学校编码：10384　　分类号_____密级_____

学号：33120120153565　　UDC_____

厦门大学

博 士 学 位 论 文

根系分泌物对红树林沉积物中多环芳烃环境行为的影响研究

Effect of root exudate on behavirors of polycyclic aromatic hydrocarbons (PAHs) in mangrove sediments

贾慧

指导教师姓名：严重玲 教授

专 业 名 称：生 态 学

论文提交日期：2016年4月

论文答辩日期：2016年5月

学位授予日期：2016年 月

2016年 6月

厦门大学学位论文原创性声明

本人呈交的学位论文是本人在导师指导下，独立完成的研究成果。本人在论文写作中参考其他个人或集体已经发表的研究成果,均在文中以适当方式明确标明，并符合法律规范和《厦门大学研究生学术活动规范（试行）》。

另外,该学位论文为（ 厦门大学环境与生态学院污染生态学 课题（组）的研究成果，获得（污染生态学 ）课题（组）经费或实验室的资助，在（ 污染生态学 ）实验室完成。（请在以上括号内填写课题或课题组负责人或实验室名称，未有此项声明内容的,可以不作特别声明。）

声明人（签名）：贾慧

2016 年 06 月 21 日

厦门大学学位论文著作权使用声明

本人同意厦门大学根据《中华人民共和国学位条例暂行实施办法》等规定保留和使用此学位论文，并向主管部门或其指定机构送交学位论文（包括纸质版和电子版），允许学位论文进入厦门大学图书馆及其数据库被查阅、借阅。本人同意厦门大学将学位论文加入全国博士、硕士学位论文共建单位数据库进行检索，将学位论文的标题和摘要汇编出版，采用影印、缩印或者其它方式合理复制学位论文。

本学位论文属于：

（　　）1.经厦门大学保密委员会审查核定的保密学位论文,于　　年　　月　　日解密，解密后适用上述授权。

（ √ ）2.不保密，适用上述授权。

（请在以上相应括号内打“√”或填上相应内容。保密学位论文应是已经厦门大学保密委员会审定过的学位论文，未经厦门大学保密委员会审定的学位论文均为公开学位论文。此声明栏不填写的，默认为公开学位论文，均适用上述授权。）

声明人（签名）：贾慧

2016 年 06 月 21 日

目录

Content

摘要

红树林是生长在热带、亚热带海岸潮间带的木本植物群落，对维护河口、海滨生态平衡和保护环境等方面具有重要意义。近年来，大量污染物被排放到红树林湿地生态系统中，其中以多环芳烃（Polycyclic aromatic hydrocarbons，PAHs）为代表的有机污染物最为明显。由于 PAHs 具有较强的致癌、致畸、致突变作用，使其极易在沉积物中被吸附固定，研究根系分泌物对沉积物中 PAHs 的活化作用，植物修复 PAHs 的根际响应机制及其在根际微环境中的降解机理，将为深入探讨 PAHs 在根际沉积物中的生物有效性、评价其污染风险、提高修复效率等提供理论依据。

本文从沉积物中 PAHs 的吸附、解吸和有效性等方面，研究了根系分泌物对沉积物中 PAHs 的活化作用；并在此基础上研究 PAHs 在根际修复过程的环境行为，围绕 PAHs 在根际微环境中的降解动态，及其随时间的变异特征；探讨白骨壤对 PAHs 的吸收、累积以及植物体内的生理生态响应。主要结果如下：

1．根系分泌物对红树湿地沉积物吸附菲的影响。结果表明，在根系分泌物的影响下，红树林沉积物对菲的等温吸附都能用 Freundlich 模型较好（R^2>0.93）地拟合。根系分泌物对沉积物吸附菲有抑制作用，且随着根系分泌物浓度的增加其抑制作用增强。随着根系分泌物浓度的升高，土壤吸附菲的 K_d（$K_d=Q/C_w$，沉积物对菲的吸附能力可用分配系数）呈现降低的趋势。与模拟根系分泌物（Artificial root exudates，ARE）相比，低分子量有机（Low-molecular- weight organic acids，LMWOA）对土壤吸附菲的抑制作用更强，根系分泌物对菲吸附的抑制作用强弱顺序为:柠檬酸>草酸>乙酸>ARE。模拟根系分泌物的效果并非是各个组分效果的单独叠加作用，这为深入地阐明根系分泌物活化根际 PAHs 的作用原理提供了重要依据。

2．研究根系分泌物对红树林沉积物中 PAHs 解吸的影响，发现根系分泌物促进了沉积物中 PAHs 的解吸，且随着根系分泌物浓度的增加，沉积物中 PAHs 解吸量也呈上升的趋势。与 ARE 相比，LMWOAs 对沉积物中菲解吸的影响更为显著。沉积物中的 PAHs 含量随着老化时间延长而降低，老化时间之

