

土壤及地下水污染整治基金 補助研究與模場試驗專案 歷年成果報告



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壹、前言

Introduction



壹、前言 Introduction

環保署自 2010 年起為推動補助土壤及地下水之污染調查、評估、底泥及整治復育等技術研發工作，辦理「土壤及地下水污染整治基金補助研究與模場試驗專案」(以下簡稱為研究與模場試驗專案)，並於 2012 年 10 月 22 日發布「土壤及地下水污染整治基金補助研究及模場試驗專案作業辦法」訂定相關作業規範，明訂補助學術研究及模場試驗專案相關規定，期能鼓勵相關公立研究機構及學術研究單位進行新穎技術研發，以精進我國土壤及地下水污染整治技術發展與政策推動。

為將研究與模場試驗專案歷年之研究成果供各界參考運用，環保署特彙整 2010 年至 2017 年歷屆專案成果(2012 年未辦理計畫徵求)，製作「土壤及地下水污染整治基金補助研究與模場專案歷年成果報告書」，期能強化專案成果與各領域之研究合作。歷年案件數及補助金額累計補助共 1.9 億元，如圖 1。

Taiwan Environmental Protection Administration (EPA) launched a funding program, namely the “Funding for Research and Demonstration Projects to address Soil and Groundwater Pollution Remediations (hereinafter referred to as research and demonstration projects)” in 2010 to promote the investigation, assessment, sediments and remediation work of soil and groundwater pollutions. The regulations of the research and demonstration projects, which was first established on October 22nd, 2012, describe details of funding opportunities for research projects and demonstration projects. The funding program pursues solutions to address environmental issues in Taiwan and supports government-owned and academic research entities to engage in research and development on the prevention and remediation of soil and groundwater pollutions.

To present the results of funded projects to all governmental and industrial sectors, the overview of the 2010-2017 funded projects’ results and highlight technologies are organized into this report. Taiwan EPA hopes to see more cross-field collaborations to tackle Taiwan’s environmental challenges. From 2010 to 2017, the amount of funding has reached NTD 190 million (Figure 1).



研究與模場試驗專案於 2010 年度至 2017 年度間依各年度政策擬定研究主題，主題涵蓋整治、調查、預防、評估及底泥等技術研發工作，且為因應土壤及地下水污染整治現況及業務需求，徵求專案類型分為模場試驗與研究計畫。歷年專案包含研究型專案 152 件及模場試驗型專案 27 件，其中研究主體整治占 52%、調查占 17%、評估占 13%、底泥占 13% 及其他 5%，如圖 2。

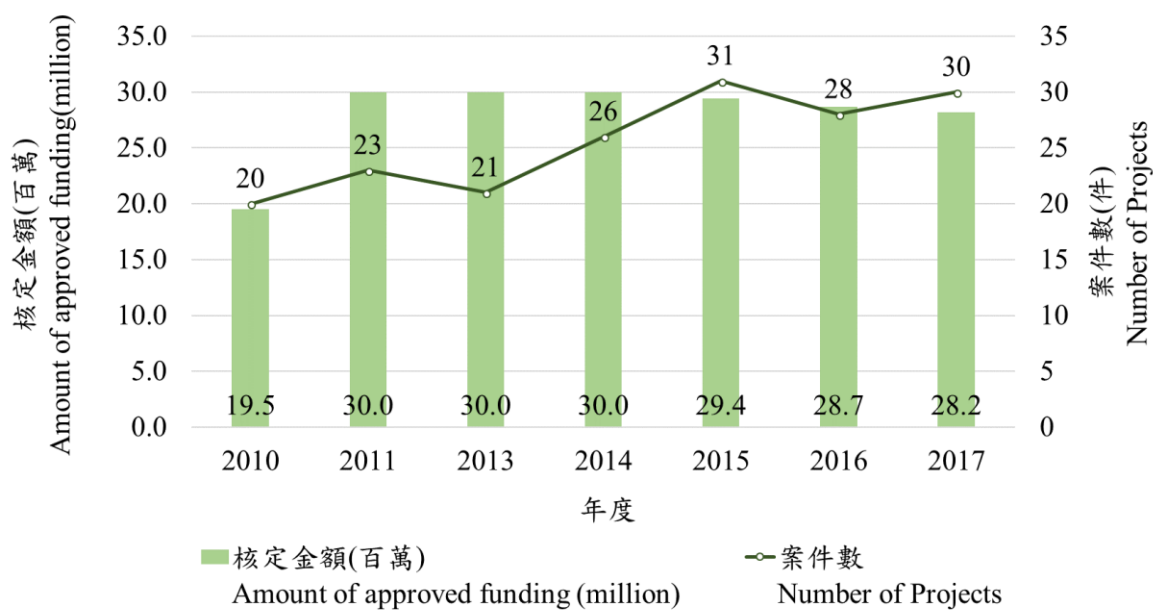
- 一、模場試驗專案：模場試驗專案(以下簡稱模場專案)僅限於現地場址試驗、調查及整治實施之現場作業。
- 二、研究計畫專案：研究計畫專案(以下簡稱研究專案)指於實驗室進行研究、現地採樣調查或進行數據彙整、電腦模擬等非於現地場址進行研究之專案。

From 2010 to 2017, Taiwan EPA decides the topics of the research and demonstration projects based on the policies set each year. The main topics usually include the remediation, investigation, prevention, assessment and sediments of polluted soil and groundwater sites.

In order to meet the requirements of the current soil and groundwater remediation work, funding projects are categorized into two types: demonstration project and research project.

- i. Demonstration Project: on-site testing, investigation, and remediation
- ii. Research Project: In-lab experiments, field surveys (sampling), statistical analysis, and computer simulations

Since 2010, a total of 152 research projects and 27 demonstration projects have been supported with funds. The selected projects cover topics ranging from remediation (52%), investigation (17%), assessment (13%), sediments (13%), and others (5%). Please refer to Figure 2 for further details.



備註：2012 年無辦理計畫徵求

Note: No project solicitation was announced in 2012

圖 1 2010-2017 年各年核定總案件數與核定總金額 / Figure 1 Number of selected projects and the amount of funding for each year (from 2010 to 2017)

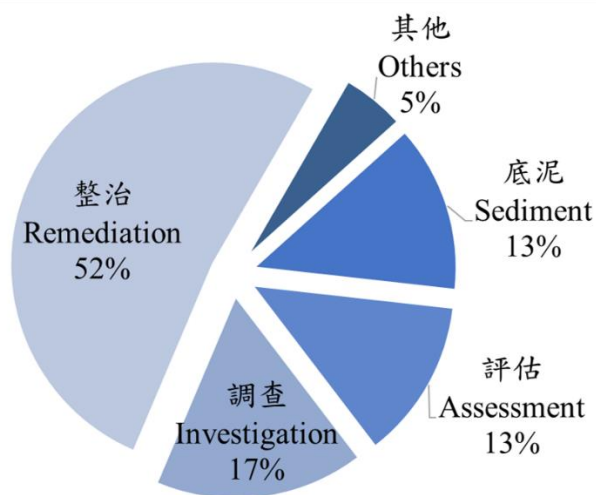


圖 2 歷年研究主題案件統計 / Figure 2 Research topics in previous years

貳、歷年成果統計

The Results Statistics for Previous
Years



貳、 歷年成果統計 The Results Statistics for Previous Years

環保署補助之研究與模場試驗專案 2010 年至 2017 年共已核定 179 案 (2012 年度未辦理計畫徵求)，統計歷年研究成果共取得 14 項專利及進行 4 項技術移轉，請參照表 1，以下依研究主題、研究類型、技術工法、目標污染物進一步分析 7 年來之計畫成果。

From 2010 to 2017, Taiwan EPA has approved and funded a total of 179 research and demonstration projects. (No project solicitation was announced in 2012). As shown in Table 1, based on the project results statistics for previous years, a total of 14 patents were received and 4 technology transfers were completed. The analysis of the project results for the past 7 years will be discussed later in this report according to research topics, project types, technology, and target pollutants.



表一 歷年取得專利及技術移轉列表 / Table 1 Patents Received and Technology Transfer Completed in Previous Years

年度 Year	主持人 Project manager	專案名稱 Titles	取得 專利 ¹	技術 移轉 ²
2010	張書奇 Chang Shu Chi	二仁溪污染底泥整治模場試驗計畫 Remediation pilot study of the contaminated sediment in Er-Ren River.	1	-
2011	張書奇 Chang Shu Chi	二仁溪污染底泥整治模場試驗計畫(第二年) Remediation pilot study of the contaminated sediment in Er-Ren River (Year 2).	1	-
2013	賈儀平 Chia Yeeping	熱脈衝流速儀應用於地下水污染場址調查之可行性研究 Feasibility study of the application of heat-pulse flowmeter to site characterization of groundwater pollution.	1	-
	張書奇 Chang Shu Chi	二仁溪污染底泥整治模場試驗計畫(第三年-苯(a)駢芘與多溴二苯醚污染整治與驗證技術開發) Remediation pilot study of the contaminated sediments in Er-Ren River (Year 3 - remediation and validation technology development for benzo(a)pyrene and polybrominated diphenylether contaminated sediments).	1	-
	劉敏信 Liu Min Hsin	利用微生物呼吸試驗探討生物通氣法對柴油污染土壤復育之成效 Using Soil Microbial Respiration to Evaluate the Efficiency of Bioventing on Diesel Contaminated Soil.	1	1
2014	吳庭年 Wu Ting Nien	封隔型雙負壓浮油回收系統於油品洩漏場址的運用 The application of dual-vacuum packer-type free product recovery system at a site contaminated with oil leakage.	2	1
	胡慶祥 Hwu Ching Shyung	底泥有機污染物生物有效性評估及應用 Assessment and Application of Bioavailability of Organic Contaminants in Sediments.	1	2
	張書奇 Chang Shu Chi	二仁溪污染底泥整治模場試驗計畫(第四年-鄰苯二甲酸酯塑化劑污染底泥之快速檢測與模場試驗) Remediation pilot study of the contaminated sediments in Er-Ren River (Year 4 -Rapid detection and remediation of phthalate ester-contaminated river sediments).	1	-
2015	張書奇 Chang Shu Chi	現地底泥整治技術研發－磁性活性炭吸附移除、電磁感熱玻璃化與粒徑分離技術研究 Innovative technology development for sediment remediation.	2	-
	林啟燦 Lin Chi tsan	以濕處理及廚餘淨化受戴奧辛污染之土壤 Clean up dioxin from contaminated soil by wet treatment and fermentation of food waste.	2	-
2016	崔碩 Tsui Lo	利用臺灣本土有益混合菌以提升水稻植生萃取重金屬鎘污染之可行性研究 Effects of applying native beneficial microorganisms on the phytoextraction of cadmium from soils by rice.	1	-

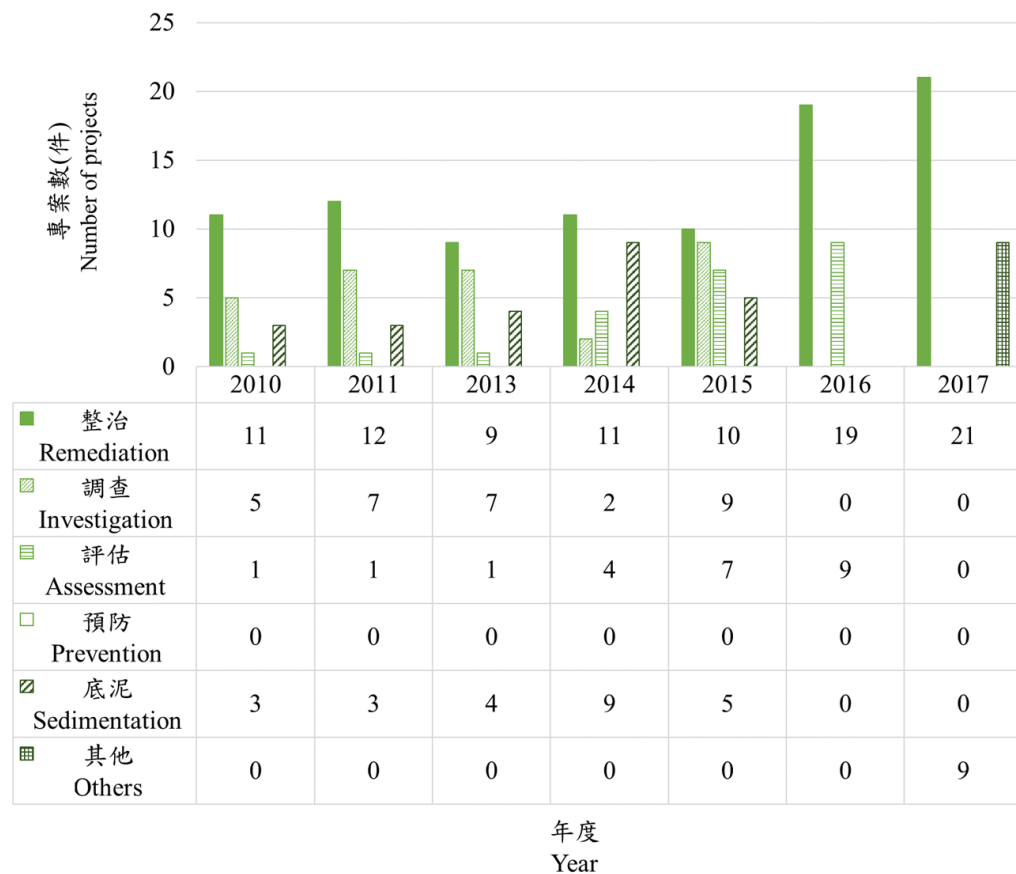
Note: ¹ Patents Received, ² Technology Transfer



一、 研究主題 Research Topics

環保署依各年度政策擬定研究與模場試驗專案之研究主題，2010 年至 2015 年徵求主題為整治、調查、評估及底泥，2016 年徵求主題為整治、預防、評估以及其他自訂類型，2017 年徵求主題則為整治、預防及其他。歷年核定專案研究主題以「整治」最多，其次為「調查」，各年度通過計畫依主題類別統計請參照圖 1。

Taiwan EPA decides the topics of the research and demonstration projects based on the policies set each year. From 2010 to 2015, the topics of the project solicitations were remediation, investigation, assessment, and sedimentation. In 2016, the topics required were remediation, prevention, assessment, and other self-decided topics while in 2017, the topics were remediation, prevention, and others. The project topic which was selected the most in previous years was remediation, followed by investigations. The selected projects from previous year is organized based on the research topics. Please refer to Figure 3 for the statistics.



備註：2012 年無辦理計畫徵求

Note: No project solicitation was announced in 2012

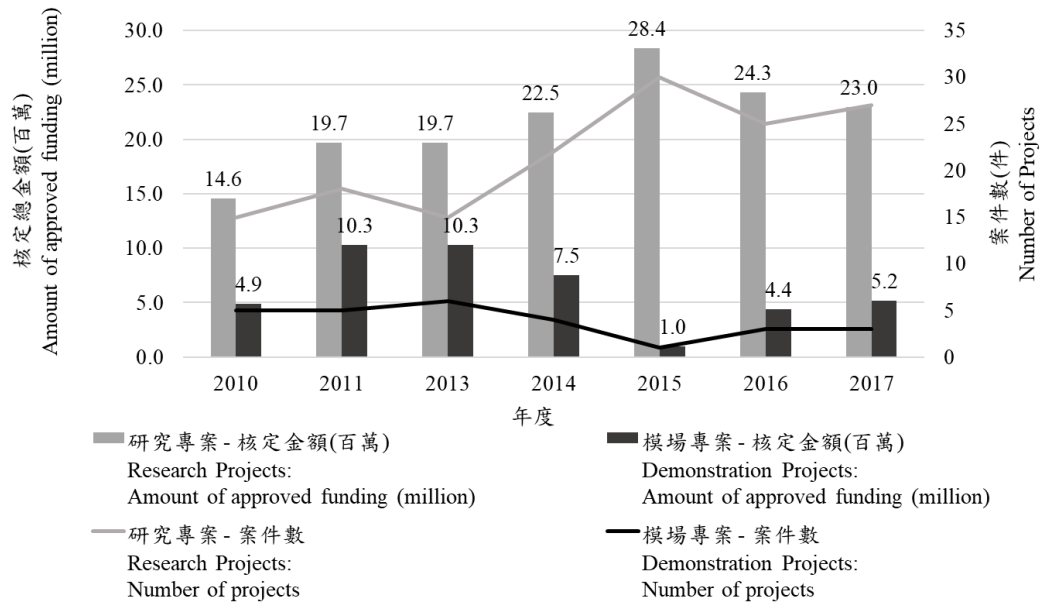
圖 1 2010-2017 年各年度專案數(依主題分) / Figure 3 The number of selected projects from 2010-2017 (categorized based on research topics)



二、 研究類型 Project Types

因應土壤及地下水污染整治現況及業務需求，徵求專案類型分為模場試驗與研究計畫。歷年總核定計畫中模場專案占 15% (共 27 件)、研究專案占 85% (共 152 件)，研究類型分類統計可參照圖 2。

Based on the current situation and work required for the remediation of soil and groundwater pollution, the project solicitation is divided into two types: research projects and demonstration projects. Demonstration projects account for 15% of the total approved projects from previous years (a total of 27 projects) while research projects comprise 85% (a total of 152 projects). The statistics of the types of project can be found below in Figure 4.



備註：2012 年無辦理計畫徵求

Note: No project solicitation was announced in 2012

圖 2 2010-2017 年各年度專案類別案件數與核定總金額比較 / Figure 4 The comparison between the two project types on the number of projects and the approved funding amount from 2010 – 2017



三、 技術工法 Technology

歷年研究與模場試驗專案依技術工法可分為整治、調查及政策等三大分類，各技術工法依其作業特性再做細部分類，請參照圖 3，整治工法可再區分為生物、化學及物理技術，調查工法可再區分為生物、物理、化學及基礎科學技術，政策工法可再區分為風險評估、保險規劃及系統，計畫以「整治」技術為主占 73%、「調查」占 27%及「政策」占 9%。各分類所佔比例請參考圖 4。

The research and demonstration projects from previous years can be divided into three major categories based on the technology and methods applied: remediation, investigation, and policy. As shown in Figure 5, each category is then divided into smaller categories. Remediation is divided into biological, chemical, and physical technologies. The Investigation category is further divided into biological technology, physical technology, chemical technology, and technology in basic science. The category of Policy is divided into risk assessment, insurance planning, and system. Projects that focus on Remediation account for 73% while the ones focusing on Investigation consists of 27%. Rest of the 9% is the projects that aim at Policies. Please refer to Figure 6 for the percentage of each technology.

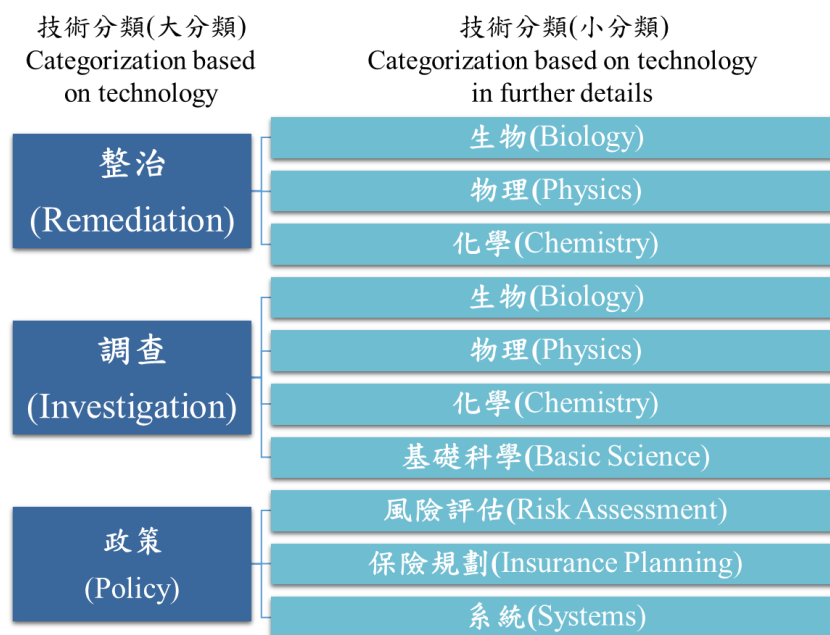
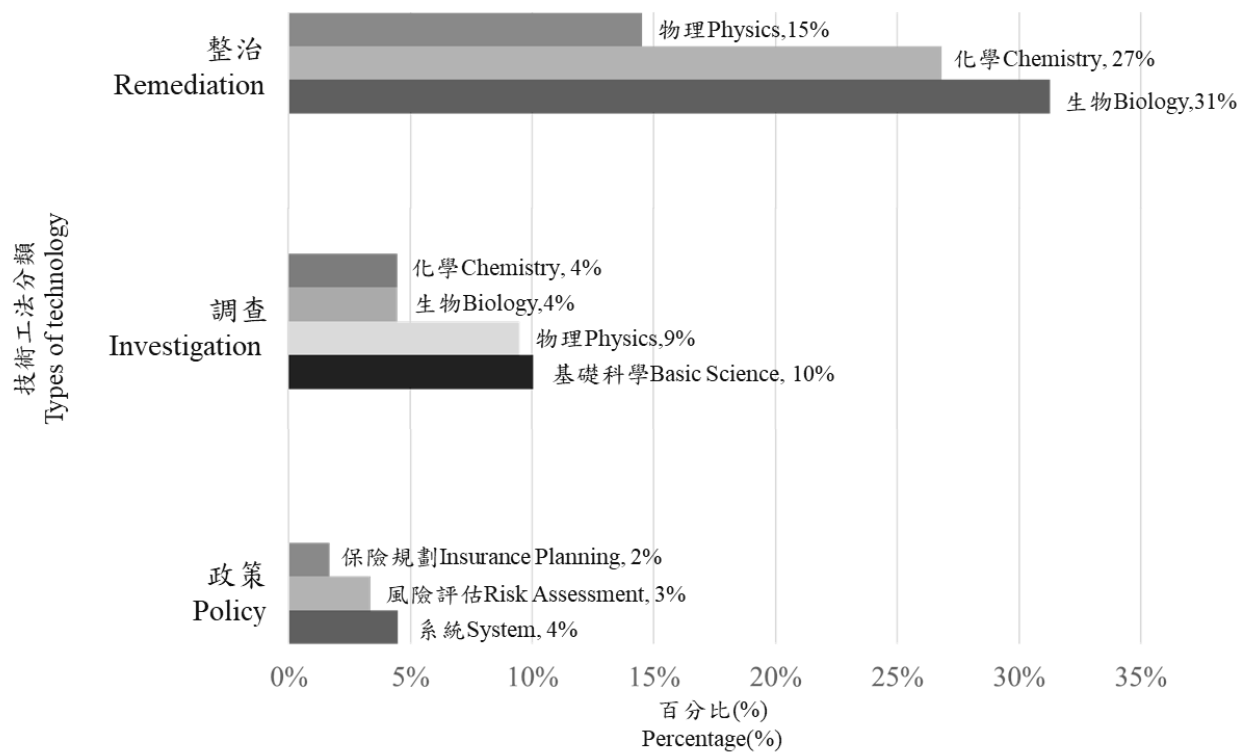


圖 3 技術工法分類圖 / Figure 5 The categorization of technology applied



備註：若計畫為整合型技術則此處分析重複計算 / Note: If a project contains more than one technology, the project is included in all the applied technologies' statistics shown here.

圖 4 技術工法分類比例圖 / Figure 6 The percentage of the types of technology applied



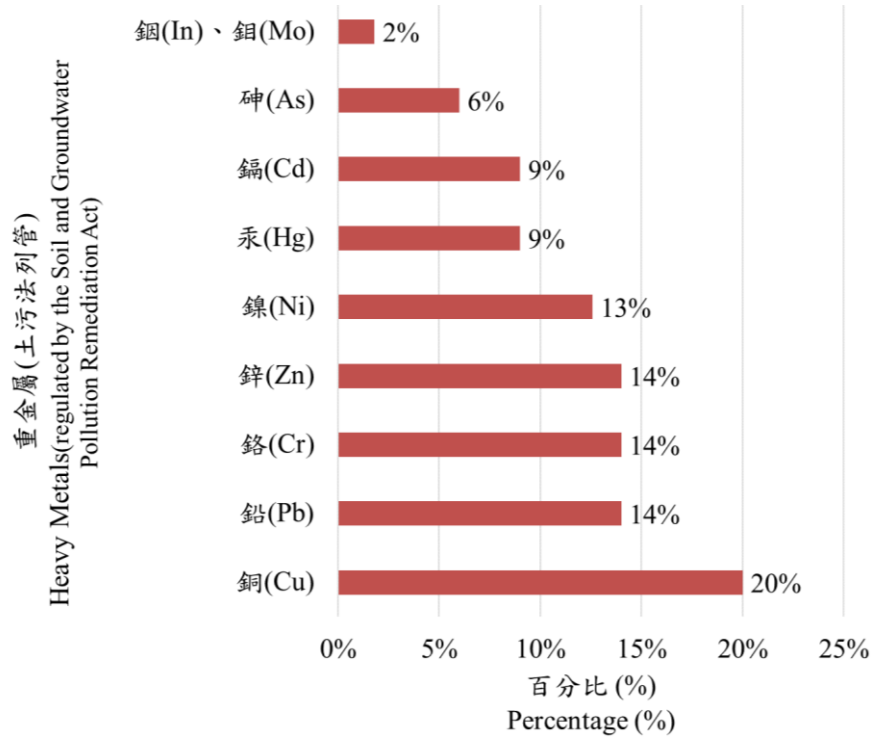
四、 目標污染物 Target Pollutants

針對研究與模場試驗專案之目標污染物，進行重金屬及有機化合物之統計分析，歷年專案之重金屬研究項目包括汞(Hg)、砷(As)、鉛(Pb)、鉻(Cr)、銅(Cu)、鋅(Zn)、鎘(Cd)、鎳(Ni)、銻(In)及鉬(Mo)，其中「銅」為最常見之目標污染物，占整體重金屬目標污染物約 20%，重金屬分類比例如圖 5 所示。

有機化合物則依總石油碳氫化合物、芳香族碳氫化合物、多氯聯苯、氯化碳氫化合物、甲基第三丁基醚、戴奧辛及其他(非土污法列管)進行統計分析，其中研究比率最高之目標污染物為「總石油碳氫化合物」占 26%，第二為「芳香族碳氫化合物」占 25%，第三為「氯化碳氫化合物」占 20%，有機化合物分類比例如圖 6 所示。

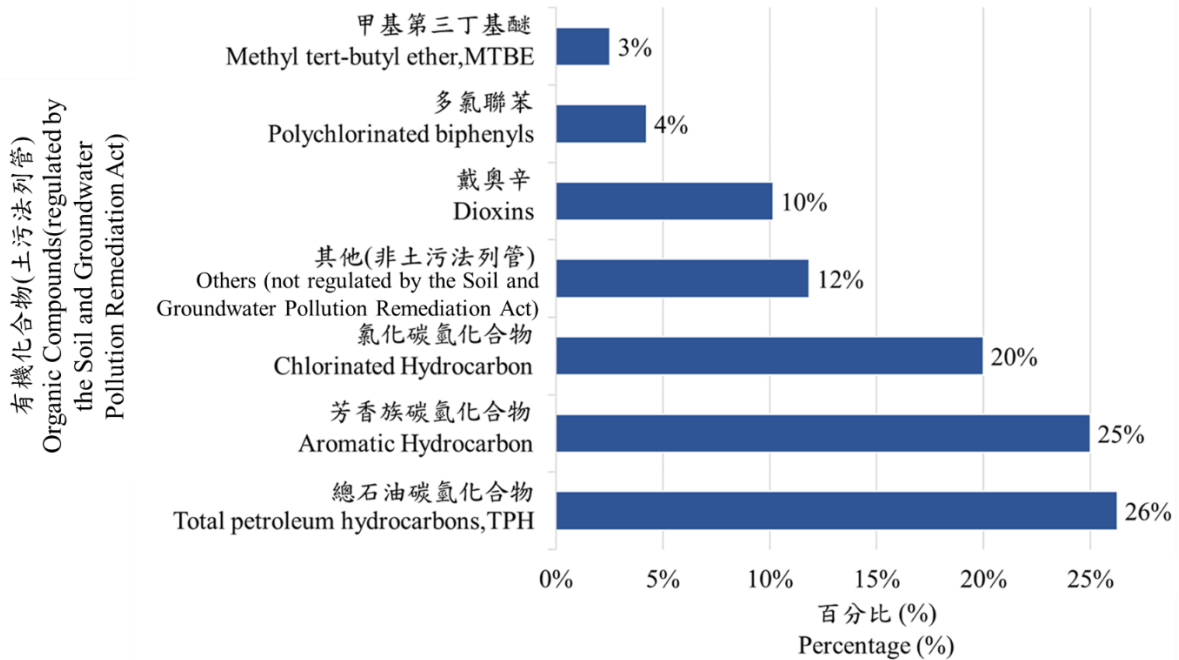
The research and demonstration projects on target pollutants include heavy metals and organic compounds, and statistical analysis was performed regarding these types of pollutants. Heavy metals that was researched in previous projects include Mercury(Hg), Arsenic(As), Lead (Pb), Chromium(Cr), Copper (Cu), Zinc(Zn), Cadmium(Cd), Nickel(Ni), Indium(In), and Molybdenum(Mo). Among these, Copper is the most commonly seen target pollutant, which accounted for roughly 20% of the overall heavy metal target pollutants. The percentage of the different types of heavy metals is shown in Figure 7.

Statistical analysis was performed on organic compounds including total petroleum hydrocarbon (TPH), aromatic hydrocarbons, polychlorinated biphenyls, chlorinated hydrocarbons, methyl tert-butyl ether (MTBE), dioxins, and others (not regulated under the Soil and Groundwater Pollution Remediation Act). In which, the target pollutants which was most researched on was “total petroleum hydrocarbon (TPH)” which accounted for 26%, followed by “aromatic hydrocarbons” which was 25%. “Chlorinated Hydrocarbons” ranked third and accounted for 20%. The percentage of different types of organic compound is shown in Figure 8.



備註：若計畫為多項污染物則此處分析重複計算 / Note: If a project tackles more than one target pollutant, the project is included in all the target pollutants' statistics shown here.

圖 5 目標污染物之重金屬計畫分類比例 / Figure 7 The percentage of target pollutants projects focusing on heavy metals



備註：若計畫為多項污染物則此處分析重複計算 / Note: If a project tackles more than one target pollutant, the project is included in all the target pollutants' statistics shown here.

圖 6 目標污染物之有機化合物計畫分類比例 / Figure 8 The percentage of target pollutants projects focusing on organic compounds

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參、計畫摘要 Project Abstracts

[001] 1,2-二氯苯污染土壤之現地永續處理技術之研究

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中文摘要

二氯苯在工業界廣泛被使用，如工業原料、農藥及中間原料與有機溶劑，因其低溶解性、高毒性及不易降解之特性，因此很難以傳統之抽取處理法進行地下環境污染之處理，一般常用之液相處理技術包括吸附法、生物處理、觸媒還原及薄膜分離法等，至於土壤處理技術較不普及。

本計畫目的即在於改變電極種類、操作流質種類及操作流質濃度等電動參數進行實驗，並藉此討論不同參數對於土相中 1,2-二氯苯處理效率之影響，本實驗使用 Ti、RuO₂/Ti(RT) 及 MnO₂/Ti(MT) 三種電極，操作流質則選用界面活性劑(SDS)、Na₂SO₄、NaOH 及 NaCl，探討電極種類、操作流質種類及操作流質濃度之影響。電滲透流係數 (Ke) 界於 $8.7 \times 10^{-4} \sim 16.1 \times 10^{-4} \text{cm}^2/\text{V}\cdot\text{s}$ ，其中以 RT-NaCl 系統為滲透系最佳。Ti 電極其處理效率為 34.4%，降解率可達 8.6%~19.8%，而使用 RT 電極於不同操作流質之處理效率為 23.3%~75.4%，其中降解率為 11.0%~29.3%，利用 MT 做為電極處理土壤時，其效率依流質不同約在 21.4~65.2%，降解率則為 9.9%~27.4%。使用 RT 電極之流質濃度改變實驗中，隨 SDS 濃度提升，整體之處理效率亦由 58.9% 提升至 75.4%，而降解率亦隨 SDS 濃度提升而由 16.2% 提升至 23.4%，使用 NaCl 做為流質時，土壤之導電性大幅增加，同時增加電化學反應及電動力行為的強度，提升降解率(25.3%至 29.3%)，隨其濃度提升處理效率亦有所增加(62.9~66.1%)。

雙金屬氧化電極特性藉由循環伏安法、SEM 及 TEM 分析之結果亦進行彙整討論。

Abstract

Dichlorobenzenes (DCB) are widely used in industrial and domestic uses, such as intermediates in the synthesis of other chemicals, solvents, and hygiene products. It results in ubiquitous in all major environmental compartments. By their nature, they are highly toxic and poorly biodegradable in environment. It is difficult to remove dichlorobenzenes from subsurface environments using traditional pump-and treat technologies. Most technologies have been focused on removal of 1,2 dichlorobenzene (1,2 DCB) in aqueous phase, such as adsorption and biotransformation, catalytic reduction, and membrane separation. However, less attention was focused on 1,2 DCB remediation in soil.

This project was aimed to investigate remediation efficiency of 1,2 DCB in soil matrix by electrokinetic process. The experimental parameters included electrode type (Ti, RuO₂/Ti, and MnO₂/Ti), processed fluid (SDS, Na₂SO₄, NaOH, and NaCl), and concentration.

Results showed that the permeability in investigated system was in range of $8.7 \times 10^{-4} \sim 16.1 \times 10^{-4} \text{cm}^2/\text{V}\cdot\text{s}$. The highest permeability was found in RT/NaCl system. The treatment / degradation efficiency for Ti, RT (RuO₂/Ti), and MT (MnO₂/Ti) were 34.4%/8.6~19.8%, 23.3~75.4%/11.0~29.3%, and 21.4~65.2%/9.9~27.4%, respectively. In RT-SDS system, the treatment / degradation efficiency increased from 58.9%/16.2% to 75.4%/23.4% as concentration of SDS increased. In RT-NaCl system, higher electrochemical reactivity and electrokinetic performance were found, which resulted from high conductivity of NaCl. The treatment /



degradation efficiency increased from 62.9%/25.3% to 66.1%/29.3% as concentration of NaCl increased.

The electrochemical properties of electrode characterized by cyclic voltammetry and the surface characteristics of electrode investigated by Scanning electron microscopy and Transmission electron microscopy were all investigated in the study.



[002] 土壤污染物水力分離成效改良之研究

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中文摘要

本研究以南部某場址土壤為例，選用3種不同類型的污染土壤（高濃度SW-3、底泥SW-4、低濃度SW-5），測試水力分離對於污染物的處理極限，研究如何提高污染分離效率且同時處理汞及戴奧辛，並嘗試找出其與土壤粒徑、酸鹼度、陽離子交換容量、總有機碳等影響因子之關聯性。土壤採集後初步篩分，將礫石及明顯雜物去除後，進行初始濃度及土壤基本性質測定，後續進行水力分離、特徵曲線分析、汞相分析及瓶杯試驗。水力分離結合浮除可去除汞72.6~86.9%及戴奧辛16.6~67.9%。特徵曲線呈U型分布，較大顆粒及細顆粒土壤皆有較高濃度汞及戴奧辛存在。瓶杯試驗顯示短時間內酸萃取對於汞的溶出效果與不添加藥劑空白組效果相近，乙醇則對戴奧辛有溶出成效。進一步分析汞相分布，本場址土壤汞相多以礦化汞的形式存在，偏向不易溶出移動的狀態，顯示處理難度較高。

Abstract

This study focus on reducing and removal the mercury and Dioxins from three different contaminate soils by hydraulic-separation and flotation. Flotation was used to polish removal of the residual mercury and Dioxins in the soils after hydraulic-separation. Soils samples, including high, medium, and low level contaminate, were collected from a contaminated site. This study also determinates the correlation of the soils diameter with mercury and Dioxins concentration. The results show the hydraulic separation removed the 72.6-86.9% mercury and 16.6-67.9% Dioxins from soils. The characteristic curves show the coarse and fine diameter soils have high level mercury and Dioxins concentration. The mercury extraction from contaminated soil by citric acid, hydrochloric acid and pure water were similar in short extraction time. The 75% ethanol extracts Dioxin from contaminated soil efficiently. HgS and element mercury were major form of mercury compound in this contaminated site soils. These two types of mercury were difficultly extracted from soil except using strong acid. Finally, this study demonstrated the hydraulic separation could be considered as a pre-treatment technique to reduce the mercury and Dioxins contaminated soils.

[003] 以現場型固體床式生物溶出技術處理受重金屬污染底泥之研究

陳勝一

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中文摘要

在河川或湖泊污染整治中，除污染源管制及興建下水道系統之外，底泥之浚渫亦是整治方案之一。底泥因已承受相當程度之污染物，浚渫後之污染底泥需經適當之處理及處置，方可達到不造成二次公害之目標。目前國內針對受污染水體底泥處理技術之研究極少，未來極需要此方面之技術，以處理浚渫後之大量底泥。本研究之主要目標為利用硫生物循環中之硫氧化作用，發展出一套應用於現場處理重金屬污染底泥之環境生物技術，以達污染預防與資源循環再利用之目的。經由研究發現，在營養鹽配方之影響方面，採用氯鹽為主之營養鹽時，硫氧化菌具有較高之活性，系統中 pH、ORP、硫酸鹽濃度變化速率因而加快，使得底泥中重金屬溶出具有較高之速率及效率。而在淋洗流量之影響方面，採用高淋洗流量之操作時，硫氧化菌之生物活性亦可有效提昇，造成底泥中重金屬之溶出速率與效率明顯升高。生物溶出程序除能有效地去除底泥中重金屬外，亦可減少殘留於底泥中重金屬之移動性及為害性。在固體床式生物溶出程序中，在經過 40 天之操作後，在重金屬之最大溶出效率中以鋅及鎳之溶出效率較高，分別可達 50% 及 60% 左右，銅之去除率偏低，只有 22%，鉛則無明顯溶出效果。

Abstract

In the restoration strategies of river and lake, besides controlling pollution sources and building sewer system, the contaminated sediment may need dredging from the rivers or lakes. Most of sediment dredged from contaminated rivers or lakes often contain substantial amount of heavy metals and thus can not be disposed of on the land and in the water body without any treatment. To date, there are relative few researches for

detoxification and decontamination processes of heavy metals in aquatic sediments in Taiwan. In future, it is important to develop the techniques for treatment of the large quantity of dredged sediments in the remediation of contaminated rivers or lakes. Sulfur cycle conversions do not only involve the elemental sulfur, but also directly influence organic matter, nitrogen and heavy metal conversions and fluxes within natural or man-made ecosystems. Therefore, one can also use the sulfur cycle as the driving force behind some specific related environmental biotechnological applications. Sulfur-oxidizing bacteria utilize reduced sulfur as an energy source for chemolithotrophic growth, producing soluble metal sulfates and sulfuric acid. A bioleaching process uses these biological oxidation processes of sulfur-oxidizing bacteria to extract and concentrate metals from polluted soils, sediments or solid waste. The purpose of this study was to develop a microbial process of sulfur cycle for the bioremediation of metal-contaminated sediments. In this project, a bioleaching process for on-site remediation of metal-contaminated sediments was studied. The results showed that the rates of pH reduction, ORP increase, sulfate production and metal solubilization obtained in the solid-bed bioleaching experiment with chloride salts (medium C) were higher than those with sulfate salts (medium S). It was found that the medium C was more suitable for sulfur-oxidizing bacteria in the solid-bed bioleaching process. On the other hand, the rate and efficiency of metal solubilization were enhanced by increasing the flowrate of process water sprinkling into the solid-bed bioreactor. After 40 days of reaction time, the highest efficiencies of heavy metals leached from sediments in this solid-bed bioleaching process were 22%, 50%, 8%



and 60% for Cu, Zn, Pb and Ni, respectively. Meanwhile, the treated sediment was stable and the residual heavy metals were no longer harmful to the environment after the bioleaching process.

[004] 地表下污染物逸散之暴露量評估研究

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地表下土壤及地下水若受揮發性污染物的影響，需要考慮其逸散的風險，環保署「土壤及地下水污染場址健康風險評估評析方法及撰寫指引」中，於第一與二層次的風險評估所推薦的簡易公式必需輸入適當的參數值，以有效的評估地表空氣相受此逸散物的影響，於第二與三層次的風險評估則推薦一些解析模式。本研究主要為評析這些計算逸散風險的簡易模式與評估Jury-finite source、BIOSCREEN解析模式及MOFAT數值模式的使用、建議相關參數的設定方式及測試其敏感性，本研究並收集現場相關資料，實際應用於這些公式與模式，以分析各別方法的使用性。

Abstract

Contaminant vapors emanating from NAPL, sorbed and dissolved phases pose a human health and environmental risk; it should be assessed by a rigorous way. Environmental Protection Agency in Taiwan provided a guideline on risk assessment and methodology for contaminated subsurface and groundwater. Exposure amount of these vapors from a variety of pathways, as suggested in the guideline for the first and second tiers of risk assessment, are estimated by empirical or theoretical methods with incorporated with some relevant parameters. Some analytical and numerical models were also suggested for the second and third tiers of risk assessment. This study aims at assessing these methods and models, specifically, Jury-finite source, BIOSCREEN and MOFAT models, for their theoretical background and usage. The relevant parameters were also analyzed for sensitivity. Some sets of field data were collected for the use of relevant methods and/or models to assess and compare their results.



[005] 利用堆肥液以提高生物溶解與降解四氯乙烯的研究

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中文摘要

四氯乙烯為主要常見的為地下水污染物之一，由於其密度高且非水溶相之特性，使其不易利用傳統的物化處理方法，將其從地下水中移除。本計畫嘗試利用廉價的堆肥液來取代商用的生物製劑，以評估堆肥液能否作為適當的界面活性劑與電子提供者，以加速四氯乙烯在地下水層中的溶解與生物降解。本計畫共測試三種不同的堆肥：三個月蔗渣堆肥(B3)、六個月蔗渣堆肥(B6)，與三個月蔗渣/廚餘混合堆肥(M3)之界面活性性質，以評估不同堆肥液對四氯乙烯的溶解效率，並利用B3堆肥進行管柱實驗，評估不同堆肥量對四氯乙烯的移除效率。實驗結果顯示，腐熟度低的堆肥，其界面活性性質較腐熟度高的堆肥為佳，而加入廚餘於蔗渣堆肥中更可提升其界面活性劑之性質。管柱實驗結果則顯示，相較於蔗渣原料，蔗渣堆肥能更有效的將下游的四氯乙烯溶出，且溶出效率隨著堆肥量的增加而提高。在近180天的培育時間過程中，堆肥能持續的維持系統中的甲烷產量，而能有效的降解四氯乙烯，同時能維持系統中近於中性的pH值。綜而言之，由於堆肥具有適度的界面活性性質以及多樣的微生物活性，使得堆肥可作為一種整治土壤地下水四氯乙烯污染的良好資材。

Abstract

Tetrachloroethene (PCE) is one of most found groundwater pollutants. Because it was denser than water and it would not mix with water easily, PCE was difficult to be removed from groundwater through traditional physical-chemical methods. Therefore, compost liquid was proposed as cheap alternative to commercial biological agents to improve the solubility and biodegradation of PCE. In this study, three compost samples: 3-month bagasse compost sample (B3), 6-month bagasse compost sample (B6), and 3-month bagasse compost/ kitchen waste mixed sample (M3) were examined for their biosurfactant property. In addition, B3 sample was selected to conduct column study to evaluate the effects of compost mass on the PCE remove efficiency. The experimental results showed that less matured sample had better biosurfactant property than more matured sample, and addition of kitchen waste would further enhance biosurfactant property. The results of column study showed that bagasse compost could dissolve more down-stream PCE when compared with bagasse sample, and the efficiency increased with increasing of compost mass. During 180 days of column study, sustainable amount of methane gas was detected in system, suggesting compost could be used as long-term electron donors to degrade PCE. The system remained at neutral pH throughout the experiment. Overall, compost contains moderate biosurfactant property and diverse microbial activity, and thus could serve as suitable media for dechlorinating groundwater PCE.

[006] 利用磁性奈米鐵氧磁體尖晶石移除水體砷污染之研究

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中文摘要

“砷(Arsenic)”，在自然水體及飲用水的污染事件中長久以來一直危害著人體生命安全，由於其廣泛被應用於除草劑、殺蟲劑、殺菌劑、乾燥劑和木材防腐劑、玻璃器皿製造、木材防腐劑、陶瓷製造業、冶金工業、製革廠、紡織業、染料廠、煉油工業、稀土金屬工業等用途，若不適當管制含砷廢棄物之流向，所造成的危害將導致環境與生態之浩劫，尤以飲用水及地下水污染問題最令人頭痛，臺灣雲林地區地下水即遭受嚴重威脅。“磁鐵礦(Magnetite, Fe_3O_4)”，又稱“鐵氧磁體(Ferrite)”，近年來被應用於吸附含砷污染之水體在國際上已漸受重視，國內相關研究則寥寥無幾。本研究團隊即以水熱合成法(hydrothermal synthesis)自行合成奈米級之鐵氧磁體尖晶石，測試其對水體中含砷污染之吸附效能。相關之研究成果為：1.完成磁性奈米鐵氧磁體生成條件之最適化研究；2.完成磁性奈米鐵氧磁體基本特性分析；3.完成鐵氧磁體(Fe_3O_4)吸附砷之最適化研究；4.五價砷之脫附及鐵氧磁體再生特性測試；5.完成等溫吸附曲線及反應動力參數之求得；6.以磁性奈米鐵氧磁體處理受砷污染之地下水。

研究成果顯示，在酸性環境下(pH 2 ~ pH 7)，吾人自製的奈米級鐵氧磁體吸附劑對砷有較佳的吸附移除效能，於不到5分鐘的時間內，即可有效的將液相中的五價砷吸附移除達95%以上，尤其在pH 3 ~ pH 4的條件下，吸附移除效率更可達99.99%以上。由等溫吸附曲線得知，pH 3、7、11的飽和吸附量分別可達14.35 mg/g、10.12 mg/g及4.88 mg/g，在pH 3至pH 11的操作區間，pH愈低，As(V)的吸附移除效率有明顯增加的趨勢，吸附平衡參數結果顯示以Langmuir Model有較佳之模擬結果，反應動力部分，自製鐵氧磁體吸附五價砷較適合以擬二

階動力模式來表示。此外，由As K-edge XANES研究結果發現，被吸附於鐵氧磁體上的五價砷並不會被其晶格內的二價鐵還原成更具毒性的三價砷，進而對水體環境產生更大的危害。

在五價砷之脫附及鐵氧磁體再生特性測試方面，本研究測試常見的六種酸類及鹽類作為五價砷之脫附劑，於脫附條件為五價砷初始濃度10 mg/L、溫度25 °C、脫附劑濃度0.1 M、鐵氧磁體0.05 g、脫附劑體積10 mL、脫附時間30分鐘的情況下，進行鐵氧磁體之砷脫附測試，結果顯示吾人測試之六種脫附劑的脫附效能以磷酸(H_3PO_4)最佳，磷酸鈉(Na_3PO_4)次之，硝酸(HNO_3)最差，脫附效能之排序為 $H_3PO_4 > Na_3PO_4 > H_2SO_4 > Na_2SO_4 > HCl > HNO_3$ ，其相應之五價砷脫附效率分別為83.52 %、63.26 %、52.80 %、43.34 %、1.56 %、0.61 %。再生特性測試結果發現，在初始五價砷濃度500 $\mu g/L$ ，溫度 25 °C、磷酸濃度0.02 M、鐵氧磁體0.002 g、磷酸體積10 mL、鐵氧磁體吸附時間30分鐘、磷酸脫附時間30分鐘的情況下，連續三次的吸脫附實驗發現，於吾人設定之操作環境下，鐵氧磁體隨著再生次數的增加對五價砷的吸附移除率有些微的降低，但移除效率仍可達93%以上，顯示自製磁性奈米鐵氧磁體具再生之可行性。

為評估自製鐵氧磁體應用於實際受砷污染地下水之整治，吾人以磁性奈米鐵氧磁體處理受砷污染之地下水體。結果發現所採集之六口井砷的濃度範圍從21.6 $\mu g/L$ 至84.3 $\mu g/L$ ，皆高於世界衛生組織(WHO)對砷所規定的飲用水標準值10 $\mu g/L$ ，若不經適當處理，則嚴重影響民眾健康。吾人於操作條件為吸附劑 Fe_3O_4 重量0.05 g，地下水體積10 mL，吸附時間4小時的條件下，測試處理六口受砷污染之地下水水樣，結果發



現，不論於中性(pH 6.84-7.65)或酸性(pH 1.61-3.30)吸附環境下，砷的移除效率皆達91.7%以上，所有地下水水樣之砷濃度均可降低至WHO所規定的飲用水標準值10 µg/L以下(最高的殘餘砷濃度為7.0 µg/L)。此外，雖然鐵氧磁體於酸性環境下(pH < 2)有些許鐵的溶出，仍然顯示吾人自製之鐵氧磁體吸附劑有應用於受砷污染地下水整治之潛力。

Abstract

Arsenic (As) in groundwater and contaminated drinking water has been a major health risk impact in Taiwan and southeast Asia countries. Arsenic has been a common added ingredient in production of various industries, including herbicide, pesticide, antiseptic, wood preservative, glass and ceramic-ware, metallurgy, leather, textile, dye, and rare metals. This can easily cause serious impacts on surrounding environments, in particular groundwater and drinking water contamination, and ecological systems if no proper waste managing strategy or controlling policy. Similar high level of As in groundwater has been reported in the Yun-Lin county in central and Chia-Nan coastal plain in southwestern Taiwan.

Magnetite (Fe_3O_4), so-called Ferrite, is a common Fe oxide with spinel structure. It has received wide attention internationally in recent year for its capability to adsorb As in aqueous solutions. However, paucity effort was dedicated to related researches in science community in Taiwan. In this proposal, we apply well developed hydrothermal method to synthesize nano-particle size of ferrite and to conduct a series of batch experiments to evaluate its capability to remove As in aqueous solution under various pH, T, solution/ferrite ratio and ion concentration conditions. Our major efforts in the past year are: (1) accomplish the optimal synthesizing conditions of magnetic nano-ferrite; (2) accomplish the characteristics analysis of magnetic nano-ferrite; and (3) accomplish some adsorption experiments for As removal by

magnetic nano-ferrite. The preliminary results showed the synthesized magnetic nano-ferrite has a great potential for removal of As even under acidic conditions, where the As(V) removal efficiency could reach more than 95% in five minutes. In pH 3-4, the As(V) removal efficiency could reach than 99.99%. From the adsorption isotherm, As(V) adsorption capacities were determined to be 14.35, 10.12 and 4.88 mg/g at pH 3, pH 7, and pH 11, respectively. In order to investigate the feasibility of magnetic nano-adsorbents in natural groundwater, six As contaminated groundwaters were sampled and tested for As removal in the laboratory. The total dissolved As concentration ranges from 21.6 to 84.3 µg/L, indicating all of the these groundwaters were potentially As contaminated groundwater (WHO limit: 10 µg/L). Our synthesized nano-ferrite were applied to remove As in these samples in the laboratory and found As removing efficiency of more than 91.7% in all cases. Currently we are further evaluating the feasibility in ferrite treatment of the polluted groundwaters in natural sites.

[007] 區域尺度土壤重金屬空間採樣策略與污染範圍劃定之研究

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本研究以彰化地區為研究區域，以該地區多種土壤種金屬為研究變數，擬發展一同時考量多變數及其保留空間分布與統計特性的採樣策略，並評估以採樣資料於污染範圍的界定之可靠性分析方法。本採樣方法提出分區條件拉丁超立方採樣方法，首先於採樣過程中先將研究區分區如網格或灌區分區，再以原始土壤採樣資料或與污染相關之變數為條件拉丁超立方採樣方法之採樣變數，以期選取的樣本於空間特性及統計特性上能更接近於原始資料或污染相關之變數之空間特性及分佈，最後各分區中選取樣區所需之樣本。

本研究適用兩種採樣情境，一為有土壤重金屬採樣資料，另一為無土壤重金屬採樣資料，若資料為原始資料調查的土壤採樣資料，則將原始資料與不同採樣方式所得的資料以逐步指標模擬法模擬研究區內重金屬濃度空間分布情形，並比較分區條件拉丁超立方採樣與原始資料之變異圖及空間特性，且計算局部和空間不確定性，並探討其污染範圍劃設之可靠性。若資料為污染相關之變數(無土壤重金屬採樣資料)，則以與污染相關變數進行分區條件拉丁超立方採樣，比較分區條件拉丁超立方採樣與原始資料之統計特性與空間變異圖特性，並與有土壤資料之採樣結果進行比較以驗證可行性，最後探討各情境下適用之採樣策略。

Abstract

The research aims to resample the multiple soil heavy metals at Chang-Hua County. The sampling model that can consider multivariate, statistic distribution and spatial information is developed. Moreover, the method is reliable for the analysis in delineating the pollution hazard. The method is a stratified conditional Latin hypercube sampling (scLHS) that includes the stratified sampling and grid sampling. Meanwhile, the consideration in spatial aspect for sampling sites in conditioned Latin hypercube sampling is also unignorable.

First, sampling is applied based on sampling data or the other correlated data, so the incorporation of spatial data, which is regarded as the spatial cLHS, might be able to drive the data closer to their original spatial allocation. Then, the spatial distribution and uncertainty of each technique, including original data without sampling, were evaluated by the sequential indicator simulation (SIS). Furthermore, the spatial cLHS could better imitate the distribution and spatial allocation of the original data.

The study considers two scenarios: with and without soil pollution data. Wherever the soil pollution occurs, the model evaluates the variogram and the spatial distribution of soil pollution based on the information offered. And then the model compares both the variogram and the spatial distribution with original data. After all the local and spatial uncertainty of the model are calculated. If there is no soil pollution at all, the model evaluates variogram and spatial distribution of soil pollution based on other information and then compares them with the original data.



[008] 港池沉積物重金屬溶出特性驗證、洗淨分級及資材化

再利用探討

張益國 許益源

中臺科技大學環境與安全衛生工程系

中文摘要

本研究應用多種溶出試驗，包括pH對初始酸鹼添加之溶出影響等溶出行為試驗(pH-dependent test)、管柱試驗(Percolation test)驗證港池沉積物重金屬溶出特性，並搭配歐盟LeachXS專家系統分析沉積物中重金屬於pH依存度之溶出行為，研判重金屬溶出或穩定之可能機制。隨後搭配水力分離技術開發，以水力漩流分離器(Hydrocyclone)分離重金屬含量較高之細顆粒港灣沉積物，再以重金屬於pH依存度之溶出行為為基礎，酸洗及螯合萃洗濃集沉積物中重金屬。並對經/未經水力分離處理、酸洗及螯合萃洗之港灣沉積物進行長期穩定特性驗證，驗證其粗細顆粒之重金屬溶出行為，評估水力漩流分離處理效能及促進粗顆粒(含重金屬量較少之顆粒)再利用。

Abstract

Contaminated sediments in the harbors remain being a significant issue during dredging operations. Numerous methods have been suggested in recent years for remove, treating and beneficial uses of harbor sediments. In this research, the basic characteristics and the geochemistry of metals in the sediments were studied, and which were subjected to pH-dependent leaching test, percolation test and column test. The results of experimental leaching tests of harbor sediments are compared with computer calculations, the LeachXS expert system. This computer program allows to predict the metal concentrations and the pH of leaching solution at equilibrium, along with the minerals that precipitate and the organic characteristics react with the metal ions forming into stable organic metal compounds.

In addition, the separation processes, hydrocyclone treatment, is designed to separate fine-grained particles by high settling velocity of particles. Combining with acid washing and chelating agent extraction, the treatment approach might achieve particle isolation and contaminant removal. Thus, this research projects might provide a basic understanding, and the statistic correlation among the sediment characteristics, metal concentration and the possible controlling factors.

[009] 超臨界二氧化碳萃取土壤中戴奧辛之研究

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本計畫已完成超臨界二氧化碳萃取系統之規劃設計，超臨界流體萃取裝置主要包括流體來源、高壓幫浦、萃取槽、控溫設備、壓力調控裝置、分離收集裝置等，相關系統組裝與試運轉業已完成。超臨界二氧化碳萃取實驗結果得知，本超臨界萃取技術確為可行之技術，在溫度120°C、甲醇濃度10%、壓力350bar下，超臨界萃取即可達約98%之去除效率。不同壓力超臨界萃取實驗結果顯示350 bar壓力下之萃取效果(97%)高於200 bar壓力下之萃取效果(90%)。不同輔溶劑比例萃取實驗結果顯示在高壓(350 bar)與高溫(120°C)下，輔溶劑比例越高，萃取效率僅可略微提升高。在偏低溫度與較低輔溶劑比例下，溫度與輔溶劑比例對萃取效率之影響皆相當顯著，但溫度上升後對萃取效率之影響比輔溶劑比例增加更趨明顯。最後，本研究以目前最佳推估之操作條件下概算每年處理10,000 m³之成本，初估平均處理成本約每方5,000新台幣。其成本與焚化處理動輒上萬之處理成本極具競爭潛力。

Abstract

In this studying, we have designed a pilot CO₂ supercritical fluid extraction (SFE) system, which is composed with gas source, high pressure pump, extraction tank, temperature controller, pressure controller and separation device. The SFE results revealed the treatment efficiency reach about 98% under 120°C, 350bar, 30g/min CO₂ and 5% methanol. It is worth to mention that pressure, co-solvent ration (v/w) and temperature play important roles in SFE system. Moreover, the high-chloride dioxins are hard to extraction than lower ones. However, co-solvent ration and chloride number of dioxin will not be critical factors under higher temperature (120°C). Finally, the cost of SFE system is about 5,000 NTD/m³, which is full of potential compare with other remediation technologies.



[010] 新穎釋氧物質於受油品污染之地下水整治與Microtox生物毒性

評估技術研發—批次與管柱試驗

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中文摘要

本計畫主要利用生物毒性偵測法 *Vibrio fischeri* light inhibition test 方法，檢測地下水污染物生物毒性範圍，若地下水具高毒性水質則採用化學法方式進行整治；若具中低毒性則以生物法方式進行復育。地下水整治方法選擇係採用釋氧型生物法與活化過硫酸鹽氧化法等二種方式進行。其中，「化學法」採用不同低價吸附劑(高爐石、轉爐石)種類與劑量，以異相活化過硫酸鹽方式進行對BTEX降解效率評估。「生物法」則以生物可分解之固化材料(聚乙烯醇)，將可降解油品污染物之分解菌種(BTEX分解菌)及釋氧物質(過氧化鈣)共同包埋而形成釋氧型固定化菌體顆粒。

在異相活化批次實驗結果得知，過硫酸鹽濃度越高，去除MTBE及BTEX所需時間將越短。當於適當條件下(以高爐石、轉爐石活化)，MTBE降解副產物—TBF與TBA亦可被有效去除，且無殘留問題產生。此外，二種吸附劑(高爐石、轉爐石)皆有活化過硫酸鹽效果，可促進污染物(BTEX與MTBE)之降解成效，未來可代替二價鐵做為活化劑之優先考量，降低整治成本及解決三價鐵沉澱問題。

研究結果顯示：以「PVA水凝膠包埋膠囊式冷凍法」包埋CaO₂製成之釋氧型固定化菌體顆粒，可獲得較高釋氧量，且添加緩衝物質(檸檬酸)可穩定釋放氧氣，同時釋氧率隨固化劑體積比減少而增加。由管柱試驗結果獲知，包埋BTEX分解菌株(*Mycobacterium* sp. CHXY119與*Pseudomonas* sp. YATO411)之釋氧型固定化菌體顆粒具可釋出氧氣，可供給包埋之菌株所需溶氧，促進微生物降解

BTEX之速率。

經由管柱實驗結果顯示，管柱內釋氧化劑物質之氧化能力約可維持6天，爾後隨釋氧化劑物質所釋出之過硫酸鹽濃度之衰退，氧化劑氧化降解污染物能力亦隨之下降。由DGGE分析菌群結構獲知，透水性釋氧反應牆長期於BTEX環境操作下，系統內之菌種變化趨於簡單化呈現；當有機負荷瞬間過高時，將導致菌群結構變動大，但隨系統逐漸趨於平穩時，菌群回復原有簡單化結構。由電子顯微鏡(SEM)拍攝結果獲知，利用PVA-alginate材料可有效包埋特定污染物之分解菌種，微生物可於顆粒內部空間中生長。

研究結果指出 *Vibrio fischeri* 對於油品污染物之生物毒性偵測具高度敏感度，污染物濃度與 *V. fischeri* 抑光率呈高度正相關；當使用 1% 過硫酸鹽及在 1 及 5 g/L 轉爐石可以有效降低污染地下水生物毒性。但使用過高過硫酸鹽(5%)，則會造成生物毒性增加。使用釋氧型固定化菌體顆粒管柱及釋氧型透水性反應牆則可有效降解污染地下水，隨污染物濃度降低，生物毒性也隨之下降。

Abstract

The objective of the project was to establish a framework for the integration remediation in a contaminated groundwater. First, the bioassay, *Vibrio fischeri* light inhibition test, was used to determine the toxicity of petroleum-contaminated groundwater. The highly toxic groundwater was treated with chemical oxidation method. In contrast, biological method was applied for groundwater of moderate-to-low toxicity. The oxygen-releasing type for a biological

method and activated persulfate oxidation were selected to remediate a BTEX-contaminated groundwater. For the biological method, novel immobilized beads for oxygen releasing were manufactured by incorporating calcium peroxide (CaO_2), with BTEX-degrading bacteria using a biodegradable material composed of polyvinyl alcohol (PVA) and alginate. For the chemical method, two types of adsorbents (blast-furnace slag (BF slag), blast oxygen furnace slag (BOF slag)) were used to activate sodium persulfate. Moreover, batch or column tests were conducted to investigate the amounts of beads and concentrations of sodium persulfate and adsorbents on BTEX decomposition for biological and chemical methods, respectively.

Both BF and BOF slags show the capability in activating sodium persulfate leading to the biodegradation of BTEX and MTBE. The activation capability was increased with the increase of the amount of slags. To reduce the remediation cost and lessen the Fe (III) precipitation commonly occurred in the groundwater remediation site, BF and BOF slag were predominantly selected as activated agents in replacing Fe (II). Moreover, the MTBE degraded by-products (TBF and TBA) were also effectively degraded under activated conditions by BF and BOF slags.

The higher oxygen released rate was observed using PVA/alginate-based hydrogel-encapsulated CaO_2 freezing method. Oxygen was also consistently released with the addition of buffering material (citric acid). The oxygen-releasing rates were increased with the decrease of the volumetric ratio of binding material, which is attributed to due to the better oxygen transfer under less amount of binding material condition.

DGGE analysis suggested that the microbial community in the PRB system acclimated by BTEX became simplified and approached to certain particular microorganisms. Microbial community structure changes were observed under transient shock organic loading conditions. However, microbial community gradually

recovered to its simplified structure when system operated in normal conditions. The SEM photographs show that PVA/alginate beads were suitable for the immobilization of microbial cells. The photograph also indicated that microorganisms could be successfully entrapped inside the pores with homogenous distribution in the PVA/alginate beads.

High sensitivity of *Vibrio fischeri* light inhibition test as a biotoxicity indicator for BTEX detection was observed. The relationship between BTEX concentrations and light inhibition rates was significantly positive. The application of 1% of persulfate with 1 and 5 g/L BOF effectively reduced the toxicity of groundwater samples. However, the application of high dose of persulfate (5%) induced the high toxicity. Both immobilized beads-BTEX degrader column and PRB system were proved to effectively degrade the groundwater pollutants, thereby decreasing their biotoxicity.



[011] 嘉南平原曾文溪流域含水層與地下水間之水-岩反應系統

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中文摘要

臺灣大量利用地下水做為飲用水之水源，但這些地下水中Fe、Mn以及許多重金屬離子含量常有過高的趨勢，除人為污染的來源外，重金屬元素多源自於天然地下水與圍岩之間的水-岩反應。常久以來，泥質沉積物被認為是這些污染物的主要供應者，因此，由土壤釋出重金屬元素的研究相形重要。本研究藉天然示蹤劑的概念做為探討這些議題的手段，並以曾文溪流域做為研究地區。地下水質分析結果顯示，此區地下水以末次冰期為界限，分為淺層含水層及深層含水層，淺層含水層因瀉湖環境具有較高的鹽度，但As與重金屬含量均低，深層含水層則因陸相沉積環境具有較低的鹽度，但As與重金屬含量均高。藉由BCR溶出試驗之分析結果，主要元素、Mn與Sr在可交換相中含量較高，可能代表在pH值大於8且略微氧化的環境；Fe、As與其他重金屬元素以鐵錳氧化物形態存在；在有機物相中富集的元素僅有Th與Li。分層結果顯示，As在深層含水層中的平均含量約為淺層的1.7倍，但其他重金屬元素則約略相等或反序，此與地下水質的分布有明顯差異。由稀土族元素的分析結果顯示，地下水含As量高者，幾乎沒有Ce負異常的現象。Ce負異常指示水體曾發生過強烈的氧化反應，顯示地下水體的As含量與氧化作用的發生有直接的關係。

Abstract

Groundwater is one of the major sources for supplying daily usage water of residents. However, the contaminants, such as Fe, Mn and heavy metals, are still a major issue in the coming years. These pollutants are generally recognized as being released by natural soils due to the water-rock interaction. In this study, a concept of natural tracer will be utilized to

establish the water chemical model. Some ultra-trace metal elements, such as rare earth elements, are very suitable to be the natural tracers. The hydrochemistry of groundwater demonstrates that the shallow groundwater is salty but arsenic and heavy metals is depleted. On the contrary, the deep groundwater is enriched with arsenic and heavy metals. The results of BCR (European Community Bureau of Reference) sequential extraction procedure show that most of heavy metals are extracted from the phase of Fe-Mn oxides while Li and Th are enriched in the phase of organic matter. Alkali and calc-alkali elements are mainly extracted from exchangeable phase in shallow aquifer. They represent the quality of pore water. It is worth to notice that the heavy metals of the BCR extracted solutions from sediments do not have the corresponding distribution in spite of As. However, arsenic in deep aquifer is almost twice the concentration in shallow aquifer. This implies that the enrichment of arsenic in sediments is not the only factor to cause high arsenic in groundwater. Some other chemical reactions are significantly involved in the water-rock interaction system. The results of rare earth elements demonstrate an interesting fact that the groundwater samples with top three arsenic concentrations do not have considerable Ce negative anomaly. On the contrary, the groundwaters with bottom three arsenic concentrations show strong Ce negative anomaly. In general, Ce negative anomaly is an excellent indicator of oxidation in aquatic system, which means that the oxidation reaction is responsible to result in minimum arsenic concentration in groundwater.

[012] 綠色整治決策支援系統之建立

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中文摘要

在國際不斷邁向低碳城市以及循環經濟等永續發展方向的趨勢下，土壤及地下水污染場址的整治必須以系統性方法為基礎，建構一綠色整治管理的決策系統。目前的整治技術決策在考量成本、時間及技術等可行性下，僅以場址符合濃度標準或風險接受度為首要目標，並以此決定整治方案；這樣的決策模式，囿於片面的評估範疇及有限的方案選項，其所產生的決策可能未能與永續發展一致。

系統性的決策架構則改善各場址獨立決策的缺點，將整治決策置於永續管理的架構中，強化並延伸整治決策所考量的面向，擴大決策空間，藉以尋求整體最適的管理方案。其所考量的範圍，第一，評估項目反應多元的衝擊類別，包括全球尺度的溫暖化效應、區域尺度的酸雨，以及地方性的生態效應等十二項評估項目。第二，決策範疇涵蓋完整的生命週期，包括支援整治階段的上游活動、整治階段，以及整治後監測，以利後續土地的維護及利用或開發。

本決策支援系統整合生命週期評估與風險評估方法，評估各種整治技術對環境與健康的綜合影響；並進行一實際案例試算以驗證其實用性。本計畫以環境與健康面向為評估重點，已建立決策系統架構與軟體介面；期以此基礎，結合經濟社會面向與決策方法，發展完整實用之管理決策系統。

Abstract

At the present practice, to determine remediation strategy for a contaminated site only considers the concentration standards and the risk acceptance along with time and cost. The remediation strategy determined under such approach is constrained with limited evaluation aspects and alternatives; it is questionable

as to whether such decision could be in line with the direction of sustainable development.

However, under the global trend of pursuing sustainable development, such as Low-Carbon City and Circular Economy, the remediation of the soil and groundwater contaminated sites should be performed with a systems approach, based on a comprehensive sustainable site management. This systems approach placed the remediation decision within the framework of sustainable site management; the evaluation dimensions and decision space are therefore enlarged to identify optimal management strategies.

The evaluation aspects of the systems approach encompass a variety of impact categories, such as global warming, regional acid rain and ecological effect, etc. In addition, the decision framework covers the complete life cycle which includes the upstream activities supporting remediation process, the remediation process itself, and the post-remediation operation & maintenance. The resource inputs and discharge outputs from the entire life cycle and the resulting primary, secondary, and tertiary environmental impacts are included in the evaluation. Thus, it is an ample approach that has wide-range issues taken into account.

The core of this decision system is Decision Supporting System integrated by life cycle assessment and risk assessment. Such integration is also an important international research subject, in which the differences in terms of data type, temporal and spatial scale, applicable levels as well as uncertainty need to be resolved.

The focus of this year research includes: the establishment of decision-making and assessment framework, the integration of life cycle assessment and



risk assessment, and conducting a case study to examine the practicality of the proposed approach. Base on the accomplishment, a practical decision-making system for sustainable site management, i.e., the green remediation, is expected to be fully developed by incorporating economic and social dimensions.

