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Author

He, Yan, Xu, Jianming, Xu, Zhihong

Published

2007

Conference Title

Linking Local Management to Global Change Challenges: The Proceedings of the International Symposium on Forest Soils and Ecosystem Health

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The environmental behavior of pentachlorophenol in the soil-plant-microbe interface

Yan He^{a,b*}, Jianming Xu^a & Zhihong Xu^b

^a College of Environmental and Natural Resource Sciences, Zhejiang University, Hangzhou 310029, China, ^b Centre for Forestry and Horticultural Research, Griffith University, Nathan, Brisbane, Queensland 4111, Australia.

Tel No +61-7 3735 7936. E-mail: yhe2006@zju.edu.cn; yhe@griffith.edu.au

Key words pentachlorophenol (PCP); soil components; interface behavior; degradation; rhizosphere; phospholipid fatty acid (PLFA)

Abstract Pentachlorophenol (PCP, C₅Cl₅OH) is an ionizable hydrophobic organic contaminant (HIOC). As a pesticide, herbicide, and antiseptic, it was once used worldwide, and has been designated as a priority pollutant and a probable human carcinogen. Understanding the behavior of PCP and its environmental risk requires an assessment of the processes influencing its fate, transport, bioactivity and persistence in soils. This paper reviewed our recent work on the environmental behavior of PCP in soil (especially sorption/desorption and degradation), and the key controlling factors involved.

Introduction

Pentachlorophenol (PCP, C₅Cl₅OH) is an ionizable hydrophobic organic contaminant (HIOC). As a pesticide, herbicide, and antiseptic, it was once used worldwide, and has been designated as a priority pollutant and a probable human carcinogen. In the 1970s PCP was popularly used in China in fighting against snail fever and as a herbicide. Due to slow biodegradation, PCP may present a toxicity risk in contaminated soils for prolonged periods of time. Hence it is not surprising that it still causes environmental problems at many locations. The highest concentrations of PCP are usually found in soil and aquatic sediments. Understanding the behavior of PCP and its environmental risk requires an assessment of the processes influencing its fate, transport, bioactivity and persistence in soils. Investigation of the environmental behavior of PCP in soil (e.g. sorption/desorption, residue and degradation), and the controlling key factors involved are thus necessary and effective.

This paper aimed to understand the environmental behavior of PCP in the soil-plant-microbe interface, by determining the potential contributions of soil physicochemical properties and its organic/inorganic components to PCP retention; evaluating the degradation of PCP in the rhizosphere and the corresponding microbiological and biochemical responses; and developing alternative rhizo-remediation techniques to decrease PCP contamination.

Potential contributions of clay minerals and organic matter to PCP retention in soils

Sorption of PCP by pure minerals and humic acids were measured to obtain additional perspective on the potential contributions of both clay minerals and soil organic matter (SOM) to the contaminant retention in soils. Four types of common soil minerals and two kinds of humic acids (HAs) were tested. The sorption affinity for PCP was in the order: HAs >> K-montmorillonite >> Ca-montmorillonite > goethite > kaolinite. Such differences in sorption capacity were attributed to the crucial control of HAs. Clay minerals also had a contribution, especially K-montmorillonite, which played an important, but not dominant, role in the process of PCP sorption. Modulating the cation type and composition on clay mineral surfaces through cation exchange processes provides an environmentally-safe protocol to manipulate the mobility and availability of organic contaminants, which could have applications in

environmental remediation. By removing 80% (on average) of the organic carbon from the soils with H₂O₂, the sorption decreased by an average of 50%. The sorption reversibility was also greatly increased. Considering the uncharged mineral fractions in soil before and after H₂O₂ treatment, the main variation in sorption behavior of the soil might thus be related to the removed organic carbon (OC) and the reduced pH. This strongly indicated the effect of the interactions between SOM and clay minerals on the PCP sorption as a function of pH (He et al., 2006a).

Detailed sorption behavior of PCP on soils and its correlation with soil properties

Insight into the sorption process of PCP and the involved exact mechanisms, e.g. adsorption (hole-filling) and partitioning, was gained by constructing highly detailed isotherms over the widest possible concentration range. Using the dual-mode model, sorption isotherms of PCP can be accurately predicted, with the quantification for sorption capacities and the distinction for sorption contribution of both adsorption (hole-filling) and partitioning respectively. Sorption-desorption hysteresis was manifested to some significant degree in ten soils with contrasting properties. Such hysteresis might result from the pore deformation and entrapment of PCP molecules within organic matter. Correlations of stepwise regression equations obtained confirmed that pH, soil OC and its fractions, and particle size distribution are the main factors responsible for the sorption and desorption hysteresis processes. These factors worked in concert in influencing the fate of PCP sorption-desorption in soil. The empirical models developed in this study accurately predict PCP sorption and desorption hysteresis phenomena for the soils (He et al., 2006b).