所以对沉积物中的 PAHs 解吸有影响是因为随着老化时间的增加降低了沉积物中 PAHs 的生物有效性。研究分析了红树林沉积物解吸菲的平衡溶液中可溶性有机质（Dissolved organic matter，DOM）的浓度，发现加入根系分泌物后溶液中 DOM 浓度增大，溶液中 DOM 与菲的结合增加则会减少沉积物对菲的吸附，这是根系分泌物促进沉积物解吸菲的主要原因。

3．采用薄层层析实验，分析根系分泌物对土壤中 PAHs 的迁移效应，结果表明，根系分泌物能够促进 PAHs 在沉积物中的迁移能力，且随着根系分泌物浓度的增大，其迁移能力随之增强。LMWOAs 对土壤的迁移能力的影响大于 ARE。

4．采用动态土柱试验法，分析根系分泌物对土壤中 PAHs 的淋溶作用。结果表明，根系分泌物对沉积物中 PAHs 有很强的林洗能力，淋溶过程中 PAHs 浓度变化均能用一阶动力学方程较好的拟合。LMWOAs 在根系分泌物活化 PAHs 中起着重要的作用。PAHs 的淋洗累积量曲线是一个连续扩散的过程，与淋洗时间成线性关系，符合菲克第一定律。加入根系分泌物后，沥出液中菲和芘的浓度的变化与可溶性有机质含量和 pH 变化均呈正相关。根系分泌物可以活化土柱 PAHs，能够提高土壤中 PAHs 的生物有效性。被有机酸淋洗的 PAHs 随着重力向下迁移，根系分泌物淋洗后菲、芘含量总体上为土柱下层（9-12 cm）>土柱中层（5-8 cm）>土柱上层（0-3 cm）。随根系分泌物浓度的提高，沉积物中菲、芘的总去除量均呈增加的趋势。

5．采用改进的自制尼龙网根袋构建白骨壤根际和非根际空间结构，分别采集第 0、15、30、60 和 120 天的白骨壤根际和非根际沉积物样品对 PAHs 降解行为进行分析。PAHs 的降解行为在不同的污染胁迫下均呈现一致的规律：根际>非根际，白骨壤根际效应加速了 PAHs 在根际微环境中的降解。白骨壤根际过程加速了 PAHs 在根际微环境的降解，越难降解的 PAHs 受到的加速效应越显著。该结果明确了植物根际微域有利于持久性 PAHs 的降解，阐明了植物根际修复技术在 PAHs 污染土壤修复中的重要作用和潜力。研究发现，根际可溶性有机碳（Dissolved organic carbon，DOC）的含量显著的低于非根际 DOC 含量，这可能是由于根系泌氧提高了根际沉积物中微生物利用 DOC 的速率，导致 DOC 含量下降。植物的根部和地上部分均有 PAHs 检出，且根部 PAHs 的富集量大于地上

部分。说明植株从沉积物中吸收的 PAHs 主要富集在植物的根部，只有少量转移至地上部分。PAHs 胁迫下白骨壤经历了抗氧化胁迫反应，抗氧化酶活性与丙二醛（Malondialdehyde，MDA）含量的增加，说明白骨壤可激发自身的防御体系，这可能与红树植物抗污染的机理有关。

关键词：红树林；多环芳烃；根系分泌物；根际；低分子量有机酸

Abstract

Mangrove wetlands, represent a complex ecological habitat distributed in the tropical and subtropical coasts. As one of the most important wetland ecosystems, they have high productivity and possess precious natural resources, and appear to possess a significant capacity to retain organic contaminants. This is especially so for the polycyclic aromatic hydrocarbons (PAHs). PAHs have been reported widely as distributed in mangrove waters and sediments, mainly from combustion by-products of organic materials and the refining of crude oil. These contaminants are well-known for their mutagenic, carcinogenic and teratogenic properties, and are becoming more and more prevalent in mangrove ecosystems particularly those near industrial cities and urban centres. Given that the toxicity caused by such contaminants has been shown as a threat to human health and ecological safety, the investigation of PAH remediation in mangrove sediments is of vital importance in terms of its ecological significance.

The aim of the study was to 1) investigate the activation and mobilization of phenanthrene by root exudates. 2) elucidate the mechanism of root exudate effects on the environmental behaviours of phenanthrene. 3) determine the distribution and bioavailability of phenanthrene and pyrene after the leaching experiments. 4) estimate the rhizosphere effect on phytoremediation in a specially designed rhizo-bag. 5) study the effect of planting time on PAH residual. 6) investigate oxidative stress response of *Avicennia marina* (Forsk.)Vierh to PAH-contaminants.

