented in Table 1.

In general, the biodegradation susceptibility of the individual hydrocarbons that constitute petroleum mixtures decreases with

Table 1
Factors determining microbial degradation of petroleum hydrocarbons in soil[a].

Factor	Optimum conditions for microbial petroleum hydrocarbon degradation*
Oxygen	>0.2 mg L^{-1} dissolved oxygen or >10% air-filled pore space for aerobic degradation
Water holding capacity	20–80% water-filled porosity
Macronutrients	C:N:P = 120:10:1 molar ratio for microbial growth
pH	5.5 to 9
Temperature	20–30 °C
Redox potential	Eh > 50 mV
Hydrocarbon concentration	5–10% soil dry weight

[a] Optimum levels based on Dibble and Bartha (1979), Shukla et al. (2010), Tibbett et al. (2011) and Vidali (2001).