[013] 熱脫附處理對土壤質地變化、汞與戴奧辛污染物去除效果 以及物種分佈探討

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中文摘要

本研究主要藉由中石化之熱脫附實驗室，以模廠級旋轉窯進行土壤熱脫附實驗。首先以實驗室熱重分析儀快速獲得數種受汞及戴奧辛污染土壤之失重行為，藉由所得之熱重損失區段初步定義可操作之脫附條件(i.e., 較適脫附操作溫度)，之後將該條件配合不同之脫附溫度、進氣量、以及延時，配合管柱實驗獲取放大數據後，應用於旋轉窯反應器，以獲得於不同脫附條件下土壤質地變化與土壤中汞與戴奧辛殘量變化情形。實驗測試包含四個土樣(以A、B、D、E代碼表示)於500或550、700及800°C脫附處理之物化特性、汞與PCDD/Fs 殘量變化情形、汞型態分佈及戴奧辛物種分佈。結果顯示加熱後土壤pH皆由原本的中性或弱鹼轉變為強鹼性，土壤中有機質含量隨加熱溫度升高而減少。土樣中之汞(6.7–480 mg kg⁻¹) 在熱脫附處理後，濃度均可降低至管制標準以下(i.e., 20 mg kg⁻¹)。PCDD/Fs毒性當量在550°C持溫2小時處理後可低於管制標準(1000 ng I-TEQ kg⁻¹)，原始土壤中 PCDD/Fs 組成顯示，OCDD及OCDF為主要化合物，熱脫附前與熱脫附後土壤中所含 PCDD/Fs 以PCDD為主。汞之型態分佈顯示，熱脫附前與熱脫附後之型態分佈均以殘餘態為主，顯示該場址之汞不論處理前後其生物可利用性均偏低。本研究促進瞭解污染物經熱處理後之再分配行為，期許所得結果能做為未來實廠建構與熱脫附參數選擇之依據。

Abstract

This study examines the effectiveness of thermal desorption of CPDC's contaminated soils using a bench-scale column reactor and a pilot-scale rotary reactor. The test parameters include desorption temperature, duration, and carrier gas flow rate. Thermo gravimetric analysis (TGA) is used to preliminarily understand the thermal characteristics of soils. Four soil samples (A, B, D, E) contained various amounts of Hg and PCDD/Fs were then tested for their desorption properties at 500, 550, 700 and 800°C. The resulting physical and chemical properties and distribution of mercury fractionations and dioxin patterns were then accessed. The experimental results showed that the soil pH changed from neutral or weak basic into a strongly basic. Soil organic matter content decreased with elevating the desorption temperature. At all of the test temperatures, Hg concentration can be reduced to < 20 mg/kg, the soil standard by Taiwan EPA, from the concentrations between 6.7–480 mg kg⁻¹. TEQ of PCDD/Fs at 550°C for 2 hours after treatment reduced to < 1000 ng I-TEQ kg⁻¹. OCDD and OCDF were the major dioxin homologues in the soils, before and after thermal desorption. Mercury fractionation examinations showed that mercury was mainly in residual form before and after thermal desorption. These results suggested that the bioavailability of mercury in the contaminated site was relatively low. This study provided better comprehension in the repartitioning of these contaminants in soil. Results presented here may provide useful suggestions for the scale-up thermal treatment processes in the future.



[014] 應用生物反應槽進行石化污染物之生物復育研究

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中文摘要

本研究利用石化污染場址中所分離的菌種(*Pseudomonas* sp. NKNU01, *Bacillus* sp. NKNU01, *Klebsiella* sp. NKNU01, *Enterobacter* sp. NKNU01, 及 *Enterobacter* sp. NKNU02) 進行甲基第三丁基醚(methyl tert butyl ether, MTBE) 生物降解實驗, 探討最具有分解 MTBE 潛力菌種及其降解途徑。

在批次實驗中以混合菌加入共代謝物質降解效果為最佳, 可降解 MTBE 約達 64%; 共代謝物質以正戊烷(Pentane)具有最佳效果, 不添加共代謝物質試驗中, 發現 *Enterobacter* sp. NKNU02 降解 MTBE 效率約達 29% 較添加共代謝物質時效率佳, 且屬單一菌種試驗中具有最佳降解 MTBE 潛力菌種。由生物反應槽試驗結果顯示 *Enterobacter* sp. NKNU02 於不添加共代謝物質之實驗可分解 MTBE 達 56%; 加入共代謝物試驗中, *Bacillus* sp. NKNU01 與 *Klebsiella* sp. NKNU01 降解 MTBE 皆約達 22%, 與批次實驗相較之下皆有顯著差異, 利用生物反應槽可促進生物降解效率提升。研究發現 *Enterobacter* sp. NKNU02 進行 MTBE 分解時, 不經過第三丁醛(tert-butyl formate, TBF)轉化, 而直接氧化生成第三丁醇(tert-butyl alcohol, TBA)進而生成 2-Propanol 與 Lactate 再進入 TCA cycle, 完成 MTBE 代謝作用。於降解實驗添加 BTEX 結果發現 *Enterobacter* sp. NKNU02 分解 MTBE 會受 BTEX 所抑制, 使降解率約減為 16%。然而, BTEX 亦會被 *Enterobacter* sp. NKNU02 分解, 甲苯被分解效果為最佳約有 36%, 苯約有 32%, 故此菌種對其他汽油污染物亦具有降解效用, 本研究結果可應用於汽油污染場址之生物復育規畫。

Abstract

The objective of this reach was to investigate the biodegradation potential of methyl tert-butyl ether (MTBE) by microorganisms specified (*Pseudomonas* sp., *Bacillus* sp., *Klebsiella* sp., *Enterobacter* sp.) at a petroleum contaminated site. It was intended to evaluate the pure culture with the best ability of biodegradability of MTBE and to explore the biodegradation pathway for these microorganisms.

Pentane was employed as the cometabolic chemical to enhance MTBE degradation. However, the pure culture (*Enterobacter* sp. NKNU02) illustrated the best degradation potential of MTBE (about 29%) without adding pentane. *Enterobacter* sp. NKNU02 could degrade about 56% of MTBE without adding pentane. *Bacillus* sp. NKNU01 and *Klebsiella* sp. NKNU01 could degrade about 22% of MTBE with adding pentane. Comparing with the batch experiments, bioreactor could significantly enhance MTBE degradation. Protein spots of interest were identified through database searching according to peptide mass fingerprints (PMFs) obtained using matrix assisted laser desorption/ionization-time of flight mass spectrometry (MALDI-TOF MS). Four metabolic enzymes including alcohol dehydrogenase, phosphoglyceromutase, transaldolase, and isocitrate dehydrogenase may be involved. The potential products of MTBE degradation including acetic acid, 2-propenoic acid, and 2-propanol were analyzed by gas chromatograph/mass spectrometer(GC/MS). *Enterobacter* sp. NKNU02 followed the pathway in the initial steps of MTBE degradation, without converting MTBE to tert-butyl formate, which was directly hydrolysed to tert-butyl alcohol, and then transformed 2-propanol and lactate to the TCA cycle



(tricarboxylic acid cycle).

Since MTBE and monoaromatics such as benzene, toluene, ethylbenzene, and xylenes (BTEX) can coexist in gasoline-contaminated groundwater, the MTBE-degradability of *Enterobacter* sp. NKNU02 could be reduced about 16%. However, it could also degrade BTEX including 36% of toluene and 32% of benzene. The effectiveness of bioremediate MTBE contaminated groundwater will serve the potential for field-scale application.



[015] 應用於土壤與地下水有機污染整治之複合技術之可行性測試

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中文摘要

本計畫擬整合雙相抽引法與高級氧化程序，開發出一套高效、可行、具有市場競爭力之複合整治技術，以解決目前土壤及地下水油品污染之問題。本計畫依選擇之污染場址特性建立一以現地污染土壤為基礎之實驗管柱進行污染物去除試驗。

實驗中抽出之液體經過簡易油水分離去除浮油後，以臭氧進階氧化技術處理水中之可溶性有機污染物，並將放流水接管至污染團地下水上游接近地表之土壤層中放流沖洗，以促進土壤孔隙中殘留的有機污染物分解並提升土壤層中的含氧量，增進土壤中有機污染物好氧分解菌生長。

實驗採集某污染場址中高污染之土壤，並以實驗室管柱模擬受污染土壤，將受污染之地下水經過高級氧化系統處理後，再將含有高濃度之臭氧與氧氣之處理水補注回土壤層中，以模擬現地之污染整治情況。現地土壤之分析結果指出，現地中最主要之污染物為總石油碳氫化合物，此污染物同時也是臺灣地區加油站超過法規標準最主要之污染物。研究結果指出，該複合方法能在 34 天內，分別去除土壤中與地下水中 93% 與 71.4% 以上之柴油總石油碳氫化合物，且符合土壤 1,000 mg/kg 與地下水 10 mg/L 之污染管制濃度。而有浮油存在之高濃度污染情形下，管柱實驗亦具有相當不錯之處理效果。

Abstract

There are quite a few petroleum organic contaminated superfund sites in Taiwan, about two billion dollars expenditure on the remediation while only taking into account the expenditure from the Soil and Groundwater Pollution Remediation Fund annually. Moreover, the whole remediation process of

contaminated sites usually needs 2-6 technologies in Taiwan. Thus, the construction costs of equipments and training costs of operators are high. A combined method of dual-phase extraction and advanced oxidation process (AOP) is employed in removing the petroleum organic compounds with the distinguishing features of rapid, effective, and economic.

A contaminated site was selected as target to perform the hydrogeological survey. The laboratory scale experimental column was developed to test the removal efficiency based on the information of hydrogeological survey. In this investigation, the dual-phase extraction, AOP, and ozonic water flushing were performed in series to complete the experiment. Dual-phase extraction is the major method for pollutant extraction in the investigation. Separate the extraction liquid into oil and water layers, and recovery the oily organic pollutant. The extraction water was then treated with ozone and flushed through groundwater level to improve the pollutant solubility. The ozonic water was flushing through surface soil layer to remove the pollutant in the pore when the float oil layer inexistence. In addition, the ozonic water can release oxygen in the soil pore to prove a good environment for the aerobic microorganisms to decompose the pollutant.

The petroleum-contaminated soil was sampled from a selected contaminated site, and stuff in a designed glass experimental column to simulate the pollutant behavior while pumped the AOP treated groundwater back into the contaminated soil. The total petroleum hydrocarbons (TPH) and benzene, toluene, ethylbenzene, and xylene (BTEX) of contaminated had been analyzed at the end of April 2011. The analyses data indicated



that the TPH is the major pollutant in the selected contaminated site. The experimental data set indicated that TPHd concentrations of contaminated soil had been below the pollution control standards of soil (1,000 mg/kg) and groundwater (10 mg/L) in a 34-day treatment. The results of the floating oil column tests also show the combined method is an effective even at a very high pollutant contamination.



[016] 二仁溪污染底泥整治模場試驗計畫

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中文摘要

河川底泥在生態系中扮演重要功能，一旦遭受持久性污染物之污染，污染物可循食物鏈進入人體及動植物體內，造成人體健康危害與生態系損害。以我國目前污染嚴重之二仁溪為例，其污染源分佈上游以畜牧廢水為最大宗，下游以燃燒廢五金、電鍍、酸洗、廢油為大宗，其下游灣裡一帶即為當年廢五金露天燃燒地區，廢氣中粒狀物質沉降及廢金屬回收酸洗廢水直接排入河川中。最引人注意之污染物包括重金屬、多環芳香烴類、多氯聯苯等。多環芳香烴類已達有害程度，多氯聯苯明顯超過標準，重金屬污染以鉻與砷有顯著風險，應進行復育，但經濟有效之復育技術付之闕如。本計畫之目的在於開發低成本高效率之奈米材料進行生物、物理化學整合之復育，去除底泥中之重金屬、萘與Aroclor1242。整體而言，本計畫於現地模場試驗設施完成後執行五個月試驗之初步成果顯示積極式工程復育之效果(最佳者重金屬移除22.6%，萘移除100%，Aroclor1242 移除91.4%) 普遍優於自然回復(重金屬移除7.2%，萘移除99%，Aroclor1242 移除61.4%)，單獨添加奈米氧化鐵或奈米乳化液不如同時添加之效果，本計畫已確認中低加量之乳化液與氧化鐵之配合為一可行之低成本高效益底泥整治技術，本計畫衍生效益為提昇本土河川底泥整治水準，了解實場整治之技術問題與克服途徑，並能保護底泥生態品質及國人健康。

Abstract

Sediments play a vital role in ecosystems. Once contaminated by persistent pollutants, the contaminants can gain access to human, plants, and other animals. This will increase human health

risk and degradation of natural ecosystem. Taking the heavily-polluted Er-Ren River as an example, the sources at the upstream are farming and livestock raising, while at the downstream scrap metal burning, metal plating, acid wash, and waste oils. Historically, the vicinity of Er-Ren River is the notorious site for scrap metal open burning. The particulate matters in the smoke and the acid wash waste water may either deposit or settle down in the river sediments. Among these pollutants, the concentration of polynuclear aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), arsenic, and chromium are either above or near to the regulated standards. The sediments in this river is in a urgent demand for a cost-effective technology to reduce the pollutant concentrations. Here we proposed to compare the removal of different approach, natural recovery, magnetite nanoparticle adsorption, nanoemulsion addition for biostimulation, and integrated remediation. The results showed that engineering intervene is better than natural recovery. The best of engineering intervene approaches can remove PAHs up to near 100%, PCBs at around 91.4% and heavy metal up to 38.8% while the natural recovery can remove 99% of PAHs, 61.4% of PCBs, and 7.2% of heavy metals. The results suggest that addition of median to low quantity of soybean oil nanoemulsion and low quantity of magnetite nanoparticle could be a cost-effective method for sediment remediation in Er-Ren River. This study can also elevate the domestic technology level in sediment remediation, gain better understanding of the scale-up remediation, and protect the health of our ecosystems and our citizens.

[017] 以模場規模之電動力法及植生技術現地鉛污染土壤之研究

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中文摘要

重金屬污染農地快速有效的整治方式具有極高研究及應用價值，特別是模場現地污染整治的試驗更顯得重要。本研究擬針對兩種現地型土壤復育技術進行模場試驗，其一為現地型物化處理技術的電動力法，另一種現地型生物處理技術為植生復育，特別是本土性植物對於土壤中重金屬具有極高的吸收能力，本研究擬以模場規模之電動力法及植生技術分別復育台中市現地鉛污染土壤，企盼藉由本計畫了解模場規模之電動力法及植生技術復育技術的關鍵因子，進而掌握兩技術最具去除效益的操作參數，最後獲得兩技術的成本效益。

本計畫採用的電動力法及植生復育的結果發現及結論如下：

在電動力法方面：

- 電動力法(CEEK)以現地規模處理鉛污染土壤，經過56天處理，土壤平均鉛濃度可從7190 mg/Kg降至約2050mg/Kg，去除效率約可達72%。
- 電動力法(CEEK)以現地規模處理鉛污染土壤，土壤之pH及導電度可維持穩定。
- 電動力法(CEEK)以現地規模處理鉛污染土壤，操作液鉛濃度於第1至14天即上升至約42mg/L後急速降低，其顯示移除鉛大多電鍍於陰極板。
- 系統對於1.0平方公尺的鉛污染土壤每去除1%所需的操作電費約為8.82元。

電動力系統停機後，無人工灑水下鬼針草種子仍能自然發芽生長，其顯示本系統整治後土壤具有相當程度的肥力。

在植生復育方面：

- 土壤含EDTA或其鈉鹽濃度1 mM以上對試驗植物鬼針草、野苧生

長明顯造成影響，且對植物對鉛之累積吸收情形並沒有正面效益。

- 現地原生植物牛筋草、水丁香、鬼針草、龍葵、尖瓣花、野苧及苦蕒等對鉛之吸收情形相當不錯。
- 鬼針草、野苧及向日葵三種植物地上部中以鬼針草對鉛有最高吸收量，其次為野苧。鬼針草對鉛有高吸收量，有相當高生質量，相當容易種植，具有做為植生復育植物潛力。

Abstract

The heavy-metal contaminated soils have threatened Taiwan agricultural development seriously and been paid attention for a long time. The fast and effective remediation techniques possess high value of research and application. Two promising in-situ soil remediation techniques will be employed in this pilot test. One is a physical-chemical remediation- electrokinetics; the other technique is the phytoremediation. Some local plants have been proven to strongly absorb heavy metals in the soil. In this study, we try to respectively use electrokinetics and phytoremediation to in-situ remediate the Pb contaminated soils in Taichung County. Hopefully, we can obtain critical operation parameters of these two remediation techniques by preceding this project and achieve satisfactory results.

Based on experimental results, several discoveries and conclusions can be drawn as the following:

For the electrokinetics:

- The Pb concentration in the soil can be removed from 7190 mg/Kg to 2050 mg/Kg (i.e., the removal efficiency is around 72%) after 56-



- day treatment by the CEEK process.
- The soil pH and conductivity can be maintained under a stable status after 56-day treatment by the CEEK process.
 - The Pb concentration in the operation solution will be increased upto 42 mg/L then decreased dramatically. Results indicate that the removed Pd is electroplated on the cathode.
 - The CEEK system operated in the pilot- scale presents that the electricity cost for removing 1% Pb from the soils is around 8.82 dollars per meter square.
 - After CEEK treatment, the *Bidens pilosa* would grow up in the treated soil which indicated the treated soil was feasible to plants.
- For the phytoremediation:*
- Soil contained EDTA, EDTA-2Na and EDTA-4Na more than 1 mM, will have significant effect on *Bidens pilosa* and *Amaranthus viridis* growth, and there is no positive effect on Pb adsorption.
 - Field plants, *Eleusine indica*, Lantern Seedbox, *Bidens pilosa*, *Solanum nigrum*, *Amaranthus viridis*, *Physalis angulata* have high Pb adsorption capacity.
 - Among, *Bidens pilosa*, *Amaranthus viridis* and *Helianthus annuus* three plants, *Bidens pilosa* has the highest Pb adsorption concentration, follow is *Amaranthus viridis*. *Bidens pilosa* has potential to be a phytoremediation plant, because it has high Pb adsorption capacity, high biomass and easy to plant.

[018] 多深度微水試驗測試段長度對水力傳導係數推估之影響

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中文摘要

含水層的異質性影響地下水流場、污染物溶解相流布、及非水相液體遷移，是設計污染整治和選用整治技術上的重要考量因素。多深度微水試驗 (multilevel slug test, MLST) 是一種單井雙封塞技術，可有效決定測試井周圍含水層水力傳導係數的垂直異質性， $K(z)$ 。在場址中不同位置的監測井執行 MLST 則可獲得場址的三維異質性 $K(x,y,z)$ 。受限於雙封塞系統的結構和 MLST 實際施作因素，測試段長度 l_s 以 0.25m 至 1m 為宜。 $K(z)$ 的解析度及 MLST 工作量均和測試段長度呈反比。本計畫的目的是評估測試段長度對 $K(z)$ 的影響，並決定兼顧 $K(z)$ 解析度和 MLST 工作量平衡的測試段長度。在三口井使用四個不同測試段長度 ($l_s=0.25\text{m}$ 、 0.5m 、 0.75m 、及 1.0m) 進行 158 次連續深度 MLSTs，和三口井的全篩段微水試驗 (full screen slug test, FST)。結果顯示在垂直異質性相當弱的局部深度範圍內，四個測試段長度所得的 $K(z)$ 分布情況和解析度相當一致，可選用最長的測試段長度 ($l_s=1\text{m}$) 以減少 MLST 工作量。在不同程度的垂直異質情況下， $l_s=1\text{m}$ 所得 $K(z)$ 的解析度最差， $l_s=0.25\text{m}$ 和 0.5m 所得 $K(z)$ 的解析度大約相同，所以使用 $l_s=0.5\text{m}$ 足以反映垂直異質性變化。由於場址異質性屬事先未知，因此建議測試段長為 0.5m (左右)，以減少 MLST 工作量及調查成本並且兼顧水文地質的變異性。FST 所得的 \bar{K} 值為全篩段的垂直平均水力傳導係數，無法有效反應垂直異質性； \bar{K} 水文地質代表性並不明確。對場址調查或污染整治設計而言， \bar{K} 較缺乏實用性，故不建議使用全層微水試驗進行場址調查。

Abstract

As an important factor in remediation design, aquifer heterogeneity significantly

influences groundwater flow field, the distribution of dissolved solutes, and migration of nonaqueous phase liquids. The multilevel slug test (MLST) is a single-well technology that employs the double-packer system for the determination of the vertical heterogeneity of hydraulic conductivity, $K(z)$. A three-dimensional $K(x,y,z)$ can be obtained by conducting the MLST in different wells at a site. Limited by the structure of the double-packer system and by the MLST operation, the test section length l_s is normally between 0.25 to 1.0 m. The test section is a perforated pipe that connects the two packers. Both the resolution associated with the $K(z)$ obtained and the work load of the MLST are inversely proportional to l_s . The purposes of this project are to evaluate the influence of l_s on $K(z)$ obtained and to determine the test section length appropriate for a balanced weight on a sufficient resolution of $K(z)$ and the work load of the MLST. In three wells, a total of 158 MLSTs using different l_s (0.25, 0.5, 0.75, and 1.0m) were conducted. In addition, three full screen slug tests (FSTs) were performed in the three wells, respectively. The results show that in some small areas of little vertical heterogeneity, the resolutions and profiles of $K(z)$ from the four different l_s are about the same, so one can choose the longest possible test section length ($l_s=1.0\text{m}$) for the MLST. Under different vertically heterogeneous conditions, however, $l_s=1.0\text{m}$ yields the worst resolution for $K(z)$, and the profiles and the resolutions of $K(z)$ from $l_s=0.25$ and 0.5m are about the same, indicating $l_s=0.5\text{m}$ is sufficient to reflect the vertical heterogeneity. Since aquifer heterogeneity is unknown a priori, it is suggested that $l_s=0.5\text{m}$ be used in the MLST in order to reduce the work load as well as to obtain sufficient resolution for $K(z)$. As far as the FST is concerned, the \bar{K} value obtained



represents the vertically averaged hydraulic conductivity over the full well screen, which fails to reflect the vertical heterogeneity and has an unclear hydrogeological meaning. Because of lacking practical usefulness of in the remediation design, it is suggested that the FST not be used for site investigation.

[019] 應用現地油污染土壤復育之系統化方法

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中文摘要

臺灣土壤及地下水受油品污染日益嚴重，污染案例不勝枚舉，以高雄煉油廠污染案為例，2005年四月，高雄市楠梓區的中油煉油廠由於油槽基礎地質侵蝕及油管破裂，造成周邊土壤及地下水受到嚴重的油漬污染，面積約為一點六公頃。當地居民因而飽受用水及土壤污染，現已被環保署列為管制區域，並要求改善復育同時要求於民國104年遷廠。油品污染一般污染途徑以地下儲油槽(Underground Storage Tanks, USTs)受腐蝕而破裂產生漏油、油管破裂、地面油品意外洩漏、及廢油品任意傾倒或掩埋等。

因此，過去八年，經由經濟部學界科專計畫補助，本計畫團隊研發出的系統化環境分子生物復育技術(Systematic Environmental Molecular Bioremediation Technology, SEMBT)，對於土壤污染檢測甚至土壤及地下水復育，將配合環保產業的需要，降低監測、整治的成本，縮短離址油污土壤復育時程，提供本土化的生物技術服務。本計畫延續前所開發出之分子生物技術，利用已建立之SEMBT為技術平台，進行離址整治模型場規模現地驗證及示範之污土生物復育。污染物的種類含柴油(C8-12 ~ C16-28)及燃料油(C28-C40)為主要污染物、BTEX為次要污染物之外，將推進並善用現址原生微生物，含柴油分解菌、重油分解菌及堆肥真菌類等，至不具揮發性、由20個碳以上的烴類混合物和其他較重的分子且較難被降解的重油(heavy fuel oil)污染場之整治。

本研究整治目標土方為20m³，在土方第0天時，預計完成各5m³土堆兩個，分別為控制組BAS0與添加150L之新鮮生物堆肥組BAS1；第7天時，BAS1經過7日生物優植與刺激後，將會產生適應土堆中碳氫化合物污染之油分解菌，將BAS1移出約1m³之土方至BAS2，同時

置入1 m³新污染土方(BAS1)，並於BAS2加入4m³新污染土方混合約5 m³土堆，此時現場將產生5m³土堆三個；爾後以此類堆，根據相同推進工法，每7天作為一間隔進行土方推進，最後將完成20m³土方整治生物堆。針對Case 6(KH-20)現場土方，經過篩器的篩選，再以日光曝曬後，所篩選出約40m³土方，進行初步土方的污染物濃度調查，其含水率約為15%以內，結果得知過篩後土方的濃度約為1100~3700 mg TPH/kg，總石油碳氫化合物污染濃度分布頗不均質，土方主要以高碳數碳氫化合物污染為主，預期能作為後續土方復育之整治目標。由微矩陣生物晶片檢測，Case 1~Case 6 之土堆發現 *Gordonia alkanivorans*、*Bacillus subtilis*、*Pseudomonas* sp.、*Sphingomonas yanoikuyae*等菌，*Gordonia desulfuricans*等原生油分解菌屬，均已廣泛被報導為具有分解碳氫化合物能力之細菌類微生物(Atlas, 1984; Bossert and Bartha., 1984; Cullen et al., 1994)。在真菌的部分，Case 1~6之土堆皆可發現 *Aspergillus fumigatus*、*Candida tropicalis* 與 *Pseudallescheria boydii*三菌種，研判可能與該土堆定期添加之活化劑有關。

Abstract

Most of petrochemical oil pollutants contain aliphatic lipid and aromatic hydrocarbon compounds that are hydrophobic to water but sticky to surface of certain materials. These widespread fuel oil pollutants (total petroleum hydrocarbon, TPH) are difficult to be removed and need to be degraded with specific microorganisms associated with abundant quantity of extracellular polymer and secreted biosurfactant. Biosurfactant with the extracellular polysaccharide and the polypeptide promoted biofilm can be developed from diverse 48 microbial consortia that are



most found in hydrocarbon contaminated soil. With the secreted biosurfactants dissolving and penetrating into the oil layer, a biodegradation process can be enhanced with the enriched microorganisms which can drill channels for mass transport of nutrients and bioproducts. In order to carry out a systematic environmental molecular biotechnological (SEMBT) remediation, three research groups are established: (1) bioagent development with molecular biotechnology, (2) molecular biomonitoring technology, and (3) biotechnology integration for environmental engineering. This research group will work out the systematic technologies of the bioagent augmentation, the biomonitoring, and the biofilm stimulation to perform an useful bioremediation process (SEMBT) in a petroleum contaminated site. Within one year, a set of ex-situ bioremediation demonstration will be established with a pilot scale plant of 20 m³ biopile treating the total petroleum hydrocarbon (TPH). These biotechnologies of ex-situ bioremediation will be transferred to the Taiwan China Petroleum Corporation, and the CHC environmental engineering firm for scale-up application in the near future. The project goal is to demonstrate a systematic environmental molecular biotechnology (SEMBT) for biodegradation technology that is feasible for remediating a large area of hydrocarbon contaminated site.

[020] 應用透水式電化學生物反應牆於受BTEX污染地下水之 現地整治研究

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中文摘要

苯 (benzene)、甲苯(toluene)、乙苯 (ethylbenzene)與對二甲苯(xylene) (簡稱 BTEX)普遍存在汽油污染的地下水中，且隨著地下水的流動，污染的範圍也隨之擴大。傳統處理方式需耗費大量動力自地下抽出污染物質或注入過氧化劑以利污染物質之氧化，各種方法中生物處理方法被認為最符合經濟效應，其中生物反應牆常被用來防止污染物質的擴散，但氧化物質(最終電子接受者)的順利提供，依然是生物反應牆在實際整治過程中最大的瓶頸。根據先期研究發現，以電極為電子接受者，在無氧的環境下，微生物可以持續進行苯的氧化反應。後續進一步在模擬土壤管柱中(反應層約15 cm)，利用實際土壤微生物作為植種菌源，在特定電壓的施加下，以電極為最終單一電子接受者，進行BTEX生物降解研究，初步發現微生物對BTEX有極佳的降解率(95%以上)，此重要結果有利於開發一微生物電化學反應牆。為使此反應牆更趨實用，本計劃將進行實際現地模廠規模(Pilot study)驗證，探討在不同停留時間、不同施加電壓與不同反應層深度下之各物質降解、中間產物累積與相關微生物分布情形。

Abstract

Benzene, toluene, ethylbenzene and xylenes isomers (BTEX) exist widely in the groundwater contaminated by gasoline and are spread by the groundwater flow. Traditional remediation methods of physical (Pump and treat) or chemical (chemical oxidation) techniques are generally costly. Biological approaches for treating BTEX in the contaminated groundwater appear to be economical and environmental friendly processes, but supply of final electron acceptors for the microbe efficiently is still a strict problem.

In our previous study, it was revealed that an electrode at a given potential could be the final electron acceptor for benzene biodegradation under anaerobic conditions. Further, the soil columns (reaction zone were 15 cm) were constructed to study the biodegradations of BTEX with carbon fiber electrode as the sole electron acceptor. The degradations of BTEX were more than 95%. This result is useful for the development of bioelectrochemical permeable reactive barrier. In order to promote this useful barrier to the on-site application in the near future, some useful parameters, such as the suitable value of applied potential for the electrode, hydraulic retention time, the efficiencies of BTEX biodegradation, and the microbial communities within the carbon fiber electrode will be organized in this pilot scale study on bioelectrochemical permeable reactive barrier.



[021] 三硝基甲苯污染土壤菌株種類之探討與具降解三硝基甲苯潛力 菌株之篩選與開發

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中文摘要

三硝基甲苯在軍事或民間用途上，均為廣泛使用的二級炸藥。在許多環境中可以見到三硝基甲苯的污染，包括火藥製造與儲存廠、試驗以及訓練場所等，另外戰爭時期遭強烈轟炸的遺址亦可能有大量三硝基甲苯的殘留，還有工礦爆破以及戰後火藥處理等都是環境遭受三硝基甲苯污染的來源。遭受三硝基甲苯污染環境包括土壤與水體都會對生物以及人體的健康造成極大的影響。因此，如何有效的對受污染的環境進行整治亦是一個在土壤與地下水的環境保護重要的課題。

本研究以臺灣南部一遭受三硝基甲苯污染場址的土壤為樣本來源，進行微生物種類之探討，並從該場址之土壤中分離純化具降解三硝基甲苯之本土微生物，作為後續進行現地整治的生物復育可行性之探討。本年度的主要研究成果，包括(1)建立使用變性梯度凝膠電泳(DGGE)直接分析土壤樣本中細菌種類的研究平台；(2)利用富集培養方法，從含有三硝基甲苯污染的土壤中篩選與分離培養具降解三硝基甲苯之本土環境微生物；(3)針對篩選出之菌株，進行純化培養與菌株之初步鑑定；(4)初步完成挑選之優勢菌株的特性分析，包括在實驗室中培養基的生長情形，使用高效液相層析儀分析培養基中三硝基甲苯的殘留量以初步評估篩選之本土菌株降解三硝基甲苯之能力。

Abstract

Trinitrotoluene (TNT) is a secondary explosive widely used both for military and civil purposes all over the world. Residual TNT could be detected as an environmental pollutant both in soil and groundwater due to the release of TNT to the environment from manufacturing or demilitarization facilities and also after munitions firing/detonation or leakage from explosive remnants of war. The presence of TNT in the soil and groundwater has been associated with adverse impacts on biological activities and human communities. Therefore, Control and remediation of TNT-containing products in soil and groundwater are critical issues in environmental protection.

In this study, we evaluated microbial diversity of a soil sample obtained from southern Taiwan which was contaminated with high concentration of TNT. Indigenous microorganisms which can degrade/utilize TNT were also isolated and characterized and their potential for using in bioremediation of TNT also evaluated. The main goals of this study include (1) Establish platform for studying microbial diversity of TNT-contaminated soil by culture independent techniques (i.e. 16S rRNA gene analysis and DGGE); (2) Isolation of TNT-degrading microorganisms from TNT contaminated soil by enrichment culture techniques; (3) Cultivation and identification of the isolated strains and (4) Characterization of TNT-degrading isolates and evaluate TNT degradation efficient by these microorganisms.

[022] 以雷射激發螢光系統建立國內油品特性光譜及風化效應影響之研究

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中文摘要

傳統調查多採分階段作業，從土壤氣體、土壤採樣、簡易井地下水採樣、監測井設置與地下水採樣檢測分析等，係屬於較剛性的定義採樣位置與數量，且由現場採樣至實驗室檢測結果取得，通常需等待數週的時間；因此，需要多階段的現場調查與採樣才能達成調查之目的。近年來新進檢測技術的發展已可提升場址評估的效率，LIF技術的應用對象係針對非屬溶解相態的「自由相態」油品污染物。因油品中含PAH化合物具有螢光之特性，利用LIF技術可提供追蹤場址中持續洩漏源、或鑑別自由相源頭之洩漏路徑和洩漏物種類。

本研究計畫針對臺灣常見油品建置LIF之螢光特性光譜資料庫，並探討地下環境中油品以混合型態存在下其螢光特性圖譜之差異；另進行風化試驗以模擬不同油品因存在於地下環境中隨時間降解，鑑別其螢光特性是否受風化程度之影響。本項研究技術之發展，將可提供另一項新穎快速場址調查技術之選擇，以應用於不同特性案場之現地調查作業，做為污染場址後續整治規劃之參考依據。

Abstract

Traditional investigation procedures are soil gas sampling, soil sampling, groundwater sampling, establishment of monitoring wells, and groundwater monitoring. Sampling positions and number of samples should be arranged in advance, and analysis result often takes several weeks of waiting. Usually, supplemental sampling and analysis are inevitable to accomplish site investigation. For the improvement of site assessment, LIF detection is designed for free-phase petroleum pollutants that contain PAH compounds possessing fluorescence characteristics. LIF can be applied to trace petroleum leakages, discover leakage transport, and identify leakage species based on their fluorescence characteristics.

This study is aimed at establishing LIF fluorescence characteristic spectrum databank of common fuels, and distinguishing LIF fluorescence characteristic spectrums among mixed fuels. Petroleum leakages may be naturally degraded in underground environment, and weather experiments are employed to identify its influence on LIF fluorescence characteristic spectrums. LIF application can provide another alternative of novel real-time site investigation for various specific sites, and present testing information for selecting site remediation schemes.



[023] 臺灣地區油品之穩定性鉛同位素鑑定技術發展與應用

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中文摘要

「環境鑑識 (environmental forensics)」定義為以系統性及科學性評估物理、化學以及歷史信息等層面，目的為要針對污染物來源及排放至環境中之時序，展現具有科學效力之法律認定。油品含鉛 (lead, Pb) 一直被視為人體鉛暴露之主要途徑之一，雖然無鉛汽油之使用後已大幅降低此風險，但依然未能完全排除。疑似人類致癌物的鉛有4個穩定性同位素 (stable lead isotopes)：²⁰⁶Pb、²⁰⁷Pb、²⁰⁸Pb 與 ²⁰⁴Pb，其天然相對豐度比分別佔 1.4%、24.1%、22.1%、52.4%。穩定性鉛同位素可作為環境污染鑑識之利器，尤其是應用於具明顯污染源 (如：鉛礦區或冶煉廠) 之處。

本研究建立油品之穩定性鉛同位素分析技術，分析臺灣地區不同廠牌之市售油品穩定性鉛同位素特徵值，並將之與環境介質鉛同位素特徵加以比對研析。採集樣品包含中油公司和台塑公司所販售之 92 無鉛汽油、95 無鉛汽油、98 無鉛汽油及超級柴油，以多頻道感應耦合電漿質譜儀 (MC-ICP-MS) 進行高精度之油品鉛同位素分析，測定 ²⁰⁸Pb/²⁰⁷Pb、²⁰⁸Pb/²⁰⁶Pb、²⁰⁷Pb/²⁰⁶Pb、²⁰⁶Pb/²⁰⁴Pb 等 4 種比值；油品鉛含量另以磁場式感應耦合電漿質譜儀 (ICP-SF-MS) 進行測定。研究結果發現，臺灣油品之鉛濃度為 10 ng g⁻¹ 至 45 ng g⁻¹ 之間。以油銷比例及廠牌市佔率加權，估算油品代表性鉛同位素特徵，²⁰⁸Pb/²⁰⁷Pb、²⁰⁷Pb/²⁰⁶Pb 分別為 2.4269、0.8710，與臺北地區氣膠之鉛同位素比值特徵 2.4270、0.8720 極為相似，顯示臺北地區氣膠中鉛來源受地域性之油品影響。

Abstract

“Environmental forensics” is defined as the systematic and scientific evaluation of physical, chemical and historical information for the purpose of developing defensible scientific and legal conclusions regarding the source or age of a contaminant release into the environment. Leaded gasoline had been regarded as one of the major source of human lead exposure. Nowadays, the health impact from unleaded gasoline is still unclear. Lead (Pb) has four stable isotopes: ²⁰⁴Pb (1.4 %), ²⁰⁶Pb (24.1 %), ²⁰⁷Pb (22.1 %), and ²⁰⁸Pb (52.4 %). Pb isotopic signatures have been demonstrated to be a robust proxy for distinguishing different sources of local and global lead pollutions.

Techniques of high-precision gasoline Pb isotopic determinations by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) were developed. The characteristics of stable lead isotope ratios, including ²⁰⁸Pb/²⁰⁷Pb, ²⁰⁸Pb/²⁰⁶Pb, ²⁰⁷Pb/²⁰⁶Pb, and ²⁰⁶Pb/²⁰⁴Pb, of different brands and environmental material were measured. Samples included a set of 92 unleaded gasoline, 95 unleaded gasoline, 98 unleaded gasoline, and diesel fuel, from the Chinese Petroleum Corporation and Formosa Plastics Corporation. Pb concentration was determined on an inductively coupled plasma sector field mass spectrometer (ICP-SF-MS). Gasoline Pb contents ranges from 10 ng g⁻¹ to 45 ng g⁻¹. There is a significant difference of Pb isotope ratios in the gas products between the two brands. The estimated Pb isotope ratios from local vehicle exhaust are ²⁰⁸Pb/²⁰⁷Pb = 2.4269 and ²⁰⁷Pb/²⁰⁶Pb = 0.8710. The ratios are respectively close



to the values of 2.4270 and 0.8720 in aerosol samples collected in Taipei area. This agreement suggests that aerosol Pb in Taipei area mainly results from local gasoline combustion.



[024] 多種同位素與地球化學分析技術(MEIGA)判釋地下水污染之

來源：以頭份工業區含氯碳氫化合物污染為例

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中文摘要

利用多種同位素和地球化學方法(Multiple-evidence of isotopic and geochemical approach, MEIGA)，研究頭份工業區地表水和地下水的同位素和地球化學特徵，判斷研究區內的地下水來源、混合、補給和運移狀況，結合污染物濃度的水準，以及研究區的地質、水文、工程等背景資料，研判含氯有機物污染源的可能來源。

自2011年11月計畫執行以來，在頭份工業區採集地表水和地下水100個，對這些樣品進行了野外物理化學參數測量、多種元素分析、氫氧碳穩定同位素分析、含氯有機物濃度的測量。通過這些樣品分析，我們目前得到：1. 研究地區天水的穩定同位素組成的曲線，它與全球天水線有所不同。2. 研究地區地下水的穩定同位素組成，顯示多數井位的水樣與地表水連通，判斷該區淺層地下水(小於100米)的補給是由大氣降水而來。氧同位素偏重($>-6.5\%$)且偏離大氣降水線較遠的樣品，是污染水源的影響。3. 水樣中的Ca和Na是關鍵元素，它們是控制導電度、硬度，與氯度平衡的主要元素。然而，Ca和Na有著不同的來源，在地表水中有強正相關，而在地下水中無相關。Ca濃度反映總硬度的變化，同時也與Mg, Sr, K, Ba等有較好的正相關。地下水和地表水的化學成分不同，顯示高Ca來源是污染源的示蹤。4. 從溶解碳與DIC $\delta^{13}\text{C}$ 的關係，可以斷定含氯有機物在地下水中降解。5. 對本研究計畫來說，多種同位素和地球化學方法(MEIGA)應當包括導電度、氯度、TOC、氯乙烯、 $\delta^{18}\text{O}$, δD , DIC $\delta^{13}\text{C}$, Ca, Na, Mg, Sr, K, Ba。6. 研究初步顯示，含氯有機物污染源有兩處：“大

坑”處和台氣頭份廠南側偏西處，污染物沿地下水流動方向從東北向西南方向運移。

Abstract

In this project, we have collected 100 samples including 85 groundwaters and 15 surface waters from Toufen Industrial Technology Area in different seasons. These 100 samples have been conducted the measurements of H, O and C stable isotopes, elemental concentrations (Na, Ca, Mg, K, Fe, Mn, Al, Ba, Sr, Li, Cu, Zn, Ni, Ga, Ti), chlorinated hydrocarbon including dichloroethane and vinyl chloride, as well as many chemical parameters such as pH, conductivity, DO, hardness, TDS, Chlorinity, ammonia nitrogen and nitrate nitrogen etc. Throughout the study, we have obtained the following conclusions: (1) We built up the local meteoric water line (LMWL) from δD and $\delta^{18}\text{O}$, and found that the groundwater supply of the studying area was mainly from rainfall. (2) Some sites with heavy $\delta^{18}\text{O}$ values and apart from the LMWL reflect contamination of chlorinated hydrocarbon. (3) The concentrations of Ca+Na strongly correlate with conductivity, TDS and Chlorinity. The Ca variations reflect hardness and strongly correlate with Mg, Sr, K, Ba. High Ca content is an indicator of high vinyl chloride. The chemical compositions of surface water are different from that of the groundwater, which is affected by contaminated water. (4) The negative relationship between dissolved carbon and its $\delta^{13}\text{C}$ value implies that chlorinated hydrocarbon occurred degradation in the groundwater. (5) For this study, the major parameters



for Multiple -evidence of isotopic and geochemical approach (MEIGA) are conductivity, Chlorinity, TOC, δD , $\delta^{18}O$, DIC $\delta^{13}C$, concentrations of Na, Ca, Mg, Sr, K, Ba and vinyl chloride. (6) Based on our study, we have found two contaminated sources: one is located at Well site of K00161, so called “The big dent” and the other is on the southwestern edge of Tai Lu Toufen factory around Well sites K00111 and K00177. The distribution of multiple geochemical parameters suggests that the contaminated chlorinated hydrocarbon migrates with groundwater from the northeast toward the southwest.



[025] 污染土壤再利用管理系統之建置

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中文摘要

建立污染土壤再生後之品質控管制度，不僅可落實污染土壤整治之執行，亦能有效管理污染物流向，藉由完整的污染土壤再利用管理系統，能確保污染土壤再利用之環境安全，故本計畫執行第一階段收集國內污染土壤物化特性，比較國內外污染特性，亦收集業界及國外污染再利用方式及管理制度，針對國內外事業廢棄物及污染土壤管理方式行分析探討，並彙整國內可行之污染土壤再生處理技術。

相較於國外如荷蘭、美國、日本及英國等，已明定污染土壤再利用管理規範，依據再利用土壤中成分含量及環境污染規範值作為分類基準，分別判定其可再利用之用途，臺灣地區相關再利用規範中僅將事業產生之污泥納入再利用範圍，尚缺乏完整的管制系統。建構健全的污染再利用管理系統執行組織架構，由政府、專業環境顧問、專業檢驗實驗室、土壤回收業、土木承包商與相關企業合作，擔任監督與技術提升之諮詢團隊，為落實與促進污染土壤再利用技術發展之首要工作，藉由團隊經驗交流與合作分工，建立污染土壤再利用管理辦法，規劃適當用量之成本效益分析評估，並結合交通部、營建署及其他再利用主管機關政策與規範研擬及執行，由第三方驗證機構定期執行審核，由專責之測試人員定期查核確保產品品質，將能有效降低天然資源使用量與促進再生資源永續利用。

Abstract

Quality control system of the regeneration of contaminated soil not only implements the implementation of the remediation of contaminated soil practically, but also controls the management of pollutant flow effectively. Integral contaminated soil management

system would ensure the safety of reuse of contaminated soil environment. Therefore this project is working to collect and compare physical and chemical properties of contaminated soil. The methods of reuse and management system of contaminated soil and regeneration processing technology are also collected.

Compare to foreign countries such as Netherlands, the United States, Japan and the United Kingdom, which have stipulated the standards for management of reused contaminated soil. The standards are according to the ingredients in the soil and environmental pollution specification as a benchmark classification and then the reuse purposes are determined respectively. The main categories of soil pollution in Taiwan include heavy metals, organic pollutants and unknown waste. In recent years, off-site treatment of contaminated soil was adopted to achieve sustainable use of harmless. However, the transport management and contaminated soil re-use patterns is still a lack of clear and complete control system.

The contaminated soil reuse management system of contaminated soil is to establish a quality control system in the contaminated soil regeneration. Government, professional environmental consultants, professional testing laboratory, soil recycling industry, civil engineering contractors in cooperation with the relevant enterprises construct sound pollution reuse organizational structure of the implementation of the management system, as a monitoring and upgrade their technology consulting team. The implementation and promotion of contaminated soil recycling technology development is the primary work. By the team experience exchanges and cooperation between the division of labor, the contaminated soil reuse management could be established. Planning for



appropriate cost-benefit analysis assessment and implementation of policies and regulations of the competent authority combined with the Ministry of Transportation, Construction and Planning Agency, and other re-use of the formulation and implementation of policies and regulations of the competent authority is necessary. Perform the audit on a regular basis by a third-party certification bodies by dedicated testers regular checks to ensure product quality, will be able to reduce the use of natural resources and the promotion of renewable resources and sustainable utilization.



[026] 利用奈米零價鐵還原降解受TNT、RDX及HMX高能火炸藥污染水體及現址整治工程技術評估及研發

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中文摘要

本研究中合成之 nano-Fe(0) 實驗乃於氫氣下經燈罩法烘乾並惰化後 XRD 圖譜文獻資料相符。由 FE-SEM 分析其粒徑為 20~50 nm，BET 量測其比表面積為 $42.6 \text{ m}^2 \text{ g}^{-1}$ 。降解研究中，以 0.1 g 之 nano-Fe(0) 降解 3 種高能火炸藥水溶液，實驗結果顯示在室溫下 ($25 \pm 1^\circ\text{C}$) 於 1 h 內可完全降解 90 ppm 之 TNT、35 ppm 之 RDX 及 5 ppm 之 HMX。在動力學研究中，將 nano-Fe(0) 降解三種不同濃度高能火炸藥實驗結果代入簡化的 Langmuir-Hinshelwood 動力學模式 $\ln(C_0/C_a) = kt$ 計算得到 $R^2 > 0.995$ ，其降解反應為一階反應。在熱力學模式研究中，則是以三種不同的高能火炸藥於 25 及 35°C 的溫度下進行實驗，並以 Arrhenius equation 計算其活化能，得到 TNT、RDX 及 HMX 的活化能分別為 9.74、10.08 及 12.46 kcal mol^{-1} 。在反應途徑研究中，由 LC/MS/MS 及 GC/MS 分析結果顯示高能火炸藥反應反應途徑是第一步為 NO_2 官能基團被還原取代成 NO 官能基團，第二步為 NO 官能基團被還原取代成 NH_2 官能基團後，導致結構不穩定而水解開環。

分析 nano-Fe(0) 與高能火炸藥反應前中後之產物，由 FE-SEM 及 TEM 分析發現有 nano-Fe(0) 顆粒數量減少及片狀產物的增加的趨勢，再以 ESCA 分析顯示其表面具有 Fe、FeO、 Fe_3O_4 、及 Fe_2O_3 等四種不同的氧化物，且其反應趨勢為 $\text{Fe}(0) \rightarrow \text{FeO} \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{Fe}_2\text{O}_3$ 。nano-Fe(0) 與高能火炸藥反應後最終產物，以 X 光吸收近邊緣結構 (XANES) 分析結果顯示，其反曲點最接近 Fe_3O_4 ，且藉由延伸 X 光吸收細微結構 (EXAFS) 分析其中心 Fe 原子配位數接近 4，表示結構可能是八面體中平面四邊形結構；Fe-O 的鍵距約為 $1.94 \pm 0.01 \text{ \AA}$ ，再以 XRPD 分析晶

形結構，其圖譜結果發現相似 Fe_3O_4 及 Fe_2O_3 。

Abstract

Zero-valent iron nanoparticles (ZVINs) with a diameter of 20-50 nm and specific surface area of $42.6 \text{ m}^2 \text{ g}^{-1}$ were measured by FE-SEM and BET. Zero-valent iron nanoparticles had a strong characteristic peak at $2\theta = 44.60$ were investigated by XRPD patterns. In the degrading experiments, 90 ppm TNT, 35 ppm RDX and 5 ppm HMX at room temperature ($25 \pm 1^\circ\text{C}$) were degraded completely with 0.1 g ZVINs in 1 h. The experimental results were placed into a simple Langmuir-Hinshelwood equation ($\ln(C_0/C_a) = kt$) and the R^2 were all upon 0.995. However, the degradation statistics corresponded to the pseudo first order kinetics. The thermodynamics study was carried on three different high-explosives under 25- 35°C and the activation energies of TNT, RDX, and HMX were calculated to 9.74, 10.08, and 12.46 kcal mol^{-1} by Arrhenius equation, respectively.

In the investigation of degradation pathway, the intermediates were identified by LC/MS/MS, and GC/MS. The substitution of high-explosives was reduced by different quantities of nitroso group into hydroxylamine. The ring structure of the explosives became destabilized when nitroso group was further reduced to a hydroxylamine group resulting into ring cleavage by a hydrolysis route eventually. In reductive degradation processing, the ZVINs were reduced and also sheet-type materials were produced. Meanwhile, the surface of Fe, FeO, Fe_3O_4 , and Fe_2O_3 was measured by ESCA and the crystalline structures were similar with Fe_3O_4 and Fe_2O_3 identified by XRPD patterns. In addition, the valence of ZVINs after degradation



was 8/3 as shown by XANES technique. The coordination numbers of Fe atom were close to 4 and the bond distance of Fe-O was about $1.94 \pm 0.01 \text{ \AA}$ as determined by EXAFS spectra.



[027] 利用現地分離之砷氧化菌作為含砷地下水生物復育之 可行性探討

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中文摘要

砷 (Arsenic, As) 的毒性影響了全世界數百萬的民眾。臺灣即使在1960年代已發現地下水砷污染的問題，然而很少文獻針對微生物與地下水砷釋放之間的關係作深入研究。在此研究當中，我們分離出現地之臺灣烏腳病疫區砷污染地下水中之砷氧化菌，命名為As7325。並利用核酸序列比對工具 (BLAST)，比對其 16S rRNA 發現As7325是與*Pseudomonas*同屬之菌種。而As7325最適宜之生長溫度和pH分別為30°C及7。As7325為一種兼性厭氧菌。除此之外，經由聚合酶鏈鎖反應技術，發現As7325具有可將砷氧化之砷氧化酶基因*aoxB*，由此可推論出As7325為具砷氧化或解毒機制之細菌。另外，As7325在好氧條件之下，可於一天以內氧化烏腳病疫區砷污染地下水含30μM (~2200 μg/L) 之三價砷成五價砷。我們更進一步利用As7325作為一種生物吸附劑移除地下水中的五價砷，結果顯示，在兩天內5g/L冷凍乾燥的As7325能分別吸附濃度為500及1000 ppb的五價砷各達37%及60%的效能；而在第六天時，其吸附效率則分別能達到87%及100%。因此，由本研究結果得知，As7325具有對於現地砷污染地下水之生物復育的重要潛能。

Abstract

Arsenic poisoning affects millions of people worldwide. Although groundwater arsenic problems in Taiwan have been recognized since 1960s, few reports have been published about the relationship between microbes and arsenic release into groundwater. In this study, we isolated an indigenous arsenite-oxidizing bacterium As7325 from arsenic contaminated shallow alluvial aquifer in the Blackfoot Disease endemic area. The Basic Local Alignment Search Tool (BLAST) search of the 16S rRNA showed that strain As7325 belongs to the genus of *Pseudomonas*. The optimal temperature for growth was 30°C and the pH was about 7. Bacterial strain As7325 is a facultative anaerobe. In addition, the cytoplasmic arsenite oxidase *aoxB* was amplified by PCR, suggesting that strain As7325 contains arsenic oxidation/detoxification mechanisms. Furthermore, strain As7325 was able to oxidize 30 μM (~ 2200 μg/L) arsenite within 1 day using environmental groundwater under aerobic conditions. We also used As7325 as a biosorbent to remove arsenic in groundwater. The results showed that 5 g/L lyophilized cell pellet of strain As7325 can adsorb 500 and 1000 ppb arsenate with 37% and 60%, respectively within 2 days. The adsorption efficiency for 500 and 1000 ppb arsenate reached 87% and 100%, respectively at 6-day. Therefore, strain As7325 shows its great potential for bioremediation of groundwater arsenic *in situ*.

[028] 利用電動力法現地整治汞污染土壤先期研究

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中文摘要

本先期研究旨在評估利用電動力程序現地整治真實汞污染土壤之可行性。臺灣早期之鹼氯工廠所產生之汞污泥及其不當處理/處置所衍生之土壤/地下水污染問題，至今仍未完全得到妥善解決。本研究利用實驗室規模之電動力整治系統氣密式砂箱反應器探討碘化鉀輔助電動力整治工法之操作參數、評估其對於汞之整治效率、及估算此工法之整治費用，進而評估此整治工法之可行性及應用潛能。砂箱反應器中所佈設之模擬未飽和層及飽和層土壤係採集自國內某實際汞污染場址土壤（汞濃度為3,000-5,000 mg/kg），並使用0.1 M KI水溶液及/或真實地下水當作陰、陽極槽液及土壤間隙水，分別以施加定電壓（1 V/cm）或定電流（20 mA）進行1-14日不同期程之8組電動力整治試驗。碘化鉀輔助電動力試驗結果顯示：(1) 汞與碘化鉀形成水溶性離子態之 HgI_4^{2-} 移向陽極端為主要處理機制，而以形成水溶液相之 Hg_2I_2 且藉由電滲透流移向陰極端為次要處理機制；(2) 經由總汞質量平衡分析，推測碘化鉀輔助電動力整治工法尚有穩定化的處理機制足以使得汞形成殘餘態金屬化合物，而無法由王水消化法予以前處理及分析；(3) 本整治工法對於汞污染土壤在整治過程並不會有汞氣體逸散之虞；及(4) 本整治工法8組試驗之平均總汞去除率為27.96-62.77%，具有技術可行性，且其整治費用（27-77元/每公克汞）與其他工法相當，具經濟可行性。因此，本先期研究採用之碘化鉀輔助電動力整治工法實具有現地整治真實汞污染土壤及底泥之應用潛能，未來如何將此整治工法實場應用仍有待進一步研究與評估。

Abstract

The objective of this preliminary study was to evaluate the feasibility of using the electrokinetic (EK) process for in situ remediation of actual Hg-contaminated soil. Subsurface mercury contamination due to improper treatment and disposal of Hg-containing sludge generated from chlor-alkali factories has been a headache in Taiwan for decades. To resolve this problem, a novel EK process was proposed in this research. In this work an EK remediation system, including a gas-tight sand-box reactor with monitoring wells & caps, DC power supply, and electrodes of various materials, was first installed. Then an actual Hg-contaminated soil (Hg concentration of 3,000 to 5,000 mg/kg) was collected, characterized, and filled in the soil compartment of sand-box reactor simulating the unsaturated zone and saturated zone. In addition, 0.1 M KI lixiviant and/or actual groundwater were used as anolyte, catholyte and soil pore water. At this stage, an electric field was applied to the EK remediation system using a constant voltage mode (i.e., 1 V/cm) or constant current mode (i.e., 20 mA) for eight tests with different remediation time ranging from 1 to 14 days. The following are the research findings obtained using the potassium iodide-assisted electrokinetic (KI-assisted EK) process in this work: (1) migration of HgI_4^{2-} (originated from chemical reaction of Hg and KI in aqueous solution) toward the anode is the primary mechanism for Hg removal, whereas the transport of dissolved Hg_2I_2 toward the cathode end by electroosmotic flow is considered the secondary removal mechanism for Hg; (2) through the mass balance of total Hg in the sand-box reactor, it is postulated that there might exist a mechanism relevant to Hg stabilization rendering the formation of unknown residual metallic Hg compound



that is non-dissolvable by aqua regia digestion and for subsequent chemical analysis; (3) the emission of Hg vapor would not take place in the KI-assisted EK process; (4) the KI-assisted EK process is considered to be technically and economically feasible as compared with other Hg remediation technologies. It is believed that further studies are needed before the KI-assisted EK process could be implemented in the real world.

[029] 利用熱脈衝流速儀量測井孔地下水流之研究

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中文摘要

地層的透水性是地下水質監測、污染物傳輸速率與污染範圍評估、地下水污染整治的重要依據，目前的污染場址調查多採用現地水力試驗來估算含水層的平均水力傳導係數，然而含水層多非均質，地下水流通常集中於少數透水性較高的區段，若能量測地層透水性隨深度變化，咸信將明顯提升地下水污染監測與整治工作效益。因此本研究嘗試在實驗室研發改進近期發展之熱脈衝流速儀，藉由設計水流模擬系統，測試與校正量測結果，在現地偵測井孔中的優勢水流，並估算含水層水力傳導係數隨深度的分布。

本研究分為「實驗室井管水流模擬系統建置」、「熱脈衝流速儀實驗室測試」及「熱脈衝流速儀現地測試」三個項目。井管模擬水流系統係藉由重力及水位差來驅動水流，並控制流速，以此分析流速儀量測流速與井管平均流速之關係，探討量測誤差大小與來源。實驗室測試結果顯示，無論裝設導流器與否，量測流速皆大於井管平均流速，兩者呈線性關係，然而其誤差隨著水流流速降低而增大，其中摩擦損失為最主要誤差來源；此外，在低流速狀態下，熱的自然對流效應顯著影響量測誤差。裝設導流器可有效增加通過流速儀的水流流速，然而當流速超過雷諾數門檻，層流狀態轉換為亂流，誤差將大幅增加。現地試驗證實熱脈衝流速儀可量測井孔中分段水流垂向流速隨深度的變化，藉由實驗室測試得到之校正公式，可解析地層垂直方向上分層透水性分布，測試結果發現在高透水性之礫石層仍存在透水性差異。本研究整合分析流速儀在實驗室和現地測試結果，經由校正分析，將可偵測出井孔中優勢地下水流；若配合現地水力試驗的分析結果，可定量分析水力傳導係數及地下水流在垂直方向上的變化，預期可提升我國地下

水污染場址水文地質調查與整治的品質與效益。

Abstract

Hydraulic conductivity of an aquifer plays a very important role in monitoring, site characterization and remediation of groundwater pollution. Hydraulic testing can be used to obtain an equivalent hydraulic conductivity of the whole aquifer. However, an aquifer is often heterogeneous and groundwater flow often concentrates in few highly permeable sections. It is desirable to delineate the preferential flow or the distribution of hydraulic conductivity. Recently developed heat-pulse flowmeter provides a promising technique for continuously characterizing the vertical distribution of hydraulic conductivity in a borehole. The objective of this project is to develop and improve heat-pulse flowmeter measurement techniques for investigating the variation of hydraulic conductivity with depth in an aquifer. A carefully designed water circulation system was established in the laboratory to evaluate the accuracy and precision of flow velocity measured by heat-pulse flowmeter in various conditions. We found a linear relationship between the measured velocity and the averaged velocity for the laminar flow. The measurement error increases as the averaged flow velocity decreases due to free convection. A calibration formula was developed based on the laboratory test data. Field test results at two sites indicated that heat-pulse flowmeter measurement can detect the locations of preferential groundwater flow in gravel aquifers. By integrating the results of hydraulic test, the vertical distribution of hydraulic conductivity in a borehole can be delineated. The result of this research is expected to provide an emerging technology which can significantly



improve the quality and efficiency of site investigation and remediation of groundwater pollution.

[030] 重金屬污染底泥整合性生物復育技術之研究

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中文摘要

目前國內針對受污染水體底泥處理技術之研究極少，未來極需要此方面之技術，以處理浚淤後之大量底泥。但是，污染底泥量增加、處理費用升高，加上更嚴格管制要求，以致於未來底泥之處理與處置技術將必須脫離傳統方法並且重新調整，始能因應實際之需要。本研究之主要目標為利用硫生物循環中之硫氧化作用，發展出一套應用於處理重金屬污染底泥之環境生物技術，以達污染預防與資源循環再利用之目的。研究結果發現，在氣提式生物溶出程序之操作過程中，由於底泥固體物含量越高時，底泥中重金屬之溶出效率會隨之降低；而當硫顆粒添加量增加時，底泥中重金屬之溶出效率則呈現增高之趨勢。在底泥固體物含量為不高於8%時，在經16天之操作時間後，銅、鋅及鎳之最終溶出效率分別可達50%、60%與50%以上，鉻之溶出效率則低於30%。底泥中重金屬之最終溶出效率中以鋅及鎳較高，其次為銅，鉻之溶出效率則為最低。由實驗設計之結果可知，本研究之零價鐵處理金屬廢液實驗中，零價鐵添加量及初始濃度設定之最佳操作值分別為2.5~4.5g/L及20~50mg/L間，金屬廢液中銅、鋅、鎳及鉻分別有100%、80%、40%及98%以上之去除效率。

Abstract

Most of sediment dredged from contaminated rivers or lakes often contain substantial amount of heavy metals and thus can not be disposed of on the land and in the water body without any treatment. To date, there are relative few researches for detoxification and decontamination processes of heavy metals in aquatic sediments in Taiwan. In future, it is important to develop the techniques for treatment of the large quantity of dredged sediments in the remediation of contaminated rivers or lakes.

The purpose of this study is to develop an integrated bioremediation technology for sediments contaminated by heavy metals. A bioleaching process employing sulfur-oxidizing bacteria for remediation of metal-contaminated sediments was first studied. Meanwhile, the zero-valent iron (ZVI) was also applied for treatment of the metal-containing solution produced from the bioleaching process. The results showed that the rates of pH reduction and metal solubilization obtained from the bioleaching experiments increased with decreasing sediment solids content and increasing sulfur concentration added. After 16 days of reaction time, the final efficiencies of Cu, Zn and Ni leached from sediments in this bioleaching process were all greater than 50% when the sediment solids content did not exceed 8%. The results of response surface methodology indicated that the maximum efficiency of metal removal was achieved at 2.5-4.5 g/l of ZVI dosage with 20-50 mg/l of initial metal concentration, where up to 100%, 80%, 40% and 98% of Cu, Zn, Ni and Cr were removed from the waste solution.



[031] 柴油污染土壤之快速整治-石灰水合反應結合現地過硫酸鹽化學氧化處理技術評估

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中文摘要

本計畫嘗試評估利用石灰(CaO)之水合反應以提供熱能及鹼性條件，活化過硫酸鹽之氧化程序對於處理柴油污染之可行性進行評估。結果顯示CaO的添加所造成之熱能及鹼性環境(例如:SPS/CaO/污染土= 0.1 M/3 g/10 g，達到約43%之柴油移除率，其中由CaO添加造成柴油濃度稀釋移除率約30%)，相較於單獨過硫酸鹽經由添加NaOH(0.05 M)之反應程序，造成約15%之柴油降解情形，得知CaO水合反應結合過硫酸鹽氧化程序尚未能達到快速柴油降解移除之成效。進一步經由其他活化過硫酸鹽氧化處理柴油污染土壤之試驗結果顯示，SPS/H₂O₂及SPS/Fe²⁺為較佳之反應程序，可快速(2天內)大幅降低柴油污染濃度(移除約60%)，但因受限於土壤存在下，造成固液相間之質量傳輸受到限制，不利氧化劑於水相中與柴油反應，因而無法使~12000 mg/kg之柴油總石油碳氫化合物(TPH)污染土壤降至法規標準以下(<1000 mg/kg)。然而，藉由改變CaO之添加順序，於氧化反應後添加適量之CaO，可避免土壤過度酸化且稀釋柴油污染濃度。

Abstract

The goal of this project was to investigate lime (CaO) hydration reaction by providing heat energy and alkaline conditions to induce persulfate activation for the treatment of diesel-contaminated soils. The results showed that addition of CaO coupled with SPS cannot trigger the effective diesel destruction (e.g., 43%) through the generated heat (~80°C) and alkaline pH (> 12). Compared with experimental conditions with SPS only, ~15% and ~43% of diesel removals were achieved in the NaOH/SPS and CaO/SPS systems, respectively. Therefore, it can be seen that the CaO/SPS process may not be an effective way for degrading diesel contaminated soils. Among all possible persulfate activation processes, SPS/H₂O₂ and SPS/Fe²⁺ appeared as the preferable options for treating diesel. Overall, activated persulfate processes can rapidly reduce diesel concentration (about 60% removal) within 2 days. Diesel removal from soils is often limited by its low water solubility and highly sorption onto soils. Hence, it is difficult to be treated and meet the soil remediation regulation (TPH < 1000 mg/kg) with an initial TPH of 12000 mg/kg. Subsequently, experiments focus on the application of CaO mixing with post-treatment soils, which process would alter soil pH and then reducing diesel concentration by dilution.

[032] 推估土壤傳輸參數現地試驗方法之改進

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土壤宿命傳輸模式的可靠性取決於模式是否適當考慮相關傳輸過程，除了選擇合適的模式，模式所需輸入參數也非常重要，延散係數為數學模式重要輸入參數，而現地入滲追蹤劑試驗為同時決定土壤縱向與側向延散係數之有效方法。本計畫進行現地入滲追蹤劑試驗以驗證其可行性，現地試驗操作的經驗將有助於改進儀器設計、操作過程與相關細節，此外本研究亦改進相關試驗數學模式與分析方法。

Abstract

The reliability of soil transport model calculations depends on the accuracy with which relevant processes for contaminant transport are implemented in fate transport model. Besides an appropriate model choice, the parameterization of the model also plays an important role. Dispersion coefficients are important parameters for soil fate and transport model. Field infiltration test with a tracer is a proposed technology for simultaneous determination of longitudinal and transverse dispersion coefficients in soil. In this study the in-situ infiltration test with a tracer was performed to verify its applicability. Experience obtained in this test was used to refine the apparatus designs, operational procedures and relevant details for the test. Moreover, the mathematical model and interpreting method for the infiltration tracer test were investigated and improved.



[033] 添加複合性副資材促進總石油碳氫化合物污染土之生物降解技術

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中文摘要

本研究期以三階段模式進行土壤之生物復育程序，第一階段利用固定土壤翻堆與灑水，配合本研究團隊之(Systematic Environmental Molecular Bioremediation Technology, SEMBT)進行監測式自然衰減復育，目標土方為污染場址中不同來源的柴重油污染風化土壤，進行土樣污染物濃度、微生物多樣以及分子生物檢測；此階段同步進行複合性副資材之實驗規模批次試驗，找出最佳複合性副資材之配比與微生物多樣性。待土壤分佈達到穩定，即進行第二階段之複合性副資材添加，並模擬現場生物復育工法之推進(BAS0→BAS6)。

本研究預期土壤污染濃度將會遭遇生物降解之高原期(plateau)，此時將定義為第三階段施工啟動，將篩選較為優勢之降解石油碳氫化合物外來菌，包含多種油分解真菌(Yeast: *Candida guilliermondii*、*Candida parapsilosis*；Mold: *Aspergillus fumigatus*、*Aspergillus versicolor*、*Fusarium oxysporum*)，以促進生物降解效果。

Abstract

In order to carry out a systematic environmental molecular biotechnological (SEMBT) remediation, three research groups are established: (1) bioagent development with molecular biotechnology, (2) molecular biomonitoring technology, and (3) biotechnology integration for environmental engineering. This research group will work out the systematic technologies of the bioagent augmentation, the biomonitoring, and the biofilm stimulation to perform an useful bioremediation process (SEMBT) in a petroleum contaminated site. Within one year, a set of ex-situ bioremediation demonstration will be established with a pilot scale plant of 2.4 kg bipiles for treating the total petroleum hydrocarbon (TPH). The project goal is to demonstrate a systematic environmental molecular biotechnology (SEMBT) for biodegradation technology that is feasible for remediating a large area of hydrocarbon contaminated site.

[034] 超臨界二氧化碳復育戴奧辛污染土壤中之最佳化與放大技術研究

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中文摘要

本計畫目的即在於承續上一年度環保署土污基管會之補助計畫，再經由一系列實驗，持續針對實場可能面臨之關鍵問題深入探討。本計畫已建立良好之 Sovova 動力模式，模擬結果顯示本試驗土壤中推估大約 18% 的污染物與土壤之間有非常強的吸附作用。預測 50 萬、10 萬、5 萬 ng I-TEQ/kg 不同起始濃度污染土壤處理至法規標準(1000 ng I-TEQ/kg)的程度，其所需要的時間分別為 398、243、以及 184 min。本研究進一步由原本 1 升萃取槽放大至 6 升萃取槽，實驗結果顯示本研究發展模式仍可準確預測放大後萃取效率。放大後萃取效率降低可歸於 superficial velocity 之降低所導致之質傳係數降低。就萃取後土壤再利用能力而言，土壤之 pH、導電度及 CEC、有效鉀、有效鈣差異不大。但隨著土壤中戴奧辛之去除，有效磷、有效鎂也會隨之減少，造成土壤肥力降低，其中又尤以有效磷之削減率最高，可達 50~90% 之削減。

以焚化飛灰進行超臨界二氧化碳萃取其戴奧辛之實驗顯示，超臨界二氧化碳萃取可達約 80~84% 之去除效率，該技術確為處理飛灰中戴奧辛可行之技術。相較飛灰與土壤之萃取條件，可能因為土壤中有機質偏多，需藉由輔溶劑增加超臨界二氧化碳與土壤中戴奧辛之親和力。然飛灰中因高溫燃燒後較無有機質，導致輔溶劑之添加無法增進萃取戴奧辛之效率。

Abstract

The results of this study, compared with other technologies, can be practically applied in commercial scale economically. Furthermore, this study will be a novel technology and in the lead of the world. The result shows that about 18% of the total contaminant is hard to remove from soil, but others could be removed within 1 hr. We have also constructed Sovova kinetic model to predict the profile of the dioxins in the soil and the results reveal it may take 398, 243, and 184 min to treat 500, 100, and 50 thousands ng I-TEQ/kg soil to 1000 ng I-TEQ/kg, respectively.

We have scaled up the extraction reactor to 6 L, and successfully predicted the extraction efficiency. The lower extraction efficiency can be attributed to mass transfer resistance. Effect-P and effect-Mg will lose during dioxins extraction, which cause the losing of soil fertility. Moreover, we have confirmed the feasibility of the supercritical CO₂ extraction on dioxins contaminated fly ash. More co-solvent will enhance soil extraction efficiency but not in fly ash extraction. It may contribute to the organic matter in the soil and reduce the affinity of CO₂ to dioxins.