Generalized models for prediction of PCP degradation dynamics in soils

Degradation of PCP in soil was investigated and its relationships with soil properties were studied. The results indicated that the degradation of extractable PCP residues can be described using first-order kinetics equation, with a half-life (T_{1/2}) ranging from 6.5 to 173.3 d. The sharply different patterns of PCP degradation in the different soils were closely related to soil properties. Correlations obtained from stepwise regression equations were significant (P < 0.01) between soil parameters and extractable PCP residues (R² = 0.974,

$P < 0.01$) as well as $T_{1/2}$ values ($R^2 = 0.882$, $P < 0.01$) The degradation dynamics of PCP in soil was most accurately predicted by using pH together with OC content and soil particle size distribution (He et al., 2007a).

Nonlinear spatial gradient of PCP degradation in the vicinity of *Lolium perenne* L. roots

A glasshouse experiment was conducted using a specially designed rhizobox where ryegrass seedlings were grown for 53 days in a soil spiked with PCP at concentrations of 8.7 ± 0.5 and 18 ± 0.5 mg kg⁻¹ soil to investigate rhizosphere effects on the degradation of PCP. The soil in the rhizobox was divided into six separate compartments at various distances from the root surface. Changes in PCP concentrations with increasing distance from the root compartment of the rhizobox were then assessed. The largest and most rapid loss of PCP in the planted soil was at 3 mm from the root zone where total PCP decreased to 0.20 and 0.65 mg kg⁻¹ respectively with the two PCP treatments. The degradation gradient followed the order: near-rhizosphere > root compartment > far-rhizosphere soil zones for both PCP concentrations where ryegrass was grown. In contrast, there was no difference in PCP concentration with distance in the unplanted soil. The increases in both soil microbial biomass carbon and the activities of soil urease and phosphatase were related to the enhanced degradation of PCP, which was higher in the near-rhizosphere than far-rhizosphere soil. The results suggest that the effect of root proximity is important in the degradation of xenobiotics such as PCP in soil (He et al., 2005a).

Profiling of PLFA: Implications for nonlinear spatial gradient of PCP degradation in the vicinity of *Lolium perenne* L. roots

Further investigations were conducted using phospholipid fatty acids (PLFAs) profiles to follow the millimeter spatial response of the soil microbial community with the purpose to illustrate the mechanism of degradation gradients of PCP in the rhizosphere of ryegrass (*Lolium perenne* L.). The response of PLFAs profiles was related to the gradient influence of root exudates and PCP degradation, showing a clear shift from hydroxyl to saturated taxa, then to fungi, then to gram-negative bacteria and gram-positive bacteria, then to actinomycetes, and then to arbuscular mycorrhizal fungi. This kind of development in the microbial community finally resulted in the enrichment of arbuscular mycorrhizal fungi, actinomycetes and bacteria in the 3 mm rhizosphere layer, where the spiked PCP also exhibited both the highest degradation rate and lowest residual level. Based on the stepwise regression analysis, the five phospholipid fatty acids of 16:1 ω 5, 16:0, 17:0, 17:1 and 18:0 were confirmed to be the most important microbial factors controlling the rhizosphere specificity of PCP degradation, strongly indicating the microbial synergistic controlling mechanisms of bacteria, arbuscular mycorrhiza and actinomycete that are involved in the accelerated process of PCP degradation in the rhizosphere (He et al., 2007b).

Stimulated rhizo-remediation of PCP polluted soil

The remediation effect and mechanisms of root exudates

on rhizo-remediation in a PCP polluted soil were studied in a simulated rhizosphere environment. The residual degradation of PCP in soil differed with the different addition rates of root exudates. There were significant correlations between the degradation of PCP and the soil biochemical indices of microbial biomass carbon (C_{mic}), nitrogen (N_{mic}), ratio of microbial biomass carbon to nitrogen (C_{mic}/N_{mic}), microbial quotient and enzyme activities in soil. At the lowest rate (13.38 TOC mg kg⁻¹), the PCP residual was smallest and remediation was most effective; at this time, the soil microbial biomass carbon, nitrogen, microbial quotient, and dehydrogenase activities showed the largest responses. The microbial biomass nitrogen, microbial quotient and dehydrogenase activities appeared to be sensitive biological indices indicating the evolution of soil environmental quality in the rhizo-remediated soil, previously polluted with PCP (He et al., 2005a).

Conclusion

Our findings in the present study led to the development of evaluation that discloses the transport behavior of PCP in soil systems. PCP may undergo natural removal process through sorption, residue and degradation. It may also undergo accelerated removal process in the plant rhizosphere, where root exudates induced modifications of microbial communities and spatially modified the dominant species within these communities, resulting in the enhanced nonlinear degradation. The information derived from this work can contribute to a better understanding of the soil-plant-microbe interactions and their impacts on the environmental behavior of organic contaminants in soils.

Acknowledgements

This work was jointly supported by the National Nature Science Foundation for Distinguished Young Scholars of China (40425007), the National Natural Science Foundation of China (40671092), and China Postdoctoral Science Foundation (20060400321).

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