Phytoremediation: PAHs, Anilines, Phenols

Phytoremediation of Polycyclic Aromatic Hydrocarbons, Anilines and Phenols

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Abstract. Phytoremediation technologies based on the combined action of plants and the microbial communities that they support within the rhizosphere hold promise in the remediation of land and waterways contaminated with hydrocarbons but they have not yet been adopted in large-scale remediation strategies. In this review plant and microbial degradative capacities, viewed as a continuum, have been dissected in order to identify where bottlenecks and limitations exist. Phenols, anilines and polycyclic aromatic hydrocarbons (PAHs) were selected as the target classes of molecule for consideration, in part because of their common patterns of distribution, but also because of the urgent need to develop techniques to overcome their toxicity to human health. Depending on the chemical and physical properties of the pollutant, the emerging picture suggests that plants will draw pollutants including PAHs into the plant rhizosphere to varying extents via the transpiration stream. Mycorrhizosphere bacteria and fungi may play a crucial role in establishing plants in degraded ecosystems. Within the rhizosphere, microbial degradative activities prevail in order to extract energy and carbon skeletons from the pollutants for microbial cell growth. There has been little systematic analysis of the changing dynamics of pollutant degradation within the rhizosphere; however, the importance of plants in supplying oxygen and nutrients to the rhizosphere via fine roots, and of the beneficial effect of microorganisms on plant root growth is stressed. In addition to their role in supporting rhizospheric degradative activities, plants may possess a limited capacity to transport some of the more mobile pollutants into roots and shoots via fine roots. In those situations where uptake does occur (i.e. only limited microbial activity in the rhizosphere) there is good evidence that the pollutant may be metabolised. However, plant uptake is frequently associated with the inhibition of plant growth and an increasing tendency to oxidant stress. Pollutant tolerance seems to correlate with the ability to deposit large quantities of pollutant metabolites in the 'bound' residue fraction of plant cell walls compared to the vacuole. In this regard, particular attention is paid to the activities of peroxidases, laccases, cytochromes P450, glucosyltransferases and ABC transporters. However, despite the seemingly large diversity of these proteins, direct proof of their participation in the metabolism of industrial aromatic pollutants is surprisingly scarce and little is known about their control in the overall metabolic scheme. Little is known about the bioavailability of bound metabolites; however, there may be a need to prevent their movement into wildlife food chains. In this regard, the application to harvested plants of composting techniques based on the degradative capacity of white-rot fungi merits attention.

Keywords: Anilines; bound residues; cytochromes P450; glucosyltransferases; oxidant stress; peroxidases; phenols; phytoremediation; polycyclic aromatic hydrocarbons; rhizosphere

Introduction

Waste products have been dumped in the environment for thousands of years assuming that the environment will adequately absorb them, but this is no longer the case (esp. with industrial compounds) and accumulating pollutants are now affecting the health of living organisms. Physical and chemical remediation techniques are commercially available (for reviews, see Bull 1992, Wilson and Jones 1993), but they are disruptive to the environment. Technologies based on plants represent an attractive alternative because they are 'clean','green', independent of an external energy supply and likely to be more publicly acceptable than the use of chemical methods. They depend on agricultural practice and are perceived to have lower costs in application. The rise in popularity of phytoremediation is borne out by recent reviews on the topic (Cunningham et al. 1996, Salt et al. 1998, Morel et al. 1999, Korte et al. 2000, Macek et al. 2000, Meagher 2000, Mejare and Bülow 2001). There is however, major concern over the time-scales associated with biological methods, both plant and microbial, for which a greater
understanding of the nature of the bottlenecks and limitations will be required if they are to be widely adopted.

In this review, information about plants, their use and biological mechanisms involved in remediating sites contaminated with anilines, phenols or the much less reactive polycyclic aromatic hydrocarbons (PAH's) is examined. Plant response in terms of metabolism, health and adaptive features are considered together with the role that plants may play in ecosystem-remediating strategies involving microorganisms.

1 Properties of Pollutants

1.1 Chemical properties

'Phenols' and 'anilines' are generic terms used to describe alcohol and amine derivatives of benzene respectively (see Fig. 1). Both derivatives exhibit octanol-water partition coefficients ($\log K_{ow}$) in the range from 0.5–3.0 and are soluble in both polar and non-polar solvents. They may also ionise as a function of pH value, anilines ($pK_a$ values = 4.6) becoming positively charged at neutral pH values and phenols, negatively charged at alkaline pH values ($pK_a$ = 7.2–8 for nitrophenols; 8.5–9 for chlorophenols and 9.9 for phenol). These properties significantly influence their potential for plant uptake.

PAHs are comprised of two or more fused benzene rings (see Fig. 2 for examples). They are largely insoluble in water (0.1 μg to 4.5 mg/L), but highly lipophilic, with $\log K_{ow}$ values ranging from 3 to 7. Lipophilicity and water insolubility tend to increase as a function of size along with a decrease in vapour pressure (Aihara 1992). PAHs partition preferentially into the humic fractions of soils rather than the aqueous phases. Those with $\log K_{ow}$ values of 4 or less partition readily across membranes into the lipophilic compartments of living cells and can be taken up by plant roots.

1.2 Bioavailability

Pollutant bioavailability is a major restricting factor in the bioremediation of organic pollutants. Bioavailability depends on the soil structure (content of humic substances, pH value, water content and porosity) and on properties of the pollut-