[035] 開發氧化還原可調控式透水性反應牆應用於地下水整治之研究

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中文摘要

本研究利用Fe/Al、Cu/Fe/Al及電子媒介體改質之複合鋁金屬(EM-Cu/Fe/Al)探討其氧化還原能力的可調控性，以做為透水性反應牆地下水整治技術之填充材料，達到可同時處理氧化性與還原性污染物之目的。研究選用四氯化碳做為還原降解之標的物，甲酸與染料作為氧化性污染物之標的物。實驗分批次與連續流管柱實驗進行，透過產物分析與EPR分析，確認上述材料個別之氧化能力與還原能力。就Fe/Al複合金屬而言，此材料為本計畫所發現最佳之材料，同時具有還原四氯化碳之能力與氧化甲酸與染料之能力；Cu/Fe/Al複合金屬具有極佳之還原四氯化碳能力；EM-Cu/Fe/Al複合金屬經超過5種以上的合成技術的嘗試，發現以維生素B12為電子媒介體者(B12-Cu/Fe/Al)，無法有效固定於材料表面，故效果不佳，然而，以TPPS為電子媒介體者(TPPS-Cu/Fe/Al)，則可以固定於材料表面，達到較佳之還原四氯化碳之效率。就還原能力而言，Fe/Al在pH=4的情況下最好，在4小時之內，去除率達76%；而Cu/Fe/Al在pH=10的情況下最好，在0.5 hr之內，去除率可達80%，去除速率 $k=1.5181$ ，相較於Fe/Al去除速率為其16倍，顯示Cu/Fe/Al在pH=10之去除效率相當快，因此兩種複合材料比較起來以Cu/Fe/Al為最佳。TPPS-Cu/Fe/Al又略優於Cu/Fe/Al，然系統性之研究仍持續進行中。就氧化能力而言，Fe/Al降解甲酸之效應與Fenton反應做比較，由TOC量測可知，Fe/Al(50g/L)去除效率可以高達93.6%，與Fenton反應相近，顯示Fe/Al複合金屬具有氧化的能力。利用EPR測定自由基，得知鐵鋁複合金屬在無添加任何藥劑時，是以甲基自由基與氫氧自由基為主要生成氧化劑物種。管柱實驗的結果顯示，Fe/Al對染料COD的長期

去除效率為43%(約1個月)，Cu/Fe/Al對四氯化碳之去除則可達96%以上，其操作時間超過7天，說明不但有很好的去除效率，也能保有長期的穩定性。

Abstract

This research is aimed at investigating the reductive and oxidative ability for Fe/Al, Cu/Fe/Al and electron mediator modified Cu/Fe/Al (EM-Cu/Fe/Al) that may serve as reactive reagents for permeable reactive barriers. The goal is to develop a new reactive reagent that can treat both oxidative and reductive contaminants simultaneously. Carbon tetrachloride was selected as the probe for reductive reactions while formic acid and dyes were used as the probe for oxidative reactions. Both batch and continuous column experiments were conducted. The product analysis and EPR analysis were carried out to investigate the reaction behaviors. For bimetallic Fe/Al, it was found to be the best material capable of simultaneous oxidizing formic acid and reducing carbon tetrachloride. Cu/Fe/Al trimetal possessed good reductive ability for carbon tetrachloride reduction. However, attempts to synthesize EM-Cu/Fe/Al were unsuccessful even though more than 5 trials were tested by using vitamin B12 as the electron mediator. Nevertheless, the use of TPPS as the electron mediator finally opened an avenue for successful synthesis of EM-Cu/Fe/Al. Cu/Fe/Al exhibited a good reductive ability, which is 16 times faster than Fe/Al. TPPS-Cu/Fe/Al is slightly better than Cu/Fe/Al, yet, further study is certainly needed. Fe/Al showed an excellent oxidative ability for the oxidation of formic acid and dye. EPR analysis indicated that methyl radicals were involved in the reaction system while hydroxyl radicals were also discovered. The column test suggested that the



longevity of both Fe/Al and Cu/Fe/Al were fairly well for potentially using in the field.

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[036] 電動力技術現地模組設立及測試之研究

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中文摘要

電動力技術係一現地(in-situ)整治技術，可藉由調整電動力操作參數及處理時間，使得地面活動及原有建物不受影響，且因具備外在驅動力及污染物擴散方向可控制之特點，特別適合應用於大多技術不適合處理之黏土層污染。

本研究實驗所使用之電極棒為空心不銹鋼棒(SUS 316)，操作流質之選用為0.05 M之乳酸(Lactic acid)，整治時間為20天，電位坡降為0.2~0.35 V/cm，電極接觸面積為28,260~37,680 cm²，以探討電極接觸面積及電位坡降之影響。

Test 1實驗(Ke)為23.9 cm²/V-s，其Zn、Cu、Pb、Cr及Ni金屬之去除效率分別為41.8 %、4.2 %、32.8 %、31.6 %及35.6 %，相較於Test 2實驗中電滲透流係數(Ke)為23.9 cm²/V-s，其Zn、Cu、Pb、Cr及Ni金屬之去除效率分別為82.4 %、81.9 %、51.6 %、88.1 %及44.9 %，主要是藉由電滲透流及離子遷移方式移除目標污染物，在陰極槽液中發現有少量污染物濃度，並推測其主要污染物皆因電鍍而在陰極電極上被發現；而在目標污染物Cu之序列萃取中發現，在電位坡降為0.35 V/cm時可有效改變其與土壤之鍵結型態，並藉由電滲透流及電子遷移方式移除；而與Test 2相同的是實驗結束後發現陰極電極有金屬污染物鍍於外層，使電極重量增加，而比較對污染物之去除效率即可發現，當降低電位坡降為0.2 V/cm時，將無法有效達到去除之成效，且在Cu之鍵結型態分析中，降低電位坡降以致無法有效改變其鍵結型態達到移除之成效，但在殘留濃度分佈中仍可發現有緩慢往陰極移動之現象。

比較Test 1及Test 2之殘留濃度分佈可發現，本研究之三維模場污染物移動方式有別於一般實驗室小型模組模擬實場整治情形，除了一般由陽極往陰極

移動之縱向去除外，明顯可看出本研究之試驗仍有一垂直向上移動之現象發生，推測應是模擬實場整治，在模場上方無額外施加壓力，以致在電動力整治過程中產生之氣體往上逸散時，同時將污染物往上推動所造成；另在土壤溫度量測部分，平均室溫為32.1 °C，期末土體平均溫度為36.6 °C，土體溫度量測結果平均高於室溫4~5 °C，是一可接受之範圍。

而在成本考量方面，電極費用佔總成本之85 %、操作流質費用佔14 %，電極是主要影響成本多寡之主因(本研究電極以每次試驗接更新計算)，而主要電極之消耗原因為槽液腐蝕及電流造成之氧化腐蝕情形，因此若能有效控制pH值及藉由試驗找出一最佳操作參數，即可使電極重複使用，將可有效降低整治成本。

Abstract

Electrokinetic (EK) process is classified as an in-situ remediation technology. It will be conducted in site without disturbing present resident activities with proper operation and reasonable treatment time. EK process is much fit in contaminated site with clay soil because pollutant will be forced to migrate by the electrical driving force. The advantages EK process includes: (1) production of uniform electroosmotic flow in heterogenous medium, especially in low permeable soil; (2) easy control of flow direction; (3) high removal and degradation efficiency; (4) high economy. To establish pilot-scale operation parameters will be beneficial to promote in application

The aim of this project is to design a 3-D pilot-scale EK modul and conduct a series of soil remediation experiments to investigate the effect of electrode area and potential gradient on remediation

efficiency.

Considering reducing cost, hollow stainless electrodes (SUS 316) are selected for test. A series of the experiments were conducted with 0.05 M lactic acid as processing fluid under potential gradient of 0.2~0.35 V/cm and electrode area of 28260 ~ 37680 cm² for 20 days. Results showed that the treatment efficiency of Zn, Cu, Pb, Cr and Ni were 41.8%, 4.2 %, 32.8 %, 31.6% and 35.6 %, respectively, conducted with potential gradient of 0.2 V/cm and electrode area of 28260 cm². As decreased to potential gradient to 0.35 V/cm, the treatment efficiency of Zn, Cu, Pb, Cr and Ni were also decreased to 82.4 %, 81.9 %, 51.6 %, 88.1 % and 44.9 %, respectively. It was found that most of removed pollutants are coating on the cathode electrode surface and part of remained in the cathode reservoir. It was concluded that the treatment mechanism was dominated by EO flow. Based on sequential extraction results, it was found that the binding strength of Cu with soil was shifted from to strong to weak after EK process and, however, it became insignificant at lower potential gradient.

Other than pollutants migrated from anode to cathode, it was also found that the pollutants were migrated from bottom layer to top layer. Such vertical migration of pollutants will be beneficial to remediate contamination in depth. The soil temperature after EK treatment was 4~5 °C higher than room temperature which was at reasonable range for in-situ remediation. For cost analysis, 85%, 14%, and less than 1% was accounted for the cost of electrodes, processing fluid and electricity, respectively. To prevent corrosion of electrode would tremendously lower the remediation cost.



[037] 應用化學指紋與生物指標鑑定受柴油污染土壤與地下水污染源之研究

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中文摘要

研究選用柴油進行試驗，油品來源包含兩大煉油公司煉製柴油和加油站市售油品。煉製柴油包含裂解(Hydrocarbon Cracking)方法煉製柴油和蒸餾(Distillation)方法煉製柴油，共15個煉製油品。市售柴油計有13個加油站油品，涵蓋在臺灣北、中、南和東部，包含7個中油公司的超級柴油(5個直營店、2個加盟店)，6個台塑公司(4個直營店、2個加盟店)的環保柴油。

煉製柴油分析結果顯示，裂解煉製的柴油所含的石油碳氫化合物在重組過程會喪失原本煉製原油的指紋圖譜和生物指標特性，使得煉製柴油皆具有相似的指紋圖譜與生物指標特性。蒸餾煉製柴油會隨著煉製原油的來源不一樣而改變煉製產品的指紋圖譜和特徵因子比值(Diagnostic Ratio)。煉製輕質柴油之特徵因子比值可由煉製油品的原油特徵因子比值結合煉製原油的比例進行預測。蒸餾煉製會保留其原油指紋圖譜與生物指標特性；也就是蒸餾方法會由於煉製原油不同，導致其柴油指紋圖譜與特徵因子比值產生差異。

市售加油站柴油結果顯示，中油公司超級柴油之總碳氫化合物生物指標化合物呈現兩個族群分佈，北臺灣加油站具有相似的 $n\text{-C}_{17}/\text{Pr}$ (1.66)、 $n\text{-C}_{18}/\text{Ph}$ (1.89)、 Pr/Ph 比值(1.41)；南臺灣加油站的比值與前述不一樣，其值為 $n\text{-C}_{17}/\text{Pr}$ (3.86)、 $n\text{-C}_{18}/\text{Ph}$ (2.44)、 Pr/Ph (0.80)。造成中油公司不同區域油品的總碳氫化合物生物指標特徵因子差異推測是供應煉油廠區不同導致。相對於中油公司不同區域油品的生物指標特徵因子差異現象，台塑石油公司六座加油站市售環保柴油具有類似的 $n\text{-C}_{17}/\text{Pr}$ 、 $n\text{-C}_{18}/\text{Ph}$ 、 Pr/Ph 比值。

藉由不同的總碳氫化合物(Total

Ion Chromatography)特徵因子比值或雙環類萜半萜烷(Bicyclic Siquiterpanes)特徵因子比值進行不同區域加油站柴油來源鑑識，發現 $n\text{-C}_{17}/\text{Pr}$ 和 $n\text{-C}_{18}/\text{Ph}$ 、 Pr/Ph 和 $n\text{-C}_{18}/\text{Ph}$ 、 Pr/Ph 和BS3/BS5這三組雙比值可將中油公司和台塑公司在不同地區的柴油來源區分成三個群組。模擬柴油風化和模擬受柴油污染土壤風化實驗顯示，在模擬時間尺度(5個月)內 Pr/Ph 和BS3/BS5生物指標特徵因子比值不易隨風化時間而改變，可應用在本研究所測試之中油和台塑公司所屬不同加油站柴油污染源的鑑識。然而，對於現地污染場址而言，現地風化條件對上述 Pr/Ph 和BS3/BS5特徵因子比值的鑑識度影響，有待後續研究討論。

Abstract

Establishment the Chemical Fingerprint and Biomarker database of refining diesel and petrol station of Chinese Petroleum Corporation (CPC) and Formosa Petroleum (FPCC) will enhance identification reliability accuracy with great benefits for the future oil leakage pollution source. In this study the diesel is used for testing and the oil source from two oil companies' refining diesel and their gas stations. Refining diesel made from Hydrocarbon Cracking method and Distillation method, a total of 15 Refined Diesel products.

There have 13 gas stations oil products were studied, covering Taiwan's northern, central, south and east. The analysis results of refining diesel fuel show that cracking refining of diesel petroleum hydrocarbons contained in the restructuring process lost the original fingerprint of the refining of crude oil and the characteristics of biological indicators, and resulting the similar fingerprint and biological indicators of characteristics in

the refining diesel. Distillation refining diesel will change the fingerprint of the refined products and Diagnostic Ratio as follow different source of refining crude oil.

Characteristic factors of the refining of light diesel oil ratio factor ratio can be predict from the refined petroleum crude oil characteristics and the proportion of the refining of crude oil. Distillation refining will retain its crude oil fingerprint and biomarker of characteristics; it indicates that distillation refining of crude oil, resulting in its diesel fingerprint characteristic factor ratios differ. Commercial diesel gas stations show that CPC's Super diesel hydrocarbons biological indicators have two groups of distribution, the gas stations of the CPC XZ, HC, ML, TX and so on gas stations in northern Taiwan region have similar $n\text{-C}_{17}/\text{Pr}$ (1.66), $n\text{-C}_{18}/\text{Ph}$ (1.89), Pr/Ph ratio (1.41); the gas stations of CPC BA, CF, CJ with the foregoing its value $n\text{-C}_{17}/\text{Pr}$ to (3.86), $n\text{-C}_{18}/\text{Ph}$ (2.44), Pr/Ph (0.80).

Total hydrocarbons and biological indicators characteristic factor differences caused by the different regions of the CPC oil supply refinery area, suggesting that the new Taipei, Hsinchu, Miaoli City and Taitung County gas station oil is supplied by the Taoyuan Refinery; and Chiayi City, Tainan City and Kaohsiung City is supplied by Kaohsiung Dalin or Linyuan Refinery. It has similar results of characteristics of biological indicators for the different areas in the stations of FPCC XZ, ML, CY, DT, DY, RL and so on six gas stations' diesel has similar $n\text{-C}_{17}/\text{Pr}$, and $n\text{-C}_{18}/\text{Ph}$ Pr/Ph .

According to the results, the ratio of diesel oil characteristics of Pr/Ph factor cannot be reasonable forensic or identify between the CPC and FPCC diesel, it must be rely on other information in order to correctly determine the oil source. Employ the characteristics of the Total Ion Chromatography factor ratio or Bicyclic Siquiterpanes factor ratio for different regions of the gas station diesel sources forensic, the contrast found $n\text{-C}_{17}/\text{Pr}$ and $n\text{-C}_{18}/\text{Ph}$, Pr/Ph and $n\text{-C}_{18}/\text{Ph}$, Pr/Ph and

BS3/BS5 those three group pairs ratio could divided CPC and FPCC's diesels into three groups.

Considerations of Isoprenoids and Bicyclic Siquiterpanes are less susceptible to the effects of biological indicators of biodegradation, Pr/Ph and BS3/BS5 characteristic factor ratios for the weathered diesel leak proposal forensics as a source of oil pollution. Diesel weathering experiments showed that in the current simulation time scale factor ratio of about five months of the characteristics of these biomarkers is not easy with the wind of change over time, a preliminary description of these parameters on the biological indicators characteristic factor ratios can be applied at different gas stations diesel sources forensic.



[038] 應用地球物理法運用於污染場址與底泥電性反應之研究

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中文摘要

現場調查已發現DNAPL仍具有穿透低滲透性地層(如黏土層或矽黏土)之風險；或低滲透性地層經長年累月所累積的大量溶質回擴至高滲透性地層，造成調查與整治之高度不確定性。而地下水污染團很可能透過滲漏機制而影響至上/下含水層，因此在調查或採樣設計上很可能需跳脫傳統僅採集至第一含水層底部或僅整治第一含水層的思維；同時界定高、低滲透性地層分佈與評估周遭污染情形，才能確實達到污染防堵與監控。傳統鑽孔調查技術所獲致之成果均屬於“點”的污染情形，DNAPL移動分佈之高度不確定性，或地下水溶解相在高、低滲透性地層之實際分佈，在實場運用上不太可能鉅細靡遺地調查，也造成其污染界定上的困難。近年來，非破壞性地球物理探勘技術已逐漸運用在污染場址之地下環境調查，搭配較少量的鑽孔資料可獲得“面與空間”資訊。目前地球物理最廣泛運用之污染調查技術為地面式之地電阻掃瞄法及透地雷達法。但地電阻掃瞄法施測會因建物阻擋或其他地面干擾物致施測距離不足，造成測深受限；透地雷達法之測深則更是受限，特別是存在厚層鋪面或鋼筋網的施測環境。而新穎之地球物理井測技術已開始應用於地下環境特徵調查，其在探測深度上更具優勢，並增加監測井或鑽孔之利用效益。井測法可透過跨孔調查建立高、低滲透性地層、優勢流徑及可能污染分佈等，並掃瞄評估不同時間序列之污染分佈、整治溶劑分佈及整治成效等。本計畫除了運用新穎地球物理井測技術，調查含氣有機溶劑在地下環境之複雜分佈，另利用感應電磁波與水上地電阻影像剖面法進行河川底泥沈積物調查，評估水上地球物理方法之適用性與初步成果。

Abstract

Many site investigations have found that DNAPL is able to penetrate the low permeable layer such as clay or silt-calcy layer in subsurface environment. The cumulated DNAPL within the low permeable Layer will gradually diffuse to the high permeable layer to affect the accuracy of investigation and remedial design. As to the deeper zone affected by the penetration of DNAPL, the conventional sampling design investigating only the first unconfined aquifer is no longer suitable for DNAPL investigation. Precisely define the boundary and the distribution of high and low permeable layer is the key to conduct a successful DNAPL investigation. "Point" information derived from the conventional bore-hole sampling is difficult to be used for locating the DNAPL pollution due to the uncertainty of DNAPL migration and the soluble-phase distribution of the DNAPL partitioned into ground water between the low and high permeable layer. Recently, non-invasive technologies such as geophysical technology have been introduced to provide the "plane and space" information of pollution in subsurface by integrating few bore-hole data. The most common used geophysical technologies are ground-penetrating radar method (GPR) and electrical resistivity tomography (ERT). Both methods have their limitations on the pollution investigation when there are interferences exist such as building structure or heavy pavement. A new geophysical technology, geophysical well logging has been developed to overcome above limitations. The information of multi-wells logging could be used to interpret the permeability of subsurface, the dominate flow path and the hot-spot for evaluating the distribution of pollution



and the efficiency of remediation in different time sequences. This study would first discuss how DNAPL and its soluble-phase components invade into the low permeable layer based on the field observation. Then, the importance of geophysical technology is introduced with comparing to the limitations of bore-hole investigation. Last, the case studies on using geophysical technologies including geophysical well logging are introduced to snapshot the complex profile of DNAPL distribution for improving future application.



[039] 二仁溪污染底泥整治模場試驗計畫(第二年)

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中文摘要

河川底泥在生態系中扮演重要角色，一旦遭受持久性有機污染物(persistent organic pollutants)或是重金屬之污染，污染物可循食物鏈進入人體及動植物體內，危害人體健康與生態系。以我國目前嚴重污染之二仁溪為例，二仁溪中下游污染物來源以燃燒廢五金、電鍍、酸洗、廢油為大宗，廢氣中粒狀物質沉降及廢金屬回收酸洗廢水直接排入河川中。最引人注意之污染物包括重金屬、多環芳香烴類、多氯聯苯等。二仁溪底泥中多環芳香烴類、多氯聯苯、重金屬銅、鉻與砷之濃度大多超過現行標準，實應進行整治復育，但經濟有效之復育技術付之闕如。本研究之目的在於開發低成本高效率之奈米材料進行生物、物理化學整合之復育，去除底泥中之重金屬、萘與Aroclor 1254。以目前進行70天之初期試驗結果而言，添加奈米乳化似乎對萘之降解有抑制效果，但對於多氯聯苯Aroclor 1254降解有良好助益，而重金屬部分因仍有排放源以致絕對去除率較低，但結合奈米乳化液與奈米氧化鐵之整合式復育法仍屬較佳之整治方案。

Abstract

River sediments play an imperative role in ecosystems, such as self-cleaning capacity, planktonic habitat, and benthic organismal habitat. Once contaminated, the contaminant may enter human body or other organisms through food chains resulting adverse effects on human health and ecosystems. Taking Er-Ren River as an example, the major pollution source is the upstream pig farm discharges. This area was famous for its metal recovery using open burning, electroplating, acid

wash, and waste oil discharge. Particulate matters deposition and acidic drainage from metal recovery caused severe contamination of this river. Among all contaminants, dioxins, polychlorinated biphenyls (PCBs), polynuclear aromatic hydrocarbons (PAHs), and heavy metals received most attentions. Most of them are either near to or above the regulated standards. However, a cost-effective remediation technology does not exist for this intermixed contamination. Here, we study a new remediation technology by integrating biological and physicochemical processes with novel nanomaterials. The first year project already showed positive result and a highly cost-effective solution seems to be feasible. Due to the evident Aroclor 1254 pattern shown on the gas chromatograph of PCBs in sediment from Er-Ren River, this year we focused on the remediation of sediment contaminated by naphthalene, Aroclor 1254, Arsenic, chromium, and copper. By conducting four different experiments in parallel, i.e. natural recovery (NR), biostimulation (BS), physicochemical adsorption (PA), and integrated remediation (IR), the results The integrated remediation will combine the nanoemulsion and magnetite nanoparticle approaches. This project has shown that within 150 days, all tested combinations can achieve higher than 97% removal of naphthalene. The best removal of Aroclor 1254 at day 189 is as high as 76.4%. For heavy metals, the highest removal percentages of As, Cr, and Cu are 14.53%, 5.17%, and 8.38%. Lead can also be removed up to 13.06%. Overall, biostimulation is better than any other test technologies in this project..

[040] 以近實場規模之現地電動力技術整治鉛污染農地之研究

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本研究以近實場規模之電動力法 (Circulation-Enhanced Electrokinetics, CEEK) 整治南投市某處鉛污染土壤，本計畫進行63天污染土壤整治及颱風淹水，主要發現及結論如下：1. 污染土壤中鉛去除率可達約64%，平均土壤鉛濃度可從7,246 mg/Kg降至約2,612 mg/Kg，2. 本系統CEEK對於1.0平方公尺的鉛污染土壤每去除1%所需的操作電費約為6.55元，3. 本電動力系統CEEK在近實場規模操作下，土壤的pH值及導電度維持在中性及穩定的狀態，4. 本電動力整治方法處理後的土壤肥力略降，需要添加適當肥料方能回復肥力，5. 由於鉛與EDTA的錯化物須經較高的電壓及較長時間電鍍，才能將土壤中的鉛電鍍於陰極板的表面。若電鍍效果不佳，應增設廢水處理設備。

Abstract

This work applied the Circulation-Enhanced Electrokinetics (CEEK) in near-real scale to clean the lead contaminated soils in Nantou City. After 63-day treatment, several conclusions and suggestions can be drawn: 1. The lead removal efficiency was about 64%; the average lead concentration was decreased from 7,246 mg/Kg to 2,612 mg/Kg. 2. The operational cost of electricity for removing 1% lead was 6.55 NT dollars in the area of 1.0 m². 3. The pH and electrical conductivity of soils could maintain neutral and stable situation. 4. The fertilizerbility of the treated soils was slightly less than that of the untreated soils. This means the addition of fertilizer is necessary. 5. If the removed lead was electroplated on the cathode with low electricity efficiency, it is necessary to integrate a wastewater treatment plant with EK system.



[041] 以綠能作物復育重金屬污染土壤之可行性研究

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中文摘要

國內有相當多的污染農地地處偏遠，原本土地利用率就不高，且其污染對週遭環境之影響風險亦不大，投入經費積極整治，其必要性實屬不高。隨著石化原料的日漸耗竭，新能源的開發是全世界共同努力的目標，綠能作物所提供之生質能源是一種綠色、環境友善的再生能源，目前世界已有相當多的國家積極投入開發。臺灣可耕地資源有限，綠能作物的推動發展未來勢必會對糧食作物的生產帶來衝擊。因此針對重金屬污染農地若能結合綠能作物推動植生復育技術不僅可提供更多能源產量，也可以經濟有效率的方法達到污染土壤整治的目標，是值得研究的方向。

本研究選擇七種富含生質能源之作物包括：玉米、甘藷、甘蔗、大豆、花生、油菜及向日葵進行重金屬鉛污染土壤現地植生復育試驗，探討七種能源作物對重金屬鉛污染土壤之適應能力以及各部位對重金屬鉛之累積吸收能力，評估適合鉛污染土壤復育之能源作物。

Abstract

In recent years, remediating farm land contaminated by heavy metals has been actively undergoing in Taiwan. It is not practical and cost-effective for remediating the contaminated farm land in remote regions because most remotely located farm land has low application rate, and its contamination poses low adverse impacts on the surrounding environment. Additionally, the increasing depleted fossil fuel energy source makes it imperative to develop substituted green energy from biomass; green crop may provide environmental friendly and sustainable energy. However, the use of green crop as an substituted energy source will squeeze the food source to adversely impact the availability of food sources, and this is an obvious problem for Taiwan that has limited farmland. If heavy metal contaminated farm land can be remediated by growing green crop to be used as green energy, the objectives of remediating the contaminated soil and providing green energy can be simultaneously achieved. In this research, seven crops that are rich in bio-energy including corn, potato, sugar cane, soy bean, peanuts, rape, and sunflower were selected for conducting the phytoremediation tests on-site in a lead-contaminated. The objective of this research was to study the adoptability of these seven plants growing in lead-contaminated soil, and the adsorption of lead by the various parts of the plants, and to assess the feasibility for use these energy crops to remediate the Pb-contaminated soil.

[042] 屏東縣九如鄉九清段1340地號生物整治現地試驗

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中文摘要

本計畫場址位於屏東縣九如鄉大坵村，地號為九清段1340地號，總面積27,550平方公尺，公告整治場址範圍為1,800平方公尺，規劃六個試驗區，除對照區CK外，BP1、BP2及BP3同時進行生物與植生復育之試驗區，而PR1與PR2進行植生復育之試驗區，生物復育試驗施作包括(1)採用紅蚯蚓(*Eisenia fetida*)分解污染土壤及(2)應用石化分解菌(*Pseudomonas sp. NKNU01*)。植生復育以間距2.5 m於場址內栽種木本植物白楊樹(*Poplars; Populus bonatii Levl.*)，六個試驗區內栽種草本植物太陽麻(*Sun Hemp; Crotalaria juncea L.*)。

三個生物復育樣區之TPH濃度在歷經五個月後均呈現降低趨勢，於監測結果發現BP1及BP2樣區，不同深度TPH有明顯移除效果，TPH減量可達41%至大於99%，BP2樣區中移除效果明顯，不同深度土壤多數已低於土壤污染管制標準。在BP3高污染樣區，TPH減量為29%至96%，整體而言TPH下降百分比比較BP1及BP2樣區為低，可能原因為高污染區不利於生物生長，甚至由於油污染氣味造成蚯蚓竄逃，導致生物量減少影響移除效果。

白楊樹由栽植日起至第四次調查日(十月中旬)共約四個月，其成長率達55~213%，但在高污染區BP-3白楊樹成長率較低。太陽麻無論是株高或乾濕重都以CK區最高，在五個處理區中，重金屬濃度最高之PR1及PR2，其測值呈現較低之現象，與白楊樹之趨勢相同，可見污染物對兩種植物之發育皆有抑制之可能。本場址之主要污染物為Zn、Cu、Cr、Ni，而植株之分析結果顯示，白楊樹與太陽麻之重金屬含量依序為Zn > Cu > Ni > Cr。雖然各區白楊樹與太陽麻之發育略

有差異，但兩種植物皆可於試驗區中生存與生長，顯示兩者對於本場址之污染物皆有相當之耐受性與適應性，有益於後續之污染物改善效果試驗。

Abstract

The contaminated site proposed in this study is located in Pingtung County with the area of 1,800 m². The site was originally used for waste oil recycling practice. The major contaminants in soil were chromium, zinc and total petroleum hydrocarbon (TPH). Groundwater did not illustrate high level of contaminants. The objectives of this study are to: (1)conduct in-situ bioremediation and phytoremediation of metal and TPH-contaminated soil, (2)to establish the pattern of site remediation administrated by local government agency, and (3)to prevent potential groundwater contamination.

Six experimental cells (6×6m) were set up. Three treatment cells were designed for bio-phytoremediation (i.e., BP1, BP2, and BP3) in the highly contaminated area. Two cells were designed for phytoremediation practice (PR1 and PR2). One control cell was used to compare the results with different remediation treatment. About 5.4 kg of earthworm was employed in BP1, BP2, and BP3 for three month interval. Petroleum degrading bacteria (*Pseudomonas sp. NKNU01*) was applied in the same cells for enhanced bioremediation. Monitoring of TPH and metals was conducted by scheduled soil sampling to evaluate removal efficiency of TPH and metals.

The apparent decrease of TPH was observed in the BP1 and BP2 zones. The removal of TPH ranged from 41% to 99% after five month of bioremediation practice.



Most of the samples in BP2 revealed that TPH is below regulation criteria. However, removal efficiency of TPH in BP3 is less effective due to highly contaminated nature in that zone. The removal efficiency varied from 29 to 96% at different depth in BP3. The highly TPH-contaminated area may affect the population of earthworm or biomass.

Poplars(*Populus bonatii* Levl.) and Sun Hemp(*Crotalaria juncea* L.) were utilized in the phytoremediation practice. Three hundred fifty poplars were planted in the site including six experimental cells. Metals in plant tissue and soil were analyzed to evaluate removal efficiency of contaminants. After four months, the growth rate of poplar ranged from 55 to 213%. It was observed that growth rate was lower in the highly contaminated area such as BP3. Certain inhibition was noticed. The heavy metal analysis of tissues revealed that $Zn > Cu > Ni > Cr$. Both species are suitable for phytoremediation. The results generated in this study will serve as a case study of green remediation and environmental decision purpose. This article provides guidance for manuscript writing for conference.

[043] 監測井多深度地下水採樣方法發展

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中文摘要

含水層由不同水力傳導係數的地質材料組成，污染團濃度自然呈現三維空間變化，其分布可自數個監測井內污染物垂直濃度變化得知。傳統地下水採樣方法提供垂直平均濃度無法反映深度變化，且低估污染程度易造成實務與法律責任爭議。本計畫的目的是發展監測井雙封塞多深度地下水採樣技術，包括建立洗井方法和採樣步驟，評估取樣段長度(l_s)對採樣結果影響，與直接貫入多深度地下水採樣結果進行比較驗證。使用微洗井採樣方法調查雙封塞系統井內移動對井水造成之影響，同時對微洗井多深度採樣方法進行評估。雙封塞技術屬封井採樣，微洗井技術屬通井採樣，直接貫入法無須使用監測井直接自含水層採樣，屬井外採樣。依本計畫研擬的雙封塞採樣步驟在一LNAPL污染場址四口監測井使用不同測試段長度($l_s = 1.0, 0.5, 0.4, 0.2$ m)進行36次不同深度的雙封塞採樣、25次微洗井採樣、及10次直接貫入法地下水採樣，共71次不同深度地下水採樣。發現(1)本計畫建立的雙封塞洗井及採樣步驟並未造成井內不同深度明顯的水質混合情況，適合用於監測井多深度採樣。(2)雙封塞測試段長度越短，採樣濃度垂直平均效應越小，越能反映井內污染物濃度垂直變化，建議使用 $l_s = 0.2$ m以獲得高解析度的污染物濃度分布。(3)雙封塞與直接貫入法所得的污染物濃度垂直分布相當一致，證實雙封塞方法可用於監測井多深度採樣，反映污染濃度垂直變化。二者所獲得的污染物濃度不必然相同。在高滲透性地層雙封塞採樣方法所得污染濃度大於直接貫入結果，在低滲透性地層則小於直接貫入結果。(4)微洗井多深度地下水採樣仍屬通井採樣，無法避免垂直平均效應，未能有效反映井內污染物濃度垂直變化，不建議使用。

Abstract

Due to the fact that aquifers are composed of geological materials of different hydraulic conductivities, the contaminant plums naturally exhibits three-dimensional concentration distributions, of which the investigation can be made use of vertical concentration distributions in a number of monitoring wells. The conventional groundwater sampling techniques yield vertically-averaged concentration that fails to provide the necessary vertical variation as well as underestimates the contamination, thereby creating practical concerns and legal liability. This project aims to develop the double-packer multilevel groundwater sampling technique used in monitoring wells. The work includes the establishment of the purge method and the sampling procedure, the evaluation of the influence of the sampling length (l_s) on the sampling results, and to verify the sampling results by comparison to the results obtained by the direct-push sampling method. Influence of the movement of the double-packer system on well water is investigated using the micropurge sampling method, of which the applicability to multilevel sampling is evaluated. The double-packer technique deals with open-well sampling, while the micropurge technique is for closed-well sampling. The direct-push technique, however, directly takes groundwater samples from the aquifer without using monitoring wells; an out-well method. In a LNAPL site, 36 times double-packer ($l_s = 1.0, 0.7, 0.4$ and 0.2 m), 25 times micropurge, and 10 times direct-push methods were implemented to gather water samples in four wells. It is discovered that (1) The purging and sampling procedures developed for the double-packer system does not create significant mixing of well water at different depths, and are suitable for multilevel sampling in monitoring wells. (2) The shorter the l_s the less the vertical



mixing and the more representation of the vertical variation, and it is recommended that $IS=0.2$ m be used for a better resolution of the concentration profile. (3) The vertical concentration profiles of the double-packer 61 and the direct-push methods are in similarity, indicating the double-packer method to be available for multilevel sampling. The concentration values obtained by these two methods are unnecessarily to be the same. Rather, the double-packer method yields higher concentration values under higher permeable conditions, while lower concentration under lower permeable conditions. (5)As an open-well sampling technique, the micropurge multilevel sampling method cannot avoid the vertical mixing, and the results obtained do not reflect the vertical variation. It is not recommended to use the micropurge technique to handle the multilevel sampling.

[044] 土壤及地下水污染責任保險之規劃

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中文摘要

本專案旨在規劃一個土污專責的污染保險，將污染所致的整治費用納入承保範圍，以便在污染情事發生時，能確保環境污染復育工作之推動。本研究參照國外之污染保險保單規劃土污專責之污染保險，並擇臺灣上市櫃之油電燃氣業、化學工業、鋼鐵工業、半導體業及光電業為研究對象進行調查，實證結果發現各項風險認知並未呈現產業別差異。其次，突發及漸進式污染事故均會影響潛在污染人的風險知覺，然潛在污染人對突發污染事故造成損害的擔憂程度甚於漸進式污染。此外，受訪者較擔心員工疏失及廢棄物污染造成的損失，但普遍輕忽自身產業的污染特質及運輸過程可能產生的污染損害。

Abstract

This project aims to enlarge the coverage to any necessary removal expenses and remediation costs induced by pollution will be covered by insurance to ensure the implementation of restoration for environmental pollution. Referring to the soil pollution insurance covered by foreign insurance policies, this study chooses Taiwan's listed companies in gas and electricity industry, chemical industry, steel industry, semiconductor industry and optoelectronics industry, to perform an investigation by questionnaire. The empirical results indicate that each risk perception does not demonstrate a difference among industries. Next, both sudden and accidental pollution and gradual pollution will affect the risk perception of potential polluters. However, potential polluters worry about the damage caused by sudden and accidental pollution events more than the damage caused by gradual pollution events. In addition, interviewees worry more about the damage caused by employee carelessness and waste pollution, but generally neglect the pollution characteristics of its own industry and the possible polluted damage occurred during the transportation procedure.



[045] 以多種同位素與地球化學分析技術(MEIGA)研究中壠工業區

地下水污染

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中文摘要

本計畫用多種同位素和地球化學方法(MEIGA)研究中壠工業區的地下水污染，同時還延續了對頭份工業區的污染調查，進一步查明臺氣頭份廠內“大坑”西南角處的污染來源。在今年的計劃執行中，我們在旱季、雨季和颱風過後分別採集地表水和地下水共81個樣品，對樣品進行野外物理化學參數測量，並進行 δD 、 $\delta^{18}O$ 、 $\delta^{13}C_{DIC}$ 、常量/微量元素和三氯乙烯的分析。

從這些樣品的地球化學數據來看，中壠工業區的地下水來源主要是地表水，常量及微量元素的濃度都很低，遠遠低於頭份工業區的地下水元素濃度，與當地地表水元素濃度相當。說明地表水在下滲過程中，沒有礦物的溶解，工業污水的滲透不明顯，污染狀況並不嚴重：1. 沒有重金屬污染；2. 氨氮的濃度還不如河水中的高，某些區段河水由於生活排放廢水導致氨氮濃度偏高(11ppm)；3. 三氯乙烯的超標只在個別井位發現。

2013年5月15號，我們在大雨中對臺氣頭份廠內“大坑”西南角處進行採樣，發現該處的水樣的pH、電導度和氫氧同位素都偏高，這些水是工業排放水。雖然三氯乙烯的分析結果未顯示出有機物的污染情況，但從pH、導電度、Na含量的指標來看，這些排放水是不合格的。中石化廠的排水和“大坑”污染處理的水可能是該處的污染來源。研究顯示，MEIGA法是一個有效的追蹤地下水污染的方法。

三氯乙烯分析結果顯示，大部分的樣品超標情況並不嚴重。但是，氫氧同位素的結果表明地表水下滲到地下水有一個時間過程，在下滲過程中，有機碳的分解和降解使得水中DIC碳同位素值偏輕。假如含氯有機物在地下水中

分解，就不易用單次抽樣測量監測。另外，工業局CL02監測井旱季時三氯乙烯超標，而在雨季採樣時濃度更是大大提升。這一現象是否表明有污染廢水在大雨時進行排放？根據目前結果，建議針對這個監測井附近進行一個完整周邊調查和密集監測，以了解地下水的污染來源。

Abstract

In this project, we use Multiple-Evidence of Isotopic and Geochemical Approach (MEIGA) to assess groundwater in Chungli Industrial Area as well as the pollution source in “Dakeng” site of Toufen Industrial Technology Area. we have collected a total of 81 samples including surface water and groundwater samples in both wet and dry seasons and measured samples for pH, DO, conductivity, NH₃-N, δD , $\delta^{18}O$, $\delta^{13}C_{DIC}$ and elemental contents of Na, K, Li, Ca, Mg, Sr, Ba, Fe, Mn, Al, Zn, Cu, Ni, Ga, and concentrations of Trichloroethene.

Based on the results, we have found that the groundwater in Chungli Industrial Technology Area comes from surface water (meteoric water), with very few influence from industrial waste water. All measured elemental concentrations are very low and no heavy metal contamination in the groundwater. The elemental concentrations in the groundwater of Chungli Industrial Technology Area are much less than these of groundwater in Toufen Industrial Technology Area. High concentrations (~11 ppm) of NH₃-N appeared in the river water near some residential area, but generally low in the groundwater samples. Only one sample shows slightly high Trichloroethene concentration. In summary, groundwater in the Chungli Industrial Technology Area



has minor contamination problem. Influences of industrial waste water discharge, mineral dissolution and seawater intrusion are not significant. However, trichloroethylene was exceeded in the water samples from well CL02 in both dry and wet seasons. We suggest that a full investigation for this monitoring well should be carried out, to understand the pollution source of groundwater.

On May 15, 2013, we have sampled the surface water at the southwest corner of “Dakeng” in Toufen Industrial Technology Area during a heavy rain. We found that surface water contained high pH and conductivity. Analyses of δD , $\delta^{18}O$ and $\delta^{13}C_{DIC}$ also indicate that the waters at this site do not come from meteoric source, but industrial waste water discharge which may be from a manufactory of CPDC and/or the treatment water of “Dakeng” pollution.

This study demonstrated that the MEIGA method that we proposed is a good approach to investigate groundwater contamination.



[046] 同時處理土壤中戴奧辛、五氯酚及汞之整合性技術開發

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中文摘要

本研究透過自主研發之連續熱裂解模組暨空氣污染物防制設備，處理同時受高濃度戴奧辛、五氯酚及汞污染之土壤。連續熱裂解模組研究結果指出當處理量為2及2.5 kg/hr(停留時間分別為33及26分鐘)時，經600°C處理後之土壤中戴奧辛及總汞濃度始可確保符合法規標準(戴奧辛<1000 ng-TEQ/kg；汞<20 mg/kg)。含高濃度污染物之氣流透過袋式集塵器、驟冷塔及流動床式活性炭吸附系統去除排氣中之各種污染物，有效控制粒狀物及其它氣相污染物排放。此外，自主開發之驟冷塔有效捕集氣流中之汞及其化合物，效率介於80~90%，冷凝液中更可發現元素汞及部份硫化汞聚集。

Abstract

For better remediation of contaminated soil in An-shun site, a continuous pyrolysis system is applied in this study. Operating temperatures of 500~750°C are applied in continuous pyrolysis system set in this study are tested for remediation of contaminated soil. However, higher than 600°C operating temperature in continuous pyrolysis system is still needed to effectively remove PCDD/Fs and mercury from contaminated soil as input rate of contaminated soil are controlled at 2 kg/hr and 2.5 kg/hr (retention times are 33 and 26 min, respectively.). In addition, high pollutant concentrations are found in flue gas of pyrolysis system outlet and baghouse, quench tower and multi-layer AC-adsorption bed as air pollution control devices are applied for effective emission control. Regarding particulate matter, lower than 3 mg/Nm³ of particulate matter concentration is obtained by baghouse. Quench tower operating at 0~3°C can effectively removal mercury from flue gas. The removal efficiencies of mercury achieved with quench tower are higher than 80%. As for the multi-layer AC-adsorption bed, 3 layers are designed in this study. Finally, the emissions of contaminants including PCDD/Fs, PCP and mercury are stably controlled to meet the emission limits of three contaminants (PCDD/Fs: 0.1 ng-TEQ/Nm³; PCP: 500 μg/Nm³; Hg: 50 μg/Nm³).

[047] 有機堆肥分解受十溴二苯醚污染底泥及其生物多樣性

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中文摘要

十溴聯苯醚 (deca-bromodiphenyl ether, DBDE) 為工業上常用之溴系火焰阻燃劑來源, DBDE 因結構穩定、水中溶解度低, 故在環境中傾向蓄積底泥, 且很難經由生物直接降解, 故易造成生態毒性, 威脅生物體健康, 是近年來受到重視的新興污染物。堆肥由於有高含量的可溶性有機碳, 具有很好的還原能力, 可當作良好電子提供者, 將不同種類的環境污染物還原, 可作為新興污染物之整治技術。本計畫是利用血清瓶建立厭氧微系統 (anaerobic microcosms), 利用臺灣地區不同有機堆肥進行厭氧生物處理受 DBDE (20mg/sediment-kg) 污染底泥, 並於實驗過程中觀察隨時間變化所生成之脫溴產物之同源異構物, 同時以分子生物技術分析微生物族群結構及其生物多樣性。實驗結果發現實驗所選用三種有機堆肥樣本 (分別標示為 C2, C6, B2) 均具有高有機質成分, 對 DBDE 具強烈吸持特性。添加有機堆肥進行厭氧生物降解 DBDE 結果可發現, 其擬一階降解速率 (k) 為 $C6 (0.0458 \text{ day}^{-1}) > C2 (0.0352 \text{ day}^{-1}) > B2 (0.0286 \text{ day}^{-1})$, 其過程共測得 23 種 PBDEs 同源異構物。微生物族群結構方面, 細菌域 (Domain Bacteria) 三種堆肥之微生物族群結構有很大不同。分子選殖結果除鑑定厭氧堆肥中常見之微生物之外, 並發現許多具降解 DBDE 能力之微生物族群, 如 *Pseudomonas* spp. 及 *Dehalococcoides* spp.。功能性基因實驗結果證實三種堆肥菌群中均具脫鹵基因, 因此在實驗中發生生物性還原脫溴反應。本研究結果說明有機堆肥的確可有效移除受污染 DBDE 底泥, 就工程實務而言, 建議將河川底泥進行疏濬後, 利用離場整治技術與底泥混合後進行厭氧生物處理, 同時達到底泥資源化之目標。

Abstract

Decabromodiphenyl ether (DBDE) is a flame retardant commonly used in the industry, and it has become an emerging contaminant in recent years. Due to its structural stability and low solubility in water, DBDE has a tendency of accumulating in the sediment, increasing the difficulty of being biodegraded. Thus, DBDE can lead to ecotoxicity and threaten the health of various organisms. The study applies the high biological activity, richness in carbons and electron donors of three different organic composts, to evaluate the initial DBDE concentration (20 mg/sediment-kg) on the biological debromination efficiency in contaminated sediment. The anaerobic microcosms will be conducted in the serum bottles with DBDE-polluted sediments and compost sample. The DBDE concentration is measured by GC/PDECD during anaerobic biodegradation. PBDE congeners are measured by GC-MS. The change of bacterial community is measured by PCR-DGGE-Cloning during DBDE biodegradation. Functional genes of bacterial species such as reductive debromination genes and dioxygenases are measured by selective specific primers.

As a result, three sampling composts (C2, C6 and B2) with high organic compounds demonstrate the significant ability of DBDE adsorption. The pseudo rate constant (k) of the first order equation for anaerobic biodegradation of DBDE is compared as $C6 (0.0458 \text{ day}^{-1}) > C2 (0.0352 \text{ day}^{-1}) > B2 (0.0286 \text{ day}^{-1})$. Metabolites including 23 PBDE congeners are measured by GC-MS. The DGGE profiles are different during anaerobic DBDE biodegradation. *Pseudomonas* spp. (ID= 97-99%) and *Dehalococcoides* spp. (ID=97%) related to DBDE biodegradation are identified in



anaerobic microcosms. Amplification of PCR-products for biological debromination are positive. An off-site approach is mentioned to combine DBDE-contaminated sediment with commercial organic compost is suggested in the practical engineering technology of remediation.

[048] 利用表面改質奈米零價鐵還原降解高能火炸藥 TNT、RDX 及 HMX

污染場址整治工程技術評估及測試

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中文摘要

本研究中合成之 nano-Fe(0) 實驗乃於氫氣下經燈罩法烘乾並惰化後 XRD 圖譜文獻資料相符。由 FE-SEM 分析其粒徑為 50-80 nm, BET 量測其比表面積為 $42.557 \text{ m}^2 \text{ g}^{-1}$ 。降解研究中, 以 0.1 g 之 nano-Fe(0) 降解 3 種高能火炸藥水溶液, 實驗結果顯示在室溫下 ($25 \pm 1^\circ\text{C}$) 於 1 h 內可完全降解 90 ppm 之 TNT、35 ppm 之 RDX 及 5 ppm 之 HMX。在動力學研究中, 將 nano-Fe(0) 降解三種不同濃度高能火炸藥實驗結果代入簡化的 Langmuir-Hinshelwood 動力學模式 $\ln(C_0/C_a) = kt$ 計算得到 R Square > 0.995 , 其降解反應為一階反應。在熱力學模式研究中, 則是以三種不同的高能火炸藥於 25 及 35°C 的溫度下進行實驗, 並以 Arrhenius equation 計算其活化能, 得到 TNT、RDX 及 HMX 的活化能分別為 9.743、10.079 及 $12.460 \text{ kcal mol}^{-1}$ 。在反應途徑研究中, 由 LC/MS/MS 及 GC/MS 分析結果顯示高能火炸藥反應反應途徑是第一步為 NO_2 官能基團被還原取代成 NO 官能基團, 第二步為 NO 官能基團被還原取代成 NH_2 官能基團後, 導致結構不穩定而水解開環。分析 nano-Fe(0) 與高能火炸藥反應前中後之產物, 由 FE-SEM 及 TEM 分析發現有 nano-Fe(0) 顆粒數量減少及片狀產物的增加的趨勢, 再以 ESCA 分析顯示其表面具有 Fe、FeO、 Fe_3O_4 、及 Fe_2O_3 等四種不同的氧化物, 且其反應趨勢為 $\text{Fe}(0) \rightarrow \text{FeO} \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{Fe}_2\text{O}_3$ 。nano-Fe(0) 與高能火炸藥反應後最終產物, 以 X 光吸收近邊緣結構 (XANES) 分析結果顯示, 其反曲點最接近 Fe_3O_4 , 且藉由延伸 X 光吸收細微結構 (EXAFS) 分析其中心 Fe 原子配位數接近 4, 表示結構可能是八面體中平面四邊形結構; Fe-O

的鍵距約為 $1.94 \pm 0.01 \text{ \AA}$, 再以 XRPD 分析晶形結構, 其圖譜結果發現相似 Fe_3O_4 及 Fe_2O_3 。

Abstract

Zero-valent iron nanoparticles (ZVINS) with a diameter of 50-80 nm and specific surface area of $42.56 \text{ m}^2/\text{g}$ were measured by FE-SEM and BET. Zero-valent iron nanoparticles had a strong characteristic peak at $2\theta = 44.6^\circ$ were investigated using XRD patterns. In the degrading experiments, 90 ppm TNT, 35 ppm RDX, and 5 ppm HMX at room temperature ($25 \pm 1^\circ\text{C}$) were degraded completely with 0.1 g ZVINS in 1 h. The experimental results were simulated using a simple Langmuir-Hinshelwood equation ($\ln(C_0/C_a) = kt$) and the R-squares were all upon 0.995. However, the degradation statistics corresponded to the pseudo first order kinetics. The thermodynamics study was carried on three different high-explosives under $25\text{-}35^\circ\text{C}$ and the activation energies of TNT, RDX, and HMX were calculated to 9.743, 10.079, and 12.460 kcal/mol by Arrhenius equation, respectively.

In the investigation of degradation pathways, the intermediates were identified by LC/MS/MS and GC/MS. The substitution of high-explosives was reduced by different quantities of nitroso group into hydroxylamine. The ring structures of the explosives were destabilized when nitroso group was further reduced to a hydroxylamine group resulting into ring cleavage by a hydrolysis route eventually. In reductive degradation processing, the ZVINS were reduced and the sheet-type materials were also found. Meanwhile, the surface containing Fe, FeO, Fe_3O_4 , and Fe_2O_3 were measured by ESCA and the



crystalline structures were similar with Fe_3O_4 and Fe_2O_3 identified by XRD patterns. In addition, the valence of ZVINS after degradation was 8/3 as shown by XANES technique. The coordination numbers of Fe atom were close to 4 and the bond distance of Fe-O was about $1.94 \pm 0.01 \text{ \AA}$ as determined by EXAFS spectra.

[049] 後勁溪底泥中之鄰苯二甲酸酯類殘留量調查及其利用新穎組合

技術現地整治之可行性研究

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中文摘要

本研究計畫旨在調查後勁溪底泥中8種鄰苯二甲酸酯類及其11種代謝物之殘留濃度，並嘗試利用奈米級 Fe_3O_4 活化過硫酸鹽氧化程序結合電動力法整治鄰苯二甲酸酯類污染底泥，期盼未來建立一本土化可行的現地整治技術，以作為後續實場應用。在後勁溪底泥中鄰苯二甲酸酯類及其代謝物之殘留濃度調查工作方面，已針對選定之7個採樣點位進行5梯次採集底泥樣品，綜合調查結果發現，於底泥中可檢出4種鄰苯二甲酸酯類及6種鄰苯二甲酸代謝物類之化合物，於楠梓溪支流的三奶壇橋處檢出 mg/kg 濃度（ ppm 濃度）等級之DEHP殘留量，其平均濃度（ $2,886 \mu\text{g/kg}$ ）及最大濃度（ $5,477 \mu\text{g/kg}$ ）分別為「底泥品質指標之分類管理及用途限制辦法」之管制下限值1.46倍及3.69倍。於鄰苯二甲酸酯類污染底泥整治工作方面，底泥反應器所充填之底泥係採集自後勁溪德惠橋處，並分別於陰、陽極槽添加過硫酸鈉或奈米級四氧化三鐵，施加定電壓（ 1 V/cm 或 2 V/cm ）進行為期14日及28日期程之6組電動力試驗。試驗結果顯示：(1)於陽極槽液中注入過硫酸鈉及奈米級四氧化三鐵，並由電滲透流移向陰極端，同時藉由反應產生之 $\text{SO}_4^{\cdot-}$ 、 OH^{\cdot} 及 H_2SO_5 等強氧化劑，可將底泥中鄰苯二甲酸酯類予以降解；(2)經由電動力第1-2組試驗（空白試驗）組別發現，單純提高施加之電場強度（ $1 \text{ V/cm} \rightarrow 2 \text{ V/cm}$ ），亦有助於鄰苯二甲酸酯類之去除，其詳細的去除機制有待進一步確認；及(3)本整治工法對於鄰苯二甲酸酯類污染底泥整治過程，其鄰苯二甲酸酯類化合物在電極槽液之殘留濃度極低（ ppt 濃度等級）。據此可知，本新穎整治

工法確實可有效整治底泥中之鄰苯二甲酸酯類。另外，本整治工法之操作成本粗估約在 $12,000$ 元/噸以下，具經濟可行性。由於本整治工法之最大優勢為可直接進行現地應用（節省龐大的開挖工程費用）及針對黏土質地亦能有整治功效，因此，對於大規模現地整治鄰苯二甲酸酯類污染底泥應具有很強的應用潛勢。

Abstract

The objectives of this study are two-fold: (1) to investigate the residual concentrations of eight phthalate esters (PAEs) and their 11 metabolites in sediment samples collected from the Houjing River; and (2) to develop and establish a localized, feasible in situ remediation technology coupling nano- $\text{Fe}_3\text{O}_4/\text{S}_2\text{O}_8^{2-}$ process and electrokinetic process for the removal of PAEs in sediments of the Houjing River. To meet the first objective, five batches of sediment sampling were conducted at seven sampling sites along the Houjing River and four PAEs and six phthalate metabolites were detected. The order of parts per million (ppm) of residual di(2-ethylhexyl) phthalate (DEHP) was detected at Sannaitan Bridge. The relevant average concentration ($2,886 \mu\text{g/kg}$) and highest concentration ($5,477 \mu\text{g/kg}$) are 1.46 and 3.69 times greater than the “Regulations for Systematic Management of Quality Indices of Sediments and Their Use Restrictions” promulgated by Taiwan EPA. To meet the second objective, six tests with a remediation time of 14 days or 28 days were carried out using the electrokinetic-assisted nano- $\text{Fe}_3\text{O}_4/\text{S}_2\text{O}_8^{2-}$ process under an electric field of 1 V/cm or 2 V/cm . Test results for the removal of PAEs in the sediment samples collected at



Dehuei Bridge of the Houjing River are given as follows: (1) injection of sodium persulfate and nanoscale magnetite into the anode reservoir would yield $\text{SO}_4^{\cdot-}$, OH^{\cdot} , and H_2SO_5 that would be transported by the electroosmotic flow from the anode end toward the cathode to degrade PAEs and their metabolites if any; (2) an increase of the electric potential gradient from 1 V/cm to 2 V/cm would enhance the removal of PAEs in control tests with no addition of sodium persulfate and nanoscale magnetite to the remediation system; and (3) the residual PAEs would not be detected in the electrode reservoirs implying an effective degradation of PAEs in the sediment compartment of this novel remediation system. Accordingly, the novel remediation process employed in this study could be considered as a viable remediation technology for the removal of PAEs from sediments. An operating cost analysis has also assured the economic competitiveness of the present remediation technology. In summary, due to its inherent nature, the electrokinetic-related processes could be applied for full-scale in situ remediation of any porous media including clayey sediments. The coupling of nano- $\text{Fe}_3\text{O}_4/\text{S}_2\text{O}_8^{2-}$ process and electrokinetic process would be a very competitive process for the treatment of PAEs-contaminated sediment in terms of remediation time and cost.

[050] 重金屬污染底泥整合性生物復育技術之效能提昇及系統改善

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中文摘要

由於目前國內針對受污染底泥處理技術之研究較少，未來極需要此方面之技術，以處理疏浚後之大量底泥。但是，污染底泥量增加、處理費用升高，加上更嚴格之法規管制要求，以致於未來底泥之處理與處置技術將必須脫離傳統方法並且重新調整，始能因應實際之需要。本研究之主目的為建立連續式重金屬污染底泥生物處理程序，並且同時以零價鐵流體化床處理生物溶出技術中所產生之金屬廢液，並探討主要操作參數對於零價鐵流體化床技術處理金屬廢液之影響，最後希望能生物溶出技術及零價鐵流體化床技術結合發展為一套經濟且實用之整合性生物復育技術用以有效處理重金屬污染底泥，並且以真正達到污染防治之目的。經研究發現，水力停留時間增加時，反應槽中之處理負荷降低，硫氧化菌之活性較佳，使得底泥中有較高之重金屬溶出效率。當水力停留時間設定為 10 天時，在連續式生物溶出程序中銅、鋅及鎳之溶出效率最高可以達到 52% ~ 60%、60% ~ 70% 與 2% ~ 70%，而鉻並無明顯之溶出效率。在連續式生物溶出程序中，增加植種量可能造成反應槽中微生物之活性降低，進而導致底泥中重金屬之溶出效率並無有效提昇之情形。另一方面，本研究之零價鐵處理金屬混合廢液實驗中，零價鐵添加量之最佳操作值應設定為 10 ~ 20 g/L，而重金屬初始濃度分別設定於銅 3 mg/L ~ 10 mg/L；鋅 7 mg/L ~ 20 mg/L；鎳 2 mg/L ~ 4 mg/L 及鉻 0.3 mg/L ~ 1 mg/L 之間時，混合廢液中銅、鋅、鎳及鉻分別有 98%、20%、25% 及 90% 以上之去除效率。

Abstract

In the restoration strategies of river and lake, besides controlling pollution sources and building sewer system, dredging of contaminated sediments from the rivers or lakes should be one of the important issues. Most of contaminated sediments often contain high content of heavy metals and thus can not be disposed of on the land without proper treatment. The purpose of this study is to develop a continuous bioleaching process for sediments contaminated by heavy metals based on the research results and findings obtained from the previous year's project. The optimal parameters and performance enhancement of the above bioleaching process were investigated in this study. Meanwhile, the fluidized bed reactor with zero-valent iron (ZVI) was applied for treatment of the metal-containing solution produced from the bioleaching process. The results showed that the pH, sulfate concentration and metal solubilization can reach the steady state after 3 hydraulic retention times (HRT) of continuous operation. At the HRT of 10 days, the maximum efficiency of heavy metals solubilized from the sediment was 52%-60%, 60%-70%, and 62%-70% for Cu, Zn and Ni, respectively. Meanwhile the efficiency of Cr solubilization was below 6%. The efficiency of heavy metals leached from sediments in this continuous bioleaching process was not enhanced by increasing the inoculum. On the other hand, the results of response surface methodology indicated that the maximum efficiency of metal removal from the bioleachate solution was achieved at 10-20 g/l of zero-valent iron (ZVI) dosage with 3-10 mg/l of Cu, 7-20 mg/l of Zn, 2-4 mg/l of Ni and 0.3-1 mg/l of Cr, respectively, where up to 98%, 20%, 25% and 90% of Cu, Zn, Ni and Cr were removed from the bio-leachate solution.



[051] 發展環境法醫技術於油品污染場址污染源鑑定

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中文摘要

本計畫目的為發展環境法醫技術，應用於國內常見之柴油污染場址之污染源判釋，評估油品污染場址之相關環境法醫鑑識分析技術，並探討風化過程對油品化學指紋特性及鑑識之影響。在建立柴油及航空燃油油品基本資料庫工作上，除了彙整過去油品相關資料外，並進行柴油(中油及台塑)及航空燃油(Jet A-1 及JP-8)基本特性分析，進一步利用分布試驗導出Jet A-1 及JP-8 目標污染物之分布係數與溶解度的理想關係式： $\log K_{fw} = -\log S + 0.689$ 與 $\log K_{fw} = -\log S + 0.724$ ，此航空燃油理想關係式可提供調查及整治規畫者在短時間內估算出碳氫化合物從有機相分布到水體的行為，將有助於在航空燃油污染時作出適當且及時的評估，以提供適切的整治方法之參考依據。

針對評估風化過程對柴油化學指紋及鑑識之影響，探討土壤受市售柴油污染後(新近及老舊污染)，風化作用對碳氫化合物濃度及組成成分間的影響，配合油品來源意義之特徵因子比值分析，從而建立柴油污染源鑑識技術。在老舊柴油及柴油污染土壤的分析分別為2000年、2002年、2003年所購置柴油所製備的柴油污染土壤以及2005年柴油與柴油污染土壤，以及在實驗室所置備新鮮柴油污染土壤，結果發現柴油中直鏈烷損失較為明顯，而類異戊二烯(isoprenoids)尚未受到劇烈影響，因此風化條件主要為蒸發作用所主導，而風化程度僅屬於輕度風化。利用多種雙環類倍半萜烷(bicyclic sesquiterpanes)比值，鑑識其原油來源的差異，分析naphthalenes 系列化合物以及phenanthrenes 系列指紋圖譜，將特徵因子進行一致性評估，並將老舊柴油及柴

油污染土壤之特徵因子比值繪製出雙比值散佈圖，結果顯示中油柴油特徵因子比值與2005 柴油及柴油污染土壤較相似，結果與柴油油品來源資訊相符。最後將本計畫累積之風化鑑識技術應用於國內污染場址樣品之洩漏來源鑑別，由結果得知雙環類倍半萜烷抗風化能力佳，污染場址受風化之樣品所含雙環類倍半萜烷尚未受到劇烈影響而消失，與中油、台塑柴油污染土壤比對結果分為二群，此部分結果與實場樣品來源資訊相符，顯示本計畫評析柴油油品污染場址的可行性環境法醫鑑識流程，所建立的柴油油品污染鑑識指標化合物及參數，以及所建立之指紋資料庫及鑑識分析技術，可作為國內柴油污染場址的鑑識參考。

Abstract

Soil and groundwater contamination by petroleum products released from underground or aboveground storage tanks is a serious and widespread environmental problem. Diesel and aviation fuels are among the most frequently spilled petroleum products and are the focus of this study. The objective of this project is to develop proper chemical analysis methodologies which are feasible to characterize and identify fuel-contaminated sites from environmental forensics prospect. By use of a two-phase liquid-liquid equilibrium model, fuel-water partition coefficients (K_{fw}) of major components were measured for civil and military aviation fuels (i.e., Jet A-1 and JP-8). Target compounds and physical and chemical properties of aviation fuels were determined. The ideal-behavior model was as following: $\log K_{fw} = -\log S + 0.689$ (Jet A-1) and $\log K_{fw} = -\log S + 0.724$ (JP-8). The models

derived using Raoult's law convention for activity coefficients and liquid solubility is presented. Soils contaminated by diesel fuel produced in 2000, 2002, 2003, and 2005 were used for our weathering effect study. The slightly degraded fuel is usually indicated by partial depletion of n-alkanes; a moderately degraded one is often indicated by heavy loss of n-alkanes and partial loss of lighter polynuclear aromatic hydrocarbons (PAHs); for highly degraded oil, the n-alkanes and branched alkanes could be completely lost, and PAHs and their alkyl homologues could be highly degraded. After the long term weathering processes of 8 and 10 years, compounds with molecular weight smaller than C₉ alkanes were disappeared in soils contaminated by diesel fuel in 2003 and 2005, respectively. Also it was found that fuel constituents with molecular weight smaller than C₁₀ alkanes were disappeared in aging contaminated soil of 2002. For soil sample through 13 years of weathering processes, compounds with molecular weight smaller than C₁₁ alkanes were degraded, furthermore, after the long term weathering processes of 365 days, compounds with molecular weight smaller than C₁₂ alkanes were disappeared in soils contaminated by diesel fuels of Chinese Petroleum Company (CPC) and Formosa (FOR). It was illustrated that Isoprenoids, bicyclic sesquiterpanes and alkylated PAHs are less susceptible to the effects of biological indicators of biodegradation. The ratios of characteristic factors such as pristane/phytane, C₁₅ sesquiterpane/8β (H)-drimane (BS3/BS5), C₁₅ sesquiterpane/8β (H)-drimane (BS4/BS5), C₁₅ sesquiterpane/C₁₅ sesquiterpane (BS4/BS6), C₁₅ sesquiterpane/8β (H)-homodrimane (BS3/BS10) and 8β (H)-drimane/8β (H)-homodrimane (BS5/BS10), methylphenanthrene Indices (MPI), methylphenanthrene ratio (MNR), methylphenanthrene ratio (MPR) can be adopted as forensic indicators in diesel contaminated sites. The results indicated

that the characteristic ratio of diesel fuel produced in 2005 with soils contaminated by diesel fuel of 2005 were similar. Apparently characteristic ratio match the information sources. Finally, source identification was attempted for samples collected from different fuel contaminated sites by using the unique pattern of sesquiterpanes. Furthermore, we demonstrated that diagnostic ratios of sesquiterpanes are largely unaffected by evaporation. It is anticipated that the information generated from this study will be adopted by decision makers to evaluate the liability of cleanup in diesel contaminated sites in Taiwan. The database, forensic criterion, and parameters established in this study should be coupled with other information such as hydrogeological condition, environmental condition of contaminated sites for better results of environmental forensics.



[052] 開發生物復育技術整治受三硝基甲苯污染之土壤-實驗室模場研究

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中文摘要

土壤及地下水(以下簡稱土水)被火炸藥類物質所污染是一個長久以來被嚴重忽視的問題。由於部分火炸藥類物質[例如三硝基甲苯(trinitrotoluene (TNT))，環三亞甲基三硝胺(hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX))，環四亞甲基四硝胺(octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX))]已確定或可能具致癌性，因此許多歐美國家均已訂出此類火炸藥類物質在土水之管制標準，並積極進行火炸藥類物質污染場址之整治。環保署目前亦已著手研訂土水之火炸藥類物質管制標準，並將於近期公告施行。屆時火炸藥類物質之土水污染場址均需提出污染改善或整治策略。目前國內針對火炸藥水體與土壤污染的處理技術主要還是使用傳統的直接焚燒法，在高溫下燃燒，達到氧化分解有毒物質的目的。但是其價格昂貴且其燃燒後的二次污染物將對生態及人體健康產生影響。因此，發展經濟有效且環境友善之火炸藥類物質污染土水整治技術有其必要性。在綠色整治(green remediation)之原則下，污染場址之調查與整治規劃必須有著和傳統不同之思維。在整治技術方面，應優先採用生物處理為主之整治系統，即儘可能減少採用物化處理為主之整治系統。本計畫之主要目的即是針對火炸藥類物質污染場址中最具代表性之 TNT 為目標污染物，探討本土分離之微生物，應用於 TNT 之生物復育之可行性評估，以達到綠色整治之目的。本研究延續上一期的成果，對篩選分離之本土 TNT 分解微生物進行完整之分析探討，主要將著重於前一期所篩選之本土菌株對 TNT 降解效率的評估，同時也將前期所建立之 DGGE 監測環境微

生物多樣性之平台應用於實驗室模場規模 TNT 污染土壤生物復育研究過程中，微生物族群狀態之觀測。研究執行內容與成果包括(1)本土分離菌株對 TNT 分解之探討；(2)環境樣本之 TNT 標準方法檢測平台技術之建立：利用 USEPA method 8330A 與環保署公佈之「火炸藥物質檢測方法—高效液相層析儀 / 紫外光偵測器法」(NIEAM804.00B)之檢測方法，建立 TNT 污染土壤中殘餘之 TNT 濃度檢測之標準流程；(3)使用高效液相層析儀建立檢測一些 TNT 代謝的可能中間產物的方法，包括苯、甲苯與二甲苯的檢測；(4)使用醱酵技術大量培養本土 TNT 分解菌株；(5)使用實驗室批次規模進行本土菌株對三硝基甲苯污染之生物復育評估以及(6)使用變性梯度凝膠電泳(DGGE)直接分析土壤樣本中細菌種類，探討 TNT 污染土壤在降解過程中微生物相之變化。這些研究初步成果將有助於我們未來規劃可應用於三硝基甲苯污染場址的原址生物復育之條件與使用之菌株。

Abstract

Soil and groundwater contaminated by munitions compounds has been a crucial issue in environmental protection. These compounds including trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) are reported as highly toxic and carcinogenic. Therefore, control and remediation of contamination of nitroaromatic compounds including TNT are very critical issues in environmental protection in Europe and United States. Control and regulation standard of these munitions compounds have also been

reviewed by Taiwan Environmental Protection Administration and will be announced recently. Proposal for the remediation of the contaminated sites will then be required. Compared to physical or chemical processes, biological remediation (microbial bioremediation and phytoremediation) are more economy and environmental friendly approaches and also more acceptable by general publics. In this study, we aim to develop bioremediation approaches for TNT by microbial degradation with indigenous microorganisms isolated from TNT contaminated soil and evaluate the feasibility of bioremediation for TNT pollution using these microorganisms.

In the present study, we continued to characterize the indigenous microbial isolates and evaluated their ability in TNT biodegradation. Microbial diversity (microbial population) of TNT contaminated soil was also examined by Denaturing Gradient Gel Electrophoresis (DGGE). The main goals and the results obtained from this project included (1) Evaluation of TNT biodegradation and biotransformation by indigenous isolates; (2) Establish the method for detection of TNT residues in the soil using High performance Liquid Chromatography (HPLC) according to USEPA method 8330A and NIEA M804.00B by EPA, Taiwan; (3) Development and evaluation of the methods for detection of intermediates produced by microbial metabolism of TNT as well as benzene, toluene and xylene by HPLC; (4) Cultivation of TNT-degrading bacterium using batch culture technique by Lab scale fermenter; (5) Development and evaluation of bioremediation of trinitrotoluene contaminated soils by indigenous microorganisms with lab-scale model; (6) Examination of microbial diversity during bioremediation of TNT contaminated soil in lab by DGGE. The preliminary results obtained from this study will help us to evaluate and propose schemes for in situ bioremediation of TNT contaminated site in the future.



