ELSEVIER

Thermochimica Acta 250 (1995) 353–358

thermochimica acta

Bioenergetics and bioremediation of contaminated soil ☆

Larry E. Erickson [a,*], Lawrence C. Davis [b], Muralidharan Narayanan [a]

Departments of Biochemistry [b] and Chemical Engineering [a], Kansas State University, Manhattan, KS 66506, USA

Received 1 July 1994; accepted 22 July 1994

Abstract

The microbial biodegradation of xenobiotic compounds in soil and ground water is constrained by the laws of thermodynamics. Bioremediation is being investigated in a rhizosphere environment in which higher plants provide carbon and energy to sustain the microbial population. Toluene, phenol, trichloroethylene and trichloroethane have been fed in separate experiments to a pilot scale system with alfalfa growing in sandy soil containing less than 10% of silt. It is well known that microbial populations are numerous in the root zone of healthy vegetation. Root exudates can stimulate aerobic microbial biodegradation of compounds which by themselves support growth poorly or not at all. Polynuclear aromatic compounds such as phenanthrene, anthracene, and pyrene, which are not very soluble in water, and chlorinated aliphatic hydrocarbons such as trichloroethylene are examples of compounds that can be biodegraded in the rhizosphere when root exudates are present to enhance and sustain microbial activity. Solar driven transport processes such as water and solute movements due to evapotranspiration increase the likelihood that the contaminants will come into contact with the microorganisms and be degraded. The thermodynamic and bioenergetic aspects of transport and biodegradation in the rhizosphere are examined through a review of the literature and the analysis of experimental data collected in the pilot scale system.

Keywords: Bioenergetics; Bioremediation; Microbe; Rhizosphere; Vegetation

* Corresponding author.

☆ Presented at the Ninth Conference of the International Society for Biological Calorimetry, Berlin-Schmerwitz, 27–31 May 1994, and dedicated to Ingolf Lamprecht on the occasion of his 60th birthday.

SSDI 0040-6031(94)002041-8

1. Introduction

Vegetation has been shown to enhance the rate and extent of biodegradation in the rhizosphere [1-3]. Root exudates provide carbon and energy, which increases the diversity and numbers of microbial species. Plants consume relatively large quantities of water when actively conducting photosynthesis. This significantly increases the net water flux through the vadose zone, where adapted microbes biodegrade many contaminants. Evapotranspiration increases the potential aeration by lowering the water table and the soil water in the vadose zone. Contaminated ground water can be transported to the root zone by natural pressure gradients, or it can be pumped into the rhizosphere as part of a managed remediation process.

Biodegradation in soil is often enhanced by gratuitous or fortuitous metabolism in which carbon and energy sources supplied by plants help sustain the microbial population that is degrading the contaminant. Enzymes required for biodegradation may be present if similar compounds are supplied as root exudates. Plants supply aliphatic and aromatic organic compounds including sugars, cellulose, other carbohydrates, amino acids, vitamins, lignin, and many other compounds which appear to be important when xenobiotic compounds that are difficult to degrade are present in soil and ground water.

2. Materials and methods

For plant growth, a 35 cm deep tank with 10 cm wide channels was filled with soil composed of sand containing less than 10% of silt [5,6]. The chamber was divided into two separate bioreactors with sampling ports along the 1.8 m axial flow path. Ground water samples which were taken from the sampling ports and the exit were analyzed for the contaminant. Toluene and phenol, respectively, were fed to separate bioreactors during the first year of operation. Trichloroethylene (TCE) and 1,1,1-trichloroethane (TCA) were fed together during the second year of operation. A spectrophotometer was used for the analysis of aqueous phase toluene at 262 nm and phenol at 265 nm [5]. Gas chromatography was employed for the analysis of TCE, TCA and methane in the ground water. Gas phase analysis above the soil surface was accomplished by enclosing the chamber and measuring the concentration of each compound with FTIR [5] spectrophotometry. The aqueous flow into and from each bioreactor was measured daily.

3. Bioenergetic analysis

The amount of carbon and energy delivered to the rhizosphere by growing plants has been reviewed by Erickson et al. [7]. Table 1 shows that 30-50% of the fixed carbon is transported to the root zone; 40-70% of this appears as root exudates. Using these values, Erickson et al. [7] estimated that ≈ 0.3 kJ (kg soil)$^{-1}$ day^{-1} is supplied as root exudates to the microbial population in the rhizosphere. This value is in general agreement with the values of 0.2 kJ (kg soil)$^{-1}$ day^{-1} estimated from CO_2 production measurements and 0.1–0.3 kJ (kg soil)$^{-1}$ day^{-1} based on rhizodeposition measurements by Whipps [10] (see Table 2).