In the present study, sorption isotherms of phenanthrene on mangrove sediments was performed using batch equilibrium analyse. The results showed that the adsorption of phenanthrene fitted well (R^2>0.93) to the Freundlich equation, In the presence of root exudates the sorption of phenanthrene was inhibited following the order: citric acid>oxalic acid>acetic acid>artificial root exudates (ARE), suggesting that low-molecular- weight organic acids (LMWOAs) predominantly affected the fate

of phenanthrene in sediments.

To evaluate their influence, comprehensive laboratory experiments were performed using batch equilibrium analyses. In the presence of root exudates, the desorption of phenanthrene were promoted, and the desorbed amounts of the phenanthrene in different treatments fitted well (R_2>0.80) by the first-order kinetics equation. Among the three representative LMWOAs (citric, oxalic and acetic acids), citric acid promoted the desorption of phenanthrene more effectively than oxalic and acetic acid. In addition, ARE enhanced phenanthrene desorption always lower than with the same concentration of LMWOAs. Furthermore, the addition of root exudates and its components could result in the increment of (Dissolved organic matter DOM) concentration in solution, which may be the main reason that the root exudates and its components promoted the phenanthrene desorption in sediments.

This work investigated the impact of root exudates on the mobility of phenanthrene using thin layer chromatography (TLC) experiment in sediments-water systems. In the presence of root exudates the mobility of phenanthrene were promoted following the order: citric acid>oxalic acid>acetic acid>ARE. Additionally, the increased extent of mobility performance enhanced as root exudates concentrations increased. The results from this study provide valuable information regarding the fate of persistent organic contaminants in the sediments-water system, and will be of importance in remedial strategies for contaminated sediments and groundwater.

In this study, column leaching experiments were used to evaluate the leachability, distribution and bioavailability of phenanthrene and pyrene by root exudates from contaminated mangrove sediments. We observed that PAH concentrations and cumulative amounts of PAH in the leachate showed an increasing trend as the concentration of root exudates and leaching duration increased. After elution, the total concentrations of phenanthrene and pyrene in sediment layers followed a descending order of bottom (9-12 cm)>middle (5-7 cm)>top (0-3 cm). Furthermore, a positive correlation between leachate pH values and PAH concentrations of the leachate was found. Consequently, the addition of root exudates can increase the leachability and

bioavailability of phenanthrene and pyrene.

A pot experiment was used to investigate the capability of *A. marina* dissipation of phenanthrene and pyrene in spiked sediments. The rhizosphere environment was set up using a self-design nylon rhizo-bag which divided the sediment into the rhizosphere and non-rhizosphere. Results showed that the dissipation of phenanthrene and pyrene were significantly enhanced in the rhizosphere compared with non-rhizosphere sediments. Residues of phenanthrene and pyrene with time in rhizosphere and non-rhizosphere sediments fitted well into the first-order equation (R_2>0.92). The accumulation of phenanthrene and pyrene in plant tissues was a negligible contribution compared to the total remediation. Plant roots promoted dissipation significantly greater than the contribution of direct plant uptake and accumulation of phenanthrene and pyrene. The activities of antioxidant and detoxification enzymes in roots and leaves significantly increased against oxidative stress with increasing PAH concentrations. Furthermore, a significant relationship (R_2>0.91) between dissolved organic carbon (DOC) concentrations and the residual of PAHs in rhizosphere and non-rhizosphere sediments developed after 120 days planting. Results indicated that rhizoremediation with *A. marina* is a useful approach to promote the depletion of PAHs in mangrove contaminated sediments.

Key words: Mangrove; PAHs; Root exudate; Rhizosphere; LMWOAs.

缩略语表

缩写	英文全称	中文全称
ARE	Artificial root exudates	模拟根系分泌物
CAT	Catalase	过氧化氢酶
DOC	Dissolved organic carbon	水溶性有机碳
DOM	Dissolved organic matter	水溶性有机物
GSH	Glutathione	谷胱甘肽
HPLC	High performance liquid chromatography	高效液相色谱
LMWOAs	Low-molecular-weight organic acids	低分子有机酸
MDA	Malondialdehyde	丙二醛
MT	Metallothioneins	金属硫蛋白
PAHs	Polycyclic aromatic hydrocarbons	多环芳烃
POD	Peroxidase	过氧化物酶
POPs	Persistent Organic Pollutants	持久性有机污染物
SOD	Super oxide dismutase	超氧化物歧化酶
ROS	Reactive oxygen species	活性氧
TLC	Thin layer chromatography	薄层层析