[053] 新興污染物於臺灣地下水體之流佈研究

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中文摘要

文獻指出新興污染物(emerging contaminants)無法以現有污水處理系統完全去除掉並已在環境水體中出現，其中以藥品和個人保健用品(pharmaceuticals and personal care products, PPCPs)、賀爾蒙和工業用化合物如全氟化合物(perfluorinated compounds, PFCs)最常被檢測出來，這些污染物可能因為各種途徑而由表面水體進入地下水體中，而臺灣地下水多用為民生用水、農業及工業用水，若新興污染物進入地下水體將可能進一步造成人體及環境上的危害。於今年度，本研究團隊根據國外相關分析方法文獻及過去建立之新興污染物於表面水體與廢水中之分析方法資料，成功建立臺灣地下水中50種新興污染物之固相萃取結合液相層析串聯式質譜儀(LC-MS/MS)之微量分析方法，其偵測極限範圍為0.05-5 ng/L。而回收率測試顯示介於67%~118%之間，除了PFDoA與Gemfibrozil之外。基於臺灣地區過去尚未有研究調查地下水中新興污染物的濃度分佈，因此本研究團隊建立了第一筆臺灣地下水體中之新興污染物流佈數據，初步調查大台北地區(14個監測井、2個場置性監測井)及新竹地區(6個監測井)之地下水，於今年度的枯水期(3月)及豐水期間(6月)各採樣一次化驗分析。檢測結果發現，絕大多數(40種)目標物之濃度皆為ng/L濃度等級，其中有3種污染物濃度達到 $\mu\text{g/L}$ 濃度等級，分別為Acetaminophen ($1.0\ \mu\text{g/L}$)、Sulfamethoxazole ($1.8\ \mu\text{g/L}$)和 17α -ethynylestradiol ($1.8\ \mu\text{g/L}$)。另就檢出頻率來看，檢出頻率最高之前十名化合物中，前八名皆為全氟化物，推測與全氟化物在環境中持久及不易分解的特性有關。此外， O_2 監測井(新竹市東門國小)之檢出目標污染物種類為最多(35種)

且濃度最高($1.8\ \mu\text{g/L}$)，明顯高於其他採樣點且兩次數據具有重複性。建議未來可持續針對特定監測井與常見之新興污染物進行相關調查。由於各監測井位置皆鄰近診所、藥局、醫院、藥廠、污水處理廠及電子科技廠，加上國外文獻與本研究團隊發表之期刊論文證實以上場址皆為新興污染物之環境污染源，因此初步研判這些場址為地下水中新興污染物之可能污染源頭。建議未來能持續進行相關調查，以釐清污染來源與後續防治策略。

Abstract

Previous studies have shown that emerging contaminants cannot be removed completely during wastewater treatment processes and have been detected in our aquatic environment. Among all emerging contaminants, most frequently detected compounds are pharmaceuticals and personal care products (PPCPs), hormones and industrial pollutants such as perfluorinated compounds (PFCs). These contaminants may enter into groundwater system from surface water through various pathways. In Taiwan, groundwaters are often used for domestic consumption, agricultural irrigation and industrial use. Consequently, the occurrence of emerging contaminants in groundwater can be a potential risk to human health. The analytical methods (solid-phase extraction combining with liquid chromatography-tandem mass spectrometry) of 50 emerging compounds in groundwater have been developed this year. The method detection limits of all target compounds range from 0.05-5 ng/L. Recoveries at this concentration level range from 67%-118% except for PFDoA and gemfibrozil. This is the first work to investigate occurrences of emerging contaminants in groundwater in Taiwan. Groundwater monitoring wells in Taipei



and Hsinchu area were monitored in March and June this year and the temporal and spatial distribution of emerging contaminants were investigated. Results showed that 40 target compounds were found to occur at the ng/L concentration level and 3 compounds reached μ g/L concentration level, including Acetaminophen (1.0μ g/L), Sulfamethoxazole (1.8μ g/L) and 17α -ethynylestradiol (1.8μ g/L). In terms of detection frequency, the most frequently detected eight compounds were all perfluorinated compounds; this is likely due to its persistent nature in the environment. On the other hand, O₂ monitoring well has the most number of target compounds found (35 PPCPs and PFCs). The result is significantly higher than the other monitoring wells and is consistent in the two times sampling. All the monitoring wells are close to clinics, pharmacies, wastewater treatment plants and electronic technology factories. Studies from other countries and the results of our previous works have identified that these sites are the sources of emerging contaminant pollution. For future investigation, it is important to continuously monitor the most frequently detected compounds as well as the specific monitoring wells which have found to have higher occurrence of emerging contaminants.



[054] 電動力技術處理重金屬污染土壤模場試驗-設計第二代現地模場 及建立本土化技術

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中文摘要

電動力技術係一現地(in-situ)整治技術，可藉由調整電動力操作參數及處理時間，使得地面活動及原有建物不受影響，且因具備外在驅動力及污染物擴散方向可控制之特點，特別適合應用於大多技術不適合處理之黏土層污染。其主要優勢為：(1)可產生均勻之電滲透流於異質且低滲透性之土壤介質中移動，(2)可有效控制電滲透之流向，(3)高降解率與移除率且具安全性，(4)為一種高經濟效益之現地永續處理技術。落實實場整治，建立本土現地操作參數，將可有效解決現有污染場址之技術瓶頸。

本計畫以100年度補助計劃成果為基礎，進行持續性研究。今年度(102)計劃重點為改良100年度設計之第一代三維現地模場，就其模場出水口位置、組裝方式及電極棒(板)規格進行改良，完成第二代三維現地模場之規劃設計，並進行電動力實驗參數之完整測試，以建立電動力技術之本土化操作參數，同時進行實場整治之相關規劃作業，俾於後續儘速進入實場進行整治。今(102)年度計畫主要內容包含：

1. 第二代三維現地模場之設計改良及組裝 — 第二代模場尺寸將改良規劃為約1 m(L) × 0.5 m(W) × 0.7 m(H)，並進行組裝方式修正，使之更具操作持久性，日後並可作為現地移動式處理設備。
2. 電動力模場測試 — 以鈦版為電極，於電位坡降0.3 V/cm，操作流質為0.05 M 乳酸，經20天整治後各金屬污染物去除率皆在75%以上；而電位坡降較低時則因移動速率較緩及電滲透流較小之故去除率未如提昇電位坡降佳；而流質濃度提升至0.5 M後因呈現稠狀，導致電滲透流流速趨緩，而於較短時間整治下無法將污染

物一出土體，以致去除率較低；而整治時間延長至40天后系可有效增加去除率，但鈦板電極經100天使用後發現腐蝕情形，使底層及中間層有污染物沉積，而影響去除率提升。

3. 與100年度計畫之結果比較後發現，電極耗損佔總成本90%以上，而第二代模場使用之鈦板電極耐腐蝕性較佳之故，整治實驗後係可繼續沿用，總成本可較第一代模場以不鏽鋼棒電極為時降低14%左右。
4. 計畫執行期間因為能尋覓適當場址，而未能執行實場整治計畫，但目前已完成實場整治規劃作業，待後續計畫若尋覓適當之場址，即可立刻進行現地整治實驗。

Abstract

Electrokinetic (EK) process is classified as an in-situ remediation technology. It will be conducted in site without disturbing present resident activities with proper operation and reasonable treatment time. EK process is much fit in contaminated site with clay soil because pollutant will be forced to migrate by the electrical driving force. The advantages EK process includes: (1) production of uniform electroosmotic flow in heterogenous medium, especially in low permeable soil; (2) easy control of flow direction; (3) high removal and degradation efficiency; (4) high economy. To establish pilot-scale operation parameters will be beneficial to promote in application

The aim of this project is to design a 3-D pilot-scale EK modul and conduct a series of soil remediation experiments investigate the effect of electrode area and potential gradient on remediation efficiency. The cooperated consulting firm will provide funding to establish the EK



modul. Three meetings were held in NUK to discuss the design criteria. The conclusions of critical designing requirement includes,

- The size of 3-D modeul is about 1 m x 1m x1m, with mobility;
- There are enough space in reservoir to put more electrodes and the electrode position can be adjusted;
- The input of processing fluid is under automatically control;
- The reservoir pH, ORP, electro current/voltage should be monitored.
- Sampling process should be convenient.

The 3-D pilot-scale EK modul has been established. Considering reducing cost, hollow stainless electrodes are selected for test. The soil loading can be flexible adjusted. Twenty-five sampling ports are set for every 25 cm depth in modul. The pH meter, ORP meter, electrovotage meter are set in the modul with continuously monitoring. After pass the preliminary test-run, a series of EK experiment will be conducted.



[055] 實場底泥污染物生物有效性評估及其在健康風險評估之應用

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中文摘要

民國99年「土壤及地下水污染整治法」修正，將底泥納入法規管制，但在健康風險評估方面，底泥尚未如同土壤及地下水污染場址有「土壤及地下水污染場址健康風險評估評析方法及撰寫指引(95年公告)」可資遵行(註)，惟依99年環保署規定，有關底泥之健康風險評估準用前述「評析方法及撰寫指引」辦理，而其所述之層次性健康風險評估中，暴露劑量大多採用污染物最大濃度(全量萃取)計算，如此雖較具保守性但可能高估風險，因為在污染場址實際環境介質中，污染物對生物受體的真實暴露劑量(actual exposure)低於污染物在環境介質中的全量。生物有效性(bioavailability)為化學物質可被生物有效接觸利用的特性，本研究證實可加以量化並推定為環境污染物對生物受體的真實暴露劑量，進而合理化風險評估，落實「土污法」中關於健康風險評估的立法意旨並達成底泥管理的政策目標。(註:「底泥環境影響與健康風險、技術及經濟效益評估方法及撰寫指引」於102年7月15日公告)

Abstract

Amendments of Soil and Groundwater Pollution Remediation Act were promulgated on February 3, 2010, in which sediment pollution is regulated. In this Act the Evaluation Methods and Writing Guidelines on Health Risk Assessment of Soil and Groundwater Pollution Sites (April 26, 2006) do not directly apply to sediment. However, the Evaluation Methods can be implemented to sediment, according to Transitional Enforcement Directions Governing the Soil and Groundwater Pollution Remediation Act after Amendment and Promulgation (May 5, 2010). Therefore, health risk assessment of sediment can be performed accordingly. The Evaluation Methods adopt a tiered health risk assessment and the highest pollutant concentrations are counted in exposure assessment, leading to conservative yet overestimated risks. In other words, the overestimated exposure during health risk assessment will result in a remediation goal too low to be accomplished. Bioavailability is characterized as the availability of chemicals to microbial degradation. Bioavailability of a chemical can be measured and regarded as actual exposure concentration. Presence in the matrix of a contaminated site, pollutants are with the actual exposure concentrations lower than their total concentrations extracted by the exhaustive extraction method indicated in regulations. The exhaustive extraction method poses a concern of overestimation on exposure. Also this study found that optimal bioavailability measurement for the sediment pollutants could be established, through which actual exposure concentrations of contaminants in sediment has been obtained.

[056] 調查焚化爐周圍水稻田地土壤及作物受現地地質化學與微生物

影響之總汞及甲基汞含量變化

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中文摘要

環境中汞的人為排放源，主要來自焚化廠及燃煤發電廠。近期文獻顯示，高濃度的甲基汞可從生長在離汞排放源相近的稻米中被檢測出來，暗示著陸地生態系統中的食物也可能成為甲基汞的攝食途徑之一。由於稻米是臺灣也是許多亞洲地區人民的主食，因此對於水稻田如何易成為甲基汞的生成環境，環境生地化循環如何涉入其過程，以及排放源造成甲基汞在稻米的累積效應為何，實有深入調查的必要。本研究即針對北投焚化廠周圍水稻田地的表水、表土(0-2 公分)和根系土的總汞與甲基汞，以及可能會影響無機汞的現地生物可得性的地質化學參數進行採樣分析。分析結果指出，水稻田的土壤及孔隙水，以及栽種在此區的稻米，其內的總汞與甲基汞含量皆無超過法規所定的環境與食米標準，且與一般的環境背景值相近，顯示焚化爐內的空污防治措施可有效管控汞的排放，未造成此區農地顯著的汞累積。根據現地地質化學與微生物族群的分析可知：(1)孔隙水中的甲基汞與無機汞濃度呈現顯著正相關；(2)硫與鐵循環所造成的孔隙水化學使得此根系環境中無機汞的生物有效性偏高；(3)硫酸鹽還原菌可能是此區最主要的汞甲基化菌群。這些因素加總起來某種程度暗示著，若此區的總汞濃度增加，其根系土環境將具有促進甲基汞生成與累積的潛力。此外，藉由添加不同形式的配位基而改變孔隙水的甲基汞化學組成後發現，配位化學可造成稻作不同程度的甲基汞的攝取及累積，然此部分的機制原理仍需進一步的探究。

Abstract

Current inventories of mercury (Hg) emissions show that coal combustion and waste incineration are the leading contributors of Hg release to the environment. Recent studies report high levels of methyl mercury (MeHg) in rice grown in the vicinity of anthropogenic Hg emission sources, suggesting that ingestion of rice may be another critical route of human exposure to MeHg. Hence, it is important to conduct a thorough investigation of this exposure pathway by examining why rice paddies are conducive for Hg methylation and how additional Hg inputs from the combustion of municipal solid waste (MSW) may lead to potential uptake and accumulation of MeHg in rice. In this study, four paddy sites within the agricultural area of the Beitou MSW incinerator were chosen to sample surface water, topsoil and root soil. Total Hg, MeHg, as well as ancillary geochemical/microbiological parameters were analyzed. Results show that levels of total Hg and MeHg in root soil, pore water and rice grains were below the regulations for soil and edible rice, suggesting that this agricultural land is not polluted by Hg and the air control device employed in the incinerator has been efficient for control Hg emission. Microbiological analysis indicated that sulfate-reducing bacteria are the principal anaerobes responsible for *in situ* MeHg-production in the rhizosphere. Geochemical analysis showed a great potential for enhanced Hg-methylation if elevated Hg inputs occurred. In addition data from MeHg chemical speciation experiments showed that complexation chemistry of pore water can influence uptake and accumulation of MeHg in rice.

[057] 整合型植生復育提升能源作物向日葵整治重金屬之研究



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中文摘要

近來高雄市區大坪頂特定區(10公頃)、屏東縣萬丹鄉大鼎飼料(0.58公頃)及新園鄉赤山巖(4.77公頃)等土壤污染場址，因面積廣闊、污染深度及污染濃度等問題，若以國內常用之翻轉稀釋、土壤酸洗及排土客土等技術估算所需經費將為龐大數字。針對此些場址以風險為考量之綠色整治技術(Green remediation)，為未來可行之策略。其包括太陽能板、風力發電等設置及生物能源，如向日葵等植生控制(phytoattenuation)，在有效之必要風險評估後之阻絕及監測規劃，應可取代目前常用之土壤整治技術。本計畫將對能源作物向日葵進行土壤重金屬之改善研析。探討整合過氧化鈣、植物生長激素與螯合劑植生復育受重金屬污染土壤，並進一步評估能源作物向日葵復育受重金屬污染土壤操作方式暨相關環境因子擬定。並藉由實驗探討過氧化鈣、植物生長激素與重金屬對植體生長情形(植體形態分析)暨重金屬累積傳輸效益之影響。另以生物可分解性螯合劑添加改變土壤重金屬生物有效性，配合植物生長激素提昇植體生長，探討植體植體重金屬累積傳輸情形。此外，亦以分子生物技術鑑定植體根系與土壤微生物之菌相，試圖尋找可以促進植物生長亦可以抵抗毒害之植物促生菌。以過氧化鈣結合生物激素與螯合劑提昇植生復育處理受重金屬污染土壤，期能以整合型植生復育法做為後續研究之綠色整治技術。

Abstract

Phytoremediation, a green technology developed to extract heavy metals from polluted soils, has drawn a great attention due to cost-effectiveness and aesthetically pleasing nature. The aim

of this research intends to assess the potential of bioenergy plant sunflower to remediate soil polluted with a mixture of heavy metals. Several pretreatments to enhance phytoremediation efficiency including adding calcium peroxide, plant growth regulators, and evaluating plant growth promoting rhizobacteria will be employed. In this study two commercially available plant growth regulators will be used to boost the assisted phytoextraction of Pb, Cu, and Zn. The effects of calcium peroxide and chelant treatment in soil will be investigated in terms of dry weight biomass, and heavy metal accumulation in the plants. In addition, the transformation mechanisms via these treatments through the pilot-scale and field-scale systems will be studied to evaluate the phytoextraction efficiency and transpiration rate. Heavy metals removed through the vegetation uptake and heavy metal soil mobility will be researched by employing sequential extraction to characterize the components that heavy metal is associated with. By virtue of understanding the mobility of heavy metals, the phytoremediation efficiency and potential environmental impact from the removed heavy metals can be addressed. The third year of this research will evaluate the potential of recycling the sunflower seeds as bioenergy and reusing the harvesting plants as biosorbents. Several related parameters, namely pH, redox potential, dissolved oxygen, microbial condition, to optimal operate laboratory-scale modules and field operation enhancing the pollutant removal will also be studied. The findings of this research might also provide the preliminary solution for combating the upcoming challenge to innovatively remediate soil pollution through phytoremediation via employing calcium peroxide, plant growth regulators, and chelants.

[058] 應用多重電極排列與感應極化法調查砂礫質地層污染之研究

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中文摘要

近年來國內外工業活動造成之土地污染案例，對國土資源與生活環境形成莫大威脅。在各類型污染一旦洩漏其移動分佈深受複雜的水文地質變化所影響，其污染流佈與調查是我們所重視的。近年來，非破壞性地球物理探勘技術已逐漸運用在污染場址之地下環境調查，搭配較少量的鑽孔資料可獲得“面與空間”資訊。目前地球物理最廣泛運用之污染調查技術為直流電阻法。

直流電阻法是一種受歡迎的地球物理探勘技術，因為其物理原理簡單且資料收集快速有效率，傳統上電阻率量測是在地球表面上施行，以配置特定電極的排列以獲得視電阻率探測曲線、視電阻率剖面或視電阻率擬似剖面，這些結果可以反應出地層電阻率水準或垂直向的變化，這種技術已廣泛應用在地下水、土木工程和環境調查上。本研究目的利用數值模擬與研究場址中常用之電極排列的二維電阻率影像之解析度與效能。電極排列包括了溫奈-施蘭卜吉、梯度法、雙極排列法、偶極偶極法等五種以上方法，並搭配感應極化法材料選用，藉此檢驗野外調查的效能(異常物效應值、訊號雜訊比)與這些排列法排繪影像的能力。並由實場調查進行檢驗，選出Dipole(偶極)系列為最佳施測電極排列法。

感應極化法發展出雙電極施測方法，利用最佳不銹鋼棒作為電流極，而最佳電位極材料為硫酸銅電極，再搭配最佳偶極偶極電極排列法為砂礫質地層中調查高電阻率污染物最佳搭配。成功利用Dipole 系列方法搭配感應極化法在油品污染場址及含氯物染場址，將污染物描繪出來，再利用採水及採土樣成功驗證本研究成果。

Abstract

DC electrical resistivity surveying is a popular geophysical exploration technique because of its simple physical principle and efficient data acquisition. Traditional resistivity measurements are carried out on the earth's surface with a specified array in order to obtain apparent-resistivity sounding curves, apparent-resistivity profiling data or apparent resistivity pseudosections, all of which qualitatively reflect the vertical or horizontal variations in subsurface resistivity. This technique is widely used in groundwater, civil engineering and environmental investigations.

Numerical simulations are used to compare the resolution and efficiency of 2D resistivity imaging surveys for 5 electrode arrays. The arrays analysed include polepole (PP), pole-dipole (PD), half-Wenner (HW), Schlumberger (SC), dipole-dipole (DD), γ -array (GM), multiple and moving gradient array (GD). Some synthetic geological models were used to examine the surveying efficiency (anomaly effects, signal-to-noise ratios) and the imaging capabilities of these arrays. The responses to variations in the data density and noise sensitivities of these electrode configurations were also investigated using robust (L1-norm) inversion and smoothness-constrained least-squares (L2-norm) inversion for the these synthetic models.

The results show the following. (i) GM and WN are less contaminated by noise than the other electrode arrays. (ii) The relative anomaly effects for the different arrays vary with the geological models. However, the relatively high anomaly effects of PP, GM and WB surveys do not always give a high-resolution image. PD, DD and GD can yield better resolution images than GM, PP, WN and WB, although they are more



susceptible to noise contamination. SC is also a strong candidate but is expected to give more edge effects. Accordingly, the GD, PD, DD and SC arrays are strongly recommended for 2D resistivity imaging, where the final choice will be determined by the expected geology, the purpose of the survey and logistical considerations.

[059] 以綠能作物復育重金屬污染土壤之可行性研究 (第二期)

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中文摘要

國內有相當多的污染農地地處偏遠，土地利用率高，污染對週遭環境之影響風險亦不大，投入經費積極整治，其必要性實屬不高。隨著化石原料的日漸耗竭，綠能作物所提供之生質能源是一種綠色、環境友善的再生能源。針對重金屬污染農地若能結合綠能作物推動植生復育技術，不僅可達到褐地再利用，提供更多生質能源產量，也可以經濟有效率的方法達到污染土壤整治的目的。本計畫以七種能源作物，於鉛污染場址進行現地栽種試驗，研究目的包括：一.了解植生復育過程植體、土壤鉛含量及土壤中鉛鍵結型態之時間序列變化。二.評估各種作物在鉛污染土壤中之產量及鉛吸收能力。三.菌根菌對作物生長、鉛吸收能力之促進作用。

Abstract

In recent years, remediating farm land contaminated by heavy metals has been actively undergoing in Taiwan; however, it is not practical and cost-effective for remediating the contaminated farm land in remote regions because most remotely located farm land has low application rate, and its contamination poses low adverse impacts on the surrounding environment. The increasing depleted fossil fuel energy source makes it imperative to develop substituted green energy from biomass; green crop may provide environmental friendly and sustainable energy. If heavy metal contaminated farm land can be remediated by growing green crop to be used as green energy, the objectives of remediating the contaminated soil and providing green energy can be simultaneously achieved. In this research, crops that are rich in bio-energy including corn, potato, sugar cane, peanuts, rape, sunflower and *Miscanthus floridulus* were selected for conducting the growth tests on-site in a lead-contaminated plot located in Nantou City, Taiwan. The purposes of research include: 1) to know the time series variation of lead content in plants and soil in vegetation process. 2) to evaluate the energy yield of various crops in the lead contaminated soil. 3) The promotion and optimal conditions of mycorrhiza fungi for plant growth and lead absorbability.



[060] 底泥中苯(a)駢芘與多溴二苯醚污染整治與驗證技術開發

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中文摘要

河川底泥在生態系中扮演重要功能，一旦遭受持久性有機污染物 (persistent organic pollutants, POPs) 污染，污染物將可循食物鏈進入人體及動植物體內，造成人體健康危害與生態系損害。以二仁溪與三爺溪沿岸底泥為例，採樣分析發現PAHs 以苯(a)駢芘 (benzo(a)pyrene, BaP) 等五環類最高且超出指標上限值10 倍；PBDEs 測值屢屢高居全國前三名，魚體脂質濃度更高居全國第一，此二者實有整治之必要。本計畫以BaP 與PBDEs 中相對濃度較高之 BDE47、BDE99 與 BDE209 為目標污染物，將食品級乳化液加入混合之後，進行油水分離回收，並以殘留之乳化液或是外加奈米過氧化鈣加速目標污染物之生物分解。初步之底泥採樣與分析確認底泥中之16 種主要PAHs 之濃度分布以五環 PAHs 為主，其中BaP濃度介於0.09-13.84 mg/kg，大部分已經超出我國現行管制辦法之上限值1.34 mg/kg 與下限值0.16mg/kg；而BDE47、BDE99 與 BDE209 之濃度為 $20.87 \pm 11.71 \mu\text{g/kg}$ 、 $27.63 \pm 10.89 \mu\text{g/kg}$ 與 $64.36 \pm 29.29 \mu\text{g/kg}$ (mean \pm SD, n=5)，與國際文獻測值比較，顯然偏高。二仁溪底泥中BaP 單次可回收達31.4%至73.6%，BDE47、BDE99 與BDE209P 單次可回收分別可達53.7%至76.1%、47.5 至91.4%與10.4 至61.8%。另外以現場底泥在未添加外來污染物情況下回收PBDEs 發現可回收達BDE209達92.7%。BaP 之生物降解最佳之組別為有加入乳化液之第4 組($t_{1/2}$ 為68.6 天)，最差者為自然回復組($t_{1/2}$ >462 天)。BDE47、BDE99 與 BDE209 之生物降解情況仍以

BDE209 最難降解，但有添加乳化液者之生物分解速率有明顯提升，自然回復組之在同時添加兩種污染物情況下之BDE209分解速率最高之情況有待進一步確認。表面增強拉曼光譜檢測BDE209 部分以氧化鐵奈米顆粒進行快速檢測部分目前仍在進行中；但微流體晶片部分已經完成至少可有效檢測90 ppb 之技術，且有效線性範圍可至少達4個數量級。

Abstract

River sediments play an imperative role in ecosystems. According to our recent sampling and analysis, the distribution of PAHs in Er-Ren River sediments has shifted from lower ring numbers to higher ring numbers and 5-ring PAHs seemed to be the most predominant ones. Further, the difficulty on confirming the remediation performance usually results from the heterogeneous distribution of high k_{ow} compounds in sediments. Thus, this research project is aimed to development removal technology of PBDEs removal with target compounds BDE47, BDE99, and BDE209 and also a new technology for reliable quantification of BDE209 using surface-enhanced Raman scattering. Our data showed that most of the analyzed sediment has benzo(a)pyrene higher than the regulated values, upper limit 1.34 mg/kg and lower limit 0.16 mg/kg. The concentrations of BDE47, BDE99, and BDE209 in the sediment samples were $20.87 \pm 11.71 \mu\text{g/kg}$, $27.63 \pm 10.89 \mu\text{g/kg}$, and $64.36 \pm 29.29 \mu\text{g/kg}$ (mean \pm SD, n=5), respectively. Single recovery operation can remove 31.4% to 73.6% of BaP, 53.7% to 76.1% of BDE47, 47.5 to 91.4%



of BDE99, and 10.4 to 61.8% of BDE209. Without addition of any BaP or PBDEs, the emulsion recovery technology can remove aged BDE209 in the real sediment up to 92.7%. It seems that fresh BDE209 is harder to remove than aged BDE209 in the sediments. For the biodegradation of BaP, it is found that the 4th tank with emulsion addition achieved the highest removal with a half-life at 68.6 days and the natural recovery group exhibited a half-life longer than 462 days. In the bioremediation of PBDEs, BDE209 is the most difficult one to remove. The natural recovery group showed the best removal in BDE209 but need to be identified by a repeat test. Surface-enhanced Raman scattering (SERS) test for magnetic nanoparticle has not reached a final conclusion yet but microfluidic SERS has yielded very good advancement. Now, the microfluidic SERS can rapidly detect BDE209 down to 90 ppb or lower and the linear relationship is good for over 4 orders of magnitude..



[061] 屏東縣九如鄉九清段1340 地號生物整治現地試驗(第二年)

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中文摘要

本計畫場址位於屏東縣九如鄉，範圍為1,800平方公尺，主要污染物為鋅、鉻、銅、鎳及總石油碳氫化合物 (TPH)。計畫之主要目的在於以生物復育法(蚯蚓與石化分解菌)與植生復育法(白楊樹與太陽麻)改善污染。在場址內共設置六個試驗區，除對照區(CK)外，其餘有三個生物復育區(BP1、BP2、BP3)，二個為植生復育區(PR1、PR2)。在兩年的試驗後發現，三個生物復育區土壤中之TPH 濃度減量百分比介於39%~100%，植生復育區則為59%~100%，且部分土層之濃度已低於土壤污染管制標準。而重金屬之測值指出，主要污染重金屬在各試驗區同一土層之濃度呈現不規則之變化，且大多數仍高於土壤污染管制標準。其次，生育調查與生理試驗之結果皆顯示，兩種復育植物在試驗區中生長良好，有益於後續之污染物改善試驗。此外，兩種植體重金屬之測值都顯示，其吸收累積量以鋅最大，其餘略呈Cu>Ni>Cr 之現象。最後以剪除植體之生質量與重金屬濃度計算其吸收移除量，結果發現，太陽麻與白楊樹對重金屬之總移除量，亦即本年度對重金屬之植生復育效益，分別為Zn(84 g)>Cu(1.93 g)>Ni(1.45 g)>Cr(0.38 g)。此移除量若與五個試驗區推估之重金屬總含量相較，其移除比例仍低，亦即復育重金屬污染所需之期程甚長。

Abstract

The contaminated site proposed in this study is located in Pingtung County with an area of 1,800 m². According to previous investigations, the major contaminants in soils were found to be

zinc, chromium, copper, nickel and total petroleum hydrocarbon (TPH). The objective of this research project is to conduct remediation in the contaminated site. Five treatment plots were designated in the highly contaminated area, in which three were designed for bio-phytoremediation (BP1, BP2, and BP3) and two for phytoremediation practice (PR1 and PR2). One control plot was used to compare the results with different remediation treatments. Earthworm (*E. fetida*) and petroleum-degrading bacteria (*Pseudomonas sp.* NKNU01) were applied for bioremediation, while Poplars (*Populus bonatii* Levl.) and Sun Hemp (*Crotalaria juncea* L.) were utilized in the phytoremediation practice. Soil analysis results showed that the removal rate of TPH in the three bio-phytoremediation plots ranged from 39% to 99% and from 59% to 99% in the two phytoremediation plots. The analysis data also revealed that TPH was below regulation criteria in some soil horizons. However, heavy metal concentrations were not reduced obviously and thus most soils were still highly contaminated. Plant growth and physiological investigations indicated that the two plants were healthy and suitable to be used in this remediation study. The concentrations of heavy metals in the plant tissues were used to evaluate the removal efficiency of the contaminants. The results of tissue analysis indicated that the four metals were absorbed and accumulated in the order of Zn > Cu > Ni > Cr. To explore in more detail, the biomass and the heavy-metal contents of the studied plants were used to evaluate the removal amounts and the results were as follows: Zn(84 g) > Cu(1.93 g) > Ni(1.45 g) > Cr(0.38 g). Comparing the heavy-metal removal amounts by plants to the total



heavy-metal contents in soils, we found that the phytoremediation effect is low and hence it takes long-term practice to reach the recovery goal.



[062] 建構自動化及專利化之實場規模現地電動力系統

-應用於整治鉛污染農地

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中文摘要

本計畫依據去年的成果進行CEEK系統改進，企盼藉由本計畫建構更具市場性的現地電動力法技術。本試驗經過100天的鉛污染土壤整治，結果與計畫目標對應後可以歸納以下若干結論：1. 本計畫確實建構一組CEEK專用的密閉式不透水渠道，克服操作液的循環量受天候影響的問題，同時避免長久操作渠道變形問題。2. 本計畫確實建構CEEK可重複使用的密閉式不透水渠道。此渠道可於整治後重複再使用，以利未來實際工程上節省初設成本3. 本電動力系統CEEK在近實場規模操作下，土壤的pH值及導電度維持在中性及穩定的狀態，呈現本系統對土壤衝擊低。4. 本電動力系統CEEK在近實場規模操作下，系統電流及電壓維持在穩定的狀態。同時，系統溫度接近大氣氣溫，呈現本系統的穩定性佳。5. 本電動力整治方法處理後的土壤肥力略降，需要添加適當肥料方能回復肥力。

Abstract

This project was proposed to improve the CEEK system based on the results from last year. We hope to establish the CEEK technique to meet the market requirements. After 100-day remediation for lead contaminated soils by the CEEK, several conclusions can be drawn: 1. A closing and uninfiltated channel for the CEEK was constructed successfully, which avoids the weather effect and deformation problem during the long-term operation. 2. A reusable channel for the CEEK was constructed, which can be reused and save the initial cost. 3. The pH and electrical conductivity of soils could maintain neutral and stable situation, which indicated the little impact on soils under such CEEK process. 4. The electrical current and voltage could maintain stable situation, which presented the great stability of the CEEK process. In addition, the temperature of operational solution was close to atmospheric temperature. 5. The fertilizerbility of the treated soils was slightly less than that of the untreated soils. This means the addition of fertilizer is necessary

[063] 運用紫外光學雷射誘發螢光系統於石化場址進行漏源追溯與組成特徵辨識

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中文摘要

紫外光學雷射誘發螢光系統(Ultra-Violet Optical laser induced fluorescence system)為一種光學檢測技術，紫外光學雷射誘發螢光技術的應用對象係針對「自由相態」(free phase)的石化污染物，有別於針對「溶解相態」有機污染物的薄膜介面探測系統(MIP)調查技術。本研究規劃於已發生洩漏狀況之場址進行地表下連續性雷射螢光檢測，以瞭解地下環境中自由相態污染物的分布情形，並配合地質水文調查期能找出優勢路徑，回推可能之洩漏來源。由紫外光學雷射誘發螢光系統現地檢測結果得知，測得污染物螢光特徵屬性經彙整歸類後大致可分為5個污染分布特徵群，進一步由環境場址評估作業(Environmental Site Assessment,ESA)歸納出3個可能污染來源區(廠區內Sulfolane洩漏之事件、試驗場址內油水分離設施、第二分離工場不明洩漏來源)與其餘2個污染混合區。從本研究調查案例經驗得知，藉由洩漏污染物質之雷射誘發螢光特徵屬性與污染團空間傳輸分布狀況，來推估場址的污染來源是可行方式。尤其在多重洩漏源情形下，運用UVOST-LIF調查可以快速釐清場址污染分布特徵。

Abstract

Ultra-violet optical laser induced fluorescence (UVOST-LIF) system belongs to optical measurement technology. The LIF detection is aimed at finding free-phase petroleum pollutants that are quite different from the membrane interface probe (MIP) detection. This study selected one soil and groundwater remediation site with potential leakage sources for the testing of in-situ continuous LIF detection. The distribution of free-phase petroleum contaminants obtained from the LIF detection was integrated with the results of hydrogeological survey to trace the possible transport pathway of leakage sources. The results of in-situ UVOST-LIF detection illustrated that site contamination can be classified into 5 types of plume distributions based on their fluorescence characteristics. Integrating with the Environmental Site Assessment (Environmental Site Assessment, ESA) work, plume distributions were roughly recognized as 3 possible source leakages (at the previous sulfolane spill site, the oil-water separation facilities, and the second separation plant) and the other 2 mixing zones of contamination. This study has demonstrated the feasibility of applying the LIF fluorescence characteristics of the leakages associated with spatial transport distribution of contaminant plumes to anatomize the possible contaminant sources in the field. The application of in-situ UVOST-LIF detection can rapidly outline the characteristics of contaminant distribution



[064] 熱脈衝流速儀應用於地下水污染場址調查之可行性研究

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中文摘要

地下水流及污染傳輸會隨著不同的水文地質特性而改變，地下水流通常集中於少數透水性較高的區段，因此瞭解地下水流在空間上的分布及水文地質特性是地下水污染場址之調查目標。本計畫採用熱脈衝流速儀量測水力傳導係數在井孔中垂向分布，研發流速校正方法，改進現地量測技術，並在地下水污染場址進行模場試驗。本研究先進行室內試驗，繼而在台大農場和南投和社水文地質試驗井場進行現地測試，經由不同地質條件及不同試驗方式之經驗與成果，瞭解熱脈衝流速儀現地量測的過程與效能。台大農場試驗井建置在未固結沉積物之含水層，同時採用抽水式及注水式流速儀試驗，試驗結果顯示該試驗井的透水性質雖然隨地層深度而改變，兩種不同試驗方式可獲得類似的結果，然而因為抽、注水速率的差異，造成兩者間存在誤差。南投和社水文地質試驗井場為裂隙岩體之含水層，試驗結果顯示熱脈衝流速儀可偵測透水的裂隙，協助瞭解優勢水流路徑。熱脈衝流速儀量測技術的模場試驗選定在中油高雄煉油廠進行，本研究在二輕附近場地建置兩口12公尺深之地下水試驗井，在探測當地的地質特性後，進行抽水式及注水式流速儀量測試驗，結果顯示當地多為中粗砂質土層，但垂向的透水性分布相當不均，深度8.0至8.25公尺間為兩口井試驗區段中最為透水的範圍，分層水力傳導係數達1.306 m/min，約為水力試驗所得平均水力傳導係數的7.6倍。兩口井的抽水式量測結果呈現相當類似的分布，然而目前注水速率穩度欠佳，解析度不如預期，未來仍需持續研究改進注水技術。模場試驗結果指出熱脈衝流速儀試驗可以量測出分層水力傳導係數，具有潛力應用於地下

水污染場址調查，協助評估地下水污染監測、污染傳輸速率、規劃污染整治、及數值模擬分析工作。

Abstract

Groundwater flow and contaminants transportation are affected by different hydrogeological conditions, therefore, it is essential to investigate the distribution of flow paths and aquifer characteristics. This project adopted heat-pulse flowmeter measurement to delineate the vertical distribution of hydraulic conductivity in the borehole. A pilot test was conducted in a groundwater contamination site. The field tests were conducted in the NTU and Heshu Hydrogeological Experimental Well Station, and the aquifers are composed of unconsolidated deposits and fractured rocks respectively. Both pumping-type and injection-type flowmeter tests were implemented in the NTU site. The test results indicate that the hydraulic conductivity varies with depth, but similar results were obtained by two methods. The results in Heshu indicated that flowmeter measurement results can locate the permeable fractures and preferential flow paths. The pilot test was conducted in the Kaohsiung Refinery of CPC. We established two wells with a depth of 12 meters. The soil samples indicate that the strata are composed primarily of sand, but the distribution of hydraulic conductivity changes significantly with depth. The most permeable zone for both wells is between the depth of 8.0 and 8.25m. The highest horizontal hydraulic conductivity is about 1.306m/min, which is 7.6 times of the equivalent hydraulic conductivity of the whole aquifer. Besides, the injection-type test results of two wells show similar distribution of groundwater flow, indicating the feasibility of the developed



technique. However, the resolution of test results from injection-type method is fair, requiring further research to improve. Heat-pulse flowmeter is a potential technique to apply in characterization and remediation of groundwater pollution, particularly in the groundwater monitoring, contamination transport, remediation design and groundwater modeling.



[065] 土壤及地下水污染整治與再開發對周邊不動產價格與 租稅收益影響之探討

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中文摘要

土壤及地下水污染場址整治後，將回復其原土地使用狀態，而該場址或周邊不動產價格似也將回復原本水準。然而，依國內桃園中壢過嶺加油站污染裁決結果，認為即使整治完成後，污名可能仍續存一段時間。但似缺乏實證結果證實，而目前文獻大多討論個別污染土地之價值與估價方法，卻甚少討論污染整治與再開發後對周邊不動產價格影響的程度、範圍與時間點。此外，於實務上，目前整治工作進行較為緩慢，係限於整治成本龐大，而整治後效益具有相當之不確定性所致。因此，如能確實評估污染整治後所能產生之經濟效益，甚而能有效地回收運用效益，並透過整體再開發計畫增加效益，則將有助於提升整治計畫的財務可行性，加速國內整治計畫之推動，且能更有效率的分配相關經費資源。

本研究透過特徵價格法、成對交易案例分析及條件評價法，估計整治前、後與再開發的不動產價格變化，並試圖釐清其影響範圍與時機。經實證分析結果，顯示特徵價格法將受到交易案例之限制，以致污染整治效益之評估有其困難性。是故建議透過條件評價法，以消費者之觀點，進行污染場址對周邊不動產價格之影響分析，藉以實證整治與再開發假設市場之願付價格。實證結果顯示 RCA 原桃園場址進行污染整治後，受訪者平均願付價格為每坪 11.58 萬元，僅略高於現況(每坪 10.5 萬元)，約 10% 之增幅，但如結合相關再開發計畫，如百貨商場、體育場、公園綠地等開發型態，其願付價格將提升至每坪 13.97 萬元，較目前現況房價增加 33%。顯示污染整治結合再開發對於房價之影響較為顯著，而未來 30 年期間將可產生

2.69 億元的地價稅增額估計數，可藉以挹注土污基金，並提高民間參與誘因。最後，建議修訂土污基金保管及收支辦法，以建立租稅增額挹注基金制度。

Abstract

When contaminated site will be remediated, it would be reused. The market price of site or the surrounding real estate may go back to its original level. However, according to the adjudication of station pollution case in Chungli, it pointed out that the stigma may still subsist for some time even if remediation is complete. But it seems lack of empirical results and most of the current literatures discuss the value of individual contaminated land and its valuation methods. There were rarely discussed the impact degree, scope and time of the surrounding real estate prices. In practice, the current remediation work more slowly that is limited to the huge cost and the considerable uncertainty after remediation. Hence, if we can really assess the economic benefits that can be derived after remediation and even can be capture this value effectively, it can abate the financing pressure of remediation and then accelerate the remediation plans to promote. Besides, we can increase the economic benefits through the brownfield redevelopment planning from the macro and long-term perspective.

This study will estimate the differences of three timing: before, after remediation and redevelopment to confirm the impact scope and timing by hedonic price method, paired sales analysis and contingent valuation method. So far, we found the HPM method will be restricted from the trading case which we can get so that it is difficult to estimate the impact. Therefore, we will estimate the



price that people are willing to pay for soil and groundwater pollution remediation or redevelopment. We found that the average WTP of remediation is 11.58 ten thousand dollars, and the average WTP of remediation combined with redevelopment is 13.97 ten thousand dollars. It show remediation combined with redevelopment had a more significant impact for prices. Finally, we propose some suggestions of the institutions and laws amendments.



[066] 以長效型氧化劑結合生物復育試驗整治受三氯乙烯之地下水：
整治列車成效及對場址影響綜合評估

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中文摘要

本研究以整治列車的概念，結合過硫酸鹽及厭氧生物復育法處理受三氯乙烯污染之地下水。整治列車系統先以過硫酸鹽降解高濃度之三氯乙烯，再以長效型厭氧生物復育試劑持續整治低濃度之三氯乙烯，最後以過硫酸鹽釋放物質於地表下長期釋放過硫酸鹽，持續將殘餘之三氯乙烯、二氯乙烯及累積之氯乙烯去除。在本研究中，我們採集一個三氯乙烯污染場址之土壤及地下水進行批次及管柱實驗。批次實驗結果顯示，1-5%過硫酸鹽添加，可於1天內迅速降解高濃度三氯乙烯(50 mg/L)，0.5%之過硫酸鹽亦可於4天內將三氯乙烯完全去除。以二價鐵活化過硫酸鹽去除污染物時，可能因過硫酸鹽迅速消耗，造成污染物之殘留。濃度2%以上之過硫酸鹽，對微生物之抑制極為顯著。微生物批次實驗結果顯示，0.5%商業化厭氧生物復育試劑Eco-Clean之添加，即可加速TCE之厭氧還原脫氯。高濃度硫酸鹽(5%)之存在，並不影響Eco-Clean對TCE之厭氧還原脫氯。分子生物技術分析結果顯示，場址中存在具有完全脫氯能力之菌種。管柱實驗結果顯示，在0.5%過硫酸鈉，1%Eco-Clean條件下，配合釋過硫酸鹽物質使用之整治列車，於每階段處理程序皆可順利銜接，並無氧化還原條件衝突之問題，可有效去除TCE及其降解副產物。此外，使用過硫酸鹽整治受污染地下水時，應定期檢測地下水中重金屬濃度，避免二次污染發生。研究結果顯示，本研究所提之整治列車，應為一可行之整治方式，惟後續仍需以現地模場試驗進行驗證，以修正相關操作參數。本計畫之成果，將可發展一套迅速有效之化學氧化結合

生物復育之整治列車，供相關污染場址整治之應用。

Abstract

In this study, a treatment train composed of chemical oxidation and anaerobic bioremediation was applied to remediate trichloroethylene (TCE)-contaminated groundwater. Soil and groundwater collected from a TCE-contaminated site were used for batch and column experiments. The treatment train used in this study consisted of persulfate oxidation, anaerobic bioremediation reagents, and persulfate release materials. Results of batch experiments show high concentrations of TCE (50 mg/L) could be removed rapidly by 1 to 5% persulfate addition during 1 day of reaction. The addition of 0.5% persulfate could also oxidize TCE completely during a 4-day reaction. Ferrous ion-activated persulfate may cause the residual of TCE due to the rapid consumption of persulfate by ferrous ions. Significant inhibition of soil bacteria was observed with the addition of persulfate higher than 2%. Results of microcosm study reveal dechlorinating bacteria were present at the site. The addition of 0.5% the commercial anaerobic bioremediation reagent, Eco-Clean, could enhance the dechlorination of TCE effectively. No significant effects on TCE removal were observed with the presence of high concentrations of sulfate (5%). The results show the proposed treatment train would be feasible for groundwater remediation. However, field pilot study needs to be conducted to further evaluate the effectiveness of the treatment train on field applications.

[067] 以新穎光催化技術處理地下水中三氯乙烯之先期研究

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中文摘要

本研究以新穎光催化技術處理地下水中三氯乙烯(TCE)，探討在不同操作條件下對於處理水中TCE之影響。研究利用高導光特性之塑膠光纖搭配浸鍍技術，將商業化光觸媒覆鍍於光纖表面製成覆膜光纖。研究先於水相條件下進行測試，實驗結果發現，光纖光觸媒覆鍍次數增加會降低光催化效率。光照強度增強以及處理時間增加皆有助於光催化效率的提升。另外，在不同pH之操作條件下發現，溶液中含有較多OH⁻時，較容易生成強氧化力之氫氧自由基(·OH)。實驗進一步以對氯苯甲酸(pCBA)作為·OH之探針(probe)進行氫氧自由基轉換濃度(R_{OH,UV})分析，結果發現，在pH10之氫氧自由基轉換效率最佳。實驗選用之觸媒則分析能隙與吸收波長。另一方面，系統之光催化反應動力模式則以L-H模式(Langmuir-Hinshelwood model)進行探討。

本實驗並分別使用屏科大土壤和石英砂填充之土壤管柱，進行模擬受TCE污染地下水之光纖光催化試驗。實驗結果顯示，含有機物之屏科土壤會抑制光催化效率。如果使用較高光照強度之LED作為光源時，可以提高R_{OH,UV}效率。土壤管柱進行不同深度地下水取樣分析時發現，結果是以靠近燈源處之光催化效率最佳。實驗最後以氯離子生成濃度與總有機碳去除效率評估光催化效率，結果皆證明光催化處理程序可提升TCE之去除效率，其中又以TiO₂觸媒之光催化效率最佳。

Abstract

This study used a novel photocatalytic technology to treat trichloroethylene (TCE) in groundwater. The effect of photocatalysis of groundwater containing TCE under different operating conditions and its treatment efficiency were investigated.

Plastic optical fibers coated with two commercialized photocatalysts on their surface were used in this study. The treatment of TCE in aqueous phase was conducted as the pre-test of the treatment of modeling groundwater in a soil column. The experimental results showed that the photocatalytic efficiency decreased as the number of coating of catalyst increased. Higher light intensity and treatment time resulted in higher photocatalytic efficiency. Furthermore, a great amount of hydroxyl radicals (·OH) was generated at alkaline pH conditions due to the higher concentration of OH⁻ existed in water samples. The para-chlorobenzoic acid (pCBA) was used to experimentally determine hydroxyl radical exposure per UV fluence (R_{OH,UV}) from the photocatalytic reaction under different operating conditions. The results showed that pH10 is the optimal pH to generate hydroxyl radicals. The energy gap of two catalysts and their specific absorption wavelength were also determined. The L-H photocatalytic reaction kinetic model (Langmuir-Hinshelwood model) was applied and discussed.

Soil columns containing test media (NPUST soil and quartz sand) were used in fiber optic catalysis to simulate the treatment of groundwater contaminated by TCE. Experimental data demonstrated that the NPUST soil containing organic matter inhibited the photocatalytic efficiency. The enhancement of light intensity promoted the value of R_{OH,UV}, which indicated that the formation of hydroxyl radicals was stimulated. Three sampling ports of the soil column with different depths were used to evaluate the effective length of optical fibers. The results showed that the efficiency of photocatalysis decreased as the optical fiber far away from the light source. Finally, the concentration of



chloride ions generated after photocatalysis and the TOC removal efficiency were investigated. The results showed that photocatalysis through optical fibers can effectively decrease the concentration of TCE, and optical fibers coated with TiO_2 catalysts showed better photocatalytic efficiency than ZnO catalysts.

[068] 北投溫泉磺港溪不同粒徑底泥砷的分佈型態之研究

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中文摘要

地熱谷溫泉形成於 18 萬年前，至今每天仍然有 2,000 噸含高礦物成分之溫泉水排出，導致在磺港溪河道底泥中因結晶、吸附等形成許多富含砷的沉積物。本研究的目的係針對磺港溪之沉積物中不同粒徑底泥透過連續逐級萃取程序(SEP)的定量方法說明砷的移動狀況及釋出機制，並進一步解釋其型態分布與鍵結狀況，以評估底泥中砷污染程度與對周遭環境的影響。本研究將底泥通過五種不同尺寸的篩號，分別為 16 號(1.19 mm)、20 號(0.84 mm)、100 號(0.15 mm)、200 號(0.075 mm)、300 號(0.05 mm)，藉由代表不同化學性質的萃取條件，研析底泥重金屬砷型態分佈之吸附過程，依序為非特定吸附態、特定吸附態、弱結晶鐵、鋁氧化物態、強結晶鐵、鋁氧化物態與殘餘型態。結果顯示磺港溪之底泥型態以弱結晶鐵、鋁氧化物態、強結晶鐵、鋁氧化物態與特定吸附態所佔比例較高，同時底泥中粒徑越小的顆粒所含的總砷濃度也越高。而其非特定吸附態(<10%)及殘餘態(<3%)所佔比例較其他三者低。本研究在分析逐級萃取所得之個別萃取階段資料發現，底泥粒徑越小的顆粒所含砷濃度也越高的現象出現差異化，在粒徑由介於 0.075~0.05 mm 轉變成小於 0.05 mm 時，砷濃度值反而下降，其中以殘餘態(F5)最明顯。逐級萃取程序有助於理解受污染農地及土壤中重金屬的型態分佈、移動狀況及釋出機制，以評估土壤污染程度與影響。

Abstract

The hot spring at Geothermal Valley was took place 180,000 years ago and the discharge of more than 2,000 tons hot spring daily containing highly mineral substance has led to the rich lead and

arsenic sediments via crystallizing and adsorbing in Huang Gang Creek up to present. The objective of this study is to investigate the distribution of arsenic concentrations by using the sequential extraction procedure(SEP) in the different particles-size sediments of Huang Gang creek. Prior to analysis, sediment samples were collected along the creek and sieved to fine-grained fractions: 1.19-0.84 mm, 0.84-0.15 mm, 0.15-0.075 mm, 0.075-0.05 mm and <0.05 mm in order to analyze the processes absorbed by arsenic via the different extraction conditions in chemistry. The SEP could obtain five chemical fractionations: the non-specifically sorbed, specifically-sorbed, amorphous and poorly-crystalline hydrous oxides of Fe and Al, well-crystallized hydrous oxides of Fe and Al, and residual phases. The results show that amorphous and poorly-crystalline hydrous oxides of Fe and Al, well-crystallized hydrous oxides of Fe and Al and specifically-sorbed were in the ascendant; in the meanwhile, finer grained sediment samples tend to have higher concentrations of As. Conversely, the percentage of the non-specifically sorbed(<10%) and residual phases(<3%) was lower than theirs. The study indicated that finer grained sediment samples don't tend to have higher concentrations of As under considering each step of SEP. in other words, arsenic concentrations decreased in the particles-size sediment from 0.075-0.05 mm to <0.05 mm, especially for residual phases.

Performing a SEP can target all potential primary chemical forms of arsenic in the soil solid phase, provide useful information to explain the agricultural land and soil heavy metal contamination, and then propose countermeasures.



[069] 同時處理土壤中戴奧辛、五氯酚及汞之整合性技術開發 (第二階段)

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中文摘要

中石化安順場址不管是在污染物形態、污染物數量與污染物濃度均為國內外罕見，受污染土壤之戴奧辛(PCDD/Fs)、五氯酚(PCP)與汞含量均遠遠超過管制標準；而此種包含不同超高濃度毒性物質之複合式污染型態，是相當棘手的污染整治場址。本團隊於102年度之研究已獲致初步成果，本年度則針對超高濃度戴奧辛污染土壤(249,000ng-TEQ/kg)、超高濃度汞污染土壤(1,860mg/kg)及含汞污泥(2,220mg/kg)等三種不同基質進行熱處理試驗。在熱處理效能方面，土壤及汞污泥中戴奧辛及總汞去除效率隨著熱裂解模組操作溫度及停留時間的提升而上升，戴奧辛及五氯酚的破壞效率可達98%以上，總汞的脫除效率最高達99%以上。為期12天的長時間系統操作試驗結果顯示操作於750°C且停留時間在60分鐘以上時，可確保處理後土壤及汞污泥中之戴奧辛/總汞濃度符合我國土壤污染管制標準(戴奧辛：1,000 ng-TEQ/kg；汞：20 mg/kg)。

排氣控制方面，高效袋式集塵器可有效去除粒狀物，集塵器出口粒狀物濃度可穩定維持在3 mg/Nm³以下；驟冷塔對戴奧辛及汞之去除效率皆隨冷凝溫度降低而提昇，90%以上的汞被捕集回收，在冷凝液中可發現汞珠(元素態汞)的聚集。在流動床式活性炭吸附塔方面，本計畫採用3層活性炭床，在1 cm/day之活性炭質床更新率下即可有效維持排放濃度符合法規標準，但因實際操作上，土壤濃度變動性高，故建議以2 cm/day為佳。經過高效袋式集塵器、驟冷塔及流動床式活性炭吸附塔處理後，排氣中戴奧辛及汞濃度皆低於我國最嚴格之排放標準(五氯酚500 µg/Nm³、戴奧辛0.1 ng-TEQ/Nm³、汞50 µg/Nm³)。由於

汞污泥在熱處理過程中會產生高濃度的SO₂，而濕式洗滌塔分別採用NaOH及Na₂CO₃吸收液對於氣流中SO₂均可達到96%以上的去除效率，並符合固定污染源最嚴格之排放標準(SO₂<100 ppm)。

本研究建立活性炭再生系統，採流動床式理念設計，活性炭吸附床中的球狀活性炭因重力往下移動至再生系統中，無氧條件下隨著反應時間增加，對戴奧辛及五氯酚的破壞效率愈高，對吸附於活性炭之戴奧辛及五氯酚的破壞效率可達98%以上，對於總汞可達99%以上的脫除效率，由於再生系統出口端含有高濃度的汞蒸氣，可將廢氣導回驟冷塔之入口端，藉由汞珠的回收將其去除，整個熱裂解系統中並無含汞廢棄物或汞污泥的產生，更能達到污染減量之目的。

Abstract

In this case study, contaminated soil containing extremely high concentrations of PCP, PCDD/F and mercury in An-shun sites is selected for remediation test. Different characteristics of these contaminants have caused the difficulty of effective remediation. For better remediation of contaminated soil in An-shun site, a continuous pyrolysis system (CPS) is designed and applied in this study. In 2013, CPS had been proved for effective removal of PCDD/Fs and mercury from contaminated soil. In this stage, contaminated soils with extremely high PCDD/F and mercury concentrations, which are 249,000 ng-TEQ/kg and 1,860 mg/kg, respectively, and mercury-containing sludge (2,220 mg/kg) are selected for treatment by CPS. Regarding the removal efficiencies achieved with CPS, PCDD/Fs and mercury are efficiently removed with increasing

operating temperature of CPS and retention time of contaminated soil. At 750°C and 60 minutes retention time, destruction efficiencies of PCDD/Fs and PCP are higher than 98% and removal efficiency of mercury is higher than 99%. After long-term test with 12 days, good performance of CPS is still effectively maintained and the residual concentrations of PCDD/Fs and mercury in remediated soil are lower than the promulgated limits of Taiwan (PCDD/Fs: 1,000 ng-TEQ/kg; Mercury: 20 mg/kg).

For air pollution control devices, baghouse (BH), quench tower (QT), multi-layer adsorption system (MAS) and wet scrubber (WS) are adopted for controlling air pollutants discharged from CPS. BH can efficiently remove particulate matter and maintain <3 mg/Nm³ of particle concentration in the exhaust after BH. 90% mercury is recovered by QT and elemental mercury significantly aggregates in the condensate of the QT. Regarding to MAS, three layers of bead-shaped activated carbons (BACs) are adopted in this study and replacement rate of 2 cm-BAC/day is suggested for effective emission control. BH, QT and MAS can efficiently remove PCDD/Fs and mercury to meet the emission limits (0.1 ng I-TEQ/Nm³ for PCDD/Fs and 50 g/Nm³ for mercury). However, SO₂ is significantly found in the exhaust of CPS with the remediation of mercury-containing sediment. WS with NaOH or Na₂CO₃ as absorbent can efficiently remove more than 90% SO₂ in the exhaust of the MAS.

For continuous operation of MAS, a system for BACs' regeneration is built with moving bed system. At oxygen-free condition (N₂ as carrier gas), increasing retention time is useful to enhance destruction efficiencies of PCDD/Fs and PCP adsorbed on BACs (>98%) and removal efficiency of mercury adsorbed on BACs (>99%). Although vaporized mercury is discharged from the regeneration stream of BACs, exhaust of regeneration system is introduced into the

flue gas before quench tower. Vaporized mercury can be efficiently recovered. Finally, CPS applied in this study can efficiently remove PCDD/Fs, PCP and mercury from contaminated soil and APCDs can also efficiently control the pollutant emission. Furthermore, secondary pollutants including BAC waste and condensate from quench tower are not discharged from CPS+APCDs. Experimental results indicate that the CPS+APCDs developed in this study is a powerful and environment-friendly remediation technology for removing PCDD/Fs and mercury from contaminated soil and sediment.



[070] 利用奈米零價鐵微粒去除DNAPLs含氯有機污染物之技術研發 及地下水污染場址整治工程評估

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中文摘要

隨著臺灣科技工業的發展，在眾多工業製程中，含氯有機化合物因具有特殊物化特性，因此被廣泛使用。而近年來意外排放和使用過程中不當處置，造成含氯有機化合物大量進入土壤和地下水層中，且含氯有機化合物具有毒性，對人體更具有致癌性及致基因突變性，因此對環境的衝擊格外受到重視。本研究之主要目的是探討利用化學還原法製備奈米零價鐵顆粒(zero-valent iron nanoparticles, ZVINS)，經由表面包覆有機分子使ZVINS懸浮於水相中並將其應用於受DNAPL污染物污染之現地場址整治，其結果藉由場發掃描式電子顯微鏡(FE-SEM)、X光粉末繞射儀(XRD)及穿透式電子顯微鏡(TEM)測試檢測ZVINS懸浮溶液與DNAPL污染地下水體反應後之變化與結構分析，以期望進一步了解利用ZVINS懸浮溶液及地電阻顯影儀(RIP)處理現地場址污染地下水體之效能及可行性。

在實驗部分，實驗室中所合成之ZVINS顆粒於氫氣下經燈罩法烘乾並惰化後XRD圖譜文獻資料相符，且自行合成之ZVINS顆粒在FE-SEM圖中為粒徑為20~50 nm之球形顆粒；而經聚乙基亞胺(PEI)改質後之ZVINS顆粒其XRD圖譜文獻資料相符，但在 $2\theta = 34.36^\circ$ 處多出一與PEI鍵結後之訊號，而由其FE-SEM圖可判定經PEI改質後之ZVINS顆粒粒徑在50~80 nm間，較未改質之前小。將表面包覆PEI之ZVINS懸浮溶液利用直接注入法應用於現地受污染場址試驗中，於注入後場址內各井位之7種主要DNAPL污染物濃度均呈現降低的趨勢，可見表面包覆PEI之ZVINS懸浮溶液隨著地下水流動至污染物殘留層將DNAPL污染物還原成無毒害之產物。此外，於實驗室中利用ZVINS懸浮溶液

與各井污染地下水體模擬現地反應後，由其測驗之結果與地下水管制項目及管制標準比較後，7種主要有機污染物其濃度經處理1天後濃度也大幅降低，甚至低於飲用水管制標準值，其結果與現地場址試驗結果相符。由實驗室中ZVINS處理各井位抽取污染水樣試驗之FE-SEM及TEM分析，可知未改質之ZVINS顆粒反應後其粒徑大小在20~50 nm之間且聚集嚴重，而表面經PEI高分子包覆改質之ZVINS顆粒其粒徑大小在50~80 nm之間。XRD、ESCA及同步輻射分析中未改質或改質之ZVINS顆粒與污染水樣反應一天後氧化為 Fe_3O_4 。可見在現場水井投入ZVINS懸浮液後，部分污染物濃度已明顯降低。實驗室測出之導電度趨勢與地電儀影樣圖判定結果相符，顯示投入之ZVINS懸浮液，確實已在地底下隨著水流移動，進而和污染物plume作用。由施測結果可知，表面PEI改質後ZVINS懸浮溶液與DNAPL污染物產生之氧化鐵為低導電率，表示地層中電阻率增加亦有表面PEI改質後ZVINS懸浮液，與DNAPL反應而還原降解所造成。本計畫已初步建立ZVINS粉體及地電阻顯影儀現地處理地下水污染之完整操作程序及技術，進而提升國內地下水污染之現地處理技術，並可做為日後污染場址的整治復育之參考，落實整治技術之本土化目標。

Abstract

In Taiwan, remediation of sites contaminated by dense non-aqueous phase liquids (DNAPLs), especially chlorinated organic compounds, is a significantly priority in the environmental field because of their widespread use in many applications. Therefore, the main objectives of the present study were to prepare surface-modified zero-valent iron

nanoparticles (ZVIN) by coating polyethyleneimine (PEI) nanofilms and *in-situ* DNAPLs-contaminated groundwater remediation. Characterization of ZVIN or PEI/ZVIN reacted with DNAPLs-polluted groundwater were also investigated by field emission-scanning electron microscopy (FE-SEM), X-ray powder diffractometer (XRD), transmission electron microscopy (TEM), electron spectroscopy for chemical analysis (ESCA) and resistivity image profiling (RIP). In addition, field tests of this study were also carried out to provide information concerning the removal efficiencies and feasibilities in the chemical reductive treatment processes for DNAPLs contaminated sites, and determined if further developments would be warranted.

Experimentally, from FE-SEM microphotos and TEM images, spherical ZVIN with a diameter of 20-50 nm were measured. ZVIN having a strong characteristic peak of PEI at $2\theta = 34.36$ was investigated by XRD patterns. The specific surface area of ZVIN measured by BET isotherms is $34.7 \text{ m}^2/\text{g}$. From ESCA spectra, the proportion of Fe/O is 1.33 on ZVIN surface including the main species of FeO, Fe_3O_4 , and FeSO_4 . In addition, ZVIN coated with PEI (PEI/ZVIN) in the form of spherical particles with a diameter of 50-80 nm were also measured by FE-SEM and TEM microphotos. PEI/ZVIN has a strong characteristic peak of Fe(0) at $2\theta = 44.83$ identified by XRD patterns and surface area of $53.4 \text{ m}^2/\text{g}$ measured by BET isotherms was also investigated. From ESCA spectra, the proportion of Fe/O is 0.39 on PEI/ZVIN surface including the main species of Fe_3O_4 and FeSO_4 . By using resistivity image profiling (RIP), the conductivity data of modified ZVINs solution and sampling groundwater were similar. It indicated that lower conductivity of FeO species was found. Obviously, the data of *in-situ* remediation

indicated that concentrations of DNAPLs after using well-injection method were notably reduced. In addition, RIP can elucidate complex subsurface DNAPLs structures by dense sampling of resistivity variation at shallow depth. The combinative technology of floating surface-modified ZVINs and RIP technique would be economically and environmentally attractive. Furthermore, the simulation calculation, basic engineering design, and economic estimation of this *in-situ* remediation technique were also performed to develop a domestic *in-situ* remediation technology in the near future. .



[071] 利用耐鹽嗜油菌與微生物富集技術強化石油碳氫化合物污染 土壤之生物復育

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中文摘要

本研究為篩選分離柴油與甲苯降解菌，並以聚合酶連鎖反應放大菌種之 16S rDNA，進行菌種之鑑定，進而探討其生理與降解特性、乳化特性、重金屬之吸附競爭或抑制代謝、不同營養源添加之共同代謝等，瞭解此等雙效微生物在土壤中降解碳氫化合物與耐受重金屬銅、鋅的行為、環境影響因子等，並應用利用實驗室集的微生物富集技術強化污染土壤之界面活性劑洗提與生物復育運作，以提供後續實際污染環境整治的參考。

研究獲致具體成果如下：

1. 篩選分離本土甲苯降解菌6株，柴油降解菌4株，共有10株，甲苯降解菌分別為T5、T6、T7、T10、T11與T12；柴油降解菌分別為D2、D5、D6及D7。
2. 研究結果顯示本研究所篩選出的部分菌株具有良好的甲苯降解效能，菌株T6、T7與T11具有較佳之甲苯降解能力。
3. 研究結果顯示本研究所篩選出的菌株具有良好的柴油降解效能，菌株D2、D5與D6具有較佳之柴油降解能力，菌株D5具有最佳之乳化效果。
4. 本研究篩選之甲苯分解菌均能忍受250 ppm Zn，柴油分解菌D2、D5與D7能忍受250 ppm Zn，高Zn濃度則對多數菌種產生抑制作用，其中T7與D5可忍受高濃度(500 ppm)；菌種之生長較易受銅影響，篩選出之菌種中僅以T7與D5能耐受高濃度Cu。本研究所分離的菌株對重金屬之吸收有良好效能。
5. 菌種之16S rDNA鑑定結果發現，主要的菌種是 *Achromobacter insolitus* (D2)，*Candida spp.* (D5)，*Xanthobacter polyaromaticivorans* (D6 and T12)，*Ochrobactrum intermedium*

(D7)，*Streptomyces caelestis* (T1 and T5)，*Gordonia amicalis* (T6)，*Brevibacillus brevis*(T10)，*Bacillus fumarioli*(T11)，另外，T7經鑑定為真菌類。

6. 本研究利用不同性質土壤，模擬甲苯或柴油污染，利用界面活性劑進行洗提，評估界面活性劑濃度、用量、洗提時間、界面活性劑重複使用對洗提效果之影響，結果顯示本研究選用之界面活性劑對不同性質土壤皆有洗提效果，惟其洗提效果高低與土壤性質有關。
7. 本研究建構實驗室微生物富集反應器系統，並於反應槽中投入本研究分離純化的3種本土柴油降解菌株 (D2、D5、D6)，用以處理模擬柴油污染土壤經界面活性劑洗提後之混合液。研究結果顯示，實驗室微生物富集反應器系統對COD的處理效果達95-97%之間，穩定且有效地處理柴油-界面活性劑洗提液。

Abstract

This project is to screen and isolate the hydrocarbonoclastic bacteria that might be suitable for bioremediation purposes to remove toluene or diesel oil from soil in presence of zinc and copper. To achieve this goal, batch cultivation of bacteria and 16S rDNA is employed to identify the target bacteria. Several sub-study such as the characteristics of isolated bacteria, degradation performance of petroleum-hydrocarbon, biosorption of heavy metals and its inhibition of bacterial metabolism, the effects of different nutrients on co-metabolism and also a lab scale of microorganism enrichment reactor system is conducted to evaluate and enhance the treatment of

surfactantwashing liquid
containingpetroleum-hydrocarbon.

1. This project has already screened and purified 6 different kinds of toluene-degrading bacteria (T5, T6, T7, T10, T11 and T12) and 4 different kinds of diesel oil-degrading bacteria (D2, D5, D6 and D7) from different sources of oil slurry.
2. Toluene-degrading bacteria T6, T7 and T11 have the high performance on toluene degradation.
3. Diesel oil-degrading bacteria D2, D5 and D6 have the high performance on diesel degradation.
4. All toluene-degrading bacteria and diesel oil-degrading bacteria D2, D5 and D7 obtained from this study have Zn tolerance of 250 ppm, the further studies showed that T7 and D5 can tolerate high metal levels of Zn and Cu. The main mechanism of metal removal in this study is absorption.
5. Results of 16S rDNA approach showed that the dominate bacteria are *Achromobacter insolitus* (D2), *Candida* spp. (D5), *Xanthobacter polyaromaticivorans* (D6 and T12), *Ochrobactrum intermedium* (D7), *Streptomyces caelestis* (T1 and T5), *Gordonia amicalis* (T6), *Brevibacillus brevis* (T10), *Bacillus fumarioli* (T11), strain T7 was identified as fungus by stain method.
6. The performance of surfactant on the flushing of diesel oil or toluene polluted soil was evaluated based on the parameters of surfactant concentration、volume、washing time and the reuse of surfactant. Ethylene Glycol mono-Butyl Ether is available for the flushing of CC, CF and SI soils with diesel or toluene and the performance depended on the property of soil.
7. Lab scale microorganism enrichment reactor system was conducted for the treatment of washing liquid, the results showed that the system was operated



[072] 利用細菌生物感測器快速篩測底泥及地下水現場污染物

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中文摘要

國內部份河川污染嚴重，然而底泥中毒性物質之污染程度與其對生態之影響，尚無法正確的評估，尤其是底泥中重金屬較易因環境擾動而釋出至水域環境與地下水，甚至直接或間接影響到生態系統及人類健康。因此，開發靈敏且降低成本之快速篩測方法是急需迫切之議題。鑑於此，本研究計畫目的為建構一系列專一性細菌生物感測器 (biosensors)，用以快速篩測底泥及地下水現場之重金屬(砷、汞與鎘)。本研究計畫已成功建構攜帶不同報告基因 (report gene) 之重金屬專一性細菌生物感測器，用以偵測重金屬砷、汞與鎘，其中所使用之報告基因包括綠色螢光蛋白 (green fluorescent protein, *gfp*)、*lacZ* 及 *luxCDABE*。

本研究利用基因工程技術，總計建構7個專一性的細菌生物感測器，其中包括：2個針對砷檢測的 *lacZ* 及 *luxCDABE* 生物感測器；2個針對鎘檢測的 *lacZ* 及 *luxCDABE* 生物感測器；3個針對汞檢測的 *gfp*、*lacZ* 及 *luxCDABE* 生物感測器。加上之前本研究室建構的2個針對砷及鎘檢測的 *gfp* 生物感測器，總計使用9個砷、汞與鎘生物感測器分析檢測環境樣品。

研究結果顯示，以 *gfp* 與 *luxCDABE* 為報告基因之細菌生物感測器對於重金屬檢測有較低之檢測極限及較高之穩定性，可以在多重污染物環境中偵測特定重金屬。本研究計畫所建構之細菌生物感測器不僅培養方便並且可以快速篩測重金屬。再者，成本分析結果顯示細菌生物感測器之檢測成本相較於化學分析法較為便宜。

整體而言，本研究計畫證明細菌生物感測器可以適用於偵測受污染底泥與地下水樣品中重金屬之生物有效性 (bioavailability)，此資訊將有助於更準

確的風險評估，提供環保署及相關單位建立更有效的環境監測策略；雖然利用細菌生物感測器對於環境相關污染物檢測的實際應用性，仍須後續更深入的研究，本研究計畫研發之細菌生物感測器對於環境相關污染物樣品檢測具有運用的潛力。本研究計畫希冀所建構之細菌生物感測器，有助於建立管理政策與預警系統，以維護環境品質。

Abstract

Certain rivers in Taiwan are heavily polluted. However, the toxicity and ecological impact of pollutants in the sediment are difficult to accurately assess. In particular, heavy metals in the sediments might be released into the aquatic environment and groundwater directly or indirectly influencing ecosystem and human health. Therefore, there is urgent need to develop sensitive and inexpensive methods for rapidly detecting pollutants in the environments. Hence, the goal of this grant was to establish a set of specific bacterial biosensors to detect heavy metals (As, Hg and Cd) in the sediment and groundwater.