Table 3 reports maintenance energy requirements for active vegetative cells, starved cells and bacterial endospores [7]. The values in Table 3 for vegetative cells can be combined with the results in Tables 1 and 2 to estimate that 10^8–10^9 active microbes (g soil)$^{-1}$ can be sustained by vegetation. Cell numbers of this magnitude have been measured in the root zone [14]. The results in Table 3 can also be used to show that the maintenance requirements for vegetative cells correspond to an endogenous metabolism coefficient of 0.01 h^{-1}. Thus, it is clear that the continuous supply of root exudates is necessary to maintain the vegetative microbes in a metabolically active state.

Table 1
Bioenergetics of photosynthetic and plant processes which support microbial populations in the rhizosphere, based on data and earlier work of Erickson et al. [7], Lips and Avissar [8], Erickson and Patel [9], and Whipps [10]

Process	Amount
Solar energy supplied	1.5 kJ cm^{-2} day^{-1}
Solar energy transformed to chemical energy (0.7–3.2%)	1.5 kJ (kg soil)$^{-1}$ day^{-1}
Fixed carbon transported to the root zone	30–50%
Chemical energy flow to the root zone	0.45–0.75 kJ (kg soil)$^{-1}$ day^{-1}
Root exudate flow to soil	40–70% of carbon flow to the root zone
Chemical energy supplied to soil microorganisms	0.18–0.52 kJ (kg soil)$^{-1}$ day^{-1}

Table 2
Measured values which have been used to estimate energy flows in root exudates

Source of data	Amount
Carbon dioxide production measurements of Davis et al. [5] in contaminated soil	0.7 mmol carbon (kg soil)$^{-1}$ day^{-1} 0.3 kJ (kg soil)$^{-1}$ day^{-1} (total) 0.2 kJ (kg soil)$^{-1}$ day^{-1} due to root exudates
Rhizodeposition measurements reported by Whipps [10]	1.2–2.9 tons carbon ha^{-1} year^{-1} 0.1–0.3 kJ (kg soil)$^{-1}$ day^{-1}

Table 3
Maintenance requirements for microbial cells, based on data and earlier work of Tijhuis et al. [11], Gray [12], Henis [13], and Erickson et al. [7]

Physiological state	Average maintenance energy, kJ (mol biomass carbon)$^{-1}$ h^{-1}
Aerobic vegetative cells at 25°C	5.7
Anaerobic vegetative cells at 25°C	3.3
Starved cells	0.16–0.24
Bacterial endospores	0.0006

Table 4
Amounts of toluene, phenol, trichloroethane and trichloroethylene flowing into and out of the chamber per day at steady state conditions

Compound	Average inflow/ mg l^{-1}	Average volume of inflow/ ml day^{-1}	Average effluent/ mg l^{-1}	Average volume of outflow/ ml day^{-1}	Percentage of water transpired	Percentage of contaminant which disappeared
Toluene	498	900	455	240	73	76.0
Phenol	497	850	23.6	250	71	99.0
Trichloroethane	47.1	875	41.1	240	73	76.0
Trichloroethylene	267	875	170	240	73	82.5

4. Biodegradation in the rhizosphere

Research on biodegradation of organic compounds in the rhizosphere has been reviewed by Anderson et al. [1], Shimp et al. [2], and Erickson et al. [3]. These reviews include the results of comparative studies with and without plants that demonstrate the beneficial effects of vegetation for degrading chlorinated compounds that are known to benefiit from co-metabolism and polynuclear aromatic hydrocarbons that are present in low aqueous phase concentrations. Results are presented in Table 4 for the contaminants fed to the bioreactors with actively growing alfalfa. Methane concentrations as large as 14 mg l^{-1} were found in the effluent ground water when TCA and TCE were being fed to the bioreactor. The measured concentrations in the ground water and in the gas phase above the soil surface provide experimental evidence that anaerobic conditions are present in the saturated zone, whereas aerobic conditions are present in many parts of the unsaturated zone. Toluene, phenol, TCE, and methane appear to be degraded aerobically in the unsaturated zone. Toluene, phenol, and methane were not found in the gas phase above the soil surface. Trace quantities of TCA and TCE were observed in the gas phase; however, most of the contaminants which disappeared appear to have been biodegraded, based on measured values of carbon dioxide production and liquid and gas phase contaminant concentrations.

5. Discussion

Plants may be viewed as solar driven pump-and-treat systems that are beneficial in the bioremediation of soil and ground water contaminated with organic compounds. In arid climates, plant evapotranspiration may be sufficient to manage a contaminated aquifer such that the region of contamination is contained and the vegetation provides inexpensive remediation. Where the contamination is at depths below the sphere of influence of the vegetation, pumps can be used to distribute the contaminated water into the rhizosphere.