In the present study, heavy metals-specific bacterial biosensors carrying different reporter genes (*gfp*, *lacZ*, and *luxCDABE*) were successfully developed to measure As, Hg, and Cd, respectively. Using genetic engineered techniques, 7 bacterial biosensors have been constructed. This includes (1) two arsenic specific biosensor carrying *lacZ* and *luxCDABE*, respectively; (2) two cadmium specific biosensor carrying *lacZ* and *luxCDABE*, respectively; and (3) three mercury specific biosensor carrying *gfp*, *lacZ* and *luxCDABE*, respectively. By combining our previously developed arsenic and cadmium biosensors using *gfp* as reporter gene, there are 9 bacterial biosensors in total for further analysis of environmental



samples.

Results from this project showed that *luxCDABE*-based and *gfp*-based biosensors were more-sensitive and stable to detect As, Hg, and Cd. In addition, the bacterial biosensors could be cultured easily and rapidly providing a cost-effective approach.

In summary, our results demonstrated that the bacterial biosensors are useful and applicable in determining the bioavailability of heavy metals in contaminated sediment and groundwater samples. This information is important for more accurate risk assessment in which the EPA and related agencies can employ effective and inexpensive environmental monitoring approaches to assess heavy metals contamination levels as well as serve as warning system against future heavy metals pollution.



[073] 利用微生物呼吸試驗探討生物通氣法對柴油污染土壤復育之成效

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中文摘要

本計畫於實驗室建立高濃度(約 20,000 mg/kg)柴油污染土壤風力驅動式生物通氣(Wind-driven Bioventing)模場,使用之土壤經質地分析為砂質壤土,適合以生物通氣設備進行污染整治,試驗中同時使用氣泡式呼吸儀(Bubble Respirometer)搭配生物泥漿法進行土壤中微生物活性監測,探討生物通氣法整治柴油污染土壤的成效與微生物活性之關係。經模場添加具柴油降解能力之三種微生物及適量營養鹽後,各通氣組皆呈現降解趨勢。Bacillus subtilis 菌(BC)及Pseudomonas putida 菌(PS)於試驗3日後之污染物濃度殘餘率(C/C0)約為0.65,而Achromobacter xylosoxidans 菌(F3B)僅約為0.80。經過試驗30日後,三種微生物混菌組(ALL)促使污染物濃度大幅降低,污染物濃度殘餘率可達0.30,相較其餘組別有最佳的降解趨勢。以氣泡式呼吸儀於降解期間對各組別進行呼吸試驗及監測,將每批次試驗開始24小時間攝氧率統計作圖可得一活性曲線,藉由曲線變化能協助操作人員評估微生物活性趨勢。由呼吸試驗結果顯示,生物通氣模場自營養鹽添加後,BC組及PS組的微生物活性可連續提高2週、F3B組活性可連續提高3週、ALL組活性則能連續提高4週後才逐漸降低。對照攝氧率活性曲線與柴油濃度變化圖後可發現,兩者在曲線中能呈現一定程度的相關性,顯示攝氧率活性曲線應能作為微生物降解柴油污染過程中成效的評估方式。

Abstract

In this study, a wind-driven bioventing pilot for the high-concentration (about 20,000 mg/kg) diesel contaminated soil was established in the laboratory. According to the analysis, the soil adopted belongs to the sandy loam, which is

suitable for the contamination remediation by using the bioventing equipment. During the experiment, a bubble respirometer complete with the bioslurry method was used to monitor the microbial activity in soil, in order to explore the relationship between the effectiveness of the diesel contaminated soil remediation with the bioventing method and the microbial activity. All venting groups presented the degradation tendency after three kinds of microorganisms having the diesel degradation ability and appropriate amount of nutrient sources were added in the pilot. The remaining ratio of diesel concentration (C/C0) of Bacillus subtilis (BC) and Pseudomonas putida (PS) was about 0.65 after 3 days of experiment and that of Achromobacter xylosoxidans (F3B) was only about 0.80. After 30 days of experiment, the mixed of the three kinds of microorganisms (ALL) resulted in the significant reduction of the contaminant concentration and the remaining ratio of contaminant concentration able to reach 0.30, which is the optimal degradation tendency compared with the rest of individual microorganism. The monitoring of microorganisms respiration were carried out with a bubble respirometer on each microorganism during the diesel degradation. An activity curve was plotted by summarizing and mapping the oxygen uptake rates during the first 24 hours of each batch of experiments. Using the curve variance, the microbial activity tendency can be assessed. The respiration tests showed that after the addition of the nutrient sources in the bioventing pilot, the microbial activity of BC and PS increased continuously for two weeks; the activity of F3B increased continuously for three weeks; and the activity of ALL only decreased gradually after four weeks of continuous increase. Comparison of the oxygen uptake rate



activity curve and the diesel degradation tendency showed that both can present a certain degree of correlation in the curves, and it is shown that the oxygen uptake rate activity curve can be used as the effectiveness assessment method in the process of diesel contaminant degradation by the microorganisms.

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治



[074] 利用鐵鋁複合金屬反應牆去除地下水污染物之 廠型規模管柱測試評估計畫

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中文摘要

透水性反應牆(Permeable reactive barrier, PRB)為近20年來最成功的地下水復育技術之一，由於施工容易，且操作成本低廉，已逐漸取代傳統之「抽出再處理技術」(Pump-and-treat)。目前最常用之填充材質為零價鐵金屬，兩者之搭配開創了地下水處理的成熟技術。然而，這類的反應牆受限於零價鐵的還原能力，僅能去除還原性污染物，及部分可被吸附之重金屬，對於地下水中常見的氧化性污染物無處理效果，殊為可惜。本計畫提出以鐵鋁複合金屬取代零價鐵金屬之規畫構想，利用鐵鋁複合金屬獨特的可同時氧化與還原之能力，進行全方位之地下水污染去除整治研究。

本計畫內容主要包括兩部分，分別為連續流管柱實驗以及實驗室模場實驗，控制因子包括污染物(氧化性污染物和重金屬)、水力因子(孔隙率、土壤組成和流速)和材料因子(配比和重量)，同時完成大量製造鐵鋁複合金屬技術之開發。實驗結果顯示，在連續流管柱實驗中，客製化PVC管柱長100 cm，內徑5 cm，重金屬移除實驗中操作流速為11 mL/min，Fe/Al填充量為450 g，結果顯示其對銅的移除具有良好的效果，累計時間為99天，處理水量達1568.16 L，經計算鐵鋁複合金屬對Cu²⁺的單位處理量為284.0g/kg。而在氧化性污染物的部分，以甲酸為污染物，操作流速為22 mL/min，Fe/Al填充量為450 g，因執行時間之限制未達貫穿即終止實驗，累計時間為32天，處理水量為506.88 L，移除率維持在50%，其單位處理量為48.9g/kg。實驗室模場實驗之模組以長100 cm、內徑100 cm的客製化模組為反應槽，污染物由模組下方進流，上方出流，模組內進流端以不鏽鋼分配管連接，使污染物可均於分佈於模組內，

Fe/Al填充量為80 kg，流速為145 mL/min，每日處理水量為208.8 L/day，因執行時間之限制未達貫穿即終止實驗，累計時間為32天，累計處理水量為6681.6 L，Cr⁶⁺移除率維持在100%，Cr⁶⁺之處理量總計為334.1 g。

Abstract

Permeable reactive barriers (PRBs) represent the most successful groundwater remediation technology in the recent 20 years. It outmatches the conventional Pump-and-Treatment technology because of the low cost and easy-to-operate. Among many packing materials, zero-valent iron (ZVI) is the most common one applied in the PRBs. However, ZVI-PRBs are applied only to the reducible contaminants such as chlorinated organics and adsorbed heavy metals. For oxidative contaminants such as petroleum chemicals, ZVI-PRBs is unable to deal with. In this proposal, we propose the use of aluminum-iron bimetal (Fe/Al) as the packing materials to integrate with PRBs (FeAl-PRBs) for effective remediation of a wide variety of contaminants including reducible, and oxidative contaminants and heavy metals.

This project consists of two parts, namely continuous column experiments and scale-up module experiments. The control factors include pollutants (oxidative contaminants and heavy metals), hydraulic factor (porosity, soil composition and flow rate) and soil types. In the continuous column experiment, customized PVC column was used (length of 100 cm and inside diameter of 5 cm). In the scale-up module experiment, customized column was used (length of 100 cm and inside diameter of 100 cm). In the heavy metal removal experiment, the amount of aluminum-iron bimetal is 450 g,



flow rate is 11 mL/min, and operating time is up to 99 days. The volume of treatment water accumulated to 1568.16 L. The capacity is 284 g/kg. In the oxidative contaminants experiment the formic acid is used as probe pollutant, the amount of aluminum-iron bimetal is 450 g, and flow rate is 22 mL/min, and operating time is up to 32 days. The volume of treatment water accumulated to 506.88 L. The formic acid removal efficiency is 50% until now, and the capacity is 48.9 g/kg. The performance of the material has not been invalidated. In the scale-up module experiment, the chromium (IV) is used as probe pollutant. , the amount of aluminum-iron bimetal is 80 kg, flow rate is 145 mL/min, and operating time is up to 32 days. The volume of treatment water accumulated to 6681.6 L. The chromium (IV) removal efficiency is 100% until now. The performance of the material has not been invalidated.



[075] 汽油污染場址之化學指紋鑑定研究

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中文摘要

隨著科技的進步與發展，環境鑑識技術所使用之分析技術與儀器設備也日趨成熟，但國內除環境檢驗所與中油探採研究所外，對於應用環境法醫技術於石化產品造成之土壤與地下水污染之案例及判識經驗相對有限，對於建制石化產品造成之地下環境污染鑑識工作所需之基本資料庫及相關作業規範屬於發展階段，為判定污染源，需掌握國內油品之基本物理及化學資訊，而此基線資訊之獲得無法單純仰賴石化業者主動提供，必須仰賴學術單位之積極建立。

本研究計畫團隊結合學術研究單位及長期進行土壤及地下水分析的國內最大環境檢驗公司，針對國內土壤及地下水污染常見之汽油油品污染，建立汽油污染場址相關的環境鑑識分析技術。本計畫目的為持續發展環境法醫技術，應用於國內常見之汽油污染場址的污染源判釋，評估汽油污染場址之相關環境法醫鑑識分析技術，並探討風化過程對油品化學指紋特性及鑑識之影響，以利國內石化污染場址污染物來源的研判及追蹤。各分項目的如下所述：

- (1) 建立及整合汽油組成、物理及化學特性、層析圖譜基本資料。
- (2) 建立汽油油品污染鑑識指標化合物及參數。
- (3) 評析汽油油品污染場址的可行性環境鑑識流程。
- (4) 分析風化過程對汽油化學指紋特性及鑑識之影響。
- (5) 評估汽油及柴油污染場址指紋及資料鑑識分析技術之適切性。

在建立汽油油品基本資料庫工作上，除了彙整過去油品相關資料外，並進行汽油(中油及台亞)及汽油混和柴油基本特性分析，並且建立油品污染鑑識指標化合物及參數。本研究將風化條件

分為三種系統，一為實驗室製備的汽油及汽油混和柴油污染土壤放置室溫(25°C)下避光且密閉之環境，二為實驗室製備的汽油及汽油混和柴油污染土壤放置室溫(25°C)下避光且開放之環境，三為實驗室製備的汽油及汽油混和柴油污染土壤放置室外，平均溫度為24°C且自然光照之環境，同時以不同有機碳含量之污染土壤進行室外實驗，觀察風化作用對methyl tert butyl ether (MTBE)、benzene、toluene、ethylbenzene、xylenes、n-propylbenzene、1,2,3-trimethylbenzene、1,2,4-trimethylbenzene、1,3,5-trimethylbenzene、1,3-diethylbenzene、1,2,4,5-tetramethylbenzene及1,2,3,5-tetramethylbenzene等14項汽油指標化合物之影響，並配合總石油碳氫化合物濃度(total petroleum hydrocarbon, TPH)、碳優指數(carbon preference index, CPI)、風化指標(weathering index, WI)、苯加甲苯對應乙苯加二甲苯比例(benzene+toluene/ethylbenzene+xylenes, B+T/E+X)以及methylnaphthalene ratio (MNR)等比值進行探討。

結果顯示，當風化時間越長，汽油污染土壤其特徵參數TPH濃度有逐漸減少的趨勢，以中油98汽油污染土壤為例，其TPH濃度由5229 mg/Kg降為319 mg/Kg，原因是n-alkanes較易受風化作用影響，而風化指標(WI)隨著時間也有遞減的趨勢，由3.97降為0.57，表示汽油中低碳數化合物因自然風化作用而有減少的現象。

針對評估風化過程對汽油化學指紋及鑑識之影響，風化鑑識技術應用於國內污染場址樣品之洩漏來源鑑別，本計畫結果顯示國內兩間油品供應商汽油中所含化合物比例皆不相同，其中烷基化naphthalene之指紋圖譜也有極大之差異，於中油各級汽油中，皆明顯含有C0-naphthalene、C1-naphthalene、C2-

naphthalene及C3-naphthalene，台亞則僅含有C0-naphthalene及C1-naphthalene，此差異性經過75天自然風化後仍然存在，但在經過165天放置室外之自然風化後，中油各級汽油中含量已有明顯改變，因此應用該鑑識工具時，應先確認其風化作用影響程度，以提高判釋之準確性，此判釋方法以及本研究所建立之汽油指標化合物，未來可依不同風化程度選擇作為油品辨識之佐證工具。

本計畫之汽油污染場址環境法醫鑑識技術相關的分析技術應用於實場樣品後，其結果顯示本計畫選用之各項鑑識指標化合物及比值參數皆能應用於評估風化過程對市售汽油化學指紋特性及鑑識之影響，以及建立鑑識流程及鑑識指標化合物。整體而言污染源的鑑定工作，宜搭配環境歷史背景調查、指紋圖譜、芳香烴化合物分析等資料綜合研判將能得到較正確的鑑識結果。

Abstract

The advances in petroleum hydrocarbon fingerprinting and data interpretation methods and approaches in the last two decades have now allowed for detailed qualitative and quantitative characterization of spilled oils. Chemical fingerprinting is a powerful tool for hydrocarbon source identification and differentiation, when it is applied properly. However, in many cases, particularly for complex mixtures of fuel products or extensively weathered and degraded fuel residues, there is no single fingerprinting technique which can meet the objectives of forensic investigation and quantitatively allocate hydrocarbons to their respective sources.

The objective of this project is to develop proper chemical analysis methodologies which are feasible to characterize and identify gasoline contaminated sites from environmental forensics prospect. In detail, the following tasks were included: (1) to obtain generic features and chemical composition of gasoline from Chinese Petroleum Company (CPC) and Formosa (FOR), (2)

to establish tiered analytical approach, (3) to develop the fingerprinting and data interpretation techniques including protocol of identifying gasoline spill, (4) to evaluate effects of weathering on hydrocarbon fingerprinting, recognition of distribution patterns of petroleum hydrocarbons, fuel type screening and differentiation, and (5) to establish source-specific marker compounds, determination of diagnostic ratios of specific fuel constituents, application of various statistical and numerical analysis tools, and application of other analytical techniques.

Various homologous series of hydrocarbons including volatile and semivolatile range of gasoline hydrocarbons were examined. In order to differentiate the chemical composition and to characterize aging processes of different grades of gasoline, the following parameters were measured: (1) benzene, toluene, ethylbenzene, and xylenes (BTEX), (2) C3 to C10 volatile hydrocarbons (3) C8 to C12 n-alkanes, (4) alkylbenzene and alkyl-naphthalene, (5) alkylcyclohexanes, and (6) oxygenated additives. Each one of these groups of hydrocarbons has a different tolerance to environmental alternation by evaporation, dissolution, and biodegradation.

For weathering effect studies, change of chemical constituent and biodegradation effect of gasoline contaminated soils are important factors to be considered, especially when there is a prolonged period of weathering processes. Methyl tert butyl ether (MTBE), benzene, toluene, ethylbenzene, xylenes, n-propylbenzene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, 1,3-diethylbenzene, 1,2,4,5-tetramethylbenzene and 1,2,3,5-tetramethylbenzene were recognized as indicator compounds in gasoline. Weathering effect onto 14 compounds along with total petroleum hydrocarbon (TPH), carbon preference index (CPI), weathering index (WI), benzene+toluene/ethylbenzene+xylenes (B+T/E+X) and methylnaphthalene ratio



(MNR) were evaluated.

The results indicated that TPH decreased with longer weathering time. TPH concentration decreased from 5229 mg/kg to 319 mg/kg in CPC gasoline (octane research number 98). It was contributed by partial depletion of n-alkanes. Weathering index demonstrated the similar trend from 3.97 to 0.57. It was indicated by loss of n-alkanes and branched alkanes.

To evaluate effects of weathering on hydrocarbon fingerprinting, and develop proper chemical analysis methodologies to characterize and identify gasoline contaminated sites from environmental forensics prospect. Composition difference of gasoline was observed in two major companies. Naphthalene, C1-naphthalene, C2-naphthalene, and C3-naphthalene were detected in all grades of CPC products. However, only C0-naphthalene and C1-naphthalene were found in FOR. With 180 days of weathering effect, such difference was existed. It may be used to discriminate between different samples of gasoline. While CPC gasoline (octane research number 98) with 165 days of weathering effect, it was contributed by partial depletion of C2-naphthalene. Therefore it is proper to confirm the impact of weathering effect for increasing the accuracy during application of the forensic tools.

After the project of gasoline contaminated sites environmental forensics technology applied to the real samples. The results showed that each biomarkers and ratios in the project can evaluate weathered process on the effect of the Chemistry fingerprint characteristics of commercially available gasoline and forensics. To establish the fingerprinting and data interpretation techniques including protocol of identifying gasoline spill. Continuous tasks will be conducted to obtain information on gasoline type recognition patterns and on the degradation level,

allowing for an estimate of residence time in gasoline contaminated soil. It is anticipated that information generated in this study will be adopted by decision makers for evaluation of liability of cleanup in gasoline contaminated sites in Taiwan.

[076] 典寶溪底泥中之新興污染物流布調查及新穎現地整治技術開發

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中文摘要

本專案研究旨在調查典寶溪底泥中 8 種鄰苯二甲酸酯類、11 種鄰苯二甲酸酯類代謝物、18 種抗生素藥物類及 10 種非抗生素藥物類之殘留濃度，並嘗試利用奈米級施威特曼石/過氧化氫氧化程序結合電動力法（簡稱“新穎現地整治技術”）整治鄰苯二甲酸酯類及藥物類污染底泥，期盼未來建立一本土化可行的現地整治技術，以作為後續實場應用。於典寶溪底泥中鄰苯二甲酸酯類、鄰苯二甲酸酯類代謝物及藥物類之殘留濃度調查工作方面，已完成針對選定之 6 個採樣點位進行 4 梯次採集底泥樣品，綜合調查結果發現，於底泥中可檢出 3 種鄰苯二甲酸酯類、6 種鄰苯二甲酸酯類代謝物及 2 種藥物類化合物，於角宿支流角宿橋處檢出 mg/kg 濃度 (ppm 濃度) 等級之 DEHP 殘留量，其最高濃度 (2458 $\mu\text{g}/\text{kg}$) 為「底泥品質指標之分類管理及用途限制辦法」之管理下限值 1.25 倍。於新穎現地整治技術方面，電動力反應系統之底泥反應器所充填之底泥係採集自聖興橋處，試驗期間則將奈米級施威特曼石及過氧化氫分別以全部注入陽極槽液及 5 等分平均注入陽極槽與底泥反應室的 4 個注入孔中，並施加定電壓 (1.5 V/cm) 進行為期 14 日及 28 日期程之 6 組電動力試驗 (含空白試驗)。試驗結果顯示：(1) 於陽極槽液中注入的奈米級施威特曼石及過氧化氫 (簡稱“新穎氧化劑”)，可分別藉由電泳及電滲透流移向陰極端，同時藉由反應產生之 $\text{OH}\cdot$ 強氧化劑，可將底泥中標的污染物 (鄰苯二甲酸酯類及藥物類) 予以降解；(2) 電動力空白試驗結果發現，單純施加電場 (1.5 V/cm) 有助於標的污染物的去除；(3) 電極極性轉換有助於鄰近初始陰極端底泥中標的污染物之去除；(4) 新穎氧化劑以 5 等分平均注入陽極槽及底泥反應室的 4 個注入孔中可提

高標的污染物之去除效率；(5) 延長電動力反應時間，有助於標的污染物的去除；(6) 氧化劑會造成整治試驗底泥之結構尺寸變小，利用電動力法可有效輔助 nano-SHM/ H_2O_2 氧化劑傳輸於底泥顆粒間隙，增加標的污染物之去除效率；及 (7) 本研究採用之工法對於整治過程，其標的污染物在電極槽液之殘留濃度極低 (ppt 濃度等級)。另外，本專案研究所開發的新穎現地整治技術其操作成本粗估約低於 5,681 元/噸，具經濟可行性。由於電動力法之最大優勢為可直接進行現地污染整治 (節省龐大的開挖工程費用)，並適用於黏土質地的土壤及底泥，因此，本整治工法對於大規模現地整治鄰苯二甲酸酯類及藥物類污染底泥 (無論其質地為砂土、粉土或黏土) 應具有強大的應用潛勢。

Abstract

The objectives of this study are two-fold: (1) to investigate the residual concentrations of eight phthalate esters (PAEs), 11 phthalate esters metabolites (PAEMs), 18 antibiotics, and 10 non-antibiotics in sediment samples collected from the Dianbao River; and (2) to develop and establish a localized, feasible *in situ* remediation technology coupling nano-schwertmannite/ H_2O_2 process and electrokinetic process (in short, “the novel *in situ* remediation technology”) for the removal of PAEs and pharmaceuticals in sediments of the Dianbao River. To meet the first objective, four batches of sediment have been sampled at six sampling sites along the Dianbao River as originally planned. Three PAEs, six PAEMs, and two pharmaceuticals were detected in sediments collected. The level of parts per million (ppm) of residual di(2-ethylhexyl) phthalate (DEHP) was detected for sediment samples collected at Jiaosu Bridge. The relevant highest concentration (2,458 $\mu\text{g}/\text{kg}$) is 1.25 times



greater than the regulatory level of the “Regulations for Systematic Management of Quality Indices of Sediments and Their Use Restrictions” promulgated by Taiwan EPA. To meet the second objective, six tests including the blank test with a remediation time of 14 days or 28 days were carried out using the novel *in situ* remediation technology under an electric potential gradient of 1.5 V/cm for sediment samples collected at Shengxing Bridge. Test results are given as follows: (1) injection of nano-schwertmannite slurry and H₂O₂ (collectively, “novel oxidants”) into the anode reservoir would yield OH• that then would be diffused into the sediment compartment and further transported by the electroosmotic flow from the anode end toward the cathode to degrade PAEs and pharmaceuticals in the sediment if any; (2) an electric potential gradient of 1.5 V/cm would help the removal of PAEs and pharmaceuticals in the blank test, which no “novel oxidants” was added to the remediation system; (3) the use of electrode polarity reversal would enhance the removal of PAEs and pharmaceuticals in sediment near the cathode for the test having the addition of “novel oxidants” to the remediation system; (4) injection of equally divided dose of 10 mL “novel oxidants” into the anode reservoir and four injection ports on the top of sediment chamber would further enhance the removal efficiency; (5) an extension of treatment time from 14 days to 28 days is beneficial to the removal efficiency as expected; (6) an employment of electrokinetics would cure the problem of decreased pore water flow in the course of remediation due to the size of sediment particles decreased; and (7) the residual concentrations of target contaminants in the anode reservoir remained at ng/L level throughout the remediation period. It was also determined that “the novel *in situ* remediation technology” is economically feasible because of its low operating cost of no greater than 195.4 USD/ton. Thus, “the novel *in situ* remediation technology”

is a viable technology for the removal of phthalate esters and pharmaceuticals from river sediments in large scale operation.

[077] 底泥有機污染物生物有效性評估及應用

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中文摘要

本研究專案採用固相微萃取技術 (solid phase microextraction, SPME) 預測有機污染物在不同真實底泥特性下的生物有效性，針對底泥常見污染物多環芳香烴(PAHs)，擇1~4 環芳香烴為目標，探討不同來源底泥、底泥現地化學整治前後、混合2 種PAHs 以及不同污染齡(aging period)對生物有效性的影響，建立適用於底泥污染物生物有效性的量化評估方法，獲得底泥PAH 的真實暴露參數(亦即荷蘭RIVM生物有效濃度代表實際暴露濃度)，提出具體科學性數據，以落實土污法中關於風險評估的立法意旨及達成底泥管理的政策目標。

研究結果發現，隨著污染齡的增加生物有效性會大幅減少，而且生物有效性在污染齡四個月之內減少的趨勢最為顯著，此結果說明了有機污染物於底泥中有明顯的貯滯作用(sequestration)，此作用降低了污染物的有效性，進而相對降低了暴露風險。在底泥有否先經現地化學整治(採persulfate 化學氧化法)對於生物有效性評估值與實際微生物降解量之相關性方面，其整體評估結果 R^2 為0.97，推斷SPME 技術應用於實場時，並不會因底泥中有機質含量不同與是否先經過化學氧化處理而影響其預測準確性。至於底泥中存在2 種PAHs 時，SPME 技術對於整體有效量稍有低估，因為SPME 無法評估出微生物在雙重污染下會產生促進降解的現象，但是SPME 能準確預測單一污染的生物有效性，不受有機質含量、污染物共存與否的影響，顯示SPME 技術在特定條件下具有良好的應用性。

綜合前述，SPME 技術可應用於底泥PAH 的生物有效性評估，其生物有效量(即SPME 萃取量)可取代底泥污染物全量，作為風險評估過程中的實際暴露量，以計算合理風險值。此外，本研

究以PAH 生物有效量試算場址污染影響潛勢評估總分(TOL)值，結果TOL介於611~989間，均低於以全量計算所得(達1200 分以上)，顯示納入生物有效性考量將實質改變底泥管理策略。

Abstract

This research was to investigate the variations of bioavailability of polycyclic aromatic hydrocarbons (PAHs) in different sediment origins, before and after in-situ chemical remediation, PAH mixture, and aging periods. Solid phase microextraction (SPME) was employed to estimate the bioavailability of PAHs in sediments. One to four-rings PAHs in sediments were selected as the target pollutants. It is expected that optimal bioavailability measurement for the sediment pollutants could be established, through which actual exposure concentrations of PAHs in sediments can be obtained. Based on the emerging policy and legal framework in the Netherlands, i.e., representing actual exposure by bioavailable fraction, and specific scientific data and information derived from this project, suggestions regarding implementation of risk assessment in sediment management could be proposed to Taiwan EPA.

Experimental results indicated that the PAH bioavailability largely decreased as aging periods increased, especially for that aged 4 months. This result illustrated that PAH sequestration occurred significantly in sediments. The sequestration reduces bioavailability and in turn decreases exposure risk. With respect to the effects of chemical oxidation (using persulfate oxidation) on the assessment of PAH bioavailability, very good relationships were found in between the extracted amount and the biodegraded, with the correlation coefficient R^2 as high as 0.97. Under the presence of a PAH mixture, SPME



slightly underestimated the bioavailable fraction due to the occurrence of synergistic degradation. However, SPME accurately estimated the bioavailability of a single PAH regardless of the organic contents.

In conclusion, SPME can be implemented to the assessment of PAH bioavailability in sediments. The bioavailable amount (SPME-extracted), representing the actual exposure, should replace the total amount in risk assessment. Further, our calculation of TOL based on the bioavailable fraction of PAH indicated that the values (611-989) were below those calculated on the basis of the total amount (over 1200). The strategy on sediment management could be totally amended when taking bioavailability into consideration.

[078] 建立臺灣褐地評估資料庫暨研擬褐地再開發機制

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中文摘要

本研究目前已參考國外經驗並結合臺灣污染土地現況，建議適用於臺灣現況的褐地定義，即為「列管中之場址與高污染潛勢土地」，並制定褐地再利用的流程架構以及研擬褐地管理平台與財務、保險政策配套工具。本研究將褐地的再利用納入現有都市計畫、區域計畫與現行環評程序的脈絡，來建立褐地評估資料庫供政策決定者在制訂國土永續發展時作為參考。

此外，本研究篩選評估褐地再利用的環境、經濟、社會方面的關鍵因子與並制定其方法學，用以評估從整治到開發及再利用期間25年內三面向的影響情形。在環境衝擊面向，由都市代謝的角度，採用能資源耗用分析，來分析在不同再利用情境之下的成本效益與環境衝擊；在經濟與社會影響面向，採用成本效益分析。因此，本研究為建立各關鍵因子之褐地評估資料庫規劃流程如下：(1) 資料表單格式制定。(2) 資料庫建置與資料品質規劃。(3) 建立資料連結性。(4) 建立自動化運算模式。(5) 計算及結果呈現。後續將依此流程建立資料庫，並以廢棄工廠做為案例，以評估褐地再利用的土地最適當利用方式，目前設定不同再利用情境為住宅區(住宅大樓)、工業區(製造業廠房)、商業區(商業大樓)、與公共設施(太陽能板)。未來待資料庫擴充，將近一步發展為褐地地圖，以利政府於規劃國土永續發展時，能更妥善地規劃我國褐地再利用方式。

Abstract

After reviewing the legal definition of 'brownfield' of other countries and the context of contaminated land in Taiwan, the research team suggested the legal definition of brownfield for Taiwan should be 'High pollution potential

sites, pollution control sites, and pollution remediation sites. Also, the research team designed the roadmap (with the assessment database) embedded into the legal framework of the current urban/suburban plans and environmental impact assessment process for the reutilization of brownfield.

In this research, the 25 year period was designed for cleanup, construction, and reutilization. The research team selected several key factors to evaluate the reutilization of brownfields on environmental, economic, and social aspects.

Regarding the environmental aspect, from the approach of urban metabolism, the usages of selected material will be collected or calculated to assess the environmental impact. Regarding the economic and social impact, the cost-benefit analysis will be utilized for the calculation. In this research, one abandoned factory was selected as the case study. Four reutilization scenarios were selected: residential use (mansion), commercial use (commercial building), industrial use (factory), and public use (solar panels).

Finally, the research team designed the framework of the assessment database as following.

- (1) The establishment of the form of the database.
- (2) The establishment of of the database and data quality control.
- (3) The establishment of Geodatabase.
- (4) The establishment of Calculation Model.
- (5) Calculation and results.

In the future, with the expanding database, the research team could develop a brownfield map that covers a larger geographical region for the policy makers to plan the reutilization of brownfield with a better scope.



[079] 建立生物畜養系統評估水生生物對底泥毒性污染物質之
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中文摘要

本報告書為”建立生物畜養系統評估水生生物對底泥污染物質之生物累積及濃縮潛能”專案計畫之期中報告，內容包括利用畜養方式建立中型生態圈 (mesocosm) 之水生生物毒性研究系統，先藉由量化此中型生態圈主要生物類群生產量、生物量與食性組成資料，建構簡單的基礎ECOPATH 生態系食物網模式，以利進一步評估提供底泥污染物生物累積及食物鏈累積模場試驗之可行性。本計畫研究規劃基本架構為將食物鏈中不同階層之水生生物包括海水青鱗魚(水中)、蝦虎魚(底棲)、豐年蝦、以及植物浮游生物飼養於同一生態系統，暴露於由野外現場 (保力溪) 採回之相同底泥污染源之水域中，以相同環境因子並控制其食性及食量，避免由於人工餌料餵飼而干擾底泥污染造成之生物累積，設計控制野外環境因子變異，進行觀察分析持久性有機污染物 (多環芳香烴; PAHs) 之生物累積與生物放大現象，進一步評估食用污染水產品其對人體健康風險之污染濃縮潛能。此計畫於上半年 (五月至七月) 建立中型生態圈 (mesocosm)，並完成三十天暴露實驗，於期中報告分析整理出個食物鏈不同階層之水生生物逐日的生物量、攝食量、代謝量、及活存狀況，建構ECOPATH 水域生態系食物網模式，同時初步分析所採用於此生態圈之保力溪底泥中以及水中PAHs 含量，於計畫下半年進行分析暴露第七天及第三十天後之各種生物體內PAHs 濃度，於此期末報告評估底泥中PAHs 對於海水青鱗魚之生物累積與毒性濃縮潛能，藉由此研究畜養系統和生態毒物累積模式應用及其他毒性污染物質和其他水生物種。

Abstract

Establishment of the degree of pollution, the quality standard, is one of the most critical issues for the decision-making of soil and groundwater pollution remediation. The Taiwan EPA evaluate soil and groundwater contamination project plans in advance to identify field studies that would solve soil and groundwater pollution problems, conduct investigation on contaminated soil and groundwater, improve the assessment and remediation technology research and development work, make research results more widely used in field remediation, and develop more innovative remediation technologies for the purpose of improving the national quality of life. The study strategy of this proposed study is to design and build a medium-sized ecosystem (mesocosm) providing aquaculture with the entire food chain in the aquatic ecosystem, in which to assess the bioaccumulation of toxic persistent organic contaminants (POPs) from sediments. The basic framework of the research program is to put different trophic levels of the aquatic food chain in the same tank. Each trophic level of the experimented species will be exposed to the same sediment pollution levels (polycyclic aromatic hydrocarbons; PAHs), environmental factors, and diet that they would have been exposed to in the wild, in order to minimize variations in the analysis of accumulation and biomagnification of the PAHs. Also, we initially establish the ECOPATH model of the food web in this mesocosm system for further development of ECOTRACER model to assess the bioaccumulation and biomagnification of many other toxic persistent contaminants.

[080] 建置漁港底泥油品污染物生物指標篩選機制之研究

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中文摘要

過去十年間如美國及加拿大等相關單位提出“底泥品質準則”(SQGs, Sediment Quality Guidelines)以瞭解並保護水生生物免於化學性之污染。然我國直至100年才有正式相關之底泥標準法規,但此種法規對目前臺灣污染狀況之規範仍明顯不足,所以必預再依研究結果作為類似法規之研擬基礎。然而不論國內、外相關底泥監測污染物均以常見之 PAHs (Polycyclic Aromatic Hydrocarbons 多環芳香族碳氫化合物)與重金屬為主,對於能鑑定污染物種之生物指標(biomarker)而且追溯至確切污染源之環境法醫鑑定程序方式並未建制並列入相關底泥法規,所以未來我國應該著重於此類研究。基於我國區域特性與東部海岸特有而且僅存、寶貴之環境品質,在整個環境改變之前必預儘速建置相關之環境基本資料庫以規劃未來趨勢。因此,本研究目的為建構相關污染物之篩選機制,本計畫擬延續過往之長年監測研究,擬於東部二個最大且為代表性之二港口亦即花蓮縣花蓮漁港與台東縣成功漁港(或稱新港)進行港口底泥採樣並檢測出成功港與花蓮港底泥,要確切釐清污染源鑑識工作需在相對區域進行現況調查,在二個港口底泥中均發現到生物指標化合物 BSs、terpanes、steranes,而 terpanes、steranes 因化學結構穩定,不易受風化作用影響,在油品的化學指紋鑑定上,是最為廣泛使用的生物指標之一。依據本研究分析結果,鑑識港口底泥受油品污染其可能主要污染來源為R68及CF潤滑油,此兩種油品因用途廣泛及價格便宜,普遍被大眾使用,而因潤滑油生物指標有不同標準化之區別,可利用其期標準化之差異性辨識不同污染來源,作為污染源鑑識有效依據之一。本研究目的為建構環境法醫程序鑑定相關污染物之三類主要生物指標化合

物類(BSs, bicyclic sesquiterpanes, C₁₄到C₁₆雙環倍半萜; terpanes, C₁₈到C₃₆萜烷; steranes, C₂₈到C₃₀甾烷)與美國環保署公告之16種代表性PAHs污染現況以利爾後相關港口底泥之污染物鑑定應用,期能以本研究生物指標研究結果提供國內其它漁港進行污染源鑑識上及提供未來我國底泥於政策規劃品質項目或進行風險評估之參考。

Abstract

In the past decades, several Sediment Quality Guidelines (SQGs) were popular adopted in the US and Canada to protect aquatic organisms. Basic concepts of “SQGs” are applying certain kinds of toxicology tests to evaluate the adverse effects to certain kinds of aquatic organisms. Before year 2011, Taiwan did not have the related sediment regulations. However, a more comprehensive laws and regulations are certainly needed for those high polluted area of Taiwan. Thus, basic researches are necessary to investigate and improve the polluted situations and being adopted into new regulations in the near future. However, PAHs (Polycyclic Aromatic Hydrocarbons) and heavy metals are the only two major listed compounds in these SQGs or sediment regulations. Environmental forensics should be take part into these regulations and especially the investigation of biomarkers among sources of pollution, polluters and polluted sites. Unlike the western coast of Taiwan, harbors that are located in the eastern part are normally less polluted environment. Thus, establishing of biomarkers’ environmental forensics technology is necessary for the future generation. Therefore, our research objectives are focus on the investigating the biomarkers and establish a proper environmental forensics technology for the two major harbors in this area. Two fishing harbors in the eastern coast were



investigated and environmental forensics technologies were applied. The biomarker compounds in the related oil products and in the sediments were studied. The studied biomarker compounds are bicyclic sesquiterpanes (BSs), terpanes, steranes and the listed major 16 PAHs by the USEPA. A series of environmental forensics procedures were conducted and the possible biomarkers in the samples were identified and quantified. The results of normalization and application of diagnostic ratios show that there are close statistic relations among studied lubricant oils and sediment samples and confirm the sources of pollution.

[081] 現場底泥電學性質感測貫入器研發

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中文摘要

由於國內各主要河川於相關法令公告後，每年應至少於豐水期及枯水期各進行底泥定期檢測及品質狀況調查，建立「底泥品質基線資料檔」，以便適時更新河川水體底泥的基線資料檔。相關底泥調查與量測需求，除現有規定之相關取樣標準作業可能受限於取樣空間代表性以及其作業效率，國內外研究計畫均初步建議配合地球物理調查方法，以可大範圍輔助底泥範圍、厚度，甚至污染潛勢等相關特性之調查，但目前其技術限制因子為探測深度以及實際量化(Quantification)方法。本研究的目的在於發展一現地可直接貫入底泥之感測桿，該量測系統具備容易組裝及操作的特性，有助於探討底泥厚度與對應之電學特性，並配合時域反射技術(Time Domain Reflectometry, TDR)於時域分析的介電度、導電度量測優勢，以及寬頻介電頻譜量測方法研擬，據以作為電學探測結果解讀與量化分析的依據，並延伸至地球物理試驗結合，提供其電學性質參數率定與驗證使用，以可充分達到快速檢測底泥範圍、厚度與對應可能污染潛勢調查。根據現場驗證的經驗，本研究研發之TDR 現場底泥電學性質感測貫入器具有高空間解析、可於高導電度環境施作以及現場簡單操作等優點，但根據目前之設計其仍有四點使用限制，其一，在底床為較堅硬之材料時以致無法貫入時，會有約5 公分的量測盲區，其二，由於其具高空間解析因此其感應量測之空間較小，易受不恰當之貫入影響，其三，對於低視介電度(<35)的量測靈敏度較差，其四，目前不建議在延長桿無側向支撐時使其超過2 公尺進行貫入，以避免感測器受損。建議未來在本研究基礎上再行加以改善。

Abstract

According to recent regulations, sediment properties of major rivers should be conducted at least once during wet season and dry season to establish the sediment quality data base and update the baseline for each major river. Current standard practice of sediment sampling may be limited in terms of spatial representativeness and working efficiency. Geophysical methods are often suggested to complement sampling for investigation of sediment coverage, thickness, and even pollution potential in large scale. However, current geophysical practice has limited investigation depth and lacks quantification approach. The difference in physical and electrical properties of sediment affects electrical current flow and electromagnetic wave propagation in sediment, providing the basis for the application of geophysical methods in sediment investigation. Therefore, there is a need to better understand the electrical properties of sediments to improve interpretation of geophysical methods. The objective of this study is to develop a field measurement penetrometer that is easy to assemble and operate for measuring sediment thickness and profiling electrical properties. The measurement will take advantages of time domain reflectometry (TDR) technique to simultaneously provide apparent dielectric constant and electrical conductivity estimation by time domain analysis. Wide-band dielectric spectroscopy method will also be developed based on TDR measurement. Penetrometer measurements developed in this study will serve the basis for quantitative interpretation of electrical geophysical method and facilitate fast investigation of sediment coverage, thickness, and pollution potential. According to the experience gaining during field examination, the developed TDR penetrometer can easily provide high



space resolution data even in highly conductive environment. However, 4 limitations should be considered in this prototype. First, 5cm blind zone would be in the bottom if the hard-to-penetrated bedrock existing. Second, un-proper penetrating control would influence the results because of the small sampling volume. Third, sensitivity would be lower for measuring apparent dielectric below 35. Last, in case of buckling, the clear section for extending rods should be less than 2m. Further modification is suggested to optimize the TDR penetrometer

[082] 運用地層剖面儀進行河口底泥物理性質之空間變異研究

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中文摘要

為了能快速且大範圍的探測河川底泥性質，本研究專案引進地球物理遙測技術-變頻聲納海底地層剖面儀(Chirp sonar sub-bottom profiler)輔以雙頻側掃聲納(dual-frequency side-scan sonar)，於淡水河口進行河床底泥質地分佈調查。地層剖面儀調查結果發現，該水域之反射係數資料顯示於河道兩側之河床部分區域被泥沙所覆蓋，屬於泥質粉砂沉積，此結果與底泥樣本分析結果吻合；而沿河道軸水深較深處，地層剖面儀資料顯示為礁岩，但現場底泥樣本分析結果卻屬於泥質或粉砂沉積物，推測該處長年受河流沖刷，因而露出硬質的岩盤，為抓泥器採集到的土樣僅為覆蓋在硬岩上的軟泥，為能反映聲波遙測所算出的反射係數分佈。本研究除了使用由地層剖面儀自身所提供的反射係數資訊來估算底泥的質地，也自行發展計算反射係數的方式。此計算方式主要修正了河床上沉積物產生懸浮現象，地層剖面儀作表層沉積物分類時，需要參考高頻測掃聲納所表現的地表地散射回訊，並以表層沉積物的厚度以解讀量測的反射係數所對應的沉積物性質

Abstract

The project investigates the acoustic surveying tools, including the chirp subbottom profiling system (SBP) and the dual-frequency side-scan sonar (SSS), to map the distribution of river sedimentary environments. The experimental sites was in the river mouth of Keelung and Tamsui Rivers. The results show that, near the relatively flat area on both sides of Tamsui River, the values of reflection coefficient (RC) measured by the SBP are between -20 to -10 dB. The SBP information indicates that the sediment is dominated by sand and silt in various amounts, which is consistent with the analysis of the in-situ grab samples. In the deeper water area the lower RCs are observed, indicating a rocky riverbed. However, the SBP information is less correlated with the grab samples. The reason might be that the deeper areas are eroded by the river flow and the bedrock is exposed with few amount of sand/silt deposited. In addition, the study uses the multiple reflections to develop an algorithm for calculating the RCs. The values of RC are corrected for the case when the sediments are resuspended from the riverbed. We find that integrating the information provided by SBP along with higher-frequency SSS can make better interpretation of the acoustic data for inference of the sediment types.



[083] 維生素C還原降解火炸藥污染物-以硝基苯為例之翻土混合工法 應用評估

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中文摘要

軍事營區內土壤及地下水遭受火炸藥類物質污染為一常見之環境問題，此類物質皆屬於硝基芳香族化合物(Nitro aromatic compounds, NACs)，其苯環上之硝基(-NO₂)具+III之N氧化態，因而具有吸收電子之特性，易行還原降解反應，硝基苯(Nitrobenzene, NB)為NACs中結構相對簡單之化合物。維生素C(即抗壞血酸, Ascorbic acid, AA)為可釋放兩電子之還原劑，因此，本研究探討AA還原降解NB之可行性，並評估反應系統中不同pH、NB濃度、AA濃度之影響。更進一步，藉由NB降解副產物推估整體反應系統之降解途徑。由不同pH條件下之實驗結果可知，於鹼性(pH > 12)之條件下，AA能有效還原降解NB，亦可觀察到亞硝基苯(Nitrosobenzene)、偶氮苯(Azobenzene)、氧化偶氮苯(Azoxybenzene)及苯胺(Aniline)等副產物之生成及降解，並推估出NB於系統中之反應降解途徑。進一步藉由NB及AA兩者對反應影響之關係推估，AA還原降解NB之反應速率式： $r = (0.89 \pm 0.11) \times 10^{-4} \text{ mM}^{1-(a+b)} \text{ h}^{-1} [\text{NB}]^a = 1.35 \pm 0.09 [\text{AA}]^b = 0.89 \pm 0.01$ 。於泥水相系統，以CaO、Ca(OH)₂或1 M NaOH作為調整反應pH之方式，雖然皆能於反應時間120小時內，有效將系統維持在鹼性(pH > 11)，但只有添加1 M NaOH於100 mM AA溶液之組別能有效還原降解泥水相NB，並可藉由提高反應水土比(100/100→200/100 ml/g)增加泥水相NB去除率(40→80%)。進一步採用攪拌及超音波震盪之方式模擬翻土混合工法(soil mixing)，皆能有效去除泥水相NB(去除率約80-90%)，因此，此研究計畫案成果證實鹼性維生素C具有處理火炸藥類物質污染土壤之潛力。

Abstract

The soil and groundwater contaminated with explosives in military bases are common environmental concerns. These explosive compounds are clarified as nitro aromatic compounds (NACs), in which structure nitrite ion (NO₂⁻) owns a +III oxidation state of the nitrogen atom and tends to gain electrons. Nitrobenzene (NB) is the simplest compound of NACs. Vitamin C (a.k.a. ascorbic acid, AA) is a two-electron reductant. Therefore, the vitamin C reductive degradation of NB was evaluated and the effects of pH, NB concentration, AA concentration were examined. Also, degradation products and pathway were assessed.

The experimental results indicated that the degradation of NB (1 mM) by AA (100 mM) is strongly pH dependent. The removal of NB can be reached above 80% at pH 12 and 13. Additionally, nitrosobenzene, azobenzene, azoxybenzene and aniline were detected as major intermediate byproducts and NB degradation pathway was thus proposed. Furthermore, the reaction kinetics were determined and revealed that the reaction rate equation: $r = (0.89 \pm 0.11) \times 10^{-4} \text{ mM}^{1-(a+b)} \text{ h}^{-1} [\text{NB}]^a = 1.35 \pm 0.09 [\text{AA}]^b = 0.89 \pm 0.01$. In the water-soil slurry system, pH was adjusted to alkaline (pH > 11) condition by adding CaO, Ca(OH)₂ or 1 M NaOH. However, even though pH was well maintained at alkaline conditions (pH > 11) within 120 h reaction, only the system of 1 M NaOH with 100 mM AA solution exhibited the ability to degrade NB. Furthermore, the removal of NB can be increased from 40% to 80% by adjusting the ratio of solution/soil from 100/100 to 200/100 ml/g. When using mechanical or ultrasonic soil mixings, the removal of NB can also reach 80-90%. Therefore, this



innovative alkaline AA reductive reaction exhibits the potential in degrading explosives contaminated soils.

調
查



[084] 緩釋型類芬頓綠色工程材料之研發與應用

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中文摘要

近年來，臺灣工業持續的發展，污染控制不當下，日積月累衍生出的土壤及地下水污染問題，已成為國內外關注的重要議題。加油站及石化工業之大型儲油槽的管線設備皆設置於地下，由於儲槽管線老舊腐蝕失修及操作管理不當等因素，洩漏機會隨使用年限增加而增加，再者油品中之 BTEX、MTBE 經地下水的流動及傳導，逐漸擴大其污染範圍至下游處，嚴重影響環境土壤及地下水水質並威脅鄰近居民生活安全。

Fenton-like 氧化法為 Fenton 法所衍生之土壤與地下水現地化學氧化復育技術，透過鐵氧化物催化 H_2O_2 產生氫氧自由基以破壞土壤或地下水中有機污染物，藉以降低污染物毒性甚至達到礦化成 H_2O 及 CO_2 之效果。Fenton-like 法因具低成本、易取得且無毒性等優點，因此具有相當大的發展潛力。本計畫擬透過自行開發之複合型鐵氧化物 Fenton-like 反應材，結合透水性混凝土製備工法，開發緩釋型類芬頓綠色工程材料，並以 BETX、MTBE 為污染物標的，期能利用外加 H_2O_2 氧化劑與透水性反應材產生異相催化反應，發展土壤地下水中有機物之氧化分解綠色整治技術，提供未來現地以緩釋型類芬頓綠色工程材料，應用於 BTEX、MTBE 破壞去除。

研究結果發現，自行合成之 A 型複合型鐵氧化物，磁鐵礦晶相較 B 型複合材顯著，系統氫氧自由基的釋放能力可以由 pCBA 的擬一階反應動力模式進行探討，其中純物質鐵氧化物反應速率常數(kobs)值普遍大於自行合成之複合型鐵氧化物，A 型鐵系複合材 Fenton-like 反應性明顯優於 B 型鐵系複合材。後續將 A 型鐵系複合材運用於管柱試驗，模擬以透水性反應牆去除土壤地下水中有機污染物。由粒狀充填

管柱與塊狀充填試驗皆可發現，隨著模擬地下水污染物於管柱行進距離越長，污染物降解濃度越高，經過 5 個採樣批次(sampling run)效果仍然不變。粒狀充填管柱試驗中，BETX 最高去除率為 94%，MTBE 最高去除率為 53%。塊狀充填管柱試驗中，BETX 最高去除率為 46%，MTBE 最高去除率為 70%。由於管柱長度僅 30 cm，從污染物降解趨勢推論，延長管柱長度應可提高污染物去除率，開發之反應材具有作為 Fenton-like 透水性反應牆之潛力。

Abstract

The continuously development of industries over the decades in Taiwan has brought about many soil and underground water pollutions. Without proper pollution control and management, it has become an important issue worldwide. The pipeline of the huge oil tank in gas stations and petrochemical factories are installed underground. The problems of the pipeline such as erosion caused by aging and poor maintenance will cause oil leakage and the chance will increased with the year of usage. Moreover, the BTEX or MTBE in the oil is spread to and contaminate the downstream by the flow of the underground water. It greatly affects the soil and underground water as well as being a threat to the living safety of the residents nearby.

Fenton-like reaction is a soil and underground chemical oxidation remediation technology derived from Fenton reaction. This remediation technology is achieved by using iron oxides to catalyze H_2O_2 and produce free hydroxyl radicals to destroy the organic pollutants in the soil or underground water, in order to lower the pollutant toxicity and mineralize them to H_2O and CO_2 . Fenton-like reaction has many great advantages including low-cost, accessible and non-

toxic, which give it a great potential to be developed. This project is to develop Fenton-like green material in sustained releasing form by developing a multi-iron oxides Fenton-like reaction material in combination with permeable concrete paving blocks, and BETX and MTBE are used as target pollutant, hoping to apply the H_2O_2 oxidative and permeable reaction material to produce heterogeneous reaction.

The preliminary result showed that the crystal intensity of magnetite in synthesis Type A iron-oxide composite material is higher than Type B. The releasing efficiency of system OH free radicals can be discussed with pCBA pseudo-first-order model. It can tell from the result that pure element iron oxides reaction coefficient (k_{obs}) is greater than Type A iron-oxide composite material. The reaction efficiency of Type A iron-oxide composite material is significantly greater than Type B iron-oxide composite material.

Further study applies Type A iron-oxide composite material to column test, to simulate permeable reactive barriers to remove ground water organic pollutant. It is showed from grinding filling column and block filling column tests that, the longer the column length, the higher the pollutant degradation concentration. The effect remains unchanged even with 5 sampling runs. In the test with grinding filling column, the highest removal rate of BETX is 94%, and the highest removal rate of MTBE is 53%. In the test with block filling column, the highest removal rate of BETX is 46%, and the highest removal rate of MTBE is 70%. The column length is 30 cm only, inferring from the tendency of pollutant degradation, lengthen the length of the column should increase the removal rate of the pollutant; and develop the reactive material which has the potential to be used as Fenton-like permeable reactive barriers.



[085] 應用雙色冷光提升戴奧辛生物快速篩選技術於土壤污染模場 試驗先行評估計畫

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中文摘要

本計畫以多方合作的方式進行土壤污染模場試驗前的評估，在本團隊開發之 Ad-(6X)DR bioassay (DRE-H4IIE 細胞) 的基礎上，由國家衛生研究院開發雙色冷光 Ad-(dual)DR bioassay，屏東科技大學負責雙色冷光 Ad-(dual)DR bioassay 之生物快篩檢測戴奧辛標準品與環境樣品，以及後續的修正與改進工作，藉此增進雙色冷光 DRE-(dual)H4IIE 細胞的穩定性與敏感度，以開發快速、有效而低成本的本土戴奧辛生物篩檢技術。目前的研究成果顯示，Ad-(dual)DR bioassay 病毒的 multiplicity of infection (MOI) 為 2 時為本研究最佳實驗條件，2,3,7,8-TCDD 檢量線最佳回推區間為 4 ~ 120 pM (RSD = 4 - 22%)，EC50 為 54.3 至 55.8 pM。Ad-(dual)DR bioassay 測試 25 件次環境基質標準品 (Certified Reference Materials, CRM)，其測值與 CRM 濃度 (466 pg-WHO1998-TEQ/g d.w.) 值相比時高了 1.25-1.61 倍。19 件次真實土壤與底泥樣本測試與 HRGC/HRMS 平均比值為 2.59 倍，兩者具有良好之關聯性 ($R^2=0.957$, $p<0.001$) 且無偽陽性之問題。40 件次樣本與 XDS-CALUX 比對平均比值為 0.974 倍，參照國際文獻 XDS-CALUX 與 HRGC/HRMS 平均比值約為 1.5-2.6 倍，顯示本研究樣本回推濃度與 HRGC/HRMS 相似。本研究所開發之 Ad-(dual)DR bioassay 病毒使用量低，在中、高濃度樣本穩定度與回推能力之表現良好，雖無法完全改善低濃度樣本穩定度表現，但比照現行規範濃度 1000 ng TEQ/kg d.w. 是非常適合推廣與應用的。

Abstract

This project is a multi-collaborated work to evaluate soil dioxins contamination before the pilot study. According to the basis of previously establishing Ad-(6X)DR bioassay (DRE-H4IIE cells) by our research team, the National Health Research Institutes develops dual luciferase detection system for detecting dioxin like compounds, namely Ad-(dual)DR bioassay, and the team members in National Pingtung University of Science and Technology test the dual system for application in detection of soil dioxins contamination and modify this system for the future dioxins survey studies. We hope our collaboration elevate the stability and sensitivity of dioxins measurements in Ad-(dual)DR bioassay to accesses a fast-screen, efficient, low-cost, and local biotechnology for AhR reporter gene assay. The current result show that the optimum multiplicity of infection (MOI) for Ad-(dual)DR bioassay is 2. The best period of the 2,3,7,8-TCDD standard curve for the Ad-(dual)DR bioassay is between 4 and 120 pM (relative standard deviation (RSD) = 4-22%). The values of EC50 in Ad-(dual)DR bioassay with MOI of 2 are ranged from 54.3 to 55.8 pM. Twenty five Certified Reference Materials (CRM) samples are examined by Ad-(dual)DR bioassay and their measurements have 1.25-1.61 folds higher than those are measured by HRGC/HRMS (466 pg-WHO1998-TEQ/g d.w.). The mean value measured by Ad-(dual)DR bioassay was 2.59 times higher than that by HRGC/HRMS in soil samples. The good correlation ($R^2= 0.957$, $p<0.001$) was found between Ad-(dual)DR bioassay and HRGC/HRMS without false negative results. Our ratio of Ad-(dual)DR bioassay v.s. HRGC/HRMS was similar to those of



XDS-CALUX v.s. HRGC/HRMS in the previous studies (Ratio=1.5-2.6). Although the small amounts of the recombinant adenovirus were used in the present study, the performance of the TCDD standard curves was robust and stable in the higher dioxin contaminated soil samples. The stability of low dioxin concentrations in soil samples was varied. It is suitable for application and development of Ad-(dual)DR bioassay in soil surveillance based on the current dioxins standard (1000 ng TEQ/kg d.w.) for the dioxin contaminated soils.



[086] 環境污染保險之需求與願付價值

曾真真

健行科技大學財務金融系所

中文摘要

價值是交易的核心，消費者購買財貨或服務會主觀認定的價值，而以貨幣形式表示其願意支付的價格，即為願付價值。事實上，保險公司設計環境污染保險係依費率基礎精算出保險費，惟所估算出的保險費是否落於潛在污染者願付價值的區間，將直接影響潛在污染者購買環境污染保險的意願，亦攸關環境污染保險能否順利推動。基於此，本計畫擬以加油站業者為研究對象，探討其對環境污染保險之願付價值。相較於連鎖加盟業者，個別加盟業在遭遇災害更無法因應，特別需要協助其規劃妥適的保險機制。基於此，本研究擬以本島的個別加盟加油站業者為施測對象，剔除地區性的重複業者加油者，共發放 999 份問卷，有效問卷計 302 份。分別採單界二分選擇模型及雙界二分選擇模型推估願付價值，分析結果顯示加油站業者願付金額介於 92,159 元至 96,761 元，落於業者精算的價格區間，故實證結果支持環境污染保險推動的可行性。

Abstract

Value is the core of transactions. When purchasing goods and service, consumers will have a subjective value, which is then turned into the monetary form as the willingness to pay. In fact, insurance companies use the rate base to accurately calculate the insurance premium when designing the environmental pollution insurance program. However, whether the calculated premium is below the willingness to pay of consumers will directly affect their purchase intention, which then determines the success of the environmental pollution insurance. Therefore, this study will target gas stations and explore their willingness to pay for environmental pollution insurance.

Compared with franchised gas stations, independently owned gas stations are less able to respond when facing disasters and especially in need of help in planning a suitable insurance mechanism. Therefore, this study targets independently owned gas stations in Taiwan and distributes 999 questionnaires. 302 returned copies are valid. Single-bounded dichotomous choice model and double-bounded dichotomous choice model are both used to estimate the willingness to pay. The analytic results indicate that the willingness to pay of gas station operators is between NTD 92,159 to NTD 96,761, which is within the price region calculated by operators. Hence, the empirical results support the feasibility to promote environmental pollution insurance.

[087] 二仁溪污染底泥整治模場試驗計畫

(第四年－鄰苯二甲酸酯塑化劑污染底泥之快速檢測與模場試驗)

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中文摘要

鄰苯二甲酸酯 (phthalate esters, PAEs) 通常用於塑膠製程中充當塑化劑之用，可增加塑膠製品之撓曲程度與黏性，但具有相當之毒性，因添加方式為物理性加入，並未形成化學鍵結，於使用時可陸續釋放至空氣、土壤與水體中，造成人體健康危害。我國目前毒性化學物質管理法所管制 PAEs 即達到 26 種之多，其中使用量最大的當屬 di-(2-ethylhexyl) phthalate (DEHP)，目前臺灣居家空氣中塵粒之塑化劑濃度為全球最高，土壤、底泥與魚體中 DEHP 濃度與世界各國比較均偏高。以我國二仁溪為例，底泥中 DEHP 濃度在 94 年之最高測值為 26.2 mg/kg (乾重) 為當年所有檢測河川底泥中之最高者，已經超過法規之上限值 19.7 mg/kg (乾重)，有進行整治技術研發之必要。並且鑒於底泥中 PAEs 之檢測分析標準方法曠日廢時，並且同樣面臨整治效果驗證之困難性。先期之二仁溪與三爺溪沿岸底泥採樣分析結果顯示，4 種受法規規範之 PAEs 有 2 種平均濃度已經超過底泥品質指標上限值。第一階段模場試驗結果顯示二仁溪底泥中微生物對 DEHP 之降解能力的確比國際間之試驗結果為佳，其半生期為國際文獻數值之 1/20 至 1/30 之間；第二階段模場試驗則顯示現場風化之 PAEs 以 BBP 最容易回收，以總去除率而言，乳化液與釋氧劑添加之工程干預仍是較佳之方案，但在 DEHP 為主要污染物且為風化型態時應謹慎使用；未進行積極整治與源頭管理，PAEs 塑化劑在二仁溪底泥中濃度可能會繼續升高。表面增強拉曼光譜用奈米金薄膜之方式進行 SERS 檢測後，靈敏性與專一性經過 40 樣品測試後均可達 100%，方法偵測極限為 6.67 mg/L，若以萃取液進行檢測，應可達到 0.67 mg/kg 之法偵

測極限。

Abstract

River sediments play an imperative role in ecosystems, such as self-cleaning capacity, planktonic habitat, and benthic organismal habitat. Once contaminated by persistent organic pollutants (POPs), the contaminant may enter human body or other organisms through food chains resulting adverse health effects and detriment of ecosystems. Taking Er-Ren River as an example according to the literatures, it is heavily polluted. In its sediment, PAEs, especially di-(2-ethylhexyl) phthalate (DEHP), are above the regulated standard. However, a cost-effective *in-situ* remediation technology does not exist yet. In the lab, the half-lives of the four regulated PAEs under aerobic conditions are less than 1 month but much longer under anaerobic conditions, which is the prevailing condition in river sediments. For example, the half-life of DEHP in sediment is as long as 347 days. Since sediment is the ultimate accumulation environmental media of PAEs, successful remediation of PAEs in sediments will substantially cut down the mass of PAEs in our surroundings and contribute greatly to the health of human. This project is aimed to remove PAEs in river sediment by implementing a pilot study at the Er-Ren River in the southern Taiwan. To meet the demand of rapid detection and quantification of DEHP in river sediment, surface-enhanced Raman scattering (SERS) detection technology is continuously developed in this research project. The results indicate that the current PAEs concentration in Er-Ren River sediment exceeds the historical values indicating the river may be polluted more heavily in recent years. Result on pilot study showed that engineering intervention may be better than natural



recovery and emulsion-recovery operation yielded the best result. If DEHP is the predominant contaminant and weathered, engineering intervention should be assessed before implementation. Method of detection limit of SERS can reach down to 6.67 mg/L in solvent extract of DEHP which could be interpreted as 0.67 mg/kg in sediment. This result indicated that SERS is probably feasible on rapid detection of DEHP in river sediments. It is recommended that PAEs concentration in Er-Ren river sediment should be monitored and the health risk should be assessed in the near future.

[088] 地下水中含氯有機污染物厭氧生物整治

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中文摘要

氯化有機溶劑常用於工業之清洗溶劑其具有低可燃、易爆、低沸點及高蒸氣壓等特性，如四氯乙烯(perchloroethene, PCE)、三氯乙烯(trichloroethene, TCE)、1,1,2-三氯乙烷(1,1,2-trichloroethane, 1,1,2-TCA)與四氯甲烷(carbon tetrachloride, CT)等。早期臺灣區域土壤及地下水污染防治觀念尚未成熟，導致人為的不當傾倒或是意外洩漏使得氯化有機溶劑造成地下水污染。生物整治法被喻為自然、環保及節能的處理技術，也是目前環境污染整治的趨勢。評估現地生物復育技術可行性其中最重要條件之一為場址本身須具有可降解污染物之微生物。當場址中可降解污染物微生物數量較低或場址整治急迫性高時，可額外添加微生物進行生物強化(Bioaugmentation)整治受污染之場址。受污染之場址皆可能含有可降解污染物之微生物存在，若能於污染降解途徑完整之場址確實鑑定出含氯污染物降解途徑中各階段之脫鹵球菌之種類及數量，將可有助於後續場址現地生物整治設計(採用生物刺激(Biostimulation)或生物強化)或作為未來生物強化之菌種純化來源。

在期末報告的研究執行內容與成果，主要是著重於評估臺南市永康鹽行段設置一模場進行含氯污染物整治試驗，本模場定期採樣偵測結果顯示有監測到含氯污染物降解之趨勢，並產生最終產物乙烯，顯示該模場降解機制完整。模場含氯污染物之降解乃為微生物進行厭氧還原脫氯機制所致。因此本計畫採用Metagenomics技術結合qPCR進行菌相分析，欲建立完整環境微生物在含氯污染場址之完整生化代謝圖譜，期末成果著重在生物營養鹽添加後是否促進氯化有機污染物降解，並建立完整環境菌相及降解

機制分析，這些成果將應用在未來不同的多氯有機污染物污染場址的生物復育研究暨菌相分析工作，作為未來場址全場整治之參考依據亦可作為菌種純化場址之參考來源地點。

Abstract

The chlorinated solvent (PCE, TCE, 1,1,2-TCA, and CT) has ignitable, explosive, low-melting, and high pressure characteristics, and are often used for cleansing solvent in industries. In the past, we did not realize the issue how we can prevent our dwelling environments near soils or groundwater from contamination, thus leading to the accidental leakage of the chlorinated solvent into the groundwater. Bioremediation is a friendly, cost-effective, and safe technique which is commonly used for remediation in contaminated sites. Bioaugmentation is to add exogenous microorganisms with the potential to degrade polluted chemicals. In this study, we hope to detect the presence of one dehalococcus species with the ability for degrading the chlorinated solvent, and then harvest it for application of bioaugmentation.

In the mid-term report, our research field trial is located in臺南市永康鹽行段 decreased to the undetected level the monitoring well, we indicated that the degradation of the chlorinated solvent occurs. To assure the success of bioremediation in our field trial, we need to confirm the presence of *Dehalococoides* for future application. In this study, we will first apply the metagenome and qPCR to detect the change of bacterial community before and after bioremediation, and prove the role of *Dehalococoides* in field trial contaminated with the chlorinated solvent. We herein emphasize that the advantages of metagenome over other molecular techniques are to prove more information



about the population of each bacterial genus and even in species within the soils or water, and also to be a fast, and high accurate technique. With this bioremediation proposal, we hope that our biomediation strategies can prove the standard model for the degradation of the chlorinated solvent in field trial.

[089] 封隔型雙負壓浮油回收系統於油品洩漏場址的運用

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中文摘要

入滲量超過土壤之吸附容量時，這些 LNAPLs 會在地下水液面形成所謂的浮油(free product)相。在油品污染類型場址整治作業中最優先採行緊急應變與污染調查作業，而須先執行污染源阻斷與瞭解污染分布情況，否則貿然進行整治作業可能增加整治費用甚或徒然無功，最嚴重是不當整治工法可能擴大污染範圍造成更大的潛在危害與損失。

本研究計畫主要是針對發生油品洩漏的污染場址，在進行整治作業前的緊急應變與前置調查作業，應用雷射激發螢光(LIF)系統先行於洩漏場址中進行地表下油相(NAPL)污染團分布調查與浮油相(Free product)移動路徑確認，接續於浮油相移動路徑上設置攔截點進行浮油相回收作業，防止浮油相污染團的擴大，最後再以 LIF 系統偵測浮油相污染團的分布以驗證執行成效。為瞭解設置之浮油回收系統效能、操作條件限制及整治方法之執行時機，本計畫導入由研究團隊開發之新型式井中浮油回收系統(Free product recovery system)：封隔型雙負壓浮油相回收系統(dual-vacuum packer type recovery system)，系統主要功能特點為以定置空間(Fixed Space)概念進行抽汲系統設置，使系統作功集中於目標污染物回收，減少不必要的虛功浪費以節省操作成本，另一方面藉由親油性填充管提高油水分離效能，降低伴隨之地下水抽取量，減少因浮油回收作業所產生之廢水處理量，以符合現行推行節能環保與效能提高目標需求，提供相關污染場址進行浮油回收應變作業的另一種選擇。

封隔型雙負壓浮油相回收系統安裝於現場經約 5 個多月的模場試驗測試，在系統作功效能提升、浮油蒐集效能、廢水減量效能與操作成本效能之比較上，相關監測數據呈現本研究新開發的

封隔雙真空式浮油回收系統皆優於傳統舊式的其他真空式浮油回收系統。

Abstract

Taiwan EPA has implemented soil and groundwater investigation at gas stations and underground storage tanks for 7 terms. The leakage of petrochemical products was found liable to contaminate subsurface environments. Petrochemical products are generally hydrophobic and lighter than water, and they are named as light non aqueous phase liquids (LNAPLs). When the leakage of LNAPLs occurred, some of them might be sorbed to soil medium or volatilize into the vadose zone. If the quantity of NAPL leakages exceeded the adsorption capacity of soil media, the residual NAPLs would reach groundwater table and form a layer of free products. For the sites contaminated with petrochemical products, the first priority works are to take emergency actions to cut off leaking sources and to investigate the spreading of contamination areas. The planning of remediation works might be in vane or greatly swell the expenses without the understandings of contamination details. The improper remediation work is liable to cause plume spreading and to increase potential health risk.

In this study, one site contaminated with petrochemical products was selected for test. Laser induced fluorescence (LIF) system was employed to detect the transport paths of free products and to investigate the distribution of contaminant plume. In order to implement emergency action, the recovery system was established on the transport paths of free products for the control of plume spreading. Finally, LIF system was employed again to delineate the distribution of contaminant plume after operating the free-product recovery system for several months. The introduced free-product recovery system was



developed by the research team, which is called dual-vacuum packer-type recovery (DVPTR) system. This novel DVPTR system is established at fixed space in the well to allow the maximum recovery of free products and minimum suction of water, which contain a lipophilic packer to increase the efficiency of oil and water separation. This novel DVPTR system was operated in such a way that the waste of energy use and the treatment of wastewater were minimalized due to the reduction of water suction. This showcase is expected to fulfill the objectives of energy saving and remediation efficiency improvement, and this novel DVPTR system is definitively an alternative of free-product recovery during implementing emergency action.

The DVPTR system was installed in field to conduct a pilot test of fuel recovery for more than 5 months. The monitoring results showed that the developed novel DVPTR system is superior to other traditional vacuum-type fuel recovery system on energy efficiency, fuel recovery, wastewater reduction, operation expense.

[090] 廢機油污染場址之綠色整治與優良本土復育樹種之篩選

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中文摘要

本計畫場址位於屏東縣九如鄉，主要污染物為鋅、鉻、銅、鎳及總石油碳氫化合物(TPH)。計畫自101年起執行迄今，主要目的在於以生物復育法(蚯蚓與石化分解菌)與植生復育法(白楊與太陽麻)改善污染，本年度並栽植本土植物構樹、血桐與田青，且評析其復育效果。在場址內共設置六個試驗區，除對照區外，另設有三個生物復育區與二個植生復育區。在三年的試驗後發現，各復育區之TPH濃度雖仍有高低之不規則變化，但大體上呈現降低趨勢，多數處理區都有不同比例之減量效果，三個生物復育區土壤中之TPH濃度減量百分比介於19%~94%，植生復育區則為43%~97%。其次，重金屬之測值指出，在各復育區同一土層之濃度呈現不規則變化，且多數仍高於土壤污染管制標準。此外，所有復育植物之生育調查與木本植物之生理試驗結果顯示，各類植物之生長與生理狀況正常，可以忍受並適應污染環境，皆可做為本場址之復育植物；而植體之重金屬測值指出，各類植物皆具吸收累積效果，其累積量依序為 $Zn > Cu > Ni > Cr$ 。最後以植體之生質量與重金屬濃度計算其吸收移除量，藉以評析植生復育效益，結果發現，所有復育植物全年之總移除量依序為 $Zn(283\text{ g}) > Cu(2.03\text{ g}) > Ni(1.78\text{ g}) > Cr(1.22\text{ g})$ 。至於三種木本植物對重金屬之移除能力依序為白楊>血桐>構樹。

Abstract

The contaminated site proposed in this study is located at Jiuru Township, Pingtung County, with an area of 1,800 m². According to previous investigations, the major contaminants in soils were found to be zinc, chromium, copper, nickel and total petroleum hydrocarbon (TPH). The objective of this research project is to conduct remediation in the contaminated site. Five treatment plots were designated in the highly contaminated area, in which three were designed for biophytoremediation (BP1, BP2, and BP3) and two for phytoremediation practice (PR1 and PR2). One control plot was used for comparison purposes. Since the initiation of this study in 2012, earthworm (*E. fetida*) and petroleum-degrading bacteria (*Pseudomonas* sp. NKNU01) have been utilized for bioremediation, while Poplars (*Populus bonatii* Levl.) and Sun Hemp (*Crotalaria juncea* L.) in the phytoremediation practice. This year, selective native plants, Macaranga (*Macaranga tanarius*), Papermulberry (*Broussonetia papyrifera*) and Indian Sesbania (*Sesbania cannabiana*), have also been planted to evaluate their remedial capabilities. Results of soil analysis showed that the removal rate of TPH within the three bio-phytoremediation plots ranged from 19%~94% and from 43%~97% in the two phytoremediation plots. However, heavy metal concentrations were not significantly reduced and thus most soils were still highly contaminated. Plant growth and physiological investigations indicated that all plants were vigorous and adaptable to the pollutants. For the purpose of further explorations, the biomass and heavy-metal contents of the studied plants were analyzed to evaluate the removal efficiency of heavy metals. The results indicated that the four metals were absorbed and removed by all studied



plants in the order of Zn(283 g) > Cu(2.03 g) > Ni (1.78 g) > Cr(1.22 g). Finally, the heavy-metal removal ability of three woody plants was found to be Poplar > Macaranga > Papermulberry.

[091] 土壤及地下水污染整治效益之區位評估與 結合跨域增值運作機制之研究

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中文摘要

依據行政院101年7月所核定之「跨域增值公共建設財務規劃方案」，其精神係希望透過各項公共計畫之整合，以長期性、整合性的地方發展視野進行全面性之都市規劃，並將計畫之外部效益予以內部化為財務效益，以助於減少計畫成本負擔，紓緩財務負擔壓力。而經去年度「土壤及地下水污染整治與再開發對周邊不動產價格與租稅收益影響之探討」計畫專案之研究成果，整治與再開發將有助於提高污染場址周邊之不動產價格與租稅增額。換言之，整治與再開發所衍生的外部效益可予以回收並作為污染整治與再開發之相關財源，而有助於提高污染行為人整治之意願，因其土地整治完成將具有更高之土地利用價值，除此之外，污染整治場址也成為地方經濟再發展之契機。然各個污染場址區位所衍生之外部效益，實具有差異性。爰此，本研究將透過FDM與ANP進行兩階段的問卷調查分析，以建構土壤及地下水污染整治之區位優先性指標體系，並評選其優先性，根據評選結果，顯示出經濟指標構面之優先性最高、社會指標構面次之，指標重要性前三名依序為居住人口(13.64%)、土地價值(13.23%)與自然資源(12.10%)，未來推動整治工作與區位決策時，可就該指標系統評估優先性，盡可能將有限資金發揮最大效果。此外，本研究亦將相關指標轉換為區位空間資訊，利用GIS針對個案(主要以加油站類型)進行區位效益之空間關聯性分析，並說明操作步驟，以供後續整合、擴充既有資料庫，並有助於未來污染整治與再開發之區位評選，以及配合相關都市規劃之推動策略的參考。最後，參考國外相關污染整治與再開發之財務運用工具，並依據國內跨域增值方案之相關操作機制，據

以研擬將整治與再開發之外部效益納入土壤及地下水污染整治基金之作業方式與相關執行建議，提供未來政策參考。

Abstract

According to “Project for Cross-Field Value-Adding in Public Works Financial Planning,” it is hoped that through the integration of the Department of Public plan to place a long-term vision of development. The plan will internalize the external benefits into financial benefits to help reduce the cost burden. The plan, A study on soil and groundwater pollution remediation and redevelopment of the surrounding real estate prices and tax revenue impact, which was executed last year revealed the result that soil and groundwater pollution remediation would cause the value of real estate around the polluted destination. In other words, external benefits of remediation and redevelopment can be internalized and used as sources of fund. Besides, pollution remediation becomes a local development opportunity as well, but the benefits will differ from location. Therefore, this study will discuss the difference of location and classify all of contaminated sites. Then, we will discuss that how to integrate “Cross-Field Value-Adding” into the work of pollution remediation.



[092] 土壤污染潛勢篩選情境之決策工具研擬

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中文摘要

土壤重金屬污染可經由多種途徑影響人體健康，為保護國家社會經濟安全，必須掌握土壤重金屬分布情形，土壤重金屬污染潛勢(Pollution Potential)圖成為污染潛勢區篩選，以及污染潛勢區篩選決策作業之重要參考資訊，然而潛勢圖大多以現有重金屬調查資料為基礎，進行潛勢之空間分布推估。但由於經費限制因素，調查資料無法涵蓋所有的區域，使未調查點之污染潛勢推估具有某程度之不確定性(Uncertainty)，進而提高推估污染潛勢區域篩選誤判之風險，並對污染區篩選及篩選決策具不同程度影響。此外，污染物之間常具有某程度之空間相關特性，若忽略此特性即各別推估污染物潛勢，此分析結果有可能遺失此污染物之空間特性。因此，研擬具科學性及可靠性(Reliable)潛勢推估工具，以提供穩健(Robust)污染潛勢範圍篩選之決策工具，為多年來土壤重金屬污染研究與實務之重要工作。

本計畫以全臺地區為研究範圍，分別以全台及灌溉小組為單位，並以農試所調查之130,772筆資料為基礎，有別於傳統克利金法及條件模擬法，本計畫結合地理統計模擬方法—高斯連續模擬與U-WEDGE法，共同模擬(Jointly simulate)研究區域內的各種土壤重金屬空間分布之可能情境(Scenarios or Realizations)，並將模擬之土壤重金屬空間分布間的空間相關性將與原始量測資料進行比較，以確定模擬之土壤重金屬空間分布間的空間相關性與原始量測資料空間是否特性一致。依據模擬結果及情境，進行空間未確定分析(Uncertainty analysis)，且依據不確定性分析及模擬情境，應用系統性的分析工具—Information-Gap Decision Theory (IGDT)進行污染潛勢區篩選不確定性之決策分析，確保因資訊不足所產生的

不確定情況下，亦能系統性地進行穩健決策分析(Robust decision analysis)，提供穩健決策，亦即當最劣的情況(worst scenario)發生時(現實情況土壤重金屬之空間分布與模擬之結果產生差異時)，所做的決策能夠恰能滿足管理者的需求；換言之，本分析方法將使上述之不確定性對污染潛勢區篩選的影響較小，同時提供污染潛勢區篩選不同情境。本計畫同時結合內梅羅指標與模擬情境，進行污染潛勢篩選，並將上述方法與系統性決策分析工具建置於地理資訊系統，並發展此系統之軟體及使用友善操作介面，完成操作介面之使用說明，並舉辦一場方法及軟體說明會。

Abstract

Potential pollution maps of heavy metals in soil play important role in screening and making specific decisions on polluted area. The distributions of the heavy metals in those maps are generated based on the existing survey data. However, without comprehensive survey data, the uncertainty caused by the estimation of distributions of the heavy metals in unsampling sites that will lead to the increasing the risk of misjudgment on contamination area, and result in the errors in screening or decision making of pollution area. Besides, spatial correlations between different heavy metals should be considered. Estimating the distribution of those heavy metals independently and without considering the spatial correlations is therefore inappropriate and may not retain the spatial correlation between each variate. Thus, to find out scientific and reliable tools for estimating pollution potential area and to provide the robust decision-making tools for screening pollution potential area are important works in heavy metals in soil. The geostatistical

approaches, such as sequential Gaussian simulation and Uniformly Weighted Exhaustive Diagonalisation with Gauss iterations (U-WEDGE), are applied in this project to jointly simulate the possible scenarios or realizations of distributions of heavy metals in soil over entire Taiwan based on the 130,772 survey data provided by the Taiwan Agricultural Research Institute, Council of Agriculture, Executive Yuan. Additionally, the estimating spatial distributions of soil heavy metals must be consistent with the spatial characteristic of original survey data. The spatial uncertainty analysis will be made according to the simulation results and scenarios. In accordance with the uncertainty analysis and the resultant simulation, a structured tool, Information-Gap Decision Theory (IGDT), is applied to make decisions on pollution potential area screening. The IGDT provides a general framework for robust decision analysis under the uncertainty caused by the insufficient information. That is this decision may still meet the needs of decision makers even in occurrence of the worst scenario, such as the significant difference between simulated and actual distributions of heavy metals in soil. In other words, this method will result in the lower impacts of uncertainties on the screening of pollution potential area and will provide the different screening scenarios. The Nemerow index and the simulation scenarios are also integrated into screening the possible polluted area. Additionally, a user-friendly GIS based tool to co-simulate the spatial distribution of heavy metals in soil, and make robust decision under sever uncertainty will be delivered. Finally, the orientation for those methods and the GIS based tool will be held.



[093] 以地電阻影像探測技術推估地下水流速流向：方法建置及驗證

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中文摘要

本研究提出以地電阻探測技術量測地下水流速流向方法並評估其敏感度及準確度。此方法主要目的為在只有一口地下水監測井的限制下，發展一套可靠且有效率之地下水流速流向測定技術。由於污染物在含水層傳輸主要藉由地下水流之對流 (advection) 及延散而使污染團向下游移動擴大。因此地下水流速流向的掌握對描繪及建構污染場址污染物在含水層傳輸的概念模式有關鍵性影響。而此概念模式正確與否，對於污染團之圍堵攔阻或污染復育對策擬定及執行具有決定成敗之重要性。本研究另一個目的為建立地電阻影像探測所得之表面導電度 (apparent conductivity) 與孔隙水導電度之關係。

技術研發將藉由在實驗槽中進行示蹤劑試驗。實驗主要步驟如下：(1)在實驗槽中填充細砂，安裝地下水監測井並維持一穩定之地下水流場；(2)以高導電度之氯化鈉溶液為示蹤劑導入至流場中；(3)以地電阻探測儀量測含水層導電度變化並推估示蹤劑濃度分布；(4)分析實驗數據與理論濃度分布值比較推估地下水流速流向；(5)利用 Archie's law 分析地電阻測得導電度與地下水導電度之關係。

實驗槽為一長 1.5 公尺，寬 0.5 公尺，高 1.0 公尺之壓克力槽。槽體長端兩端各有一寬 5 公分之定水頭槽體。細砂填充以飽和填充法以避免造成層化現象。填充完後，將安裝地下水監測井以量測水頭及地下水導電度。本研究之示蹤劑試驗將進行三維之脈衝點源及連續式點源。地電阻電極之排列為溫奈及雙偶極，電極棒之間隔為 5, 10 及 20 公分，運用不同之電極排列及間距可以分析評估此方法之準確度及敏感度。另外所測得之地下水導電度與表現導電度，可由 Archie's law 算出含水層之

formation factor。本研究將探討不同之電極排列及間距和輸入電流對 formation factor 之影響。

本研究預期將可研發出一經濟且準確之地下水流速流向測定技術，在未來污染場址調查或場址復育，污染源調查乃至於地下水污染潛勢調查及使用管理都具有重要貢獻。

研究結果顯示，ERT 重複性良好、敏感性佳，可測得鹽水導電度 600、800、1000、1200 $\mu\text{S}/\text{cm}$ 之差異。由 Archie's law 可驗證鹽水電阻與 ERT 量測含鹽水之石英砂電阻之關係，顯示施測結果具有準確性。Dipole-dipole 排列法下，輸出電流大小對於靜態實驗槽之 ERT 視電阻率量測結果無顯著差異。相同電極數量，偶極間距越短，施測時間越長，可探測地層範圍之資料點數越多，解析度越高。改變電極插入地表的深度，可明顯發現越接近地下水，探測得電阻率越低。

脈衝式與連續式示蹤劑試驗結果，顯示 ERT 可明顯地捕捉到示蹤劑於地下水中流動造成電阻值改變之訊息，此成果可應用於地下水流速流向之推算。而增加測線數量，可提高流場流向判斷的解析能力。由單測線試驗計算地下水流速與控制流速相差 $\pm 10\%$ 以內，並發現深度增加，流速有降低的趨勢。多測線試驗計算流速高於控制流速，可能受流場非均質性及短流影響，實際流動面積小於槽體截面積，或槽體底部石英砂密度與空隙率受重力壓實影響，導致地下水主要流動發生在上層，亦可能為 ERT 示蹤劑試驗計算流速較高的可能原因。以監測井量測的地下水電阻變化與 ERT 監測結果，透過 Archie's law 關係修正後比較，顯示觀測值與推估值兩者相近，表示驗證結果良好。

Abstract

The main purpose of this research is to develop a technique for directly measuring groundwater velocity and direction based on electrical resistivity tomography (ERT). The motivation for this technique is to be able to accurately and effectively identify the direction of groundwater flow and direction with only one monitoring well. Accurate knowledge of groundwater velocity and direction is essential for constructing a conceptual model for groundwater water and soil transport in a contaminated site as advection is the main mechanism for contaminant transport. Without an accurate model for the transport of contaminants, the containment and remediation efforts for groundwater and soil contamination have very little chance of success. The other objective of this research is to evaluate the relationship between the apparent electrical conductivity and groundwater electrical conductivity.

Tracer studies will be conducted to achieve the objectives. The main procedures for the tracer studies are as the following: (1) fill the sandbox with sand, install groundwater monitoring wells, and maintain a steady groundwater flow in the sandbox; (2) inject high electrical conductivity sodium chloride solution into the flow; (3) use ERT to calculate the change in electrical conductivity and use it as the change in sodium chloride concentration; (4) obtain groundwater velocity and direction by comparing the observed concentration with the theoretical values; (5) evaluate the relationship between apparent electrical conductivity and groundwater electrical conductivity using Archie's law.

The sandbox is made of acrylic plates and has dimensions of 1.5 m in length, 0.5 m in width, and 1.0 m in height. One 5-cm-wide compartment is attached to each end of the sandbox for use as a constant head boundary. The packing of sand will be conducted using sequential saturation method to prevent layer formation. Groundwater monitoring wells for water

head and pore water electrical conductivity measurements will be installed after packing. The tracer experiments will be conducted under instantaneous point source and continuous point source modes. The ERT will be obtained using two different electrode arrays (Wenner and dipole-dipole array) and three electrode spacing (5, 10, and 20 cm). Results from these different settings of electrodes will be used to evaluate the accuracy and sensitivity of the technique. Archie's law will be used to evaluate the groundwater electrical conductivity and apparent conductivity and obtain the formation factor for the simulated aquifer. The effect of electrode arrays and spacing and input current on formation factor will be evaluated.

The research will develop a new technique for accurately and cost-effectively measuring groundwater velocity and direction with only one monitoring well. Therefore, it could be very useful in the application of site characterization and site remediation, locating contaminant sources, and even in groundwater management and containment of groundwater pollution plumes.

The results from reliability and sensitivity of the ERT experiments are acceptable. The Archie's law can be validated with the apparent resistivity from the ERT experiments and the solution resistivity, which means the ERT technique can accurately detect the change in solution resistivity. Using a dipole-dipole array setup, the effect of the applied current strength on the apparent resistivity is insignificant. The apparent resistivity decreases with the depth of the electrodes.

The velocity and direction of groundwater was measured using the ERT technique under both impulse and continuous tracer injection schemes. The results from both schemes show the technique can detect the groundwater velocity and direction. The measured groundwater velocity from both schemes is within 10 percent of the actual velocity. It is observed that the flow regime in the



sandbox was non-homogeneous although great effort was put into packing the sand during experiment setup; this non-homogeneous flow regime is detected by the ERT technique.

The results indicate that it is feasible to measure groundwater velocity and direction using the ERT technique presented in this report. Additional study in a real test site is needed to further verify the practical and potential use of this technique.

[094] 以能源作物向日葵整治重金屬鎘污染土壤之研析

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中文摘要

本計畫將對能源作物向日葵進行土壤重金屬鎘之改善研析，探討整合植物生長激素與螯合劑植生復育受重金屬污染土壤，並進一步評估能源作物向日葵復育受重金屬污染土壤操作方式暨相關環境因子擬定。並藉由實驗探討植物生長激素與重金屬鎘對植體生長情形(植體形態分析)。實驗結果證明，GA3 可以提升植物的生長速率：單純添加重金屬組的平均生長高度為 18.9 公分；Cd+GA3 組的平均生長高度為 19.5 公分；Cd+EDDS 組的平均生長高度為 19.0 公分；Cd+GA3+EDDS 組的平均生長高度為 20.4 公分。實驗結果證明，EDDS 能增加重金屬在土壤中的流動性且增加整體植生復育的效果：單純添加重金屬組的植體累積濃度為 7.635 ± 0.14 mg/kg；Cd+GA3 組的植體累積濃度為 10.522 ± 0.212 mg/kg；Cd+EDDS 組的植體累積濃度為 17.037 ± 0.637 mg/kg；Cd+GA3+EDDS 組的植體累積濃度為 16.216 ± 1.503 mg/kg。相較於傳統植生復育，整合型植生復育能有效地促進植物生長。

Abstract

This project will be carried out to improve energy crops Sunflower Research and Analysis of heavy metals in the soil. Explore the integration of plant growth hormones and chelating vegetation restoration soils contaminated with heavy metals and further assessment of energy crops Sunflower heavy-metal contamination of soil remediation operation -cum- related environmental factors intended. By experiment and explore plant growth hormones and heavy metals on the growth scenario explants (explants morphological analysis). The experiment's results indicate that GA3 can increase the growth rate of the plant: The average increment of the heavy-metal-added-only group is 18.89 cm; the average increment of the GA3-added group is 19.5 cm; the average increment of the EDDS-added group is 19.0 cm; the average increment of the GA3+EDDS-added group is 20.4 cm. The experiment's results indicate that EDDS can increase the solubility of heavy metals in soil and enhance phytoextraction: the plant accumulates a concentration of the heavy-metal-added-only group is 7.635 ± 0.14 mg/kg; the plant accumulates a concentration of the GA3-added group is 10.522 ± 0.212 mg/kg; the plant accumulates a concentration of the EDDS-added group is 17.037 ± 0.637 mg/kg; the plant accumulates a concentration of the GA3+EDDS-added group is 16.216 ± 1.503 mg/kg. Compared with the conventional methods of phytoremediation, these integrated measures can actually spur the growth of plants.



[095] 以添加胺基氮源生物刺激方式開發受三硝基甲苯污染土壤之 高效能生物復育-實驗室模場研究

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中文摘要

大量使用之 2,4,6-三硝基甲苯已造成土壤與地下水污染。本研究從受 TNT 污染土壤中分離出具降解 TNT 的細菌，根據不同的菌落型態和它們的 16S rDNA 序列這些分離出具 TNT 降解能力的菌，其中一株菌 *C. youngestrain* E4 在沒有外源的胺基氮源和碳源添加時並無法降解 TNT。但若同時添加胺基氮源和碳源則能有效提升其降解 TNT 的能力，且 TNT 降解能力會隨添加量增加呈正向關係。因此 *C. youngestrain* E4，降解 TNT 的能力可以確認是因共代謝現象所造成。同時我們發現外源性胺基氮源的添加除了增加細菌生長以外，也會提高降解 TNT 相關酵素例如 NemaA、NfsA 和 NfsB 的表現量，所以胺基氮源應該與誘導氮代謝的相關酵素有關。值得注意的是若用銨基取代胺基，TNT 降解的生物刺激效用並不明顯，而且細菌生長可能會受有毒 TNT 代謝物的累積而被受抑制，故銨基氮源並非合適生物刺激營養添加物。此外 *C. youngae* strain E4 應用到土壤泥漿相降解 TNT 污染土，雖然 TNT 污染土的濃度比較高但只要氮或碳源存在，則 TNT 降解的效率就會明顯的提高，故胺基氮源添加成為有效生物復育 TNT 污染的方法。雖然添加外源性胺基氮源和碳源可有效提升 TNT 被 *C. youngae* strain E4 降解，但其間的 TNT 代謝物對生物毒性的分析，發現經三天有氧培養條件所產生的 TNT 代謝物混合對日虎斑猛水蚤的毒性較為降解的 TNT 為高，顯示普遍使用的生物復育 TNT 仍有生物毒性累積的風險。本研究結果顯示當土壤受到 TNT 污染可藉生物刺激的方式並協同生物強化去除土壤中的污染，但仍須注意 TNT 代謝物所造成的生物毒性。

Abstract

Massively used 2,4,6-trinitrotoluene (TNT) caused soil and groundwater contaminations. Bioremediation is a currently important method to remove TNT contamination. In the present study, we isolated TNT-degradable bacteria strains from TNT-contaminated site through repeated enrichment process. As a consequence, bacterial clones of highly TNT-degradable capability were identified by distinct visualized colony morphology and categorized into different genera: *Enterbacter*, *Pseudomonas*, *Achromobacter*, *Serratia*, *Kelbeseiella* and *Citrobacter*, based on 16S rDNA sequences. Subsequently, these bacterial strains were inoculated into a TNT-NFG medium containing TNT with/without amino-nitrogen amendment composed of yeast extract and peptone hydrolysate as biostimulation. These collected TNT-degradable bacterial strains subjected to amino-nitrogen amendment exhibited a significantly higher TNT degradation capability than that of culture in a defined medium composed of TNT as sole nitrogen source. In particular, a most responsive isolate *Citrobacter* sp., which was further verified as *C. youngae* and named strain E4 with biochemical test kit API 20E, was used to assess the capacity of microbial degradation of TNT more detail in culture medium with/without exogenous nitrogen and carbon sources. As a consequence, *C. youngae* strain E4 was incapable of transforming TNT without exogenous nutrient amendment; however, the addition of amino-nitrogen and carbon amendments dramatically enhanced the efficacy of TNT degradation in a dose-dependent manner. Thus, metabolizing exogenous nutrient sources with simultaneous TNT degradation was verified as a process of cometabolism. The

biostimulation, in terms of nutrient amendment on TNT degradation, was mediated by not only an increase in the cell number but also the up-regulation of TNT nitroreductases, including Nema, NfsA and NfsB. The nitrogen amendment might be responsible for the induction of these enzymes relevant to nitrogen metabolism. It is noted that when ammonia instead of amino-nitrogen was used as nitrogen source, TNT degradation was only slightly increased, and surprisingly bacterial growth was inhibited probably due to toxic TNT metabolite accumulation. Thus, it seems only amino-nitrogen but not ammonia as effective exogenous nitrogen amendment for biostimulation. Moreover, when *C. youngae* strain E4 was applied to a TNT-contaminated soil slurry in the presence of nitrogen and carbon amendments, TNT degradation was effectively enhanced, albeit with a higher concentration of TNT in the contaminated soil. However, it is noted that the mixture of *C. youngae* mediated TNT metabolites was more toxic compared to TNT to *Tigriopus japonicus*. Taken together, our results indicate that consortia isolated from TNT-contaminated soil were able to degrade TNT through exogenous amino-nitrogen biostimulation. Still, the toxicity of TNT metabolite mixture needs to be further investigated.



[096] 以電容去離子技術移除地下水中砷之研究

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中文摘要

砷的毒害是一種全球性的地下水污染問題，而臺灣現有之地下水質砷污染來源包含土壤污染列管場址，因土壤中砷傳輸至地下水體，導致地下水中砷濃度超過地下水污染管制標準，以及砷來源主要來自於岩層的西南沿海與宜蘭地區地下水，若農業及漁業用水引用當地地下水做為水源，造成對生物或人體的潛在危害性。電容去離子技術(Capacitive Deionization, CDI)為一種節能、清淨、無需使用化學藥劑，且不產生二次污染物之新穎電化學處理技術，其原理是利用外加電場的控制與奈米孔洞碳電極的高比表面積，基於電荷分離機制，先以外部供電方式充電，在處理水體中產生電場，利用庫倫作用力將水中離子電吸附於電極表面上，在奈米孔洞間形成電雙層，進而產出乾淨水體。值得注意的是，與傳統的砷處理技術相比，CDI更適合處理含低濃度污染物之水體，恰符合砷在天然水體中低濃度之特性，且處理過程中能源需求低、無須添加化學藥劑，不會產生二次污染物，且電極可重覆使用。故與傳統的砷處理技術相比，利用CDI去除水中砷相當具有競爭優勢與應用潛力。

本研究計畫之目的在於評估CDI技術於移除地下水中無機砷之可行性，顯著提升對於五價砷與三價砷的去除效能，達到其與水體分離的目的。研究內容包含研析五價砷與三價砷之去除機制與移除效率，瞭解電場對於砷型態間的轉變之影響，與地下水體中不同物質的存在對於砷選擇性之影響，並發展實驗室規模CDI模組系統，應用於處理含砷地下水體，評估CDI技術應用於模擬/實場水體中移除砷之發展潛力。本研究試驗結果顯示，CDI對於水中低濃度的砷(如0.2 mg/L)具有良好的移除效果，其中五價砷以帶有負電荷之 H_2AsO_4^-

或 HAsO_4^{2-} 型態存在溶液中，在電場作用下(1.2 V)，容易以電吸附方式被去除；三價砷則是在電場作用下，與陽極反應被氧化成五價砷，再電吸附於電極表面而被去除。故五價砷之因其帶電荷型態，CDI對其有較佳的去除效率。另外，三價砷與五價砷在CDI系統中之吸附行為，皆符合傳統之Langmuir與Freundlich等溫吸附模式，以及擬一階動力學。在CDI的單元連續式實驗中，活性碳電極具有良好的再生性與穩定性，且藉由對連續吸脫附實驗後之電極表面進行分析，證實砷於電容去離子系統中主要是以電吸附機制被去除，電沉積還原機制並不顯著。再者，於競爭性分析中可知含砷溶液中其它物質，如氯化鈉或天然有機物質皆會對砷之電吸附效果造成影響。研究中進一步使用實驗室規模的電容去離子技術模組系統處理實場含砷地下水(含有天然有機物質及多種溶解性離子)時，砷去除率達70.5%，可使砷濃度從0.138 mg/L降至符合飲用水水源標準及農業灌溉用水標準(0.05 mg/L)之下，故以電容去離子技術處理含砷地下水體具有良好之移除效率與穩定性，具有發展潛力。

Abstract

Arsenic poisoning via groundwater is one of worldwide problems. Arsenic can be introduced in groundwater through nature sources and anthropogenic sources. Importantly, it is found that in some areas of Taiwan, the arsenic concentrations are much higher than the groundwater quality standards. However, traditional water treatments, such as adsorption, reverse osmosis, and ion exchange, have many limits for the removal of arsenic from aqueous solutions at low concentrations.

Capacitive deionization (CDI), or referred to electrosorption process, has been regarded as a novel water

purification technology, which has many advantages including low operating pressure, low energy consumption, no secondary waste, and easy regeneration. The mechanism behind CDI to remove ionic species from water is based on the charge separation, in which nanoporous carbon electrodes are charged and discharged to store and to release large quantities of ions, respectively.

As evidenced by this study, CDI process can be applied to effectively separate arsenic at low concentrations (0.2 mg/L) from aqueous solutions under an external electric field of 1.2 V. The removal capacity of activated carbon electrodes strongly depends on the applied voltage and initial arsenic concentration. Arsenate (As(V)) can be directly removed by the electro-sorption process at 1.2 V because of its negative charge. The mechanism of arsenite (As(III)) removal in the CDI system could be involved with the oxidation of As(III) to As(V), and thereby they can be further removed by the electro-sorption process. The electro-sorption/desorption experiments and electrode surface analysis provided evidence that the arsenic removal can be mainly attributed to electro-sorption rather than electrodeposition in this electrochemically assisted process. However, the presence of sodium chloride or natural organic matter causes a significant decrease in arsenic removal. For remediating natural groundwater, 70.5% removal efficiency of arsenic can be achieved, and the treated groundwater can reach the drinking water resource standard and agricultural irrigation water standard (< 0.05 mg/L). The results provide a fundamental understanding of the removal mechanisms for arsenic in an electro-sorption process, which is beneficial for the practical application of CDI techniques for the remediation of arsenic-contaminated groundwater.



[097] 同時處理底泥中持久性有機污染物及汞之整合性技術開發

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中文摘要

中石化安順場址不管是在污染物形態、污染物數量與污染物濃度均為國內外罕見，受污染土壤中所存在之戴奧辛(PCDD/Fs)、五氯酚(PCP)與汞含量均遠超過管制標準；而此種包含不同超高濃度毒性物質之複合式污染型態，是最難處理的污染整治場址。本研究於102~103年度已獲致初步成果，在第三年研究計畫中，本計畫分別以受中石化安順場址污染之海水池底泥及河川底泥為探討對象。結果指出處理海水池底泥時若操作溫度 600°C 且停留時間在 46 分鐘，可確保處理後底泥中戴奧辛/汞濃度可低於我國戴奧辛及汞之「底泥品質指標」之上限值(戴奧辛：68.2 ng-TEQ/kg；汞：0.87 mg/kg)。由於河川底泥之戴奧辛濃度約為海水池底泥的兩倍，處理後的河川底泥戴奧辛濃度若要低於「底泥品質指標」之上限值，則旋轉窯溫度在 600°C 條件下停留時間必需達 62 分鐘。

排氣控制方面，高效袋式集塵器可有效去除粒狀物，集塵器出口粒狀物濃度可穩定保持在 3 mg/Nm³ 以下；驟冷塔對戴奧辛及汞之去除效率皆隨冷凝溫度降低而提昇；流動床式活性碳吸附塔於 0.5 cm/day 之活性碳置換率下即可有效維持排放濃度符合法規標準，但因實際操作上，土壤濃度變動性高，故建議以 1 cm/day 為最佳之活性碳置換率。經過高效袋式集塵器、驟冷塔及流動床式活性碳吸附塔處理後，排氣中戴奧辛及汞濃度皆可低於我國最嚴格之排放標準(戴奧辛：0.1 ng-TEQ/Nm³；汞：50 µg/Nm³；SO₂ < 100 ppm)。本研究建立活性碳再生系統，採流動床式理念設計，活性碳吸附床中的球狀活性碳因重力往下移動至再生系統中，無氧條件下隨著反應時間增加，對戴奧辛及五氯酚的破壞效率愈高，對吸附於活性碳之戴奧

辛及五氯酚的破壞效率可達 98% 以上，對於總汞可達 99% 以上的脫除效率，由於再生系統出口端含有高濃度的汞蒸氣，可將廢氣導回驟冷塔之入口端，藉由汞珠的回收將其去除，整個熱裂解系統中並無含汞廢棄物或汞污泥的產生，更能達到污染減量之目的。

Abstract

In this case study, contaminated sediment containing extremely high concentrations of PCP, PCDD/F and mercury in An-shun site is selected for remediation test. Different characteristics of these contaminants have caused the difficulty of its effective remediation. For better remediation of contaminated sediment in An-shun site, a continuous pyrolysis system (CPS) is designed and applied in this study. In 2013~2014, CPS had been proved for effective removal of PCDD/Fs and mercury from contaminated soil. In this stage of the project, contaminated sediments collected from sea-water ponds or channels of An-shun site are remediated with self-developed CPS. Regarding the sediment in sea-water ponds, PCDD/F and mercury in the sediment is efficiently removed with the operating temperature of 600°C and the retention time of 46 min., and the concentrations are lower than the limits of sediment quality index (PCDD/Fs: 68.2 ng-TEQ/kg; mercury: 0.87 mg/kg). As for the sediment in the river, the operating parameters with 600°C and 62 min. are needed to meet the limits set for sediment because PCDD/F concentration in the sediment of river is two times of that in the sediment of sea-water pond.

Moreover, air pollution control devices (APCDs) including bag filter, quench tower and multi-layer adsorption system are tested simultaneously. Bag filter can effectively remove particulate

matter (PM) and keep the PM concentration lower than 3 mg/Nm^3 at bag filter outlet. Furthermore, removal efficiencies of PCDD/Fs and mercury achieved with the quench tower increase with decreasing operating temperature and multi-layer adsorption system (MAS) highly efficient to ensure that emission concentrations of PCDD/Fs and mercury are lower than the emission standards with AC replacing rate of 1 cm/day. However, SO_2 is significantly found in the exhaust of CPS with the remediation of sediment. WS with NaOH as absorbent can efficiently remove more than 90% SO_2 in the exhaust of the MAS.

For continuous operation of MAS, a system for BACs' regeneration is built with moving bed system. At oxygen-free condition (N_2 as carrier gas), increasing retention time is beneficial to enhance destruction efficiencies of PCDD/Fs and PCP adsorbed on BACs (>98%) and removal efficiency of mercury adsorbed on BACs (>99%). Although vaporized mercury is discharged from the regeneration stream of BACs, exhaust of regeneration system is introduced into the flue gas before the quench tower and gaseous mercury can be efficiently recovered. Finally, the CPS applied in this study is demonstrated to efficiently remove PCDD/Fs, PCP and mercury from contaminated soil and APCDs applied can also effectively reduce the pollutant emission to meet the Standards. Furthermore, secondary pollutants including waste BACs and condensate from quench tower are not discharged from CPS+APCDs. Experimental results indicate that the CPS+APCDs developed in this study is a powerful and environment-friendly remediation technology for removing PCDD/Fs and mercury from contaminated soil and sediment.



[098] 地下水污染環境法醫:發展高通量微生物偵測技術

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中文摘要

國內土水污染的環境法醫學主要以地層水文、化學性證據分析為主，尚缺乏生物性證據分析技術與相關知識。為填補此空白，本研究將導入高通量次世代定序 (Next-generation high-throughput sequencing, HTS) 與階層寡核苷酸引子延伸 (Hierarchical Oligonucleotide Primer Extension, HOPE) 等尖端分子生物分析技術，分析多氯乙烯地下水污染場址菌群結構與還原脫氯菌豐富度，以建立多氯乙烯污染的微生物指紋譜與污染指標菌群資料庫，結合多氯乙烯在厭氧還原脫氯過程微生物動態的關聯性，發展微生物追蹤法醫技術，相關研究結果並提供多氯乙烯生物整治所需的微生物學資訊。本計畫新設計偵測四屬脫氯菌的專一性引子，最佳化測試結果顯示 HOPE 分析技術能以低成本高通量的方式快速偵測於污染場址中相對豐富度高於 0.4% 的 *Dehalococcoides*、*Dehalobacter*、*Desulfitobacterium* 和 *Geobacter* 脫氯族群，或改以另一策略分析相對量更低的 *Dehalococcoides* 次族群，如與其他分生技術如分子選殖、定量 PCR 搭配運用，可快速提供場址整治過程脫氯菌群相關資訊。另一方面，本計畫導入土水微生物的高通量定序技術與大數據分析，除了全面性監測脫氯菌群之外，並探討土水微生物族群結構與含氯有機物的關聯性，提供地下水含氯有機物污染微生物分析診斷的基礎。本計畫建立的整合性地下水微生物分析平台、資料庫及相關知識，將有助於提升國內多氯乙烯生物整治技術之水平，增加土水產業之國際競爭力。

Abstract

Currently, environmental forensics for groundwater pollutions is mainly relied on the analysis of hydrology and chemistry evidence. The microbiological evidence analysis is also compulsory but still in its infancy. This study applies the cutting-edge molecular biotechnology such as next-generation high-throughput sequencing and hierarchical oligonucleotide primer extension to analyze the microbial community structure and abundance of the anaerobic dechlorinators in the polychlorinated ethylene contaminating sites with an attempt to build up the relevant microbial fingerprint and indicator microorganism database. We have developed specific oligonucleotide primers and combined with hierarchical oligonucleotide primer extension (HOPE) to detect the common dechlorinators, including *Dehalococcoides*、*Dehalobacter*、*Desulfitobacterium* and *Geobacter*. With the optimal conditions obtained, the method can detect the targets at the abundance as low as 0.4% with respect to total bacterial population. Also, it can detect the three subgroup of *Dehalococcoides*. On the other hand, high-throughput sequencing (HTS) technology and big data analysis were used to study the microbial community structure in aquifers contaminated with chlorinated compounds. Together with HOPE and HTS, the results obtained with the field samples suggest the efficacy of the methods used in this study to quantitative analysis of the dechlorinating populations, and providing relevant microbial diagnostic information for the improved management for polychlorinated contaminant bioremediation.

[099] 好/厭氧環境整治工法於滯水層氣體分布調查技術研發

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中文摘要

生物整治為目前進行污染場址整治的常用技術，其主要採用厭氧菌與好氧菌對污染物進行降解，以破壞、轉化或移動／遲滯污染物，以達到污染整治之目標。然而好/厭氧環境之營造成效檢驗為一具有技術重點之工作，相較於直接調查污染物之降解狀態，調查營造好/厭氧環境過程所產生氣體的範圍，以此作為有效整治區域得界定為一極為有效且快速的方式，並可回饋作為整治中厭氧或充氧環境營造手段的評估與調整之用。介電度之量測為進行氣體含量量化量測之高潛力技術，有鑑於此，本研究利用具發展性之時域反射技術(TDR)，採用單棒式三叉感測器設計，而訊號分析採用頻率域相位波速分析法進行，建立快速且便捷可量測監測井周邊氣體含量量測技術，並提出採用時序性的跨孔雷達井測進行氣體含量調查之分析方法，透過孔內透地雷達進行飽和土體中2維氣體分布之調查評估，建立有效之滯水層中氣體含量分布調查工具。室內試驗已驗證本計畫所提兩項技術之可行性，而在台南市的電極電解水生物整治工法試驗模場所進行之測試，相隔15天的監測結果顯示土體無明顯氣體變化，反饋與模場試驗方，使其發現設備電源損壞之問題，間接顯示相關監測之重要性。

Abstract

On site bioremediation is one the most popular technique applied in treatment of groundwater contamination. Usually, aerobic and anaerobic condition would be created to increase the efficiency of biological treatment. Assessment of the treatment directly from monitoring the concentration of the sources of contamination is not efficiency and it probably may slow down the process to adjust the design of the remediation. Comparing to this, measuring the distribution of air in aquitard would be an alternative method to evaluate the performance of the design. Dielectric constant measurement of the multiphase material has high potential to measure the air concentration. Accordingly, the purpose of the project is to develop an efficient air content distribution investigation technology in aquitard. A system based on time domain reflectometry (TDR) technique was developed to measure the air content around the monitoring well and borehole ground penetrating radar system was applied to investigate the distribution of air content in 2D which is based the a time-lapes model proposed by the project.



[100] 利用全底泥及孔隙水毒性鑑定評估進行二仁溪底泥相關污染物

確認

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中文摘要

本研究主要目的為利用端足目動物(*Hyalella azteca*)做為底泥生物毒性試驗物種，篩選二仁溪(ER1~ER10)及三爺溪(SY1~SY5)污染底泥進行毒性試驗，運用全底泥(whole sediment)和孔隙水(porewater)毒性鑑定評估(Toxicity Identification Evaluation, TIE)技術描述和鑑定溪流底泥的主要毒性來源。本研究 TIEs 主要探討氨、重金屬和多環芳烴三類化合物。兩階段 TIE 處理程序係運用添加沸石、EDTA、陽離子交換樹脂和粉狀椰子炭/固相萃取來鑑定全底泥和孔隙水中造成毒性之污染物。生物毒性部份則為使用 *Hyalella azteca* 進行全底泥 10 天/ 孔隙水 48h 之毒性試驗。三爺溪檢出重金屬(鉻、鎳、鋅、鉛及銅)和多環芳烴(CHR, BbF, BaA, Ant, and BaP)，且檢出濃度均超過底泥品質指標之下限值。全底泥結果顯示 TIE 樣站 ER8 及 SY5，主要毒性來源為氨氮，添加沸石會顯著降低毒性；而樣站 ER4、ER9 是由氨氮及重金屬(Zn、Cd、Cr、As)所引起的毒性；樣站 ER6 為 Cr 金屬導致其毒性。本研究結果顯示孔隙水 TIE 樣站 ER8，主要毒性是氨氮，添加沸石會顯著降低毒性；樣站 ER2，主要毒性是氨氮及 Σ PAHs，添加沸石及固相萃取後會顯著降低毒性；而樣站 ER3、SY1 及 SY3 是由於重金屬(Zn、Ni、Pb、Cd、Cr、As)所引起的毒性，添加 EDTA 會顯著降低其毒性。TIE 是用於毒性測試，再配合特定化學品分析之綜合方法，這種方法可以更容易地追蹤毒物的來源，以降低毒性。總體而言，環境底泥及孔隙水樣品中不同類別的化合物(有機和無機)和毒性之間存在顯著相關性，但這些相關性並不代表兩者和毒性之間存在著直接的因果關係，包括可能存在於底泥中有機碳或孔隙水萃取流程

中會改變底泥動態平衡都可能是影響毒性的因子。由於全底泥和孔隙水 TIE 研究的底泥毒性不同，使用兩種 TIE 方法分別進行風險評估，未來也將探討其相關性，可提供底泥毒性更準確的風險評估。

Abstract

This study utilized freshwater amphipods (*Hyalella azteca*) as the sediment toxicity test species for assessing sediment-associated contaminants in order to screen for risk levels in the Erren River (ER1-ER10) and San-ye River (SY1-SY5). Two-phase toxicity identification evaluations (TIEs) using zeolite, ethylenediaminetetraacetic acid (EDTA) chelation, cation exchange (CE), powdered charcoal/solid phase extraction, and various other analytical techniques on whole-sediment and pore water samples were conducted to determine the causative contaminants. Untreated (baseline) and TIE-treated sediment and pore water samples were evaluated for toxicity using *H. azteca* 48-h and 10-day survival tests. Heavy metals (Cr, Ni, Zn, Pb, and Cu) and polycyclic aromatic hydrocarbons (CHR, BbF, BaA, Ant, and BaP) were detected in the San-ye River and exceeded the lower limits of sediment quality guidelines. The TIE focused on three classes of contaminants: ammonia, metals, and PAHs. Whole-sediment TIE indicated that the major toxicant at sampling sites ER8 and SY5 was ammonia and that its toxicity was significantly reduced by the addition of zeolite. Toxicity at sampling sites ER4 and ER9 was induced by ammonia and heavy metals (Zn, Cd, Cr, As), whereas metallic Cr was at toxic levels at ER6. Pore water TIE indicated that the major toxicant at sampling site ER8 was ammonia, but zeolite significantly reduced its levels.



Toxicity at sampling site ER2 was induced by ammonia and Σ PAHs at sampling sites ER3, SY1, and SY3, and was caused by heavy metals (Zn, Ni, Pb, Cd, Cr, and As) that were identified by adding a chelating agent (EDTA). TIE can be used to confirm that a causative toxicant has been correctly identified and quantitatively correlate its measured toxicity to its concentration. This study revealed that different compounds (organic or inorganic) in whole sediment and porewater are highly characteristic of specific toxicants; however, other factors, chemicals, or organic carbons defy identification and are still cryptic. Due to the different toxicities of whole sediment and porewaters, TIE studies conducted to assess risks and correlations are discussed in order to reveal the causes of toxicity.



[101] 利用滲透灌注技術於地下水生物整治之應用研究

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中文摘要

現地生物整治法係為現今常被應用於地下水受含氯有機物污染之整治方式。此法常利用重力流方式，將基質或營養鹽注入，使其自然沈降並擴散，來加強微生物生長與降解反應，達到分解污染物之效果。但此種方式不易確認基質是否能有效的滲透且均勻的散佈於欲整治範圍。

爰此，本計畫應用大地工程中常用於土壤改良之滲透灌漿技術，進行基質注入技術之研究試驗，針對基質注入砂柱試體滲透性及持續時間等指標，評估不同土層條件下之各種基質適用性。

本年度計畫為建置一套滲透灌注試驗設備，以低壓滲透的方式，將市售三種基質灌注於四種不同粒徑分佈的砂柱試體，針對其滲透性與持續性等進行探討。

試驗結果發現，中砂($D_{50}=0.51\text{mm}$)試體中，三種基質皆能達到目標灌注高度；再者，A 砂($D_{50}=0.45\text{mm}$)、B 砂($D_{50}=0.30\text{mm}$)及細砂($D_{50}=0.23\text{mm}$)方面，僅 EcoClean 能達到目標灌注高度。而 HRC 與 EOS 可能由於黏滯性較高、稀釋濃度較濃的影響，致使最終未能達到目標高度；持續性試驗結果顯示，HRC 的殘留率最高，EOS 次之，而 EcoClean 較其他二者為差。

綜合而言，HRC 的持續性最佳，但仍有在質地較細的試體中無法達到目標灌注高度的問題。建議未來可針對基質的稀釋比例、灌注體積或灌注壓力的調整等面向，進行更深入之探討，藉以找尋最佳的灌注條件，來達到預期之灌注目標。

Abstract

In-situ bioremediation is a method which has been often used to treat the groundwater polluted by the chlorinated

organic compounds. To inject the substrates into groundwater, the method by gravity flow is commonly used, so that the substrates or nutrients are injected and they will settle and diffuse freely.

To enhance microorganisms growth and degradation reaction, consequently, the pollutants can be decomposed. However, it is difficult to recognize whether the substrates are distributed effectively and evenly in the areas to be treated.

Therefore, in this project, a method of permeation grouting which has been frequently used in geotechnical engineering to improve the soil was applied. Using this method, experiments are conducted to evaluate the index of the permeability and persistence of the substrates in the column-shaped specimen, and to estimate the suitability of different substrates in different soil conditions.

In this year, an experimental equipment for permeation grouting was established. Using this equipment, a method of low pressure permeation was applied to injected 3 different kinds of commercial products of substrates (namely, EOS, HRC and EcoClean) into the column-shaped specimens of the soils with different particle size distribution to observe the permeability and persistence of the substrates.

Test results are as follows. For the specimens of medium sand ($D_{50}=0.51\text{mm}$), the targeted heights of permeation grouting was reached for the 3 kinds of substrates. As for the specimens of sand A ($D_{50}=0.45\text{mm}$), sand B ($D_{50}=0.30\text{mm}$) and fine sand ($D_{50}=0.23\text{mm}$), only EcoClean could reach the targeted heights. Because of greater viscosity and higher concentration, HRC and EOS could not reach the targeted heights. The results of persistence showed that the retention rates of the substrates, in decreasing order, were



HRC, EOS and EcoClean.

In general, HRC has the best persistence, however, for some specimens with finer soils, it can not reach the targeted heights of permeation grouting. It is suggested dilution ratios of the substrates, volumes and pressures of permeation grouting be studied and adjusted in the future to obtain the optimum permeation grouting condition to achieve the goal of permeation grouting.



[102] 汞污染土壤之二階段式生物復育技術開發

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中文摘要

土壤和水是地球上最重要的自然資源，然而，在過去數十年中，由於工業化、人口的大量增加和城市化，環境重金屬污染問題日益嚴重。其中，汞因其具高毒性及生物累積等特性，對生物體及環境可能影響或危害，具有高風險 (Clarkson et al., 2003; Canuel et al., 2009)，因此汞污染需優先被進行整治 (USEPA, 2007)。利用生物復育程序 (Bioremediation) 進行環境污染整治是屬於對環境最友善的技術，而且也具有包括經濟效益所需花費少，容易操作且較易受社會大眾接受等優點。

本計畫建立了污染場址耐汞細菌菌株的篩選方法，並建立以 DGGE 結合 16S rDNA 鑑定菌株的菌種方法，篩選出的三株菌株，最高皆可耐受 100 ppm 汞濃度，應可耐受原污染場址 60 ppm 汞濃度環境，篩選出菌株帶有 merA 基因，可將汞離子還原成元素汞，揮發至大氣中稀釋。

利用次世代定序技術分析加汞前後菌種基因變化發現，菌種會改變細胞膜結構並加強能量的攝取以因應重金屬汞壓力，細菌會利用硫的吸收與同化路徑合成 Glutathionein 等抗氧化基因抵抗重金屬汞產生的氧化壓力，並大量表現熱休克蛋白與伴隨蛋白修復汞導致的蛋白質錯誤，最後利用汞操縱組將環境中汞移除。

改良菌株所需要的 pHERD20T 載體已測試完成，可以用此載體系統將本土菌株 A46 改良表現綠螢光蛋白，未來可利用此載體系統改良本土菌株，依照不同需求使菌體表現不同蛋白質。

Abstract

Soil and water are the most important natural resources on earth. However, environmental pollution of heavy metal is

escalating due to industrialization, huge population and urbanization. Mercury has been reported as highly toxic and need priority treat. Bioremediation is economy and environmental friendly approaches and also acceptable by general public. However, due to very low solubility of mercury compounds. It's not easy to be used by microbes. Therefore, using chelating agent to make mercury compound in soil transferred from solid phase to liquid phase is an effective way for bioremediation.

We set up filter conditions of mercury-resistant bacteria in contaminated sites, and identification of bacteria strains method by 16S rDNA DGGE combination. In the above experiment results, among the three strains tolerance to limit of 100 ppm mercury wherefore be able to tolerance to 60 ppm mercury concentration in contaminated sites.

In the results of Next Generation Sequencing analyze bacteria genome changes of treatment mercury before and after. Heavy metal stress will change cell membrane structure and strengthen energy intake. Bacterial synthesize of glutathione antioxidant genes in order to resistant to mercury produced oxidative stress via sulfur uptake and assimilation route. Overexpression of heat shock protein and chaperon will recover misfolded protein. At last, bacterium removed mercury in the environment by mercury operon.

The current progress of the experiment, improved strains require pHERD20T vector testing has been completed. Furthermore, the future can be used this vector improved native strain, that is according to different requirement make bacterial expression different protein.

[103] 長途管線偵漏系統開發研究

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中文摘要

本研究發展之串聯式水平多孔隙管偵漏系統，可應用在長途輸油管線及油料儲槽土壤氣體之監測，為一新型長途管線洩漏偵測土壤氣體技術。新的洩漏偵測系統可沿著地下管線或油料儲槽進行鋪設，為不滲透聚乙烯管等間距串聯連接橡膠多孔隙管。傳統土壤氣體採樣技術有兩種，分別是：被動式採樣和動態採樣。被動式採樣為使用吸附劑捕捉在土壤氣體中擴散的污染物，通常需要埋在淺層土壤中數天至數周，再取出送至實驗室進行脫附分析。動態採樣為使用探針或是土壤鑽孔方式到地表下方包氣帶，再使用泵浦抽取土壤氣體樣本。動態採樣的方便性是可配合移動式實驗室或攜帶型儀器於現地進行即時分析。然而，常規的土壤氣體採樣方式應用在長途管線偵漏時，通常需要大量的土壤氣體樣本進行分析。

新的洩漏偵測系統可使得在長途輸油管線進行洩漏偵測時，大量減少土壤氣體採樣分析樣本數量及採樣鑽頭消耗數量。本研究開發的新偵測系統的有效檢測距離能達到至少 20 米，而傳統的土壤氣體採樣影響範圍只有 5 米。由串聯式多孔隙偵漏試驗結果證實在粗砂的環境下，汽油以及柴油的漏源在 20 米內皆可被偵漏出來。而在細砂環境下，只有汽油可以被偵出。本研究也發展出數學模式預測串聯式水平多孔隙管偵漏系統內不同位置及距離之空氣流體的分布。

Abstract

This project presents a new leak detection system for a long-distance pipeline using soil-gas techniques. The new leak detection system runs underground along the nearby pipeline and consists of intermittent porous tubes

connected in series with impermeable polyethylene tubes. Conventional sampling techniques used in soil-gas surveying fall into two categories: passive sampling and dynamic grab sampling. Passive sampling uses an adsorbent to trap contaminants that diffuse through the soil gases. Passive adsorbent samplers are buried in the shallow soil for a period of days to weeks. The adsorbent is then retrieved from the soil and transported to a laboratory where desorption and chemical analyses are performed. Dynamic grab sampling requires the installation of probe or soil boring in the vadose zone followed by the withdrawal of soil gas with a pump. Applying conventional soil-gas techniques to long-distance pipelines for leak detection usually requires a large number of soil-gas samples and analyses.

Applying the new detection system to long-distance pipelines for leak detection can reduce the large number of soil-gas samples and analyses that are required when conventional soil-gas probes are employed. The effective detection distance of the new system is determined at least 20 m, while the effective detection radius from the conventional soil-gas probes is only ~5 m. Laboratory leak tests confirm that both gasoline and diesel can be detected at a distance of 20 m in the media of coarse sand. In the media of fine sand, only gasoline can be detected at a distance of 20 m. A mathematical model is developed to predict the distribution of airflow in the new leak detection system for each porous tube at various distances from the extraction end. The model is useful in designing the distribution of airflow in a new detection system to monitor fuel leakage from a long-distance pipeline.



[104] 前鎮河底泥中之環境荷爾蒙流布調查及現地加強式生物整治 結合電動力法之研究

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中文摘要

本研究計畫旨在調查前鎮河(含鳳山溪)底泥中之環境荷爾蒙(包括:8種鄰苯二甲酸酯類、11種鄰苯二甲酸酯類代謝物、壬基酚及雙酚A)之殘留濃度,並嘗試開發加強式生物整治程序結合電動力法(簡稱“現地加強式生物-電動力整治技術”)整治環境荷爾蒙污染底泥,期盼建立一本土化可行的現地整治技術。於前鎮河(含鳳山溪)底泥中鄰苯二甲酸酯類、鄰苯二甲酸酯類代謝物、壬基酚及雙酚A殘留濃度調查工作方面,已完成針對選定之5個採樣點位進行4梯次(枯水期)採集底泥樣品,綜合調查結果發現,於底泥中可檢出雙酚A、5種鄰苯二甲酸酯類及7種鄰苯二甲酸酯類代謝物化合物。其中,於紅毛港路橋處檢出mg/kg濃度(ppm濃度)等級之鄰苯二甲酸二(2-乙基己基)酯(DEHP)殘留量,其最高濃度(2.944mg/kg)為「底泥品質指標之分類管理及用途限制辦法」管理下限值之1.49倍。而屬於鳳山溪流域的各採樣點位之鄰苯二甲酸二異壬酯(DiNP)殘留濃度有相近之趨勢(甚至高於DEHP)。於現地加強式生物-電動力整治技術方面,電動力反應系統之底泥反應器所充填之底泥係採集自紅毛港路橋處,試驗期間則分別在陽極槽及底泥反應室中添加釋氧劑(以營養鹽為基質之稀釋過氧化氫溶液),並施加定電壓(1.5V/cm)進行為期14日及28日期程之5組電動力試驗(含1組對照組)。試驗結果顯示:(1)單純施加電場(1.5V/cm)結合現地微生物,有助於鄰苯二甲酸酯類之去除,因施加電場所產生之電滲透流可促使吸附於底泥之有機污染物釋出,提高污染物之生物可利用度;(2)釋氧劑於底泥反應室注入不僅能減緩底泥pH值受電動力之酸鋒與鹼鋒之影響(平均

pH=7.50),並降低釋氧劑於傳輸過程中之損失,使其更直接被生物利用為生長碳源及氧氣來源,藉此提高降解標的污染物之效果;(3)將釋氧劑注入於陽極槽液雖可藉由電動力傳輸供微生物利用,但於傳輸過程中之損失,將降低促進微生物生長之效果;(4)由分子生物技術(PCR-DGGE)分析得知,添加釋氧劑及施加電場皆可促進現地微生物之生長,使菌相較為豐富;及(5)由定序結果發現,電動力輔助生物降解系統中,Flavobacterium sp.、Bacillus sp.、Pseudomonas sp.及Rhodococcus sp.為可降解鄰苯二甲酸酯類(PAEs)之菌株。此外,本研究專案之組合整治技術其操作成本粗估約為1,298元/噸,具經濟可行性。綜合上述結果顯示,本組合整治技術應是一種可行的整治技術。

Abstract

The objectives of this study are two-fold: (1) to investigate the residual concentrations of environmental hormones including eight phthalate esters (PAEs), 11 phthalate esters metabolites (PAEMs), nonylphenol (NP), and bisphenol A (BPA) in sediment samples collected from the Cianjhen River; and (2) to develop an in situ enhanced bioremediation coupled with electrokinetic process (in short, “the in situ enhanced bio-EK remediation technology”) for the removal of environmental hormones of concern in sediments of the Cianjhen River. To meet the first objective, four batches of sediment have been sampled at five sampling sites along the Cianjhen River during the low water season. Total of BPA, five PAEs and seven PAEM were detected in the sediment samples. On the other hand, NP were below their method

detection limits (i.e., < 100 ng/L). However, the level of parts per million (mg/kg) of residual di(2-ethylhexyl) phthalate (DEHP) was detected for sediment samples collected at Hungmaokang-Road Bridge. The relevant highest concentration (2.944 mg/kg) is 1.49 times greater than the lower management level of the “Regulations for Systematic Management of Quality Indices of Sediments and Their Use Restrictions” promulgated by Taiwan EPA. To meet the second objective, five tests (including one control test) with a remediation time of 14 d and 28 d, were carried out using the in situ enhanced bio-EK remediation technology under an electric potential gradient of 1.5 V/cm for sediment samples collected at Hungmaokang-Road Bridge. During the test period, diluted hydrogen peroxide in the nutrient matrix was injected into the anode compartment and sediment compartment, respectively. Test results are given as follows: (1) enhanced removal of PAEs was obtained by simply coupling EK and intrinsic microbial because the electroosmotic flow would render the desorption of organic pollutants from sediment particles resulting in an increased bioavailability; (2) injection of oxidant into the sediment compartment not only would alleviate the pH variation due to acid front and base front (maintaining at neutral pH), but would be directly utilized as the carbon source and oxygen source for microbial growth resulting in an enhanced degradation of organic pollutants; (3) as compared with the case of injecting oxidant into the sediment compartment, injection of oxidant into the anode compartment would yield a lower degree of microbial growth due to a loss of oxidant during the transport by EK; (4) through the analysis of molecular biotechnology (specifically, PCR-DGGE) it was found that both addition of oxidant and application of external electric field would be beneficial to the growth of intrinsic microbial and

abundance of microflora; (5) the sequencing result showed that PAEs could be degraded by the following four strains: *Flavobacterium* sp., *Bacillus* sp., *Pseudomonas* sp., and *Rhodococcus* sp. It was also determined that “in situ enhanced bio-EK remediation technology” is economically feasible because of its low operating cost of no greater than 40 USD/ton. Based on the preliminary test results obtained, the in situ enhanced bio-EK remediation technology appears to be promising.



[105] 建立污染(潛勢)土地結合再生能源利用評估機制

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中文摘要

美國環保署在近年來進行對褐地、超級基金場址、掩埋場、廢棄礦場等結合發展再生能源的研究。目前，美國環保署聯合了美國再生能源實驗室(NREL)加快污染土地可再生能源的發展。評估項目包括確定在褐地發展再生能源項目的最佳技術及安裝方式、潛在的發電能力、投資回報預估和經濟可行性。目前(2014)，美國已完成 709.8 MW 之再生能源裝置容量於污染土地。

目前臺灣列管中的場址總面積約 1375 公頃，另外，具高污染潛勢之廢棄工廠三萬四千家，由目前統計結果可知，已有 54.43%(19095 家)轉為住宅、商業、文教、建築等其他用途使用。剩下的 45.57%高污染潛勢之廢棄工廠中，少數(1158 家)位於敏感性農業用地與水產養殖用地，多數(14000 家)為工業使用土地(行政院環保署，2012)。其總面積約 1400 公頃。重金屬高污染潛勢農地則約 15000 公頃。亦即，目前臺灣的列管場址與高污染潛勢土地總面積共約一萬七千公頃，且多為農地。

由於農地污染之特色為傳統整治工法時常破壞地力，配合我國永續發展之整體政策與農地農用政策、農地再生政策之一環，利用污染農地以發展再生能源(如太陽能、生質作物)，除了可節省整治經費，亦可作為未來再生能源政策參考。本研究已計算農地場址之再生能源潛力與 GIS 地圖，並建置經濟與環境成本效益計算之方法論。估算全台污染農地場址總面積(共 347 公頃)來計算，顯示仍是以發展太陽能發電潛力為最高，潛力大小為太陽能>甘蔗酒精>甘藷酒精>培地茅發電。生質能所需場址數與污染農地面積高過太陽能需求，培地茅發電經濟

效益為此四種再生能源類別為最低。另外，太陽能則是不管於發電潛力與所需污染農地面積分析，都是為四種再生能源最具有潛力，不僅發電潛力高，所需污染農地面積亦是最少的。若以縣市來估算污染農地發展再生能源環境效益，前五大潛力縣市為彰化縣、桃園市、台中市、台南市、及雲林縣，總環境效益分別以太陽能 379,773,904 元為最高。其中，彰化縣不僅發電潛力居第二，其再生能源發電總環境效益亦是最高，代表該縣市發展再生能源對於環境助益也是較大的。

Abstract

Recently, the USEPA and National Renewable Energy Laboratory (NREL) launched RE-Powering America's Land program to promote the re-power contaminated lands with renewable energy and evaluated the feasibility of technologies and installations, energy potential and economic performance. EPA developed national level site screening criteria in partnership with the National Renewable Energy Laboratory (NREL), U.S. Department of Energy (DOE) for wind, solar, biomass, and geothermal facilities. By 2014, there has been 709.8MW installed capacity on the contaminated lands in the U.S., including contaminated lands, landfills, and mine sites

Currently the total area of listed contaminated sites in Taiwan is about 1375 hectares. As a part of the national sustainable development plan, the combination of contaminated lands and renewable energy (solar, biomass) could not only save the cost of remediation but could contribute to the goals of the national green energy plan. In addition, the EPA could collect money flow back



from this approach to clean up more contaminated lands. We already calculated the potential of the selected green energy on the farm land sites and developed the GIS map. The method was also developed to calculate the monetary benefit from the green energy.

This study draft on the experience of the U.S. and set up the criteria of solar, and biomass for the contaminated lands based on the environmental limitation of Taiwan. The solar power potential was the highest on polluted agricultural land, total area of was about 347 ha in Taiwan. In addition, the high contribution of renewable power and environmental benefits for five cities were Changhua County, Taoyuan City, Taichung, Tainan and Yunlin counties. Changhua County was not only second on power potential, but also was highest on environmental benefit of renewable energy on polluted land.

Based on the collected information, we also developed the GIS map and calculated the economic and environmental cost and benefit under various scenarios to provide the reference for the policy makers.



[106] 建立專一性、廣效性及耐酸性細菌生物感測器快速篩測 環境底泥中的污染物

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中文摘要

臺灣重點河川底泥常見重金屬污染物，其中以砷、鎘、銅、汞、鉛及鋅等為主。除了重金屬外，底泥中亦存在其他毒性物質，因此，除了檢測底泥中存在的特定重金屬外，檢測底泥中的其他毒性物質的存在亦為重要的課題。再者近年來，環境酸化污染事件日益增加，使得底泥中重金屬與毒性污染物對生態之影響性更加難以正確地評估。因此，發展高靈敏度、低成本、且能反應生物有效性之檢測法，用以偵測底泥中重金屬與其他毒性物質是急需迫切之議題。本研究計畫完成針對銅、鋅專一性生物感測器，以及針對基因毒性(SOS response)與熱休克(heat shock)壓力之廣效性生物感測器之研發，並且完成其靈敏性與穩定性之評估以及環境樣品檢測。此外，本計畫亦成功應用陽明山篩選出之嗜酸性菌種 Y10 完成耐酸性廣效性生物感測器，藉由鐵氧化能力受毒性物質之影響，進而產生呈色差異。由於其可藉由肉眼直接觀測可應用於酸性環境，在現地及酸性環境使用上具有非常大的優勢。此外，本研究計畫所建構之生物感測器具有以下優點：不僅培養方便，同時也可以快速篩測鋅、銅與其他毒性，提供生物有效性的資訊，以及檢測成本相較於化學分析法更為便宜。本研究計畫成果將有助於更準確的環境風險評估，提供環保署及相關單位建立更有效的環境監測策略。

Abstract

Heavy metals including As, Cd, Cu, Hg, Pb, and Zn were highly polluted in several major rivers in Taiwan. In addition to heavy metals, other toxic chemicals are

present in the sediment. Therefore, in addition to analyze the presence of the specific heavy metal, it is also important to detect the presence of toxic chemicals in the sediment. Recently, acidic pollution events in river were increasingly reported. This makes more difficult to accurately assess the toxicity and ecological impact of heavy metals and other toxic chemicals in the sediment. Therefore, there is an urgent need to develop highly sensitive, inexpensive, and reflecting bioavailability methods to rapidly detect toxic pollutants in the rivers and sediments. The present study has established a series of specific bacterial biosensors (for Zn and Cu) and non-specific bacterial biosensors (for SOS response and heat shock). In addition, the developed bacterial biosensors were further analyzed for their sensitivity and stability toward toxicants and environmental samples. Moreover, an acidic bacterium Y10 was isolated and characterized from Yangmingshan soil. The acidic bacterium Y10 was evaluated as a non-specific biosensor in acidic environment based on the inhibition of the toxicants to the iron-oxidizing ability of this bacterium, resulting in color change in solution. In addition, this bacterium can be used as a biosensor in acidic environment and observed by eyes, which makes it having potential for on line analysis. Furthermore, results from this study showed that the developed bacterial biosensors providing advantages including: easily cultured, rapid detection for Cu, Zn, and toxicity, providing bioavailability information for pollutants, and less expensive than that of chemical methods. Results from this research thus provide valuable information to Taiwan EPA and other agencies for effective and inexpensive environmental monitoring approaches and strategies.

[107] 建置碳足跡盤查及評估程序協助綠色整治技術之決策分析研究

— 以農地重金屬污染場址為例

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中文摘要

綠色整治(green remediation)依據場址特徵進行環境調查且選擇整治技術前，進行減碳為目標之碳足跡盤查與計算，以了解排碳熱點，做為整體減少碳排放之決策分析。臺灣地區農地污染大部分因臨近工廠/場之廢水不當排放，或非法棄置/掩埋。如桃園、彰化及台中皆產生過錳米，為保護國人健康需銷毀農作物且進行農地整治復育以恢復地力。至102年底止，累積公告農地控制場址共2437筆(面積315公頃)，已解除列管1965筆(面積430公頃)。目前已列管農地污染改善方式如(1)含銻、銅、鎳、鋅且濃度較低採「翻土混合稀釋法」；(2)含鎘、鉛、汞及濃度較高農地採「酸洗法」或部分污染土壤採「熱處理法」、「排土法」、「客土法」。故本研究擬進行過去完成及現在正進行之污染重金屬農地復育技術之碳足跡盤查，以提供政府及業者綠色整治之管理決策參考。共收集並盤查計算11個案例，結果顯示不同工法差異大，如單純使用翻轉混合稀釋法5個場址，碳足跡計算結果 $0.28-2.18 \text{ kgCO}_2/\text{m}^2$ ； $0.92-3.63 \text{ kgCO}_2/\text{m}^3$ ； $0.57-2.79 \text{ kgCO}_2/\text{ton}$ 。當翻轉混合稀釋搭配排客土法6個場址之計算結果較高 $0.57-11.48 \text{ KgCO}_2/\text{m}^2$ ； $1.91-19.96 \text{ KgCO}_2/\text{m}^3$ ； $1.19-12.48 \text{ KgCO}_2/\text{ton}$ 。差異來自於排客土的車輛運送土方量較多故消耗油量較多，故碳排放量較高。在整治中消耗油量最多為挖土機進行翻土，貢獻較高的碳排放，故可在機具選擇如使用碳排放係數較低燃料或省油之機械等。此外，本研究完成一個簡易計算器以提供未來政府及業者應用於農地重金屬污染場址之碳足跡盤查計算。同時整合綠色整治6個核心元素以工法管理概念與執行，避免整治污染場址而產生二次污染，造成環境品質惡化。例如：(1)能源需求：儘量減少自場址外輸送進來電力的依

賴、提昇省電設備的能源使用效率到最高點、對於高耗能設備定期檢討提昇其能源使用效率；(2)廢氣排放：應有效率使用重型設備並妥善保養、使用柴油的重型設備應改良其引擎以使用潔淨能源(低含硫量柴油)、作業流程應妥善規劃以減少設備運轉及怠轉時間；(3)水資源需求及保護：整治過程中儘可能減少使用淡水(fresh water)並儘可能重複使用、回收再利用處理過的水、避免因過度使用肥料或農藥而影響表面水或地下水的水質；(4)土地及生態系統：儘量減少使用具破壞性的現地整治技術、儘量減少對土壤或動植物生長環境干擾、採用生態復育技術；(5)材料消耗與廢棄物產量：使用低廢棄物產量的技術、回收及再利用材料(包括建築物拆解後的廢棄物)、儘量減少使用或移除未受污染土壤、減少廢棄物產量；(6)長期的環境保護與復育：減少二氧化碳、甲烷及其他溫室氣體排放、採用利於長期整治及未來經濟發展的可再生能源系統、設計可重複使用的整治設備。建議適用於農地重金屬污染場址之綠色整治工法管理概念與執行如(1)能源需求：儘量減少自場址外輸送電力、提昇省電設備的能源使用效率、對於高耗能設備定期檢討提昇其能源使用效率；(2)廢氣排放：有效率使用重型設備並妥善保養、使用柴油的重型設備應改良其引擎以使用潔淨能源(低含硫量柴油)、作業流程應妥善規劃以減少設備運轉及怠轉時間；(3)水資源需求及保護：整治過程中儘可能減少使用淡水(fresh water)並儘可能重複使用、回收再利用處理過的水。此外，建議：(1)未來整治過程中，可依據碳排放熱點做為改善依據，思考更好的替代方案。(2)因應目前我國現行整治技術選擇以使用翻轉稀釋法及排客土法兩種工法為主，未來可評估其他整治工法以



達到既能解決農地重金屬污染問題，亦可有效進行低碳排放。(3)本研究之數據取得來源整治廠商提供歷史資料，可能在機具耗油上填報之資料較不精確，影響計算之數據品質。但由於歷史資料無法改善，建議未來整治工程進行時，當日直接填寫機具耗油紀錄於工作日誌上，以獲得即時正確的資料，又可避免事過境遷發生遺忘或疏漏問題。(4)本研究建置碳足跡盤查計算之系統邊界為各農地坵塊之邊界，且以整治施工期間之機具耗油、XRF篩測及肥力恢復等項列入計算。其他如人員差勤、整治設備運送、採樣/樣品運送/分析及處理機構之碳排放皆未納入計算。故建議為更充分反應場址整治實況，未來可規劃示範計畫，除可驗證修正本研究提供之簡易計算器外，且評估擴充各項碳排放因子。

Abstract

Green remediation is the trend of cleanup actions that calculates the carbon "footprint" of investigation and remediation prior making technology decisions for obtaining the hot spot of carbon emission which may avoid the potential environmental damage of further remediation. In Taiwan, the farmlands contaminated with heavy metals from industrial wastewaters and illegal hazardous wastes disposal have produced cadmium rices such as in Taoyuan, Changhua and Taichung area which were destroyed by incineration for protecting the public health. Afterwards, the farmlands have remediated to recover the ability of planting. By the end of year 2013, there were accumulated 2437 control contaminated sites (area 315 acre) and 1965 control contaminated sites (area 430 acre) were released. The remediation technologies applied in contaminated farmlands were (1) turnover and mixing for lower concentrations of Cr, Cu, Ni and Zn; (2) acid washing for Cd, Pb, Hg and higher concentration; or parts of the remediations of farmlands by incineration, excavation, clean soil of higher

concentrations. Therefore, the objective of this study is to collect and compare with the remediation technologies of Taiwan area as well as develop innovative green remediation strategy and the process establishment of carbon footprints inventory for the heavy metal farmland contaminated sites. There were 11 cases collected and obtained the inventory including the turnover and mixing of 5 sites : 0.28-2.18 KgCO₂/m²; 0.92-3.63KgCO₂/m³; 0.57-2.79KgCO₂/ton . The higher results were obtained while the turnover and mixing integration of excavation and foreign soil of 6 sites: 0.57-11.48 KgCO₂/m²; 1.91-19.96KgCO₂/m³; 1.19-12.48KgCO₂/ton. The results of two remediation technologies were differed because of the transportation of contaminated and clean soil from excavation and foreign soil. The diggers were the most contribution by diesel consuming for carbon emission. Therefore, choice of the lower carbon emission factor or lower diesel consuming type machine will be suggested for future that a carbon calculator was developed for quick check by government and the application of consulting organizations. Meanwhile, integration of 6 core elements of the green remediation and engineering management and implement avoid the second pollution during remediation to damage the environmental quality such as (1)Energy demand: reduction the electricity from outside sites, the highest energy efficiencies, maintenance of high energy-consuming equipment. (2)Air pollution: clean energy (low sulfur content of diesel) of heavy duty equipment engines, reduction time of operation and idle time. (3)water resources: reduction of fresh water, recycling and reuse of the treated wastewater, avoiding overdose of fertilizers or pesticide to impact the quality of surface water or groundwater. (4)Land and ecological system: reduction of the damage in-situ remediation technology and growth interference of soil or animals and plants, bioremediation.