Direct and indirect calorimetry may be applied to investigate the microbial processes and root respiration in the soil. Measurements of heat production, oxygen consumption and carbon dioxide production may be made. Since, above ground, photosynthesis converts energy and carbon dioxide into plant biomass and oxygen, it is important to try to separate these processes from the processes which occur in the soil.

The research and field studies with vegetaton indicate that many beneficial applications may be commercialized. These include the remediation of contaminated soil and ground water, containment of contamination through managed evapotranspiration of contaminated ground water, and wetlands that treat wastewater. Grasses and trees have been planted at the edges of fields along the banks of streams to capture and transform pesticides and fertilizers [3]. Vegetation has also been planted to prevent pollution associated with landfill leachate [3].

6. Conclusions

Root exudates associated with vegetation can provide sufficient carbon and energy to support $\approx 10^8-10^9$ vegetative microbes per gram of soil in the rhizosphere. Microbial biodegradation of toluene, phenol, TCA and TCE was observed in laboratory bioreactors with alfalfa plants growing in sandy soil. Methane was one of the biodegradation products that was found in the ground water, but not in the gas phase above the soil, when TCA and TCE were fed to the bioreactor.

Plant roots provide a distributed system which draws water into the plant. This results in the movement of dissolved contaminants from the saturated zone into the vadose zone, where aerobic biodegradation occurs near the plant roots.

Acknowledgments

This research was partially supported by the U.S. EPA under assistance agreements R-815709 and R-819653 to the Great Plains–Rocky Mountain Hazardous Substance Research Center for Regions 7 and 8. It has not been submitted to the EPA for peer review and therefore may not necessarily reflect the views of the agency, and no official endorsement should be inferred. The U.S. Department of Energy, Office of Restoration and Waste Management, Office of Technology Development and the Center for Hazardous Substance Research also provided partial support.

References

[1] T.A. Anderson, E.A. Guthrie and B.T. Walton, Environ. Sci. Technol., 27 (1993) 2630.

[2] J.F. Shimp, J.C. Tracy, L.C. Davis, E. Lee, W. Huang, L.E. Erickson and J.L. Schnoor, Crit. Rev. Environ. Sci. Technol., 23 (1993) 41.

[3] L.E. Erickson, M.K. Banks, L.C. Davis, A.P. Schwab, N. Muralidharan, K. Reilley and J.C. Tracy, Environ. Prog., 13 (1994), in press.
[4] L.C. Davis, L.E. Erickson, E. Lee, J.F. Shimp and J.C. Tracy, Environ. Prog., 12 (1993) 67.
[5] L.C. Davis, C. Chaffin, N. Muralidharan, V.P. Visser, W.G. Fateley, L.E. Erickson and R.M. Hammaker, Proceedings of the Eighth Annual Conference on Hazardous Waste Research, Kansas State University, Manhattan, KS, 1993, pp. 236–249.
[6] L.C. Davis, N. Muralidharan, V.P. Visser, C. Chaffin, W.G. Fateley, L.E. Erickson and R.M. Hammaker, in T.A. Anderson and J.R. Coats (Eds.), Bioremediation through Rhizosphere Technology, ACS Symposium Series, 563 (1994) 112–122.
[7] L.E. Erickson, L.C. Davis, S.K. Santharam, S.C. Kim, N. Muralidharan and C.W. Rice, Proceedings of the 87th Air and Waste Management Annual Meeting and Exhibition, Cincinnati, OH, 1994, Paper 94-WA86.04.
[8] S.H. Lips and Y.J. Avissar, in A. Richmond (Ed.), Handbook of Microalgal Mass Culture, CRC Press, Boca Raton, FL, 1986, p. 46.
[9] L.E. Erickson and S.S. Patel, Crit. Rev. Biomed. Eng., 8 (1982) 311.
[10] J.M. Whipps, in J.M. Lynch (Ed.), The Rhizosphere, Wiley, New York, 1990, pp. 59–97.
[11] L. Tijhuis, M.C.M. van Loosdrecht and J.J. Heijnen, Biotechnol. Bioeng., 42 (1993) 509.
[12] T.R.G. Gray, in T.R.G. Gray and J.R. Postgate (Eds.), The Survival of Vegetative Microbes, Cambridge University Press, Cambridge, UK, 1976, pp. 327–364.
[13] Y. Henis, in Y. Henis (Ed.), Survival and Dormancy of Microorganisms, Wiley, New York, 1987, pp. 1–108.
[14] R. Campbell, Microbial Ecology, Blackwell Scientific, London, 1977, pp. 63–91.