(5)Waste minimization: recycling and reuse materials, reduction use and removal of uncontaminated soil, waste reduction.

(6)The long term environmental conservation and remediation: reduction of carbon dioxide, methane and greenhouse gases emission, renewable energies, design of reuse remediation equipment. The suggests: (1)The better alternatives for improvement of carbon emission hot spot. (2)The low carbon remediation technology. (3)The historical data was possible incorrect that it's better to record the site data on site daily. (4)The fuel consumption, XRF screen and fertilizer quantities were calculated in the carbon calculator. The demonstration project is suggesting to verify the carbon calculator as well as add the carbon emission factors such as employee transportation and travelling, haul of the remediation equipment, sampling/ship/analysis and the treatment plants of contaminated soil.



[108] 重金屬監測離子交換樹脂縮時膠囊之設計研發

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中文摘要

鑑於偷排廢水事件含有不定時、延時短、污染濃度高且地點廣泛等特性，故偷排行為難以防範。連續監測成本高昂，因此違法行為始終難以全面掌控。本研究利用樹脂離子交換為基材做成重金屬監測包(稱之為「樹脂縮時記錄膠囊」)，大量將其投放於監測之區域，一段時間後收回監測包測定所吸附之重金屬，污染源之分布特性即被有效掌握，輔以環境指紋辨識方法之科學證據，污染行為人無所遁形。本計畫研發「樹脂縮時記錄膠囊」之架構分為實驗室與現地試驗兩個方向進行。實驗室試驗結果顯示陽離子交換樹脂與水體接觸的通量越大，其吸附重金屬的效率越好；兩者接觸時間達30分鐘時，陽離子交換樹脂對重金屬的吸附效率可達40%以上；在離子交換樹脂之交換容量未達飽和的情況下，重金屬濃度的高低對離子交換樹脂吸附效率的多寡並無顯著差異。針對現地試驗部分，「樹脂縮時記錄膠囊」投放在彰化縣東西二、三圳灌溉區域，涵蓋面積8.8平方公里。監測時間最長達21天，期間共回收404個陽離子樹脂膠囊(回收率89.2%)與28個陰離子樹脂膠囊(回收率93.9%)。根據監測膠囊回收數據顯示，背景元素監測資料特性會隨著時間的累積，水體中因一直存在穩定含量，讓交換形式持續進行，導致背景元素含量有增加的趨勢，以鈣跟鋁為主；另類則是以人為形式(如工廠排放、農業施肥等)加諸於環境水體之中，在特定時間與地點的大量排放，使得「樹脂縮時記錄膠囊」中重金屬元素在特定點位異常增加。本研究透過研發「樹脂縮時記錄膠囊」發展為環境指紋辨識的方法是有效且可行，能夠協助鎖定廢水違法排放之區域，提供政府相關單位能利用有限稽查資源為土壤環境品質監督做最佳把關。

Abstract

It is difficult to block wastewater illegal discharge behavior owing to the high cost of continuous monitoring, and therefore illegal situation always difficult to fully control. In this study, the heavy metal monitoring package (called "Resin Lapse recording capsule ") made of ion-exchange resin as a substrate was developed. It is an effective monitor device with low cost and rapidly analytic surveillance would be a way to suppress illegal emissions under the limited resource. The goals of this project were divided into the laboratory and the field experiment on two trails direction to carry on. The laboratory experiments to show that the cation exchanges a flux of resin and water body contact affect the adsorb efficiency of heavy metals. The contact time with the heavy metal and cation exchange resin in solution for 30 minutes, cation exchange resin adsorption efficiency of heavy metals can reached 40%. Under the unsaturated condition for the commutation capacity in the ion exchange resin, the level of concentration of heavy metals to the ion exchange resin is no significant difference in the amount of adsorption efficiency. For the field experiment, launch and recovery operations for "Resin Lapse Recording Capsule" had been completed. There were 151 points, covering an area of approximately 8.8 square kilometers. Each site placed three capsules for monitoring time covering 21 days with interval of 7 days. 453 cation resin capsules and 30 anion resin capsules were totally launched in the research areas. After the monitoring, cationic resin capsule recovery was 89.6%; anion resin capsule recovery was 93.9%. Finally, "Resin Lapse Recording Capsule" was carried out to be one of the environmental fingerprint recognitions and also provided



the official inspector to identify the specific areas of the illegal pollution emissions under the limited resource condition.

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[109] 強化被動式生物通氣系統應用於污染場址之操作參數探討

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中文摘要

本年度計畫於實驗室建立風力驅動式生物通氣(Wind-driven Bioventing)模場應用於風化超過2年的柴油污染土壤，使用之土壤經質地分析認定為壤質砂土，適合以生物通氣設備進行污染整治；試驗中同時使用氣泡式呼吸儀 (Bubble Respirometer) 搭配生物泥漿法進行土壤中微生物活性監測，探討生物通氣法整治柴油污染土壤的成效與微生物活性之關係。經 103 年度成果報告可得知，*Bacillus cereus* 菌(代號 BC)、*Achromobacter xylosoxidans* 菌(代號 F3B)、*Pseudomonas putida* 菌(代號 PS)等 3 株菌具有柴油降解能力，因此本計畫持續 103 年度計畫，模場實驗組別為五組，分別為三組添單一菌種組、一組添加混菌組(Mixture 組)及空白(Blank)組，Blank 組為未植菌且未通氣空白試驗組，土壤中營養源比例為碳、氮、磷比 100:10:1，採樣點固定為距中央通氣管 15 cm 處，同時本實驗事先以少量柴油馴化此三種植菌，再搭配強化被動式生物通氣系統，探討降解風化柴油污染土壤之成效。以氣泡式呼吸儀於降解期間對各組別進行呼吸試驗及監測，將每批次試驗開始 24 小時間攝氧率統計作圖可得一活性曲線，藉由曲線變化能協助操作人員評估微生物活性趨勢。呼吸試驗結果顯示，在七週的柴油降解試驗中，5 日的總累積攝氧量以 BC 組與 PS 組微生物具有良好的攝氧條件，相較於其他 3 個組別，有較平穩的狀態下呈現攝氧情形，結果亦發現添加營養鹽確實有效增加微生物的活性。由批次翻拌好氧反應槽試驗結果顯示，BC 菌組較適合生存於高濃度柴油污染土壤中，提高其事先馴化柴油濃度有助於降解之成效，F3B 和 PS 菌組在試驗 14 天後，馴化組及未馴化

組會出現明顯的降解效果差異。PS 菌組在試驗 21 天時皆出現 2 週的降解平緩現象，在試驗 49 天後馴化 8,000 $\mu\text{L/L}$ 組降解率達 79.5% 為最佳。馴化 8,000 $\mu\text{L/L}$ 組中，三種菌組皆有較好的降解成效。提高 F3B 菌組之馴化濃度有助於降解成效，但過高的馴化濃度無法提供更好的效果。經強化被動式生物通氣系統試驗結果顯示，各組對風化柴油皆有相當穩定的降解趨勢，添加菌種 *Achromobacter xylosoxidans* 的 F3B 組柴油殘餘率(C/C0)0.25 為最低，尤其 F3B 組於添加營養鹽後可出現明顯降解之成效。

Abstract

Major effort of this year's research is devoted to pilot study on measuring the effectiveness of wind-driven bioventing in remediating the diesel fuel contaminated soil. Tested soil was identified as loamy sand, conducive to bioremediation with wind-driven bioventing. Soil was seeded with each of 3 microorganism species, *Bacillus cereus* (BC), *Achromobacter xylosoxidans* (F3B) and *Pseudomonas putida* (PS); these microorganisms are capable to biodegrade diesel fuel as identified in previous yearly report. One soil was seeded with all three microorganisms' Mixture and another soil was functioning a blank without seeding and ventilation. The soils were nutrient balanced with 100:10:1 CNP ratio. All testing samples were taken from locations 15cm away from the central venting casing. Concomitantly, 24-hr oxygen uptakes were measured with a bubble respirometer collocated with bioslurry method and analyzed graphically to estimate the viability of microorganisms employed. These viability data were then compared with the effectiveness of remediation data with a purpose to



uncover the possible relation between the two sets of data. During 7-week bioventing pilot study, BC and PS groups showed better 5-day cumulative oxygen uptake than the rest, both in terms of the amount of accumulation and steadiness. In the study of batch aeration and mixing test, the results showed that the BC group is more active than the rest in high diesel environmental condition. The microorganisms were acclimated with diesel prior to applying to high diesel contaminated soil, the degradation efficiency of F3B and PS groups also showed the difference between with and without acclimation of microorganisms. The degradation curve revealed that PS group became gentle in two weeks, the optimal condition was to use 8,000 $\mu\text{L/L}$ diesel acclimation concentration in 49-day experiment, and the diesel degradation efficiency could approach to 79.5%. However, the higher acclimation concentration was not suitable for any microorganism. The results also appear to show the biological viability is enhanced by the supplement of nutrients. This yearly study clearly demonstrates that the concentrations of diesel fuel contaminants were trending down steadily, with relative diesel concentrations (C/C_0) of 0.25 by F3B seeding and possible lower with nutrient addition.



[110] 現地底泥整治技術研發－磁性活性炭吸附移除、 電磁感應加熱玻璃化與粒徑分離技術研究

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中文摘要

臺灣地區之底泥污染情況相當嚴重，多項有機污染物與重金屬污染濃度在全世界之監測濃度均名列前茅。針對污染物分布之差異性，本計畫將針對底泥中之重金屬與有機污染物進行磁性活性炭吸附與回收、針對局部高污染成分底泥進行現地玻璃化、針對容易懸浮之微小顆粒底泥則以改良式凝膠過濾法進行去除。現行活性炭添加法因活性炭本身具有漂浮性而可輕易遷移到較低污染或是無污染之底泥區域而釋放出污染物導致污染範圍擴大，故研發磁性活性炭複合材 (magnetic activated carbon composite) 於完成污染物吸附平衡後立即回收；局部高污染區塊之現地玻璃化 (in situ vitrification) 技術係針對表層底泥污染物固定提出一快速電磁感應加熱進行底泥現地玻璃化技術研發；現行浚渫法 (dredging) 往往將具高污染濃度之微小底泥顆粒再懸浮於水相中，沉降後導致表層底泥仍具有高濃度污染而無法達成整治目標，本計畫將利用改良式凝膠過濾法進行現地底泥表層微小顆粒之現地分選 (in situ fractionation)。目前計畫依預定進度執行，三項技術研發均已顯現成效，磁性活性炭經證實對砷及汞重金屬具有良好吸附效果且遵循擬二階動力方程式，添加於底泥後之較佳回收時間為 1 至 4 小時之間，Aroclor1254 之最佳去除率可達 81.9%。電磁感應加熱玻璃化之重金屬可固定 97.0-100.0% 之重金屬，1400°C 下直接玻璃化法經測試三處之底泥均能達到標準，進一步改良添加玻璃砂方法可將溫度進一步降至 1000°C，經測試三處底泥，也均能達到標準。改良之凝膠已可初步分離粒徑不同之底泥顆粒，對最小粒徑範圍 (2.0 μm) 去除

率約 56%，尚未達到理想目標。本計畫已經完成可提供我國底泥整治產業三項新技術，並已完成 1 篇 SCI 論文論文投稿，二項專利申請中。

Abstract

Sediment contamination in Taiwan is an imperative environmental problem. Concentration levels of some organic pollutants and heavy metals are ranked at the front all over the world. Aimed at this uneven distribution of contaminants in sediment, this project will focus on development of three different strategic technologies, i.e., magnetic activated carbon (MAC) for organic contaminant removal, in-situ rapid vitrification for highly contaminated sediment, and modified gel filtration for in-situ fine particle fractionation. Up to now, all three technologies has shown good results. Magnetic activated carbon showed good removal on mercury and arsenic and their adsorption followed pseudo- second order kinetics. The better recovery time interval after MAC addition is between one and four hours and the highest removal of Aroclor1254 was 81.9%. Induction heating showed very good confinement of heavy metals up to 97.0-100.0% stabilization of tested eight heavy metals and have tested on sediment from three sampling sites and all passed the regulated limits. A new vitrification method was successfully developed and now vitrifying sediment at 1000°C is feasible. This method has been applied to the sediments from three sampling site and showed all passed the regulated limits. Refined gels can successfully separate the sediment particles into two different groups but the efficiency need to be further improved. Up to now, all have been implemented and one SCI paper is submitted and two



invention patents are filing application.
The proposed three new technologies are
proved to be feasible as in situ remediation
options.



[111] 植生復育重金屬污染土壤及其生命週期評估

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中文摘要

植生復育(Phytoremediation)是利用植物來移除污染物的技術。植生復育定義為使用高等植物經由吸收、分解、傳輸或累積方式移除環境中的污染物或是使之轉化成無害物質，可以應用存在於固體物質(土壤)、溶液物質(水)及空氣中的有機或無機污染物。植生復育在國外有許多相關的報導，發現具有重金屬富集作用的植物，如部分十字花科植物對於鎳具有富集效果。但若引進國外植物不僅有氣候適應的問題，對於環境上的衝擊也是有疑慮，因此本計畫擬利用本土種植物進行綠色整治試驗研究，以現地含有重金屬銅、鎳、鉻的土壤作為植物種植的來源，目前規畫以本土常見與具有能源潛力作物，如狼尾草、芒草、十字花科-油菜、水稗進行重金屬吸附試驗。

本研究已完成狼尾草、芒草、水稗及油菜以重金屬污染土壤鎳、鉻及銅蓄積效果。從結果來看水稗及油菜對於這三種重金屬具有富集效果，對於土壤重金屬的移除將可獲得良好的助益，然而以生物量來看，狼尾草可獲得最大的生物量，並且可以進行後續的再利用。從目前結果來看狼尾草所獲得的生物量最大，其次為芒草、水稗、油菜，而在重金屬鎳的環境下，狼尾草的植體每平方公尺，一次收穫可移除 11.99~27.30 mg 之間的鎳，芒草為 5.26-15.05 mg 之間、水稗為 0.40-2.24 mg 之間，油菜為 0.13-1.92 mg 之間；在重金屬鉻的環境下，狼尾草的植體每平方公尺，可移除 26.69-53.82 mg 之間的銅，芒草為 2.10-25.80 mg 之間，水稗為 1.01-2.59 mg 之間、油菜為 0.83-1.58 mg 之間；在重金屬銅的環境之下，狼尾草的植體每平方公尺，可移除 27.34-92.52

mg 之間的銅，芒草為 5.92-52.66 mg 之間，水稗為 0.43-2.26 mg 之間，油菜為 0.18-5.10 之間，油菜及水稗雖較具有富集現象，但若以生物量來估算，狼尾草及芒草可移除重金屬量則較大。

植生復育法在實行時對於現地場址的生態破壞程度較低，為一永續性的污染整治方式，但在考慮到場址重金屬污染濃度，較嚴重污染的土壤將影響到植生復育植物的生長及未來的富集量，因此使用傳統排土客土工法將對環境衝擊較低，然而若污染濃度較低，使用植生復育工法所造成的環境衝擊則較低，另外污染土壤之污染深度也是需考量的點，若污染場址的污染情形為深度污染的話，植生復育工法的移除將是有限的，因植物的根系大多不深，因此需要較長時間的移除，使用傳統排土客土工法造成的環境衝擊則較低；使用植生復育將考量植株之轉移係數及收穫量等因素，相較於傳統排土客土工法而言，單純使用植生復育法整治並不一定對環境來的友善，但是若將收穫後之生物量再進一步作為能源使用，植生復育整治技術對於環境造成的衝擊會有所下降，所獲得的環境友善都是正向的，因此，為提升環境品質，維護環境資源，追求永續發展，植生復育法搭配生質物再利用仍是一具有潛力的整治技術。

Abstract

Phytoremediation utilizes the plant to remove pollutants and is defined by utilizing higher plants to absorb, degrade, transport and accumulate environmental pollutants and/or transformed them into harmless substances. Phytoremediation could be utilized to remediate pollutants in ground, water and air phases.

Phytoremediation examples were globally reported, including many plants (e. g. Brassicaceae plants) found able to enrich heavy metals. However, introducing foreign plants would face issues such as adaptabilities toward local environments and raising additional environmental concerns. This project will use indigenous plants for green remediation by using site soil containing Cu, Ni, Cr. Plants with bio-energy raw material supply potentials like switchgrass, miscanthus, rapeseed and barnyard grass. After remediation, bioenergy producing potential by harvested plant biomass will also be assessed.

This study has been completed Pennisetum, Miscanthus, water and rapeseed barnyard heavy metal contaminated soils nickel, chromium and copper accumulation effect. From the results, water barnyardgrass and rapeseed for the three heavy metals enrichment effect, for the removal of heavy metals in the soil will get good help, but the biological point of view, Pennisetum obtain the maximum biomass, and can be for subsequent reuse. From the current results, Pennisetum maximum biomass obtained, followed by silver grass, water barnyard, rape, and in the environment of heavy metals nickel, Pennisetum explants per square meter, the first harvest can remove 11.99 ~ Nickel 27.30 mg between Miscanthus between 5.26-15.05 mg, water barnyard between 0.40-2.24 mg, cole between 0.13-1.92 mg; chromium in the environment, explants per square Pennisetum meters, a removable copper, between 26.69-53.82 mg Mans dish between 2.10-25.80 mg, water barnyard between 1.01-2.59 mg, cole between 0.83-1.58 mg; in the environment of heavy metals copper under Pennisetum of explants per square meter can be removed between 27.34-92.52 mg copper, silver grass between 5.92-52.66 mg, water barnyard between 0.43-2.26 mg, rapeseed is 0.18-5.10 between, rape and barnyard although water has a more enrichment, but if in order to estimate the biomass,

Pennisetum and Miscanthus is a large amount of heavy metals can be removed.

Vegetation Restoration Act in the exercise of the extent of ecological damage to the site is now low, as a sustainable way of remediation, but in consideration of the concentration of heavy metal pollution site presence, the more heavily contaminated soil will affect the Vegetation Restoration plants growth and enrichment of the future, the use of conventional passenger geotextile Dumping Act would lower environmental impact, but if contamination is low, the use of plant repopulation impact the aquatic environment caused by the construction method were lower, while the contaminated soil Pollution is also a need to consider the depth of the point, if the pollution situation of contaminated sites contaminated depth, then remove Vegetation Restoration labor law will be limited, because most of the plant roots are not deep, it takes a long time to remove, use environmental impact of traditional dump-off caused by the lower geotextile law; use Vegetation Restoration will consider the amount of transfer coefficient and harvest the plants of factors, in terms of traditional indigenous dump-off Compared to the simple use of Vegetation Restoration Act and Regulation not necessarily friendly to the environment, but after the harvest biomass If further as energy use, Vegetation Restoration Treatment Technology for the environment impact will decline, obtained environmentally friendly are positive, therefore, for the improve environmental quality, safeguard environmental resources, the pursuit of sustainable development, with the Vegetation Restoration Act was re-utilization of biomass is still a potential remediation technologies.



[112] 發展三維螢光光譜技術追蹤污染場址污染來源之可行性

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中文摘要

近年來，為了落實環境污染稽查工作與預防環境污染事件之發生，發展更新穎之環境法醫技術釐清污染責任有其必要性。三維螢光光譜具有很高的敏感性與專一性，可以由此複雜的列陣確認污染物來源。該方法具有高選擇性、樣品使用量少、快速而準確等特性，非常適合應用於實地受地下水與土壤污染之場址。本研究結合三維螢光光譜、ATP 冷光分析與化學分析方法，評估桃園地區受三氯乙烯 (Trichloroethylene, TCE) 與順-1, 2-二氯乙烯 (cis-1,2-Dichloroethane, c-DCE) 之場址污染概況。本次研究結果顯示，24 件次地下水樣本中 TCE 之分析結果普遍高於地下水污染管制標準，且在深度 15m 與 55m 測得較高之 TCE 濃度。地下水樣本中 DOC 濃度、UV-Vis 光譜分析與螢光光譜分析結果顯示，類黃酸與腐植酸螢光強度與 TCE 與 c-DCE 濃度呈現顯著正相關性，可藉由評估上述兩項參數來追蹤 TCE 與 c-DCE 之污染程度。

Abstract

In the recent year, the importance of developing a new environment forensic technique for inspecting sources of environment pollution and in monitoring the changes of environmental contaminants has been the focus of many studies. Due to high sensitivity, specificity, accuracy, rapidity, and it only requires small volume of sample, the three-dimensional excitation-emission-matrix fluorescence technique for qualitative analysis of aromatic compounds is used to confirm the fingerprint of contamination by complicated mixture of aromatic compounds. Therefore, this method may be suitable in tracing the contaminant sources in groundwater and soil. In this study, we combine the three-dimensional excitation-emission-matrix fluorescence technique, ATP luciferase analysis, and chemical analysis to evaluate the trichloroethene (TCE) and cis-1,2-dichloroethene (c-DCE) contaminants' distribution in a highly contaminated ground water site. The concentrations of TCE in 54 groundwater samples detected in this study were higher than the groundwater pollution control standard, and the highest concentrations were detected at a depth of 15m and 55m. Levels of DOC, UV-Vis and fluorescence in 216 groundwater samples were detected by three-dimensional excitation-emission-matrix fluorescence technique. Two fluorescence parameters (FLF fluorescence level and humic acid fluorescence level) were found to have a positive correlation with TCE and c-DCE. In the future, these two parameters may be important in evaluating and tracing the contaminant sources in groundwater.

[113] 開發可用於現場檢測重金屬之低成本紙基快篩檢測平台

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中文摘要

本計畫為開發現場檢測汞污染之低成本紙基快速篩檢平台之研究，將結合紙質基材、奈米粒子，以及智慧型手機來進行地下水及底泥中含汞離子實際樣品的快速檢測。在常見的重金屬污染中，汞離子可以經由飲用水或是透過食物鏈的方式累積在人體中，普遍認為對生物體造成相當大的毒性及危害。因此，在本計畫中，我們將利用奈米金屬粒子的表面電漿共振效應，結合比色分析法，整合智慧型手機及應用程式，進而設計出具有低成本、容易操作、攜帶方便、高靈敏度之汞離子快速檢測平台。

在期中成果報告中，我們成功利用奈米轉印技術，將單層奈米金屬粒子陣列轉印到紙質基板上，當含有汞離子的待測液接觸到奈米粒子陣列時，會立即發生置換反應，並隨著汞離子濃度的差異，造成吸收色譜的顯著變化。透過合成不同奈米粒子，包括銀奈米粒子、中空銀金粒子、中空銀殼層粒子，並探討其與汞離子反應之後的色譜變化，我們發現銀奈米粒子具有最佳的靈敏度，最低檢測濃度可達 2 ppb，並對汞離子具有顯著的選擇性。

在期末成果報告中，我們透過調控製程參數、奈米粒子表面修飾及形貌，成功優化此低成本感測器，以及利用智慧型手機記錄快篩試片上之彩色光學影像，並透過應用程式快速判讀檢測結果。由反射光譜分析結果顯示，此感測器之最低檢測濃度可達 1 nM (0.2 ppb)；而當結合智慧型手機取得光學影像，進行色彩分析結果顯示，此感測器之最低檢測濃度可達 5 nM (1 ppb)；更重要的是，當濃度達 10 nM (2 ppb) 以上時，其顏色變化即可以用肉眼判斷之。最後，我們利用最佳化條件之快篩試片，進行實際含汞污染之地下水試樣的半定量分析，並結合感應耦合電漿質譜分析儀來比對快篩試片之可靠性。

Abstract

The excessive number of plants constructed in Taiwan produce serious discharged toxic heavy metal ions, such as mercury ions, may ultimately accumulate in human bodies through the food chain. In this project, we will investigate the development of paper-based analytical platforms for on-site detection of mercury ions. Combining with colorimetry analysis and smartphones, the metal nanoparticles arrays are designed for novel optical chemical sensors with easy-to-use, portability, low-cost, and excellent sensitivity.

Previously, we successfully fabricated the novel colorimetry paper sensors by transferring the metal nanoparticles monolayer from glass molds to paper substrates via the reversal nanoimprinting method. When mercury ions are reacted with the surfaces of the nanoparticles, they will induced a significant reduction of the absorbance peak for the silver or copper nanoparticles, which is originated from surface plasmon resonance (SPR). We monitored the change in their reflectance spectra with increasing mercury concentration and found the lowest detection concentration of 2 ppb by using silver solid nanoparticles. The sensor also displayed a good selectivity against other metal ions.

Herein, we optimized the plasmonic sensors to further enhance their sensibility through modifying their particle number density, surface coating layers and morphology. After that, the spectroscopic change could be also quickly detected through a smartphone: the colorful optical images were easily recorded and their RGB values were analyzed rapidly. In our case, the limit of detection has been improved to 0.2 ppb by a spectrometer, to 1 ppb by a smartphone, and to 2 ppb by naked eyes. Finally, the plasmonic sensors



were used to analyze the real samples from mercury-polluted water sources. Furthermore, inductively coupled plasma mass spectrometry (ICPMS) was utilized to examine the reliability of the colorimetric sensors.

[114] 新興無機污染物於河川底泥中之流佈調查與循環機制—

以烏溪流域為例

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中文摘要

由於半導體產業的蓬勃發展，在製程上應用了許多微量金屬來改進薄膜成長(thin film growth)、化學蝕刻(chemical polishing)、微影(photolithography)等製程效能。然而，這些微量金屬的應用所產生的衍生副產物和殘餘的化學物質可能會因此進入到廢水中，並隨後隨著廢水排放至周遭流域中。舉例來說，硒(Se)、鎵(Ga)、銦(In)與鉬(Mo)已經被廣泛的應用於半導體光電產業的製程之中。而同時這幾個元素亦為植物與動物的必須元素，然而其介於生物必須及產生生物毒性的濃度範圍極窄。即便這些微量金屬在環境中的具有相對較低的濃度，但因這些微量金屬在生態系統中是可累積的，由這些產業所釋放至環境中的量可能會導致顯著的生物放大效應，對生態系統造成重大風險。本計畫及針對筏子溪、烏溪中工業區廢水排放口的底泥重金屬與微量金屬進行調查。

根據位於筏子溪流域與烏溪流域中 12 個監測點所獲得的結果，其水體樣品中的重金屬與微量金屬含量均符合灌溉用水之標準，但在烏溪流域中科放流口下游接近出海口的監測點的水體樣品中 Se 與 Mo 含量均高於其監測點。部分筏子溪流域底泥樣品中均有 Cu、Zn 與 Ni 超過底泥品質標準上限之問題，可能會對於敏感底棲生物與小型生物造成影響。而烏溪流域具有較大水流量，僅有少部分底泥樣品的重金屬濃度超過底泥品質標準上限。根據 Pearson 相關分析矩陣(Pearson correlation matrix)與主成分分析(principal component analysis, PCA)之結果結果發現水體樣品中的重金屬與微量金屬元素，可能受到其排放源所影響可以被歸類成三個不同的群組。但底泥的分析結果並未發

現與水體有相同的趨勢，統計結果顯示底泥中的重金屬與微量金屬元素均與有機質與無定型鐵鋁氧化物三個環境因子有緊密關係，其可能是控制重金屬與微量金屬元素在環境中累積的主要因素。而 X 光吸收光譜(Cryo-X-ray absorption spectroscopy, XAS)的分析結果顯示筏子溪與烏溪的底泥與懸浮微粒中 Se 的主要物種為 FeSe、元素 Se 以及三甲基 Se，並且在烏溪下游的底泥中有觀察到毒性較強的四價 Se。

Se 等元素對於水中生物會以食物鏈方式對於水中生物產生超累積效應，對於水中生物造成毒害或者生態上的破壞，因此建議針對筏子溪與烏溪流域在未來繼續進行底泥與水體進行中長期的調查，持續監測其濃度變化，評估放流水中重金屬與微量金屬排放造成的潛在風險。

Abstract

Due to the intensive development in semiconductor industry, the manufacturing processes have embraced a boom in the application of trace metals to improve the performance of thin film growth, chemical polishing, photolithography, etc. However, such application may result in the complicated intermediate byproducts and residual chemicals that could be released to the wastewater and subsequent discharged to the surrounding river basin. For example, trace elements such as selenium (Se), gallium (Ga), indium (In), and molybdenum (Mo) have been widely applied in the product process. These elements are essential for the metabolism of plants and animals. Contents of such elements is of environmental interest because of a narrow range between nutritionally required and toxic effect concentrations in many organisms. Even if



environmental levels of the trace elements are relatively low, the effect of biomagnification may result in an essential accumulation of trace elements in ecosystems. In this project, our objective was to develop the distribution of not only heavy metals but trace elements in the basin of the Fazih and the Wu River, which has been received the wastewater effluent from hospitals, the Taichung Industrial Park, and the Central Taiwan Science Park.

According to our results, contents of heavy metals in the river water of the Fazih and the Wu River were lower than the criteria for the agriculture irrigation water. Regarding the trace elements, however, we observed an increase in Se and Mo contents for the river water sampled from the downstream Wu River. The sampling site was near the effluent location of wastewater generated from the Central Taiwan Science Park. In terms of sediment samples, those collected from the Fazih River contained higher amounts of Cu, Zn, and Ni. Levels of such metals exceeded the top limits of sediment quality criteria, suggesting that the benthic and small aquatic organisms in the associated watershed have been subjected to permanent damage. Due to the relatively higher flow rate in the Wu River, the heavy metal contents in sediment samples collected from the Wu River were generally lower than the top limits of sediment quality criteria. We found that the sediment sampled from the Fazih River watershed contained relatively higher amounts of Se, Ga, In, and Mo than that in the Wu River, although we observed an increasing Se and Mo concentrations in the Wu river water. Results of Pearson correlation and principal component analysis (PCA) show metals in river water could be classified into three groups, implying the discharged metals might come from three different sources. However, the PCA results for sediment samples didn't show the same trend. All the metals are correlated to total

organic carbon (TOC) and amorphous Fe/Al, suggesting that TOC and amorphous might be the major environmental factors controlling the accumulation of metals. In addition, the linear combination fitting (LCF) for the Se-XANES spectra indicated that the Se species in the sediment and suspension particles could generally be described as FeSe, elemental Se and trimethyl Se. Selenate, which is more toxicity than other Se species, was also found at sediment sample of downstream Wu River.

Such results indicated that sampling sites with higher TOC contents pose a high risk for ecosystems due to the accumulation for heavy metals and trace elements. Hence, we suggest a continuous monitoring for the levels of metal accumulation in sediment samples. Such information could eventually serve as scientific results for authority to develop the related regulations.

[115] 精進現場即時篩測工具提升土壤及地下水含氯污染物濃度判識之成效

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中文摘要

國內使用含氯溶劑工廠遍及各類業別，致癌風險性高，污染洩漏後其移動分佈深受複雜的水質地質變化所影響，其污染流佈與調查及整治技術迥異於重金屬或油品類污染。近十年現地快篩技術所使用之分析技術與儀器設備也逐漸發展及提升其應用性，因此在適合的地質條件下，含氯場址污染調查工作，往往先使用如薄膜界面探測系統(Membrane Interface Probe, MIP)初步探索污染位置與範圍，但僅能以高低總量訊號值判斷污染潛勢，無法進一步辨識污染物種類與地下環境中污染物濃度。

本計畫目的為評估現場快速篩檢工具 MIP 在含氯有機溶劑污染場址之應用性及限制性，研究中分別設計實驗室穩定條件下之操作試驗，及不同水質地質條件下污染場址調查及驗證，期望由現場篩測結果透過所產出之經驗方程式可回推辨別土壤及地下水污染程度，作為調查階段及整治階段重要之判識工具。本計畫選擇 7 種目標污染物，包括氯仿、氯苯、1,2-二氯乙烷、1,1,2-三氯乙烷、二氯甲烷、三氯乙烯及四氯乙烯等。本研究主要分為兩個部分，包括實驗室試驗及污染場址污染調查，其中實驗室工作區分為兩階段，第一階段建立含氯有機溶劑在土壤與空氣兩相吸附與脫附之平衡狀態所需時間。第二階段則是使用第一階段求得之平衡時間參數，建立管柱試驗進行評估，透過現場篩測儀器薄膜界面探測結合電子捕獲偵測器(electron capture detector, ECD)及攜帶型飛行時間質譜儀(time of flight mass spectrometer, TOF-MS)進行含氯有機溶劑污染分析，依據現場篩測儀器進行不同環境介質條件及不同濃度測試，推估 MIP-ECD 及 MIP-TOF-MS 偵測之相容性及差異，並評估極佳

化偵測條件及可能之限制因子。

第二部分工作則為含氯有機溶劑污染場址進行實際污染調查，配合進行污染採樣及全量分析，同時分析實驗室數據與現場篩測數值之相關性，驗證實驗室試驗所推算出經驗方程式是否符合，期以此方式讓實場進行污染初步篩測過程中，可以同步獲得含氯有機溶劑在土壤及地下水中污染濃度。

實驗結果以薄膜界面進入模擬地下水中到離開地下水水層前這段時間所收集到的響應值進行統計，MIP-ECD 偵測氯仿、三氯乙烯、四氯乙烯及 1,1,2-三氯乙烷具較佳線性關係，對氯苯及二氯甲烷之線性關係較差，而對 1,2-二氯乙烷線性反應不良，呈現負相關，將 MIP-ECD 與實驗室內 GC-MS 分析的地下水數據進行相關性分析，結果以三氯乙烯的線性關係較高(R^2 為 0.996; $y=0.0024x-12.29$)，對氯苯及二氯甲烷之 ECD/GC-MS 線性關係較差，顯示 MIP-ECD 對於地下水體中含氯化合物的測定雖具敏感度與相關性，但其線性關係仍具化合物選擇性。而連結 MIP 的 FID 對七種化合物具較佳線性關係，將 MIP-FID 與 GC-MS 分析的地下水數據進行相關性分析，以 1,2-二氯乙烷的線性關係較高(R^2 為 0.987; $y=0.0056x-37.92$)，顯示 MIP-FID 對水中含氯化合物亦有可接受的線性關係，但基於偵測含氯化合物的靈敏度不建議使用 FID。TOF-MS 對七種含氯溶劑具較佳線性關係(R^2 為 0.927-0.996)，TOF-MS 偵測二氯甲烷的線性反應最佳，將薄膜界面探測系統結合 TOF-MS 與實驗室 GC-MS 分析進行相關性分析，則以 1,1,2-三氯乙烷的線性關係最高(R^2 為 0.987; $y=2.3354x-50.56$)，而其他含氯化合物的現場偵測與實測值(GC-MS)之 R^2 則皆在 0.923 以上，MIP-TOF-MS 對於這七



種含氯化合物偵測較 ECD 具有較佳線性關係，但 TOF-MS 的分析濃度皆低於預設濃度的 1000 倍，其中推估可能係 MIP 系統須將化合物加熱蒸發成氣相，同時載氣傳輸至 TOF-MS 時也會造成被分析物損失，因此每個濃度中皆呈現低於目標濃度的 1000 倍。因此就目前設計上 MIP-TOF-MS 的分析上無法達成現場即時定量的功效，但對於化合物具甄別性可提供現場調查佈點及整治規畫之判釋。

針對 MIP 系統分別以 ECD、FID 與 TOF-MS 進行不飽和層土壤中含氯化合物的分析，類似地下水偵測結果，MIP-ECD 偵測土壤中四氯乙烯具較佳線性關係，對二氯甲烷及氯仿之線性關係較差，而對其餘化合物線性反應不良，呈現負相關，將 MIP-ECD 與 GC-MS 分析的數據進行相關性分析，結果僅四氯乙烯的線性關係較高 (R^2 為 0.903； $y=0.0377x-182.9$)，對氯苯及二氯甲烷之 ECD/GC-MS 線性關係較差，顯示 MIP-ECD 對於不飽和層土壤中含氯化合物的測定具反應性及敏感度，僅能提供是否有含氯化合物之資訊。

TOF-MS 對土壤中六種含氯溶劑具較佳線性關係 (R^2 為 0.915-0.976)，以三氯乙烯的線性反應最高，對氯仿之線性關係較差，將薄膜界面探測系統結合 TOF-MS 與實驗室 GC-MS 分析進行相關性分析，則以四氯乙烯的線性關係較高 (R^2 為 0.964； $y=863.19x-20.56$)，而其他含氯化合物的現場偵測與實測值 (GC-MS) 之 R^2 則皆在 0.825 以上，MIP-TOF-MS 對於土壤中含氯化合物偵測較 ECD 具有較佳線性關係。

不同污染場址之數據顯示不論是地下水樣品或土壤樣品的含氯化合物濃度均偏低(地下水樣品:不同化合物濃度範圍介於 0 mg/L-2.59 mg/L；土壤樣品:不同化合物濃度範圍介於:0 mg/kg-13 mg/kg)，在套用實驗室推演出之經驗方程式後，發現現場數據皆落於回歸線下，顯示實場數據較預期值為低，亦即現場篩測顯示之數據為低估，其可能原

因為本計畫建立經驗程式之濃度範圍較大(地下水 20-100 mg/L 及土壤 20-100 mg/kg)，由於污染場址之偵測數據濃度較低，因此可能不適用此線性範圍區間，為提升現場篩測工具所得數據之應用性及有效性，也許必須審視污染物可能出現之濃度範圍，面對不同水文地質條件，及時修正及重新建立經驗程式，如此方可提供有效即可利用之現場篩測數據，就目前 MIP-TOF-MS 的技術發展及應用性，雖然無法達成現場即時定量的功效，但對於化合物具甄別性，此特性是傳統 ECD 無法提供的，同時 MIP-TOF-MS 可提供含氯化合物即時半定量之解析，這些資訊可提供場址現場調查佈點及整治規畫之判釋。

Abstract

Chlorinated solvents are widely used in various industries in Taiwan. Once the leakage and spread of chlorinated solvent into the subsurface may result in high mobility of contaminant in the heterogeneous hydrogeological conditions. The investigation and remediation are generally more difficult than heavy metals and petroleum hydrocarbons. Membrane Interface Probe (MIP) is a semi-quantitative and field-screening device that can detect volatile organic compounds in soil and groundwater. It can be used to define the soil and groundwater contamination potential of VOCs; however, it can't directly quantify the concentration of individual compound. Additional sensors may be added to the probe to facilitate soil logging and analyze contaminant concentrations. Thus, the analytical results produced by a MIP are relatively contamination potential but not identification of contaminants in the source zone.

The objective of this study was to evaluate applicability and limitation of in-situ analysis of chlorinated organic compounds by MIP coupled with different types of detectors such as electron capture detector (ECD), flame ionization detector (FID) and Time-of-flight mass

spectrometer (TOF-MS). This study intended to establish empirical equation between laboratory and field-screening analyses in chlorinated solvent contaminated sites.

Seven target compounds including dichloromethane, trichloroethylene (TCE), tetrachloroethylene (PCE), 1,2-dichloroethane, 1,1,2-Trichloroethane, chloroform and chlorobenzene were selected in this study. Experimental design covered laboratory and field study. The stainless steel column (120×15 cm, lenth×diameter) packed with contaminated soil or groundwater was used in the laboratory study.

The integrated MIP-detector system was tested in chlorinated solvent-spiked aqueous and soil samples at five different concentration levels (i.e., 20 to 100 mg/L in water and 20 to 100 mg/kg in soil) in the laboratory study. For target compounds tested in water, linear response was considered acceptable for four compounds (i.e., chloroform, TCE, PCE, and 1,1,2 trichloroethane) detected by the MIP-ECD system. However, chlorobenzene and dichloromethane showed less promising linearity with coefficient of determination equalled 0.751 and 0.760, respectively. The response of ECD was not proportional to increased concentrations of 1,2 dichloromethane. It was noted that the response of ECD while analyzing 1,2 dichloromethane may vary factor of nine at the depth of 4.25 m to 3.61m in the laboratory study. Response of ECD at different depth contributed variation in this study for certain compounds. Chlorinated organic compounds were first vaporized in MIP and transports the vapor through tubing to ECD. It was suspected that abnormal diffusion pattern of vaporized 1,2 dichloroethane acrossing the membrane might be the cause of poor response by ECD measurement.

If the sample matrix was switched to soil, acceptable linear response was only observed for tetrachloroethylene and 1,2 dichloroethane among the target compounds measured by the MIP-ECD system. The linear response of ECD was

not observed corresponding with the increased concentrations of chlorobenzene, trichloroethylene, dichloromethane, or 1,1,2 trichloroethane in soils. Poor linearity of chloroform was observed by the MIP-ECD system. Apparently the field-screening device such as MIP-ECD did not warrant qualitative results as anticipated in the laboratory study. Notably the MIP-FID system demonstrated high linearity for samples measured in water and soil in the laboratory study. Theoretically FID is more sensitive for detection of aliphatic and aromatic hydrocarbon and ECD is sensitive to chlorinated organic compounds. However, the results of FID showed better linearity (0.975 to 0.997 and 0.905 to 0.999 in water and soil, respectively) than ECD in the laboratory study.

Overall TOF-MS illustrated acceptable linearity for measuring chlorinated compounds in water. It should be noted that the concentration reported in TOF-MS is ppb level. Measurement of water contaminated by different concentration levels of chlorinated compound indicated that linearity of tetrachloroethene was the best (0.964) and the linearity of the rest of six compounds was considered acceptable by TOF-MS. The coefficient of determination ranged from dichloromethane (0.825) to tetrachloroethene (0.964). Chlorobenzene did not demonstrate good linearity by ECD measurement and the linearity by TOF-MS was better though the lowest coefficient of determination among the target compounds. Also TOF-MS did provide acceptable linearity for 1,2 dichloroethane while the linear response of ECD was not observed with the increased concentration.

Detection of soil contaminated by different chlorinated compounds indicated that linearity of trichloroethylene was the best ($R^2= 0.976$) and the linearity of the rest of six compounds was considered acceptable by TOF-MS except chloroform ($R^2= 0.641$). The coefficient of



determination (R^2) ranged from 0.915 (1,2 dichloroethane) to 0.976 (trichloroethylene). In contrast to results of ECD, we considered that TOF-MS can offer more promising in-situ monitoring. Besides chloroform, most compounds illustrated acceptable linearity ($R^2=0.915$ to 0.976) in soil samples by TOF-MS analysis.

Comparing the results measured by ECD, TOFMS or FID with analyses by GC/MS, it was evident that most of the results obtained from field-screening device were compatible with conventional laboratory analysis. Evaluating the performance of different detectors coupled with MIP, measurement of chlorobenzene and dichloromethane by ECD may caused higher artifacts. For the rest of compounds, compatibility is relatively high between various in situ detectors. Other than chloroform in soil, the coefficient of determination was relatively high for TOF-MS and GC/MS as shown. Compatible results were anticipated while employing the MIP-TOF-MS system.

Five contaminated sites were selected for the evaluation of the MIP system in the field study. Based upon the field condition, MIP measurement of 34 sampling points were conducted in this study. In total, 51 measurement were performed (MIP-ECD, $n=21$; MIP-TOF-MS, $n=9$; MIP-FID, $n=21$). The empirical equations established in our laboratory study were adopted to estimate the concentration in the contaminated sites. Most of the analytical results of groundwater and soil indicated that they were underestimated by TOF-MS. Vaporized sample was indeed in split mode, only part of the gaseous sample was measured by TOF-MS. Therefore, the reported value by TOF-MS can only serve as semiquantative results in contrast to the sample analyzed by GC/MS in the laboratory. One of the advantage of TOF-MS is compound differentiation in

field condition. ECD gets response while detecting chlorinated compounds but compound differentiation should rely on device such as TOF-MS. However, based upon the applicability of current field-screening devices, full scale quantitative results were not well established. It is reasonable to suggest that only semiquantitative results can be generated. However, this will serve a useful tool for site remediation decision-making process. Consequently, a better identification of the contamination with depth is possible at low concentration level. In relation to the qualitative analyses, it was found that the configuration of the MIP-system with the built-in detectors are useful to carry out on-site analyses, thus allowing a better identification of the contamination in a vertical profile.

[116] 增溶劑結合電透析技術處理含重金屬及氯污染之土壤及地下水

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中文摘要

本研究主要是探討兩種類型的糊精：hydroxypropyl- β -cyclodextrin (HPCD) 和 carboxymethyl- β -cyclodextrin (CMCD) 對土壤中之含氯有機污染物和鉻離子的脫附效果。其中，HPCD 對四氯乙烯的脫附效果將與三種不同類型的界面活性劑做比較。此外，本研究亦測試以電透析技術處理鉻化物廢水的效率。研究結果顯示，在外觀溶解度實驗中，HPCD 的濃度越高，PCE 之外觀溶解度亦相對增加，兩者之間呈現迴歸性良好的直線關係。在不同有機質含量的土壤對四氯乙烯之吸附量實驗方面，研究結果顯示以高有機質含量的土壤對四氯乙烯之吸附能力最佳。在 HPCD 對吸附於土壤中 PCE 的脫附能力的研究上顯示，HPCD 濃度的增加，可以有效地提高土壤中 PCE 的脫附效果。但是，HPCD 對土壤中 PCE 的脫附效率受限於土壤中有機質含量的多寡。有機質含量愈高，脫附效率愈低。界面活性劑雖然增加水中 PCE 溶解度的能力優於 HPCD；但是 HPCD 在自低有機質含量土壤中脫附 PCE 的效能卻高於實驗中的三種界面活性劑。在 HPCD 和 CMCD 脫附土壤中 TCE 的效果方面，HPCD 反應時間愈長，脫附效果愈佳。在反應三天後，10% HPCD 可脫附 87% 的 TCE。相較之下，CMCD 對 TCE 的脫附效率約只有 20%。在鉻化物的脫附效率方面，CMCD 和 HPCD 都呈現出反應時間愈長，脫附效果愈佳的趨勢。在反應三天後，1% CMCD 可脫附約 90% 的 TCE；相較之下，1% 和 10% HPCD 對 TCE 的脫附效率約為 68% 和 70%。在以電透析技術處理鉻化物廢水的效率方面，電極液導電度固定為 5470 μ S/cm 時，設定流速 7 L/min、固定電壓 20V，淡水槽脫鹽率達 47.2% 時，所需的操作時間為 420 分鐘。此時，所對應到淡水槽中，鉻離子的去除率可達 85.5%。因此，HPCD 和 CMCD

在污染場址的整治和復育上，具有相當高的可行性與應用價值；電透析技術亦可有效處理含鉻化物的廢水。

Abstract

Due to the low solubility of chlorinated organic solvents, they will form dense non-aqueous phase liquids (dNAPLs) in the aquifer and adsorb to the soil easily. Once it contaminates the aquifer, it is hard to remove completely. Heavy metals in the form of anions are also possibly sorbed to the soil. The mobility of those heavy metals is limited in the aquifer. So far, there are some sites which are contaminated by heavy metals and chlorinated organic solvents in Taiwan. Those sites are very difficultly to remediate. Cyclodextrins and surfactants have the ability to enhance desorption and solubilization. The main purposes of this study are: (1) to test the solubilization effect of solubilization agents (including cyclodextrins and surfactants) to the chlorinated organic contaminants; (2) to test the desorption effect of solubilization agents (including cyclodextrins and surfactants) to sorbed chlorinated organic contaminants and chromium compounds; (3) to use different ratios of HPCD and CMCD testing the desorption effect of chlorinated organic contaminants and chromium compounds; (4) to examine the enhancement effect of a sequence application of CMCD and surfactant approach on the removal of TCE; (5) to examine the enhancement effect of a sequence application of surfactant and CMCD approach on the removal of TCE. In this study, the target contaminants are TCE, PCE, and CrO_3 ; the solubilization agents include carboxymethyl- β -cyclodextrin (CMCD), HPCD, and three different surfactants. The results showed that HPCD is better than the CMCD on the desorption effect of TCE. Compared with the desorption



effect of HPCD, CMCD, and a mixture of HPCD and CMCD on the sorbed TCE, a mixture of HPCD and CMCD is better. Especially, the ratio of HPCD and CMCD is 80 to 20. For the sorbed CrO_3 , CMCD can desorb 51% and HPCD can desorb 29%, after one day

[117] 醇類加入受污染地下水增加空氣注入法對有機污染物

去除效率之研究

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中文摘要

空氣注入法與土壤蒸氣萃取法均為土壤地下水受到有機物污染時常見的處理方法，但可惜的是受限於有機物的揮發速率，常需要花費許多時間才能達到整治目標，若能有效增加有機物之揮發量，則能提高空氣注入法與土壤蒸氣萃取法之處理效率，本計畫主要研究目標即為添加醇類至地下水中增加有機在空氣注入法配合土壤蒸氣萃取法處理時的揮發量，同時考慮由上述主題延伸發展的兩項主題，包括發展新的吸附劑降低在上述處理程序中去除有機物之成本與添加醇類是否影響有機物生物分解效率。

本研究考慮研究的有機物包括石化產生常見的單環類芳香族化合物(甲苯與乙苯)與直鏈型化合物(正己烷與正庚烷)，同時也研究含氯有機溶劑(1,1,2-三氯乙烷與四氯乙烯)，所使用的醇類則包括正戊醇、正己醇與正庚醇，先醇類以 2ppm、6ppm 與 10ppm 三種濃度與指定有機物混合成溶液，在控制溫度 25°C 與流量 50ml/min 下將有機物帶出不同有機質含量之土壤，在指定時間下以吸附管吸附揮發出的有機物並分析其揮發量。此外，也以合成奈米鈦管將表面以有機物十六烷基三甲基溴化銨(HDTMA)與十八烷基三氯矽烷(OTS)改質成為吸附劑，並以電子顯微鏡、穿透式電子顯微鏡、XRD、接觸角、FTIR 圖譜與元素分析儀分析改質前後表面性質，再以此吸附劑吸附有機蒸氣，最後利用 Thomas 方程式評估對 VOCs 之吸附容量，並與商用活性炭進行比較。此外亦同時進行有機物分解試驗，考慮醇類存在時對是否對有機物分解產生之影響，經由醇類與有機物混合後，測定在不同時間下 OP600 吸光值，做為評定之依據。

研究的結果顯示，醇類存在時確實可以增加上述有機物之揮發量，其對揮發量影響大小呈現正庚醇>正己醇>正戊醇，且揮發效率隨醇類濃度增加而增加，高有機質的土壤則會導致有機物傳送效率被抑制，揮發效率愈低的條件下抑制愈明顯。所合成之奈米鈦管經改質後表面由親水性變成疏水性，揮發性有機物除可吸附於改質奈米鈦管之表面，也可利用分佈方式進入鈦管上的有機物質，因此可增加鈦管的吸附量，其吸附量與表面疏水性順序相同為 OTS-TNT >HDTMA-TNT >TNT，且 OTS-TNT 對有機物吸附量可高於商用活性炭，對於不同有機物而言，由於化學結構影響，吸附量呈現芳香族有機物>含氯有機溶劑>直鏈型碳氫化合物。所選擇的醇類容易被生物分解，且 1,1,2-三氯乙烷與四氯乙烯存在並不會對醇類分解產生影響，加入芳香族有機與直鏈型有機物則醇類與芳香族有機物皆可被微生物分解。

Abstract

Air sparging (AS) and soil vapor extraction (SVE) are frequently used to remediate contaminated soil and groundwater by organic compounds. When the target contaminants are low volatile organic compounds, it will be a very long schedule to finish the remediation. If we can find a way to increase emissions of organic compounds, improving the remediation schedule for the removal efficiencies of organic contaminants. The objective of this study is to added alcohol to groundwater for the increase in volatilization of organic compounds in the processes of AS and SVE. In addition, we also intend to develop a low-cost adsorbent which can adsorb organic compounds releasing from air sparging and soil vapor extraction.



Furthermore, we examine the effects of added alcohol on biodegradation of carbon hydrogen compounds and chlorinated organic solvents.

In this study, the target organic compounds include aliphatic compounds (n-hexane and n-heptane), aromatic compounds (toluene and ethylbenzene) and chlorinated organic compounds (1,1,2-trichloroethane and tetrachloroethene). The n-pentanol, n-hexanol and n-heptanol with 2, 6, and 10ppm were added the solution mixing with an target organic compound. Air with a given flow rate 50 ml/min was used to purge the solution at 25 °C for 3h. The release of VOCs was adsorbed using a commercial adsorption tube. The adsorptive amounts of VOCs were discussed in various environmental conditions. Moreover, the soils with high or low organic matter were applied to evaluate the transportation of organic compounds in the soil-water system. In this study, we also intended to use an organic substance (HDTMA and OTS) modified titanate nanotube (TNT) to remove VOCs from the processes of AS and SVE. The properties of synthesized adsorbents were characterized with SEM, TEM, XRD, contact angle, FTIR and element analysis instrument. Thomas equation was applied to estimate adsorption capacities of the test VOCs. The adsorptive amounts of VOCs on the produced adsorbents were compared with those on commercial activated carbon. In addition, bioavailability of added alcohol toward the VOCs was discussed. We measured OP 600 in given interval to understand the biodegradation when the alcohols mixed with the test VOCs in the solution.

The results indicated the added alcohols can effectively increase the volatilization of the VOCs. The n-heptanol can generate the highest increase in volatilization for the all VOCs. The volatile amounts of VOCs increase with the increasing alcohol concentrations. The

soil with the high organic matter might reduce the volatilization of VOC in the soil-water system. The modified TNT using HDTMA and OTS possessing the hydrophobic surface can uptake organic vapor. VOCs might adsorb on the surface of modified TNT and partition to the organic substance on TNT. The partitioning behavior can increase the sorption of VOCs on adsorbent. The adsorptive amounts of test organic compounds were in the decreasing order : OTS-TNT > HDTMA-TNT > TNT. The adsorptive amounts of VOCs on the OTS-TNT were higher than those on the commercial activated carbon. In addition, the obtained results indicated the presence of alcohol in groundwater can be degraded by microorganism. Moreover, the added alcohols do not affect the biodegradation of the test VOCs.

[118] 整治場址能耗與環境足跡之本土化評估系統建立及應用

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中文摘要

國內推動土壤地下水污染防治工作，已近十五年。諸多控制以及整治場址，礙於技術以及經費，經常耗時多年，而且費用高昂所費不貲，甚至整治無以為繼。不僅戟傷案場土地復育時程，亦影響案場及鄰近社區與經濟發展甚鉅；致使案場業主等污染土地關係人、社區居民及/或政府機關等利害關係人均蒙其害。究其關鍵，應與整治過程未評估能源耗用特性，且缺乏評估其他環境介質足跡之方法，以致連帶影響環境會計/成本、整治經濟/成本、甚至社群乃至社會成本。為了彌補這方面之不足，本研究已規劃協助環保署全面導入並且極力推動對環境更為友善之可持續性綠色整治 (Green Sustainable Remediation, 簡稱 GSR)。希望在進行污染整治時，亦能兼顧環境保護、經濟發展及社群共識，取得三者之間均衡發展。

目前，國際間正開發環境足跡分析工具，且無統一之評估工具，因此由於各工具評估範疇與邊界不同，不同工具間評估結果並不適合互相比較，而本研究分析美國環保署提出之環境足跡分析試算表 (Spreadsheets for Environmental Footprint Analysis, SEFA)，其評估工具是用以計算整治過程之環境足跡等相關參數，以及定性描述土地及生態系統。

本研究已提出一套污染土地可持續性綠色整治架構流程，並利用三合法控管作業原則，建立一套流程及層次性整治策略；為能盡速與國際接軌，本研究已將 ASTM 準則導入此系統，且草擬出可持續性綠色指標來因應污染案場之整治規劃；在兼顧環境、經濟及社會相輔相成之下，發展所需考量之各項因素，並區分各項因素之正向指標及負向指標。使用 SEFA 評估工具導入可持續性綠色指標，在推動土地整治之方案時，需同時考量相關因素，降低其負向指標

並提高整體效益，協助我國綠色整治策略朝向定量模式發展。

本研究以某供油中心大型生物復育場作為研究案場，且導入評估軟體，共分為能源、空氣、水資源、原料耗材與廢棄物、土地與生態系等五大範疇要素。其中土地及生態部分目前以定性方式呈現，但本計畫嘗試將此範疇定量，因此針對油污染土壤健綠整治進行土壤及生態指標，其評估項目依序有以下幾項(1) 土壤肥力指標 (2) 成長狀況 (3) 收成狀況 (4) 蔬果成品品質狀況。研究結果發現，如欲導入並落實綠色可持續性整治，能源管理與現行各類相關環境申報機制若納入整治計畫/控制計畫，並予審查、稽核追蹤與要求落實，不僅可促使國內案場落實綠色可持續性整治，亦可活絡甚至衍生其他相關綠色經濟，有助污染土地社會經濟環保各面向更均衡之永續發展。

Abstract

In order to construct the mainframe of green and sustainable remediation policy, a systematic evaluation mechanism was developed. Such evaluation tool was established according to the requirement of Taiwan Soil and Groundwater Remediation Act, and was referring from sustainable remediation case examples of USEPA and other US governmental agencies, and the American Society of Testing Materials (ASTM). The established Chinese version of Green and Sustainable Remediation Evaluation Tool has considered energy consumptions and environmental footprints in five aspects include: energy, air, water, materials and solid wastes, as well as land and ecological aspects. To test the comprehensiveness of the GSR Evaluation Tool, a field scale of TPH contaminated soils bio-remediation case was applied and found successful. To the administrative concerns, it is suggested



that energy consumptions and the related environmental footprint data should be estimated and reported in the site remediation plan or the site control plan. Then the administrators should follow up the implementation plan via auditing program to enforce the completeness of the plan. Enforcing green and sustainable remediation policy, not only can cultivate green remediation business opportunities, but also can harmonize and balance society, economic, and environment groups; thus, a sustainable future can be expected

[119] 應用自然電位法檢測迷失電流之研究

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中文摘要

本研究以數值模擬與砂箱實驗設計出一套以自然電位法偵測地下迷失電流源的分析方法，闡述自然電位法應用在環境監測之可行性及優勢。第一階段的污染擴散砂箱實驗中，同時以地電阻影像法及自然電位法進行量測，成果說明地電阻影像法較適用於單次的調查與time-lapse的研究分析；自然電位法則適用於長時間的「觀察監測」。地電阻影像法應用在環境調查上，電性差異約需20%以上較能反應出現象的改變；自然電位的原始數據則具有偵檢環境中微小事件發生的能力。第二階段以自然電位法於人造迷失電流之砂箱進行實驗，資料逆推演算後的成果可使用電位分布的具體影像及電流密度量指出迷失電流源的位置。地電阻影像法是目前最常應用於協助土壤及地下水污染問題的地球物理探勘技術，而自然電位法量測之設備與地電阻影像法相似，因此具有同時收集電阻率及自然電位兩種資料之可行性，本研究結果擴大了地球物理探勘技術中電測法在土壤及地下水污染之應用層面，除了研判污染分布之外，還可偵檢可能潛在的迷失電流問題，亦有助於長期地下水管理之成效落實。

Abstract

This study proposes an innovative idea by applying the self-potential (SP) method to detect stray currents throughout the implement of numerical simulations and sandbox experiments. This research also expounds the feasibility and advantage of SP for monitoring in the field. We have conducted the sandbox design, literature and theory review, preliminary simulations on electrical resistivity imaging / tomography (ERI / ERT), together with laboratory sandbox experiments for various conditions of contaminants. The results of experiments illustrated, while the ERI is good for site investigation and time-lapse comparison, the SP method is preferred in the long-term monitoring. Importantly, the criterion for the ERI application could be the contrast in the resistivity larger than 20%. On the other hand, the SP method is capable of detecting a small environmental event in magnitude. We have applied the SP method for synthetic stray currents in sandbox experiments. The results of inversion showed the position of stray currents can be imaged by the electrical potential distribution and current density. ERI is the most popular approach to survey the issue of soil and ground-water contamination. The instrument of SP method is similar to ERI, therefore it also has feasibility to measure the signals of ERI and SP at the same time. The results of this study extend applied range of the electrical methods in geophysical exploration for the problem of soil and ground water pollution. It not only determines the pollution distribution but also detects the potential problem of stray currents benefiting the management of potential leakage of petroleum and natural gas.



[120] 應用電動力技術整治雲林虎尾含鎘及鉛污染土壤之研究

章日行

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中文摘要

循環加強式電動力法(Circulation-Enhanced Electrokinetics, CEEK)對鉛污染物整治已有很好的成效，為了未來能將本技術廣泛應用於各地污染場址，整治並獲得其他重金屬之處理效率有其必要性。透過本研究計畫之執行，若能證實 CEEK 技術可有效去除多種重金屬並達到污染物資源化之目標，則更提高本技術的實用性。本計畫將 CEEK 縮小規模建置於實驗室中，整治同時含鎘及鉛污染農地之現場土壤，進一步探討相關處理效率、問題及成本，並評估本技術對於鎘及鉛現場土壤的處理效益。

本計畫實驗按照計畫書執行內容進行，目前已完成污染土壤的物化特性分析、重金屬的移除效率、陰極電鍍回收、不透水層材料測試及部分中國大陸的專利申請，試驗結果可以歸納如下：

本電動力系統 CEEK 經不斷改良下，系統具有簡便、組裝容易、運送輕便及可重複使用性，有利未來推展與實際進行。

污染土壤鎘及鉛金屬於電動力系統下，鎘及鉛濃度皆能符合土壤監測標準；鉛濃度更能低於食用作物農地之監測基準。

本電動力技術對於鎘及鉛金屬的回收率最高可分別達到 85% 和 70%，能有效使金屬電鍍於陰極電極表面上。

不織布夾層對於未來現地整治應用提供一個好的選擇，能促使金屬污染物資源化的目標予以落實。

Abstract

The Circulation-Enhanced Electrokinetics (CEEK) effectively remediation the Pb contaminated soil. In order to this technique can be widely used around the contaminated sites, it is necessary for remediating and getting the removal efficiency of various heavy-metal

contaminated. In this study, the CEEK was constructed in the laboratory for remediating the Cd and Pb contaminated soil, to further explore the treatment efficiency, problems and operation cost. To obtain the appropriate operational parameters makes the CEEK technique cost-effective.

The execution of experimental program according to the previous plans, the analysis of physical-chemical characterization of soil, removal efficiency of heavy metal, cathode plating recycling, impermeable layer of material testing and apply the patents in mainland China have been obtained. Several conclusions and suggestions can be drawn:

- After continuous improvement, the CEEK system possesses some features such as: more concise, easy construction, easy transport, and reusable. These features are beneficial to promote in the future.
- The concentration of Cd and Pb contaminated soil conform with law standards under the CEEK operation, specially the concentration of Pb less than the standard for monitoring of food crop agricultural land.
- The recovery efficiency of Cd and Pb in the CEEK was about 85% and 70%, respectively. The metal ions could effective plating on the cathode electrode surface.
- In order to obtain the element Cd and Pb, the non-woven can offer a good choice in-site treatment, which to enhance the effectiveness of cathode plating.

[121] 綠色整治廢機油污染場址之管理與效益評估

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大仁科技大學環境與職業安全衛生系

中文摘要

本計畫場址位於屏東縣九如鄉，主要污染物為鋅、鉻、銅、鎳及總石油碳氫化合物(TPH)。計畫自 101 年起執行迄今，主要目的在於以生物復育法(蚯蚓 與石化分解菌)與植生復育法(白楊、構樹、血桐、太陽麻與牛筋草)改善污染。在場址內共設置六個試驗區，除對照區外，另設有三個生物復育區與二個為植生復育區。在三年餘的試驗後發現，各復育區之 TPH 濃度多呈現降低趨勢，三個生物復育區土壤中之 TPH 濃度減量百分比介於 33%~97%，植生復育區則為 19%~81%；而重金屬之測值指出，各復育區同一土層之濃度呈現無規則變化，不過，多數土層中之污染物濃度仍高於土壤污染管制標準。其次，生理試驗結果顯示，除白楊因正值落葉期以致光合潛力較差外，其餘植物已能適應污染環境。此外，本年度進行之木本及草本植體重金測值顯示，所有復育植物都具吸收累積效果，其吸收量依序為 Zn>Cu>Cr>Ni。最後以所有復育植物修剪或收成 植體之生質量與重金測值計算其吸收移除量，藉以評析植生復育效益，結果發現總移除量為 Zn(618.1 g)>Cu(12.07 g)>Cr(11.39 g)>Ni(10.07 g)。至於復育植物對重金測值之移除能力，木本植物依序為白楊>血桐>構樹，而草本植物則為牛筋草>太陽麻。

Abstract

The contaminated site proposed in this study is located at Jiuru Township, Pingtung County, with an area of 1,800 m². According to previous investigations, the major contaminants in soils were found to be zinc, chromium, copper, nickel and total petroleum hydrocarbon (TPH). The objective of this research project is to conduct remediation in the contaminated

site. Five treatment plots were designated in the highly contaminated area, in which three were designed for bio-phytoremediation (BP1, BP2, and BP3) and two for phytoremediation practice (PR1 and PR2). One control plot was used for comparison purposes. Since the initiation of this study in 2012, earthworm (*E. fetida*) and petroleum-degrading bacteria (*Pseudomonas* sp. NKNU01) have been utilized for bioremediation, while Poplars (*Populus bonatii* Levl.) and Sun Hemp (*Crotalaria juncea* L.) in the phytoremediation practice. Selective native plants, namely Macaranga (*Macaranga tanarius*) and Papermulberry (*Broussonetia papyrifera*) have also been planted to evaluate their remedial capabilities in 2014, while a dominant weed *Eleusine indica* was chosen for the same evaluation this year. The results of soil analysis showed a trend of decreasing TPH concentrations in most treatment plots, and the removal rate of TPH within the three bio-phytoremediation plots ranged from 33%~97% and from 19%~81% in the two phytoremediation plots. However, heavy metal concentrations were not significantly reduced and thus most soils were still highly contaminated. Plant growth and physiological investigations indicated that Poplars, Papermulberry and Macaranga were adaptable to the pollutants. For the purpose of further explorations, biomass and heavy-metal contents of the studied plants were analyzed to evaluate the removal efficiency of heavy metals. The results indicated that the four metals were absorbed and removed by all studied plants in the order of Zn(618.1 g)>Cu(12.07 g)>Cr(11.39 g)>Ni (10.07 g). The heavy-metal removal ability of the woody plants was found to be Poplars > Macaranga > Papermulberry and *Eleusine indica* > Sun Hemp for the



herbaceous plants.

[122] Itrax應用於環境鑑識之探討

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中文摘要

違法偷排含重金屬廢水或廢棄物在臺灣是造成土壤與底泥污染的最大威脅，對環境的殘害與影響正逐漸對生活在這片土地的居民產生傷害。本研究以桃園市大園區滲眉埤污染案為探討對象，利用 Itrax 岩芯掃描儀針對底泥進行元素種類判定、元素半定量快速篩測與非彈性和彈性散射之比值 (Mo inc/coh)，評估該儀器所提供大量且多元的數據資料對於研判環境污染物質來源之適用性。研究資料顯示滲眉埤岩芯所含元素包括矽、鈣、鐵、錳、鎳、銅、鉛、鉻與鋅等 9 種。其中，錳、鋅、銅與鈣的濃度含量在不同底泥岩芯剖面深度的變化趨勢有相似之處。合理懷疑該工廠利用大雨或假日將時，連帶將噴入大量碳酸鈉和石灰溶液至滌塵器中使其和煙道氣發生酸鹼中和的物質一併連同非法污水與污泥排入滲眉埤所致。如果採用傳統底泥混樣的分析方式，會因底泥所含重金屬濃度均勻化而無法顯示出金屬濃度隨岩芯深度而有連續檢測數據的特性，這也正是凸顯 Itrax 檢測技術的優勢所在。最後，本計畫認為 Itrax 岩芯掃描儀之檢測數據靈敏度佳、元素種類判定多元與岩芯連續掃描等特性，可作為國內未來環境鑑識科學中釐清污染來源責任歸屬問題的分析工具之一。

Abstract

Illegal wastewater discharge containing heavy metals pose the greatest threat to Taiwan's soil and sediment contamination. The impact on the environment and gradually harmed on the people living in this land. In Sheng-Mei pond pollution case study, we aimed to use Itrax core scanner patterns for sediment samples to determine the type of elements,

the elements and the ratio of the inelastic scattering and elastic (incoherent over coherent scattering, inc/coh), further evaluate the suitability of large and diverse data sources to environmental pollutants judgments of the instruments provided. Research data show the "Sheng-Mei pond" core contains elements include nine kinds of silicon, calcium, iron, manganese, nickel, copper, lead, chromium and zinc and so on. Manganese, zinc and copper content concentration consistent in different sediment core cross-sectional trends depth. In heavy rain or on holidays, reasonably suspect that the plant will be sprayed with a large number of sodium carbonate and lime solution to the dust and the flue gas to acid-base neutralization of the material together with the illegal sewage and sludge discharged into the pond due. If the traditional method of sediment mixing sample analysis, sediment concentration of heavy metals contained in the metal concentration can not be shown with the core depth and continuous testing data characteristics. It is also highlighting the advantages of the Itrax detection technology. Finally, the project considered that the detection data of Itrax core scanner had good sensitivity, multi-element classification and continuous scan of core, which could be used as one of the analytical tools to clarify the attribution of pollution source responsibility, especially as one of the environmental forensics tool to clarify the sources of pollution in future.



[123] 木麻黃植物 (Casuarina spp.) 根部共生微生物對於重金屬累積之影響

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中文摘要

重金屬 (heavy metal) 為最具警示性及毒性之無機物質，造成土地大面積之污染，而植生復育 (phytoremediation) 為利用植物與微生物之共生及相關之技術，木麻黃科 (Casuarinaceae) 為臺灣海岸地區主要造林樹種之一，可與土壤中多種微生物進行共生，可降低環境逆境，幫助植物生長。本研究嘗試釐清接種不同類型之共生微生物是否影響木麻黃植物重金屬吸收量。研究結果顯示，木麻黃植物 (*Casuarina equisetifolia*) 能與三種類型微生物共生，包括叢枝菌根菌 (arbuscular mycorrhizal fungi, AMF)、暗色隔膜內生菌 (dark septate endophytes, DSE) 及固氮放線菌 (nitrogen-fixing actinobacteria, NFB)。7 株暗色隔膜內生菌分別進行重金屬耐受試驗，3 株菌株 (CkDB5、Rk1 及 RrtHH10) 具有耐受 1 mg/mL ZnCl₂ 濃度處理之能力。CkDB5 菌株進一步進行 0-3.2 mg/mL ZnCl₂ 濃度處理，試驗結果顯示 ZnCl₂ 對於菌株完全抑制濃度為 2.4 mg/mL，於 1.6 mg/mL 濃度處理時，菌絲 Zn 含量可達約 156.9 mg/g，具有高度之重金屬 Zn 吸附能力。以 0-4 mg/mL ZnCl₂ 水溶液進行木麻黃苗木重金屬吸收試驗，並探討微生物之影響。試驗結果顯示 AMF、DSE 及 NFB 幫助木麻黃苗木耐受 Zn 之能力，並降低植體內重金屬 Zn 含量，但卻能增加植物生長量，進而增加整體重金屬累積量並提升植生復育之效益。

Abstract

Heavy metals are the most alarming and the most toxic inorganic substances which have contaminated a large area of land. Phytoremediation can be defined as an in situ remediation strategy that uses

vegetation and associated microbiota to remove environmental contaminants or render them harmless. Casuarinaceae plants which are one of the main reproducing trees in the eastern coast of Taiwan are able to be associated with different symbiotic soil microorganisms that mitigate the adverse effect of stress and improve plant performance in environments. We try to figure out the effects of heavy metal accumulation by different symbiotic microorganisms in *Casuarina* plants. The study result demonstrates that *Casuarina* plants can symbiosis with three kinds of microorganisms including arbuscular mycorrhizal fungi (AMF), dark septate endophytes (DSE) and nitrogen-fixing actinobacteria (NFB). Seven strains of DSE separately test the tolerance capability of heavy metals. The three strains (CkDB5, Rk1 and RrtHH10) show the tolerance capability in 1 mg/mL ZnCl₂ concentration. CkDB5 strains further test the tolerance capability by 0-3.2 mg/mL ZnCl₂ concentration treatments. The minimum inhibitory concentration (MIC) values of ZnCl₂ to CkDB5 strains were about 2.4 mg/mL. In 1.6 mg/mL ZnCl₂ treatment, the Zn accumulations of mycelium were about 156.9 mg/g. The CkDB5 strains have highly ability to accumulate Zn in mycelium. In the experiment of heavy metal uptake by *Casuarina* seedlings via 0-4 mg/mL ZnCl₂ solutions as irrigating water, and figure out the effects of microorganisms. The result demonstrates that AMF, DSE and NFB enhance the tolerance ability of Zn in *Casuarina* seedlings, and reduced the Zn accumulations in plant. But they can promote the growth of plant and then enhance the heavy metal accumulations in total.

[124] 以巨量資料預測土壤及地下水污染趨勢與優先補助整治評估模式 李家儂

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中文摘要

本研究從近年國外諸多研究中，發現巨量資料(Big Data)之概念已被廣泛運用於各項領域，其資料重複性使用可由大量看似雜亂的數據中推測出潛在相關性，不僅有助於瞭解這個世界，更能以此改善決策方式達到重塑社會的走向。因此，為有效推動污染整治工作，本研究透過巨量資料的應用，使之在整治前即充分運用污染場址過去的工業活動進行評估，且借以不同場址各項污染程度為評估基準，進行一系列污染整治優先順序評定，勢必能使基金運用更有效率，且有助於加速與擴大整治工作的進行，並能有效解決土壤及地下水污染影響議題。本研究已完成運用科學性分析工具之評估篩選與指標權重計算及排序，並以此進行各項環境潛在因素之相關性分析與再利用評估之使用，本研究計畫成果內容說明簡述如下：

本研究係以 Big Data 數據基礎為考量，首先以運用所建立之優先整治補助評估指標，以及指標權重計算與排序，如第一階段(FDM)研究中研擬出「土地使用指標」、「公共設施服務指標」、「環境空間指標」、「巨量資料指標」、「未來潛力指標」、「成本收益指標」與「政策供給指標」等七項評估構面，並據以建立出 35 項代表指標，以此完成 FDM 專家共識值分析之評估篩選，以透過 FDM 專家共識值檢定與 Grey-ANP 計算得之權重白值「土地使用指標(23.76%)」、「公共設施服務指標(15.96%)」、「環境空間指標(14.17%)」、「巨量資料指標(12.12%)」、「未來潛力指標(34%)」五項評估構面，以及 14 項評估指標與權重，以完成建立 PFA 優先整治補助之評估指標體系，以此計算出各項指標之灰色權重值與優先排序，使之具有「決策彈性」。

最後，本研究以此指標體系進行桃園市大園區實際案例之應用，藉以客觀

數據改善決策方式，使之在案例場址中，評估其最具急迫性的優先整治區域(PFA)及場址之排序，輔以透過地理資訊系統(GIS)呈現，以提出區域性策略建議，以供相關單位日後對於棕地的治理可以更有效進行排程，以至縮短整治作業，更讓基金能投資於適當對象，使基金運用更有效率，以達加速與擴大整治工作的進行。

Abstract

In this study, the concept of "Big Data" has been widely used in many fields in recent years. The repeated use of data can be used to infer the potential relevance from a large number of seemingly cluttered data. Help to understand the world, but also to improve the way decision-making to remold the trend of society. Therefore, in order to effectively promote the pollution remediation work, this study, through the application of huge amount of data, makes full use of the past industrial activities of contaminated sites before remediation, and predicts the future pollution trends of different sites. A series of pollution remediation priorities will be used to evaluate the pollution trend, which will make the fund more efficient. It will also help to speed up and expand the remediation work, and effectively solve the soil and groundwater pollution impact issues. The results of this study have been completed by the use of scientific analysis tools to assess the selection and weight calculation and ranking, and to conduct the analysis of the correlation between environmental factors and the use of re-use assessment, the research project at this stage (The first draft) content description briefly as follows:

In the first stage (FDM) research, the author uses the Big Data data base as the basis for the research. The first step is to use the established evaluation index of priority remediation subsidy and the index



weight calculation and ranking. , "Indicators of Utilities", "Utilities Service Indicators", "Environmental Space Indicators", "Bulk Data Indicators", "Future Potentials Indicators", "Cost-Benefit Indicators" and "Policy Supply Indicators". To establish 35 representative indicators in order to complete the FDM expert consensus analysis of the assessment of screening, through expert consensus value of the "land use indicators", "public facilities service indicators", "environmental space indicators", "huge Five Indicators of Future Potential Indicators, and 14 assessment indicators to establish a framework for assessing the indicators' performance. Then, Gray-ANP is used to complete the evaluation index system of Gray-ANP in the second stage (Gray-ANP). The gray value of each index and the prioritization are calculated to make it have "decision elasticity".

Finally, the practical case is applied to improve the decision-making mode by using objective data to evaluate the PFA and site ranking in the most urgent cases in the case site, and then through geographic information system (GIS) In order to propose regional strategies for the relevant units in the future for brownfield governance can be more effective scheduling, as well as shorten the remediation operations, leaving the Fund to invest in the appropriate object, the use of funds more efficient, to accelerate And expand the rectification work carried out.

[125] 以生物界面活性劑進行土壤淋洗促進植生復育重金屬污染土壤

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中文摘要

植生復育(Phytoremediation)是利用植物來移除污染物的技術。因此本計畫擬利用本土種植物進行綠色整治試驗研究，以取得現地已污染含有重金屬鎘、鉻、銅的土壤作為植物種植的介質來源，目前規畫以本土常見與具有能源潛力作物，如狼尾草、臺灣藜、肥皂草進行重金屬吸附試驗，待植物收成後除移除，亦可能作為生質能源作物料源來源。另因肥皂草含有大量的皂素(Saponin)成分，為生物界面活性劑，本研究利用其所含有羧基與金屬結合的能力來對土壤中重金屬進行吸附，將皂素溶液對於土壤進行淋洗，藉此提高植生復育的重金屬吸附量，並於生物可分解淋洗螯合劑EDDS及傳統淋洗螯合劑EDTA進行比較。

從目前來看狼尾草所獲得的生物量最大，其次為臺灣藜及肥皂草，以EDTA、EDDS及皂素為淋洗液的環境下，EDTA及EDDS對於生物量的減少較為明顯，皂素則對於生物量的影響較小。

而以EDTA、EDDS及皂素為淋洗液的環境下，狼尾草植體重金屬銅的濃度，分別為100.9 mg/kg、117.8 mg/kg及32.7 mg/kg，臺灣藜植體重金屬銅的濃度分別為761.0 mg/kg、891.5 mg/kg及461.5 mg/kg，肥皂草植體重金屬銅的濃度分別為294.5 mg/kg、281.6 mg/kg及128.4 mg/kg，顯示以EDDS為淋洗液，所獲得的植體重金屬吸收較EDTA來的好，比皂素的影響來的高。狼尾草在EDDS的環境下，所能移除的重金屬Cu移除量最多，每 m^2 可移除約112.2~142.3 mg的Cu，在EDTA的環境下每 m^2 可移除約42.6~67.9 mg的Cu，在皂素的環境下每 m^2 可移除約43.2~64.9 mg的Cu。臺灣藜在EDDS的

環境下，所能移除的重金屬Cu移除量最多，每 m^2 可移除約36.1~40.5 mg的Cu，在EDTA的環境下每 m^2 可移除約5.1~18.7 mg的Cu，在皂素的環境下每 m^2 可移除約13.1~17.5 mg的Cu。肥皂草在EDTA的環境下，所能移除的重金屬Cu移除量最多，每 m^2 可移除約30.9~40.7 mg的Cu，在EDDS的環境下每 m^2 可移除約27.3~34.7 mg的Cu，在皂素的環境下每 m^2 可移除約21.3~30.5 mg的Cu。皂素的淋洗液可被生物降解，不會對於環境造成二次污染。植生復育若搭配淋洗做為灌溉用水，將有助於植體吸收重金屬的增加，若能再搭配耐酸性環境下植體作物，將可提升植體吸將重金屬的效率。

Abstract

Phytoremediation technology is the use of plants to remove contaminants. Therefore, this project intends to use the native species of green Experimental Study on Regulation in order to achieve now be contaminated energy potential crops contain heavy metals cadmium, chromium, soil copper as plant cultivation media source currently planning to local common and have, as a wolf tail grass, quinoa Taiwan, soap grass heavy metal assay, in addition to the plant to be removed after harvest, may also be used as source material for biomass energy sources. Another soap because grass contains large amounts of saponin (Saponin) component of biological surfactants, carboxyl and metal binding ability of the present study, it contains benefit to the adsorption of heavy metals in soil, the soil saponin solution to rinse, thereby increasing the amount of adsorption of heavy metals Vegetation restoration and rinsed in biodegradable chelating agent EDDS chelator EDTA and leaching traditional comparison.



The biomass of *Pennisetum purpureum* was the largest, followed by Taiwan *Chenopodium album* and soap. The EDTA, EDDS and EDS were the most important factors to decrease the biomass. The effect on the biomass is small.

The concentrations of Cu in the plants were 100.9 mg/kg, 117.8 mg/kg and 32.7 mg/kg, respectively, and EDTA, EDDS and saponin were used as eluents. 891.5 mg/kg and 461.5 mg/kg, respectively. The concentration of copper in the soap grass plant was 294.5 mg/kg, 281.6 mg/kg and 128.4 mg/kg, respectively. The obtained heavy metal absorption than EDTA to the good, higher than the impact of saponin to high. *Pennisetum* in the EDDS environment, the removal of heavy metals can be the most Cu removal, removal of about 112.2~142.3 mg/m² of Cu, in the EDTA environment can be removed per m² of about 42.6~67.9 mg Cu, in the saponin environment can be removed per m² about 43.2~64.9 mg of Cu. In the environment of EDDS, the removal of heavy metal Cu in the environment of EDDS could remove about 36.1~40.5 mg of Cu per m², and remove about 5.1 ~ 18.7 mg of Cu per m² in EDTA. , In the saponin environment can be removed per m² about 13.1~17.5 mg Cu/kg . In the environment of EDTA, the removal of heavy metal Cu in the environment of EDTA was the most, about 30.9~40.7 mg Cu/kg was removed per m², and about 27.3~34.7 mg of Cu in the environment of EDDS was removed , In the saponin environment can be removed per m² about 21.3~30.5 mg of Cu. Saponin eluents can be biodegraded and will not cause secondary pollution to the environment. If the irrigation with irrigation with water, will help the plant to absorb heavy metals increased, if again with acid-resistant environment, plant crops, will be able to enhance the absorption of heavy metals plant efficiency.

[126] 以地電阻影像探測技術推估地下水流速流向：實場驗證

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中文摘要

本計畫為去年度計畫的延續。主要目的為對以地電阻探測技術量測地下水流速流向方法進行實場驗證。此方法主要目的為在只有一口地下水監測井的限制下，發展一套可靠且有效率之地下水流速流向測定技術。去年度計畫砂箱實驗結果顯示量測地電阻變化可有效量測地下水流速流向。因此本年度以實場展示此技術之可行性。並藉由實驗建立現場量測基本流程與方法。實驗共可分為五個主要部分：(1)場址及實驗設置；(2)示蹤劑試驗；(3)場址示蹤劑傳輸模式模擬；(4)地電阻試驗；(5)地電阻推估地下水流速流向。

本計畫選擇雲林科技大學校園內做為進行實場示蹤劑及地電阻試驗場址，該場址內既有監測井為 17 口，含水層約 20 m，監測井完全貫穿含水層，開篩長度從地表下 1.5 m 至 20 m。地電阻試驗分為兩階段，第一階段為方法驗證。第二階段為地下水流速流向推估。本計畫搭配雲科大溫志超教授研究團隊進行的抽水試驗，抽水井連續抽水三天，在抽水試驗的第三天流場穩定後，即進行示蹤劑地電阻試驗，以固定體積的高導電度鹽水(NaCl；濃度約 2.45 g/L，導電度 5000 $\mu\text{S}/\text{cm}$)的鹽水從上游的注入井注入，同時下游抽水井以固定流量持續抽水。

本計畫地電阻監測共執行六次，分別編號為試驗 No. 1 至 No. 6，試驗 No. 1 至 No. 3 為五測線、試驗 No. 4 為三測線、試驗 No. 5 至 No. 6 為單測線。每 1 m 設置一電極，共設置 16 至 32 支。示蹤劑以脈衝式點源 (instantaneous point source) 注入，成分為濃度約為 2.45 g/L NaCl 水溶液(導電度 5000 $\mu\text{S}/\text{cm}$)，注入體積為 100 至 250 公升，注入時間約 1 至 2 小時。當鹽水注入後，注入井將停止注水，但抽水井則會繼續抽水。同時開始進行監測井中導電度與地電阻量

測，地電阻間測時間分別為 5、5、8、8、23 及 21 小時。

本計畫目前獲得之研究數據指出，地電阻確實能感測到實場地下水受高導電度示蹤劑影響，產生較背景值為低的電阻，且電阻峰值隨時間有降低的趨勢。透過此電阻變化量隨時空變化的趨勢，應能解析地下水流場流速流向等訊息。但目前數據分析結果顯示，地電阻資料未能明確掌握示蹤劑的移動變化，主要原因可能是流場流速太慢，以至於在有限時間內測量的視電阻峰值的移動距離較地電阻電極間距短(1 m)，故無法解析出示蹤劑的移動方向。

地下水流場以 MODFLOW 模擬，而示蹤劑傳輸以 MT3D 模擬，模擬結果顯示抽水產生的人為流場，其地下水流速約為 0.5 至 1.2 m/d，說明地下水流場流速確實較慢。實際監測時間內示蹤劑團移動的距離小於地電阻電極間距 1 m。表示監測時間 8 至 24 小時的地電阻試驗，不足以偵測到示蹤劑團有顯著的移動，然而，注入井位置基本上仍會有高導電度的示蹤劑團，此現象與實場試驗結果相符。

根據本研究實場試驗結果，發現砂箱試驗與實場規模的試驗結果的不同，注入點及附近除了有電阻較背景值降低的現象，亦會發有電阻較背景值增加情況發生。表示高導電度示蹤劑進入地下水，不止是改變電場的分佈，更可能改變電流的路徑分佈，產生電壓差上升，結果以電阻增加的結果呈現，與一般的定電流的假設有所差異。

Abstract

This research extends the works of last year's project. The main objective is to directly measure groundwater velocity and direction based on electrical resistivity tomography (ERT). The motivation for this technique is to be able to accurately and effectively identify the direction and



velocity of groundwater flow with only one monitoring well. Last year's project has validated the feasibility of this technique by conducting sandbox experiments. This research will validate the effectiveness of this technique in a real groundwater flow field. This research includes five main tasks: (1) setup experimental site; (2) conduct tracer tests; (3) construct and validate a numerical model for groundwater and solute transport of the tracer tests; (4) conduct electrical resistivity tomography tests; (5) measure the direction and velocity of groundwater flow of the test site.

The site for this study is located in National Yuanlin University of Science and Technology. The aquifer within the site is about 20 m in depth. There are 17 monitoring wells, each screened between depths of 1.5 and 20 m, within the site. The tracer study is divided into two stages: verification of technique and measurement of groundwater velocity and direction. Concurrent pumping tests were conducted during the ERT experiments. Therefore, the tracer experiments were conducted after the groundwater flow reached equilibrium, which was approximately 2 days after the pumping started. The tracer tests are conducted using an injection approach. Solutions containing 2.45 g/L (5000 S/cm) of sodium chloride was injected into the aquifer. The ERT technique in the test site was consisted of 5 testing lines, each with 16 electrodes of 1 m apart. The 5 testing lines were parallel with each other with a spacing of 1 m. The injection volume is 250 L and the injection process lasted 5 min. One tracer was conducted so far.

The results of the tracer study indicate the change in groundwater electrical conductivity can be detected by the ERT technique. However, the ERT results show insignificant movement of the concentration plume. The main reason is that the groundwater velocity induced by the pumping process is only

0.1 m/h, which means the concentration front moved less than 1 m during the 5 h of ERT monitoring period.

Consequently, the setup of the ERT electrode needs to be modified to address this problem. In future tracer studies, the equilibrium groundwater flow will be analyzed before the tracer studies and the spacing between each ERT line will be decreased to 0.25 m, whereas the distance between electrodes will be still 1 m.

A model for the groundwater flow within the test site will be constructed using MODFLOW. The model will be calibrated and validated with the data from the pumping tests. Afterwards, the model will be used to generate groundwater flow field for a solute transport model constructed using MT3D.

The expected outcome of this project is to validate the technique for effectively and accurately measuring groundwater velocity and direction.

[127] 以植物復育整治受汞污染土壤之可行性研究

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中文摘要

本研究之目的是利用植生復育技術處理受汞污染之土壤，以盆栽實驗評估出具有最佳耐受性與最佳汞累積能力的植物種。實驗之植物種為耐鹽、耐旱的臺灣原生種濱海植物，包含水黃皮、白茅、蘆葦、蘆竹、五節芒、甜根子草。植物放在半開放空間下，添加汞污染土壤實驗150天。實驗結果顯示，(1)本研究選用之六種植物確能透過植物萃取及植物穩定化機制吸收汞。(2)六種植物之根、莖及葉部位皆會吸收汞。(3)整株植體汞累積量越高，但該植體單位生物質量汞累積濃度不一定越高，非呈正向關係。(4)植株生長率以甜根子草最佳，但因其累積濃度較少，推測此種植物較不易吸收汞，但是耐受度較佳。(5)六種植物之汞累積顯示在空白組中並無明顯吸收作用，因此可推估該六種植物對大氣中的汞蒸氣並無吸收的情況發生。(6)雖然整株植體汞累積量以水黃皮最高，但是植體單位生物質量汞累積濃度以蘆竹最高。因此，未來建議以單位面積植株樹木來評估何種植物為最佳植生復育汞污染土壤之植物種。

Abstract

The purpose of this study is feasibility study of phytoremediation treatment of mercury-contaminated soils. The plant species were evaluated with best endurance ability and best mercury accumulation ability by pot experiment. The experimental plant species is the salt-tolerant, drought-tolerant native plant species of seashore in Taiwan, including *Millettia oraria*, *Imperata cylindrical*, *Phragmites australis*, *Arundo formosana* Hack., *Miscanthus floridulus* and *Saccharum spontaneum*. plants were added to mercury contaminated soils for 150 days in a semi-open space. The experimental results show that (1) the six plant species used in this study are able to absorb mercury through Phytoextraction and Phytostabilization.(2) These plants roots, shoots and leaves absorb heavy metal mercury in all six plants. (3) The higher the mercury accumulation in plant tissue, but the concentration of mercury in plant tissue is not necessarily higher, not strictly correlated. (4) The growth rate of *Saccharum spontaneum* is the best, but its mercury accumulation ability is less. It is presumed that *Saccharum spontaneum* is not easy to absorb mercury, but mercury accumulation ability is better. (5) The controls of six plants had no significant change in the mercury accumulation ability. Therefore, it can be inferred that the six plants do not absorb mercury vapor in the atmosphere. (6) Although the mercury accumulation capacity in plant tissue was highest in *Millettia oraria*, but the concentration of mercury in plant tissue was the highest in *Arundo formosana* Hack. Therefore, it is recommended to use the plant number per area to evaluate which plant has the best phytoremediation ability for mercury contaminated soils.



[128] 以超臨界流體氧化技術同時處理土壤中戴奧辛、五氯酚及汞之 整合性系統開發

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中文摘要

近年來國內陸續發生彰化地區戴奧辛鴨蛋事件、高雄市大坪頂與彰化段台61線非法棄置案及台南中石化安順廠週邊土壤受戴奧辛污染等事件，土壤及地下水污染議題再度受到民眾與環保單位高度的關切與重視。其中，中石化安順場址不管是在污染物形態、污染土壤量與污染物濃度方面均為國內外罕見，受污染土壤之戴奧辛(PCDD/Fs)、五氯酚(PCP)與汞含量均遠遠超過管制標準；而此種包含不同超高濃度毒性物質之複合式污染型態，是最難整治的污染場址。本研究以中石化安順場受污染土壤為對象，透過本研究群自主研發的超臨界流體氧化(SCWO)處理模組進行試驗，以評估不同操作參數條件下(包含操作溫度、操作壓力、停留時間及氧化劑添加量等)對戴奧辛、五氯酚之去除及汞回收效率進行系統性評估。在後段空氣污染控制技術方面，則搭配本研究群研發的驟冷塔進行氣相汞的回收，再藉由流動床式活性碳吸附/熱解/再生系統(發明第I424877號)將汞與戴奧辛等有機污染物同步進行吸附及破壞。此外，在廢水處理技術方面，採用鈀觸媒(Pd/Al₂O₃)加氫脫氯技術達到戴奧辛減量之目的，避免戴奧辛殘留於環境，達到全面解決(total solution)之境界，本研究所開發之相關技術及執行成果可提供國內相關產業於戴奧辛及汞控制上的新選擇。

初步研究結果顯示污染土壤中戴奧辛及五氯酚的去除效率隨著SCWO操作溫度、壓力、氧化劑濃度(H₂O₂)及反應時間的增加而提升。使用100%過氧量，反應溫度為380°C，壓力為22MPa及停留時間為20分鐘條件下，對戴奧辛及五氯酚的破壞效率則達到99.9%以上，土壤中各污染物之殘餘濃度皆可符合

法規標準(戴奧辛<1000 ng-TEQ/kg；汞<20 mg/kg)。在後段空氣污染控制方面，實驗結果顯示驟冷塔除冷凝水氣外，更可有效捕集氣流中之汞及其化合物，捕集效率介於74~96%，冷凝液中可發現液態汞珠的聚集。而廢氣通過流動床式活性碳吸附塔後，各污染物濃度皆低於我國之排放標準(五氯酚500 µg/Nm³、戴奧辛0.1 ng-TEQ/Nm³、汞50 µg/Nm³)。

本研究建立活性碳再生系統，採流動床式理念設計，活性碳吸附床中的球狀活性碳因重力往下移動至再生系統中，於無氧條件下隨著反應時間增加，對戴奧辛及五氯酚的破壞效率愈高，對吸附於活性碳之戴奧辛及五氯酚的破壞效率可達98%以上，對於總汞可達99%以上的脫除效率，由於再生系統出口端含有高濃度的汞蒸氣，可將廢氣導回驟冷塔之入口端，藉由汞珠的回收將其去除，整個系統並無含汞廢棄物或汞污泥的產生，更能達到污染減量之目的。

Abstract

Recently, various sites of contaminated soil, such as dioxin-containing eggs in Changhua, hazardous wastes in Kaohsiung and soil contaminated by dioxin and mercury in Tainan, are discovered. These issues have attracted much attention from government and general public. Among these cases, contaminated soil in An-shun site simultaneously contains extremely high concentrations of PCP, PCDD/F and mercury. Different characteristics of these contaminants have caused the difficulty for effective remediation. In this study, super-critical water oxidation (SCWO) technology is self-developed for remediation of the soil contaminated with PCDD/Fs, PCP and mercury. For efficient removal of the contaminants, relevant

operating parameters including temperature, pressure, reaction time and oxidative added are tested. For well controlling pollutant emission, especially mercury, a novel quench tower is designed for recovering gas-phase mercury and condensing organic compounds. After that, the residual gaseous pollutants are further collected and destroyed via multi-layer adsorption/pyrolysis/regeneration system (Patent No I424877). Pollutants in contaminated soil, including PCDD/Fs, PCP and mercury, can be effectively destroyed and recovered via the integrated system of continuous pyrolysis system and multi-layer adsorption/pyrolysis/regeneration setup developed in this study. In addition, the wastewater collected in quench tower contains high-concentration contaminants. The chlorinated contaminants in the wastewater are further removed via hydro-dechlorination for total solution. The fruitful results obtained in this study will support the novel technology for remediation of the contaminated soil.

The preliminary results indicate that the removal efficiencies of PCDD/Fs and PCP in the contaminated soil increase with increasing operating temperatures, pressure, oxidant (H_2O_2) added and retention time. The destruction efficiencies of PCDD/Fs and PCP in the contaminated soil are more than 99.9% with 100% of stoichiometric demand, 380°C operating temperature, 22 MPa operating pressure and 20 min. retention time. The target pollutants in the remediated soil treated with above operation parameters of SCWO system meet the regulation of Taiwan EPA (PCDD/Fs < 1,000 ng-TEQ/kg; Mercury < 20 mg/kg). Regarding the pollutants emitted from APCDs, gas-phase mercury are effectively removed by the quench tower with 74 ~ 96% removal efficiencies. The elemental mercury (Hg^0) is also found in the condensed water of the quench tower. After the quench tower, the pollutants in the flue gas are further removed with multi-layer adsorption

system. In the emission, all concentrations of pollutants are lower than the emission standards regulated by Taiwan EPA, including PCP < 500 $\mu\text{g}/\text{Nm}^3$, PCDD/Fs < 0.1 ng I-TEQ/ Nm^3 and mercury < 50 $\mu\text{g}/\text{Nm}^3$. The PCDD/F- and mercury-containing wastes are not generated via the SCWO system developed in this study. Hence, total solution of remediating the soil heavily contaminated with PCP, PCDD/Fs and mercury is accomplished.

For BACs' reuse, a system for BACs' regeneration is built with moving-bed design. At oxygen-free condition (N_2 as carrier gas), increasing retention time is useful to enhance destruction efficiencies of PCDD/Fs and PCP adsorbed on BACs (>98%) and removal efficiencies of mercury adsorbed on BACs (>99%). Although vaporized mercury is discharged regeneration system of BACs, exhaust of regeneration system is induced back to the flue gas before quench tower and vaporized mercury can be efficiently recovered. Finally, SCWO developed in this study can efficiently remove PCDD/Fs, PCP and mercury from contaminated soil and APCDs can also efficiently control the pollutant emission. Furthermore, secondary pollutants including emission, BACs waste and condensate from quench tower are not been discharged from SCWO+APCDs. SCWO+APCDs designed in this study is a powerful and environment-friendly remediation technology for PCDD/F and mercury removal from contaminated soil and sediment.



[129] 以濕處理及廚餘淨化受戴奧辛污染之土壤

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中文摘要

本研究係導入綠色及可持續性整治 (Green and Sustainable Remediation, GSR), 採取以濕處理液洗及堆肥之非熱處理整治技術, 處理受戴奧辛污土, 更符合環境友善綠色整治, 並減少空污、水污、廢棄物等二次污染環境足跡, 且更經濟低廉以使整治得以持續順利進行。期能將土壤戴奧辛濃度處理至符合法規標準 1000 ng I-TEQ/Kg 以下, 洗土成本低於每公噸污土 6000 元。

本研究之污染土壤, 濕篩採取粒徑 0.105~0.250 公厘之砂質土壤, 使用厭氧液肥、水產生漿、及甘蔗酒三種配方, 進行洗土試驗, 以評估清洗戴奧辛污土潛勢, 另外利用好氧堆肥試驗將含戴奧辛污土降至法規標準。

洗土試驗為戴奧辛污土與上述三類洗土配方皆以 1:2.5 之重量比(土壤約 200 公克, 萃取液約 500 公克)混合, 攝氏 30 度, 40kHz 超音波震盪器。本研究洗土結果顯示, 水產物生漿其戴奧辛濃度由未萃取前 22,080 ng-TEQ/Kg, 水洗後結果為 1,298 ng-TEQ/Kg, 去除效率為 94.1%, 接近法規標準 1,000 ng-TEQ/Kg; 厭氧液肥水洗後其濃度為 2,961 ng-TEQ/Kg, 去除率為 87%; 最後甘蔗酒水洗後其去除率為 80%。此外, 本團隊藉由上述之結果, 選擇兩種去除效率較佳之溶劑(厭氧液肥及水產物生漿), 亦試驗高濃度之土壤, 其戴奧辛濃度介於 110,000 至 130,000 ng-TEQ/Kg。其中, 厭氧液肥洗土後, 其濃度由 113,565 ng-TEQ/Kg 降至殘餘為 4,841 ng-TEQ/Kg, 去除率為 95.74%; 水產物生漿洗土後其濃度由 134,709 ng-TEQ/Kg 降至 6,237 ng-TEQ/Kg, 去除率為 95.37%。

本團隊之好氧堆肥實驗, 以負壓箱作為反應器進行好氧堆肥實驗, 將戴奧辛污土與廚餘以濕重比為 1:3, 經充分

混拌後, 總重 5.6 公斤。該混合物之戴奧辛初始濃度為 2,491 ng-TEQ/kg, 歷時 63 天反應後, 其殘留濃度為 751 ng-TEQ/kg, 去除率為 69.9%, 且達到土壤污染管制標準 1,000 ng-TEQ/kg 以下。因此, 本團隊藉由上述之結果, 嘗試對於只經濕式篩分但未經厭氧液肥或水產物生漿或甘蔗酒等搓洗過後之土壤, 進行兩批次好氧堆肥反應器實驗, 充分混拌戴奧辛污土與廚餘(濕重比 3:7, 廚餘成分以生魚肉為主), 單組總重 80 公斤, 該堆肥混合物戴奧辛初始濃度各別為 7,462 及 6,048 ng-TEQ/kg, 經 42 與 47 天反應後, 其殘留濃度各為 1,916 及 1,604 ng-TEQ/kg, 去除率為 74.3% 及 73.5%, 最終殘餘濃度亦近於土壤污染管制標準值。

由此三批次之好氧堆肥實驗結果顯示出對於戴奧辛降解均為有效, 且負壓箱與反應器之戴奧辛降解趨勢為吻合。本計畫提出含有戴奧辛污染土壤解除法規管制標準之最佳路徑, 為將污土先經由洗劑搓洗將戴奧辛濃度降至 5,000 至 7,000 ng-TEQ/Kg 後, 再由好氧堆肥處理, 亦將殘留餘土壤中戴奧辛濃度降解至本計畫之目標值。

Abstract

Green and sustainable remediation (GSR) is commonly recognized in the recent years. Going for GSR, air, water, waste, energy and ecological impacts are emphasized to reduce secondary pollutions and to minimize environmental footprints. In this research, we are aiming to explore both technical and economic feasibility of soil washing and composting to treat Dioxin contaminated soils in order to compensate current thermal desorption and thermal destruction treatment in the aspect of reducing energy consumption and CO₂ emission. Moreover, the treated soil must comply with the 1000 ng I-

TEQ/Kg control criteria. Competitive and affordable treatment cost is expected for less than NTD\$6000/ton.

A pretreatment, namely soil screening/sieving, is conducted for obtaining a glance at particle distribution of the soil. The result shows that fine sand is the major component of the soil, accounting for more than 60% of the total mass. Both fish broth and anaerobic compost tea were chosen as probe of greener washing fluids. A combined treatment of ultrasonification and mechanical double-blade agitation is employed, which proves to be considerably efficient, achieving more than 85% (6 washing cycles) and 95% (10 washing cycles) of total removal efficiencies for medium and highly contaminated soils respectively under ambient temperature, soil/liquid ratio 1:2.5, 700 ppm and relatively short duration. As that for the fish broth, 94% and 96% removal were achieved in a parallel experiments. Though fish broth has achieved higher efficiency, anaerobic compost tea is chosen for the cost consideration. Those high efficiencies of anaerobic compost tea washing can be explained by the collision and penetration effects brought about by an innovatively designed combination of mechanical agitation and ultrasonic power; therefore, the partitioning between the particles and anaerobic compost tea rises benefiting the treatment. It is the first time a natural solvent is used for dioxin contaminated soil washing. Anaerobic compost tea, which is rich of bio-surfactants, e.g. alcohols, humic acids, etc., provides no harm to the environment during the treatment and also possesses the ability to improve bioavailability and bioactivity of the soil so that further bio-attenuation and full recuperation may take place in a faster manner.

The feasibility of degrading highly dioxin contaminated field soil by the aerobic co-composting process with food waste. The initial toxic equivalent

quantities (TEQ) of the soil was 16,004 ng-TEQ/kg dry weight, which then decreased to 7,642 after mixing with the bulking agents. The final TEQ value after 42 day incubation was 1,916 ng-TEQ/kg dry weight (approximately 74.3 % degradation) which is still higher than the standard limit (1,000 ng-TEQ/kg dry weight). Profiles of temperature, moisture, pH and ammonia presented favorable conditions for aerobic organisms. In another attempt, a washing soil with initial dioxin concentrations at 2,491 ng-TEQ/kg after mixing with foodwaste at 1:3 ratio has demonstrated 69.9% of removal in 63 days, and the residual concentration was 751 ng-TEQ/kg that is lower than the 1,000 ng-TEQ/kg regulatory limit.

Above findings have demonstrated the feasibility in combining anaerobic compost tea washing and the aerobic organic waste composting techniques to remediate dioxin contaminated field soils. The proposed technologies serve as alternatives in choosing greener technology for remediation other than traditional thermal treatment approach. In order to meet the regulatory control limit, a treatment train consists of anaerobic compost tea washing, followed by organic waste composting is proposed.



[130] 臺灣南部溪流底泥硫化物鍵結金屬的生物有效性與生態風險評估

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中文摘要

底泥為許多底棲生物棲息之場所，亦為溪流水體潛在污染來源，在水域環境佔重要一環。本研究結合化學評估和生物毒性測試來預測底泥和孔隙水中重金屬的毒性。將使用平衡分配模式的酸揮發性硫化物及同時提取金屬分析進行不同污染程度的臺灣南部 8 條溪流(後勁溪、東港溪、鹽水溪、三爺溪、典寶溪、阿公店溪、武洛溪及牛稠溪)之底泥重金屬生物可利用性評估，運用 SEM-AVS、SEM/AVS 及 (SEM-AVS)/foc 模式來判斷底泥中重金屬之生物可利用性，並以底棲端足蟲 *Hyalella azteca*(10 天全底泥及 48 小時孔隙水)進行水生生態系統危害程度(Tier 1、Tier 2 及 Tier 3)之毒性評估，另外也利用潛在生態風險指數 (potential risk index) 來判斷各樣站底泥之風險等級。研究數據未來可被用來釐清 AVS 和 EqP 數據是否能取代複雜或昂貴的測量，當作底泥快速金屬毒性篩選的工具。

本計畫結果顯示底泥中重金屬鉻、鎳、銅、鋅、鉛與鎘濃度範圍分別介於 8.86~132、12.68~223.53、5.68~683.56、63.24~910.60、4.11~57.17 及 ND~0.36 mg/kg；而孔隙水中重金屬鉻、鎳、銅、鋅與鉛濃度最高可達 0.212、0.256、0.126、3.609、0.045 mg/L，鎘濃度均低於檢測極限。本研究透過溪流底泥基本物化性質可得知後勁溪、武洛溪、東港溪底泥的粉粒與黏粒較高，而牛稠溪及阿公店溪底泥則以砂粒為主。八條溪流 35 個測站底泥總有機碳介於 0.47%~5.46%，而底泥與總有機碳含量相關性分析結果顯示鎳、銅、鋅、鉛及鎘均具有顯著性相關，證實底泥中重金屬濃度分布受有機質含量影響會較其它物化特性如粒徑大。底泥 - 孔隙水間的分配係數 (sediment-pore water partition coefficient) Koc 值大小變化關

係為銅>鉛>鎳>鉻>鋅，顯示本研究重金屬污染物中鋅最易釋出於孔隙水，而銅最易吸附於底泥。潛在生態危害係數評估結果顯示，僅 SY3 樣站之潛在風險指數為中高度污染，其餘樣站均屬於低度風險。整體來看，八條溪流流域生態風險指數由大至小依序為三爺溪>牛稠溪>武洛溪>鹽水溪>後勁溪>典寶溪>阿公店溪>東港溪。另外，以 Σ SEM-AVS 數據評估結果顯示，典寶溪、三爺溪及阿公店溪風險程度均為 Tier 1(即最高風險之不利影響)，後勁溪、牛稠溪及武洛溪風險程度為 Tier 2，而鹽水溪及東港溪風險程度則為 Tier 3。此外， Σ SEM/AVS 及 Σ SEM-AVS/foc 結果與 Σ SEM-AVS 相似(以典寶溪、三爺溪及阿公店溪為最高風險)。

全底泥毒性試驗方面，典寶溪、三爺溪、後勁溪及牛稠溪之存活率較阿公店溪、武洛溪、鹽水溪及東港溪低。此外，孔隙水急毒性試驗結果顯示，三爺溪及牛稠溪存活率最低。對底棲生物 *Hyalella* 而言，孔隙水較全底泥試驗更具毒性，但孔隙水毒性可能因孔隙水中物理化學變化，導致不再與富含金屬的底泥顆粒接觸，故其試驗結果不能與全底泥試驗直接進行比較。

綜合所有評估方法得知，三爺溪及牛稠溪為 8 條調查之溪流中污染最嚴重的兩條溪流，為瞭解引起毒性之污染物種類，未來應進行毒性鑑定評估。

Abstract

Sediment not only provides habitat for benthic organisms, but also is a potential source of contamination of streams and therefore has a significant influence on the aquatic environment. A combination of chemical assessment and biological toxicity testing was conducted to predict the toxicity of metals in sediment or pore-water. Equilibrium

partitioning models using acid volatile sulfide (AVS) were applied simultaneously with extracted metals (SEM) analyses to evaluate the bioavailability of heavy metals in sediments from eight rivers (Houjin (HJ), Donggang (DG), Yanshuei (YS), Sanye (SY), Dianbao (BD), Agongdian (AGD), Wuluo (WR), and Niuchou(LK)) exhibiting a wide range of contamination in southern Taiwan. Their bioavailabilities were evaluated with [SEM-AVS], [SEM/AVS], and [(SEM-AVS)/foc] approaches. In addition, their toxic effects were evaluated using the amphipod *Hyalella azteca* (10 d for whole sediment and 48 hr for pore water) to assess their hazard levels (Tiers 1- 3) to aquatic ecosystems. The potential risk index was applied to clarify the degree of ecological risk in the tested sediments. Additional information could be provided if AVS and EqP data replace other more expensive or complex methods of measurement.

Preliminary results showed that concentration ranges were Cr, 8.86~132; Ni, 12.68~ 223.53; Cu, 5.68~683.56; Zn, 63.24~910.60; Pb, 4.11~57.17; and Cd, ND~0.36 in sediments (in mg/kg dry weight). Maximum concentrations of Cr, Ni, Cu, Zn, and Pb in porewaters were 0.212, 0.256, 0.126, 3.609, and 0.045 mg/L, respectively. Cd levels in porewaters were all below the detection limit. Particle size analysis showed that the HJ, WR, and DG Rivers contained high quantities of silt and clay, while LK and AGD river sediments were composed primarily of sand. Total organic carbon (TOC) concentrations varied from 0.47 to 5.46%. Furthermore, significant relationships were observed between TOC content and Ni, Cu, Zn, Pb, and Cd concentrations. Our results confirmed that heavy metals concentrations in sediments were influenced more by organic matter content than other factors. In addition, sediment-pore water partition coefficients (Koc values) for metals, in decreasing

magnitude, were $Cu > Pb > Ni > Cr > Zn$. Zn was the most easily remobilized heavy metal in porewaters and Cu the most easily adsorbed in sediments. The average potential ecological risk index (RI) of station SY3 was 165.3, suggesting a moderate ecological risk, whereas all other samples exhibited low ecological risk. Overall, the ecological risk index showed that the degree of potential ecological risk to eight stream basins were: $SY > LK > WR > YS > HJ > BD > AGD > DG$ Rivers. The use of $\Sigma SEM-AVS$ showed that the Dianbao, Sanye, and Agongdian Rivers were classified as Tier 1, (i.e., highest risk for adverse effects), the Houjin, Niuchou, and Wuluo Rivers were classified as Tier 2, while the Yanshuei and Donggang Rivers were classified as Tier 3. Furthermore, $\Sigma SEM/AVS$ and $\Sigma SEM-AVS/foc$ results were similar to those of $\Sigma SEM-AVS$, with higher risk being found in the Dianbao, Sanye, and Agongdian Rivers).

In whole-sediment toxicity tests, survival rates were lower in the Dianbao, Sanye, Houjin, and Niuchou Rivers than in the Agongdian, Wuluo, Yanshuei, and Donggang Rivers. In addition, pore-water acute toxicity testing showed that survival rates in the Sanye and Niuchou Rivers were low. Pore waters were more toxic to *Hyalella* than whole-sediment tests. However, pore-water toxicity tests were not directly comparable to whole-sediment testing due to the physicochemical changes in pore waters no longer in contact with metal-rich sediment particles.

Our study revealed that the Sanye and Niuchou Rivers are two of the most contaminated rivers among the eight rivers investigated. Toxicity identification evaluations should be conducted in the future in order to understand the causative agents.



[131] 本土異化性金屬還原菌 *Shewanella* sp. KR12 整治水體中
含氯有機污染物之研究

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中文摘要

本土異化性金屬還原菌 *Shewanella* sp. KR-12，篩選自臺灣新竹客雅溪。*Shewanella* 菌屬在厭氧環境缺乏含氧鹽類時，能以金屬氧化物作為電子接受者並從中獲得生長之能量，且此菌屬為兼性好氧菌，具有能在好氧環境下迅速增殖培養之優點，在環境污染復育領域具有相當之潛力。在以菌株直接降解水體中三氯乙烯和四氯乙烯之試驗中，三氯乙烯和四氯乙烯在不同處理天數組別的濃度無明顯差異，顯示 KR-12 應不具有脫氯酶，無法在厭氧環境中以還原脫氯作用直接降解三氯乙烯及四氯乙烯。而部分異化性金屬還原菌會在還原金屬氧化物的同時，於菌體生成生物性奈米金屬顆粒，其中 ZnS、Pd(0) 奈米顆粒被認為具有催化之功能。在不同金屬蓄積試驗中，KR-12 可成功將 Ag^+ 、 Pb^{2+} (環境中含有磷酸根)、 Zn^{2+} (環境中含有硫酸根)、 Pd^{2+} 還原，形成奈米顆粒分布於菌體表面。將嘗試這些由 KR-12 形成之生物性奈米金屬顆粒，當作催化劑使用，應用於厭氧環境水體中三氯乙烯和四氯乙烯之降解。

Abstract

The local dissimilatory metal reduction strain *Shewanella* sp. KR12 (strain KR12) was isolated from Ke-Ya River in Taiwan. The genus of *Shewanella* have ability of dissimilatory metal reducing and facultative anaerobic bacteria. Previous studies and reviews shown *Shewanella* has the ability of bioremediation. Strain KR-12 could not degrade trichloroethylene (TCE) and tetrachlorethylene (PCE) directly owing to the lack of dehalogenase. Fortunately, strain KR-12 has a significant ability for metal accumulation and the potential to produce bionanoparticles. It could form bio-nanoparticle Ag, Pb, Pd, ZnS on cell surface. This project would to evaluate strain KR12 for bioremediation of trichloroethylene (TCE) and tetrachlorethylene (PCE) by using the bio-nano metal particle as a catalyst to hydrodechlorination and degradation of TCE and PCE

[132] 光觸媒覆膜光纖集束(COFB)光催化地下水中三氯乙烯之 現地綠色整治技術開發

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中文摘要

本研究以新穎之光催化覆膜光纖集束(COFB)反應牆(permeable reactive barrier, PRB)系統處理地下水中之三氯乙烯(TCE),探討採用多支光纖集束,在不同操作條件下,處理系統應用於模擬土壤箱中,對於 TCE 去除效率之影響。研究首先使用 20W LED 搭配電源模組作為實驗之光源,並使用 POF 建立光纖集束透水性反應牆於模擬土壤箱中,用以設置實驗之處理系統。實驗將先利用對氯苯甲酸(pCBA)作為氫氧自由基之探針(probe),評估使用直徑 2 mm 光纖應用於光降解 COFB 處理程序之氫氧自由基轉換濃度($R_{OH,UV}$)。研究第一階段選用 3 種直徑之光纖(2 mm、6 mm、14 mm),在相同光纖支數(1 支)或是不同支數但是總直徑相當之光纖集束(2 mm 7 支、6 mm 3 支、14 mm 1 支)應用於光降解系統,探討其對於去除 TCE 效果之影響。此外,後續(第二階段)之研究選用 TiO_2 作為光觸媒,並使用市售之小型噴槍在簡便之操作條件下製備 TiO_2 覆膜光纖,評估 PRB 處理系統對於模擬土壤箱中 TCE 之去除效果。場發式電子顯微鏡(field-emission scanning electron microscopy, FE-SEM)以及擴散反射光譜儀(spectrophotometer with diffuse reflectance spectra, DRS)等設備將用於觀察覆膜光纖使用前後之表面變化和計算光觸媒能隙(energy gap)。

Abstract

A novel photocatalytic coated-optical-fiber bundle (COFB) installed in a permeable reactive barrier (PRB) system is used in this study to treat trichloroethylene (TCE) in simulated groundwater. The effects of various operating conditions on the removal of

TCE by using a multiple optical fiber bundle in a soil box are investigated. A 20W light-emitting diode (LED) with power module is used as the light source of the system as well as using POF to build the PRB in a soil box. The par-chlorobenzoic acid (pCBA) was used as a probe of the hydroxyl radicals to evaluate the converted concentration of hydroxyl radicals during photodegradation of pCBA in the system by using an optical fiber with 2 mm diameters. In the first stage of study, optical fibers with 3 different diameters (2 mm, 6 mm and 14 mm) were used in the PRB system. The effects of 1 optical fiber with different diameters or different number of optical fibers with the same bundle diameter, which was 14 mm when using 7 2mm fibers, 3 6 mm fibers and 1 14 mm fiber, on the removal of TCE were investigated, respectively. Furthermore, in the following second stage of our study, titanium dioxide (TiO_2) nano powders will be use as photocatalysts. A commercially available small spray gun will be used to spray TiO_2 on optical fibers to prepare coated optical fibers, which will be used in PRB system to evaluate the effects of system on the TCE removal efficiency in the soil box. A field emission scanning electron microscopy (FE-SEM) and a spectrophotometer with diffuse reflectance spectra (DRS) will be used to observe the surface of coated optical fibers before and after experiments and to calculate the energy gap of photocatalysts.



[133] 地下水污染溯源環域與風險評估線上模擬平台開發

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中文摘要

如何有效地判斷、評估與預測地下水污染傳輸機制，為污染場址管理、污染事件應變以及場址整治成功的重要關鍵。本計畫將導入序率污染物溯源追蹤與水井捕集區之概念，建置以物理模式為基礎的線上分析平台，結合環保署既有土壤地下水管理資訊系統與外部單位開放資料，達到與使用者互動、即時與快速分析潛在污染來源的目的。分析平台將考量跨系統、跨平台操作，使相關調查人員能在網路連接情形下，使用行動裝置如智慧型手機或平板電腦，進行線上分析評估。為提高分析成果的理解與評估，平台將使用 GIS 架構，並藉由結合政府單位之開放資料，以 Google 地圖進行空間上污染團遷移或特定地下水捕集區視覺展示。在此架構下，使用者能藉由簡易輸入現地污染物調查區位、通報地點或取水井位置，即時推估污染團的歷史遷移與空間分布，以及特定水井於不同時間下之捕集區範圍，成果將更有效率地結合既有土壤地下水管理系統，協助搜尋潛在污染行為人。對特定水井捕集區之範圍，則能用於水井保護區範圍劃定，降低水井受到污染物之污染機率，並藉此保護民眾用水安全。為了考量現地含水層異質性以及其他外部資訊不準確性造成推估不確定性，本研究另外導入序率分析概念，提供污染團或捕集區在不同異質性與外部資訊不準確性程度下，可能的空間與時間分布，作為污染風險分析的參考。本計畫於已完成以下工作項目(1)蒐集如環保署、水利署以及地質調查所之土水相關圖資，並且已成功建置至資料庫並連動至平台展示；(2)建置平台入口、繪圖以及圖層資訊展示等相關工具；(3)開發模擬平台之繪圖介面規劃與建置；(4)透過既有資料庫進行初步數值模擬測試，成功將觀測井內部屬性值(如地

下水水位)進行差值分析並展示於平台上(5)開發水井捕集區模式，並且成功進行單機版測試例；(6)完成水井捕集區以及污染傳輸溯源模式之模式開發，並植入至平台計算引擎，完成線上地下水數值模式模擬以及建構相關模式平台之互動式圖形介面。

Abstract

Efficient identification, assessment, and prediction of groundwater flow and contaminant transport behaviors have become the key process for site management, strategy design of emergency events, and remediation of contaminated sites. This study aims to develop real-time and online platform for modeling stochastic source tracking and capture zones in groundwater systems. The physical-based analysis integrates the available data in soil groundwater management (SGM) system and other open source. The platform enables users to analyze and identify potential contaminant sources with online interactive environment. In this study the platform was designed to compatible with different operation systems and platforms and the platform was allowed to operate with smart phones and other mobile devices. The GIS-based platform enhances the usefulness of the results because the solutions and data are designed to map to the Google map for visualization. The users can freely input desired locations for plumes and contaminant events or pumping wells and real-time visualize the spatial and temporal variations of plumes and capture zones. With the available SGM data, the preliminary identifications of potential contaminant sources become possible and the analysis is expected to be efficient for most cases. The delineation of well capture zones can be used to define well head protection areas (WHPAs) for



safety used of groundwater resources. Additionally, the stochastic analysis of the source trackings and capture zones can be the important information of risk analysis for specified contamination events, locations, and groundwater supply systems.



[134] 地電阻影像探測監控土壤與地下水污染整治的技術發展

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中文摘要

近期國內土壤與地下水研究進入實場整治階段，整治藥劑的灌入狀況為整治成效的重要步驟，但在滲透性差之地層中，重力或加壓方式勢必造成整治藥劑僅會沿優勢流徑(如砂層)傳輸，除容易流失藥劑，亦無法改善已擴散進入坩黏土層之污染溶質，造成持久性污染而持續影響周遭地下水。為求有最佳整治效果，整治者可以根據藥劑擴散半徑適時調整整治參數達到最佳效益，所以對於藥劑灌入的傳輸路徑監測非常重要。在藥劑傳輸路徑的監測上，利用量測地層電學性質之地電阻影像探測法進行是極具效益的方法，將此技術搭配既有標準監測井進行孔內施測可有助解決其單在地表施測會有深度解析能力較為不足的問題，但其現場施作之最佳參數目前並未有最佳的應用準則，此外，為可採用既有標準監測井進行施測，發展可重複使用的移動式電極具有其實用性，因此本計畫之主要目的有二：1. 電極排列方式的優化探討 2. 移動式孔內電極的研發。本研究最終將前述研發成果擇一試驗場址，利用地電阻影像探測方法監測藥劑在低滲透地層中的傳輸範圍與路徑，並測試移動式孔內電極的現地應用效果。以模組化之方式研發出第一代之移動式孔內電極雛形，具有簡便延長展距，與便利局部更換之優點，現場測試具備現地適用性；電極排列方式之優化由數模之結果顯示孔對地之施測建議採用地表合併孔內 Wenner-schlumberger 序列施作，地表測線與鑽孔長度建議以 1:1 為主，增加地表測線長度對施測成效之助益不大。

Abstract

Currently the study of soil and ground water contamination in Taiwan has recently initiated in-situ remediation

phase. The distribution of the chemical agents after injection is a key factor for the remediation effectiveness. In practice, however, injection into low conductivity layer (such as silt-clay layers) is difficult as most of the treating agents would most likely be dispersed into high conductivity layer (for example, sandy layers). Consequently the contaminant within silty or clayey layers could not be easily remediated and would continuously affect the underground water environment. In order to enhance site remediation effectiveness, site operators can adjust the parameters of the injection plan according to the in-situ monitoring result on the dispersed radius of chemical agents. Electrical Resistivity Tomography (ERT) is an effective geophysical technique to monitor the distribution of in-situ injection by measuring the electrical properties distribution of the underlying ground layers. Conducting both surface ERT and borehole ERT within existing monitoring wells can greatly increase the resolution in depth compared to conventional surface ERT survey. However, proper application guideline for optimizing field survey parameters is not readily available yet. Moreover, with the intention of utilizing the existing monitoring well for borehole ERT survey, a recoverable borehole electrode and cable should be developed for economical and convenience purpose. Aim of this project is to 1. Study the optimized field parameters of electrode array setup 2. Develop a recoverable and mobile borehole electrode and cable. This project examines the aforementioned study in an in-situ contaminated site, by applying ERT to monitor the dispersed region and path and examine the in-situ application recoverable borehole electrode-cable system.

[135] 污染底泥之微生物多樣性與生物整治可行性之評估

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中文摘要

由於底泥為細微顆粒及有機質組成，通常具較高吸附性而同時含有有機及無機等有害物質。因此在環境整治上是一個相當的複雜問題。目前已經有許多整治方法被提出，包括界面活性劑淋洗法去除底泥有機質，化學氧化法降解底泥中有機物，以及化學萃取法回收底泥中重金屬等。但是具潛力的底泥生物修復方法依然較未清楚。高雄港上游河流的廢水每天大量地將污染物輸進高雄港，使得水域中的底泥成為污染物長期累積的儲存庫。本計畫我們提出的宏觀基因體學分析高雄港底泥的環境微生物多樣性。我們從不同位置收集到高雄港的底泥，包括愛河(LR)，前鎮河(CR)，二仁溪(JR)，以及鹽水溪(SR)四河的流入口。這些河流流經高度的民生活動和工業區域。另外，高雄港 1 號入港口(E1)作為一個參考測站。從高雄港底泥中萃取總 DNA，並通過一連串的品保分析測試每個步驟的 DNA 和 16S rRNA 序列組製備的流程，確保 DNA 品質。然後利用次世代定序分析環境微生物的多樣性。我們找到每個樣點極具代表性的菌株，如 *Ruegeria lacuscaerulensis*、*Desulfotalea arctica*、*Lutimonas vermicola*、*Amphritea atlantica*、*Polaribacter dokdonensis*、*Fusibacter paucivorans*、*Polaribacter butkevichii*、*Kribbella ginsengisoli* 只單獨存在於 E1 中，屬於專一性之海洋菌種，代表未受污染的近海菌種，如果這些菌種較多時，顯示環境相對較未受到污染。大量且專一性存在 LR、CR 與 JR 樣點的 *Dehalogenimonas lykanthroporepellens*、*Desulfobacterium aniline*、*Desulfomonile tiedjei* 的這三個菌種能分解有機氯化物。*Desulfuromonas acetoxidans* 大量的富集於具有高度鉻污染的前鎮河口。這結果顯示這些細菌都可作為的當地的污染指標。接著我們利用生物資訊分析各樣

點的菌相功能，發現在物質代謝與物質合成與運輸的功能上，港區內的細菌與港區外的細菌有顯著性差異。表示港區內的菌叢的確發展出代謝污染物的能力。最後，我們交叉分析環境微生物的富集度與底泥的物理和化學特性，然後評估微生物應用於生物修復的潛在可能性。由本實驗的成果，我們確實能從複雜的河港交界底泥中，找出不同河口的特殊菌種，並找出具有生物復育潛力的菌種。

Abstract

The sediments are majorly composed of the ultra-fine silts and organic compounds; it would have high affinity to organic and inorganic hazardous matters. Potential techniques for remediating the sediments were evaluated in recent years, including rinse method, chemical oxidation, and chemical leaching. However, the potential bioremediation methods for the sediments are still large unknow. Waste water from upstream rivers is flowed into Kaohsiung Harbor through the Kaohsiung city every day and which also bring large flux of pollutants into the Kaohsiung Harbor. The aquatic sediment becomes a long-term sink for all pollutants in the Kaohsiung Harbor. To reveal environmental microbial phase of sediments isolated from Kaohsiung Harbor, we collected sediments from different location in the Kaohsiung Harbor including the stream inlet of four rivers of Love River (LR), Canon River (CR), Jen-Gen River (JR), and Salt River (SR). The harbor entrance 1 (E1) was selected as a reference site. We analyzed the environmental microbial community by 16S rDNA metagenomic analysis. Some specific bacteria for each sample site was found, such as *Ruegeria lacuscaerulensis*, *Desulfotalea arctica*, *Lutimonas vermicola*, *Amphritea atlantica*, *Polaribacter dokdonensis*, *Fusibacter paucivorans*,



Polaribacter butkevichii and *Kribbella ginsengisoli* were specifically lived in E1, indicating that they are naturally lived in the ocean. Therefore, the more natural bacteria means the environment are more similar to normal condition. *Dehalogenimonas lykanthroporepellens*, *Desulfobacterium aniline* and *Desulfomonile tiedjei* are capable of degrading the chlorinated volatile organic compounds (VOCs), which may be used as biomarker for the pollution of VOCs. *Desulfuromonas acetoxidans* is enriched in JR which is polluted by Cr. These data suggests that these bacteria could be used as a biomarker for these sites. Functional prediction was performed by using bioinformatics analysis, and significantly difference were found in metabolism, biosynthesis, and transportation, thus suggesting bacteria in Kaohsiun Harbor indeed developed ability to metabolize pollutants. Finally, we cross analyzed the environmental microbial phase with the physical and chemical characteristics and then evaluate the potential and possibility to apply the microbes to bioremediation. In this study, we demonstrated that we can find specific bacteria with potential of bioremediation form the complex sediments.

[136] 利用臺灣本土有益混合菌以提升水稻植生萃取重金屬鎘污染之 可行性研究

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中文摘要

本研究測試利用本土有益混合菌的酸性特性，對土壤重金屬鎘的清除效率，並與不同的化學萃取劑，包含氯化鉀、氯化鈣、氯化鐵、鹽酸、檸檬酸、醋酸、以及兩種重金屬螯合劑 EDTA 與 DTPA，比較其對重金屬鎘的萃取效率。初步的實驗結果顯示，對於經石灰調整後的土壤，由於鹽酸與氯化鐵的萃取溶液 pH 值最低，所以有最佳的萃取效果，不過有益菌的 pH 值高於檸檬酸，但是對重金屬鎘的萃取效率卻優於檸檬酸，顯示酸性有益菌可做為潛在的土壤重金屬萃取劑。稀釋序列萃取實驗顯示，酸性有益菌主要移除土壤中的可交換性鎘，不過檸檬酸卻可移除較多的鐵錳氧化態鎘。盆栽實驗顯示，添加有益菌的水稻，對重金屬鎘有較佳的耐受性。

Abstract

Native beneficial microorganisms were selected as the soil heavy metal extraction agent, and its efficiency for removing soil cadmium was compared with other chemicals, including KCl, CaCl₂, FeCl₃, HCl, citric acid, and acetic acid. The results showed that the soil treated with HCl and FeCl₃ had the lowest solution pH, and thus had the greatest cadmium removal efficiency. However, the soil treated with beneficial microorganisms had higher pH than that treated with citric acid, but beneficial microorganisms could extract more cadmium from soil, suggesting they could serve as potential extraction agents. The sequential extraction procedure suggested that beneficial microorganisms could remove more exchangeable cadmium from soil, but citric acid could extract more heavy metal from the fraction of Fe and Mn oxide occluded. The potting test showed that the rice seedling growing with beneficial microorganisms could have better tolerance for heavy metal when compared with the plants growing without beneficial microorganisms.



[137] 利用滲透灌注技術進行基質最佳稀釋比例於地下水生物整治之 應用研究

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中文摘要

現地生物整治法係為現今常被應用於地下水受含氯有機物污染之整治方式。此法常利用重力流方式，使其自然沈降並擴散，但此種方式不易確認基質是否能有效的滲透且均勻的散佈於欲整治範圍。

爰此，本計畫應用大地工程中常用於土壤改良之滲透灌漿技術，進行基質注入技術之研究試驗，針對基質注入砂柱試體滲透性及持續時間等指標，評估不同土層條件下之各種基質適用性。

本年度計畫可分為二部分，第一部分改變基質 HRC 之稀釋比例，探討其在砂柱試體中之滲透性與持續性，期望能提出該基質適用稀釋比例之建議；第二部分針對極細砂試體進行滲透灌注之試驗，期望能提出適用之基質之建議。

由第一部分的試驗結果發現，稀釋比例之改變能改善基質滲透之情形，在 A 砂試體 ($D_{50}=0.45\text{mm}$)、B 砂試體 ($D_{50}=0.30\text{mm}$) 及細砂試體 ($D_{50}=0.23\text{mm}$) 中，提高 HRC 之稀釋比例至 1:20 可以灌注到目標高度。

第二部分的極細砂試體試驗，研究發現以滲透灌漿之技術無論是 EOS、HRC 或是 EcoClean 皆無法於 C 砂 ($D_{50}=0.01\text{mm}$) 及 D 砂 ($D_{50}=0.05\text{mm}$) 中滲透，而在 E 砂 ($D_{50}=0.25\text{mm}$)、F 砂 ($D_{50}=0.27\text{mm}$) 中，HRC、EOS 及 EcoClean 三種基質僅可分別滲透至分別約為 50 及 60 公分；持續性方面在 E 砂即 F 砂中則分別高達 90% 及 70%。

緣此，稀釋比例之改變可以改善無法有效滲透之現象。極細砂部分，HRC 之滲透性最佳，持續性部分三者皆差不多。針對滲透性較差的土壤，未來則建議朝向提高稀釋比例、增加灌注壓力等方向努力，以改善滲透不佳之情形。

Abstract

The method of in-situ bioremediation has been widely used to treat the groundwater polluted by chlorinated organic compounds. To inject the substrates into groundwater, the method by gravity flow is commonly used, so that the substrates or nutrients are injected, and then they will settle and diffuse freely. However, it is difficult to recognize whether the substrates are distributed effectively and evenly in the areas to be treated.

Therefore, in this project, a method of permeation grouting which has been often used in geotechnical engineering to improve the soil was applied. Using this method, experiments are conducted to evaluate the indexes of the permeability and persistence of the substrates in the column-shaped specimens, and to estimate the suitability of different substrates in different soil conditions.

In this year, the project is divided into two parts. First, the dilution ratio of the substrate of HRC is varied to investigate the permeability and persistence in the column-shaped specimens, so that appropriate dilution ratio for the substrate may be proposed. Second, tests of permeation grouting are conducted for the specimens with very fine sand, so that appropriate substrates may be suggested for the sites with similar soil conditions.

The results show the permeation of the substrates can be improved because of the change of dilution ratio. For the specimens made of Sand A ($D_{50}=0.45\text{mm}$), Sand B ($D_{50}=0.30\text{mm}$) and fine Sand ($D_{50}=0.23\text{mm}$), while the dilution ratio for the substrate of HRC is 1:20, the targeted heights of permeation grouting can be achieved. It is found that the specimens with sand C and sand D (D_{50} are 0.01 and 0.05mm respectively) cannot be



permeated by neither substrate EOS, HRC nor EcoClean. While the specimens with Sand E($D_{50}=0.25\text{mm}$) are used, the permeation heights for the substrates of HRC, EOS and EcoClean are 48, 42 and 43mm respectively. The persistence for all the three substrates is found 94% are remained 7 days after the clean water flow through the specimens.

Up to now, it is found the conditions in which the substrates cannot permeate the specimens may be improved by changing the dilution ratio. For Sand E, the permeability of HRC is found the best, while the persistence of the three substrates are similar. The tasks to be completed in this project are: (1) to find the appropriate substrates for the specimens with sand F($D_{50}=0.27\text{mm}$); (2) to suggest the dilution ratio of the substrates for the specimens with Sand C, Sand D, Sand E and sand F.



[138] 長效性氧化電極進行複合污染場址整治及環境地工離心機模擬 長期整治成效之研究

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中文摘要

臺灣污染現況顯示重金屬及有機物之複合式污染已成為土地污染常態，電動力技術係一現地整治技術，可藉由電極種類、操作流質、處理時間及電位坡降等參數，又整治技術長期整治成效無法預期成為技術盲點，故急需翻轉原小尺度窠臼，探討長時間與大尺度之整治行為，才可有效掌握整治時程。本專案將以整治具苯系有機物及重金屬污染之複合污染場址為目標，製備具降解性、長效性及高經濟效益之 Fe/Al 氧化電極進行電動力模組試驗，並利用環境地工離心機以縮小之時間尺度模擬長期之污染物行為，將可作為後續實場整治之重要參考依據。

電動力模組實驗成果，操作流質為 DI water、SDS 與 NaCl 其移除效果為 17.3 %、26~37.6 % 及 23.9~33.9 %，降解率分別為 45.6 %、50.8~62.2 % 及 62.2~73.7 %，當操作流質為 NaCl 時有最佳降解率，其因於陽極電解產生 OCl⁻，又 NaCl 為強電解質，於電動力實驗中增加離子遷移效果，可提升污染物降解之效能，使其處理效率大幅提升。電位坡降由 0.5 V/cm- 2 V/cm 對於苯之處理結果，當使用 1 V/cm 即可達 96.9 %，提升至 2 V/cm 再提升至 99.0 %，但因高電位環境對電極耗損大，故以 1 V/cm 為最佳操作參數。複合污染物處理成果顯示，其苯之降解效能並未受銅影響，但電解反應使土壤 pH 值提升形成金屬沉澱物造成阻塞，致無法有效將土壤中苯移至電解槽中，苯污染僅以 5 天即可處理至 87.2-95.2 %，而銅處理延長至 20 天也僅為 38.9 % 之移除率，因電解反應產生金屬錯合物阻塞，而始銅移除效能不明顯，後續可藉由延長處理時間或提升電位坡降等提升移除效果。

目前已完成地工離心機試驗箱設

計與測試，並進行染料縮時模擬試驗、電動力技術模擬測試與重金屬於地下傳輸行為模擬測試，模擬 1:50 水力坡降之砂質與黏質土壤中重金屬銅傳輸現象，僅 2 L 實驗模組僅運作 15-30 分鐘短時間內，即可得知重金屬於長 16 m x 寬 8 m x 深 8 m 之地下環境中 26-133 天之傳輸現象，砂質土壤中，由 X 方向可明顯觀察出銅由高水頭往低水頭移動；Z 方向則明顯由淺層往深層移動。黏質土壤中，繞機 30 分鐘，相當於原型之 133 天，於 Z 方向可觀察土壤中銅之濃度由淺層往深層移動，並未於 X 方向觀察到明顯濃度行為，而電動力實驗僅通電 10-20 天即可將 20 公分長土體中污染物移除，由此結果得知以模擬地工離心機模擬污染物/標的物傳輸之可行性，結果顯示，電動力技術可將深層污染物向淺層上抬移動，克服污染物受長期重力傳輸往深層移動而增加整治困難性，又以可克服數值模擬結果無法有效驗證之瓶頸。

Abstract

A polluted land contaminated with organic and heavy metal is very common in Taiwan. The Electrokinetic process is an in-situ remediation technology. It is fitted for remediation of metals/organics contaminated sites by choosing appropriate electrodes, processing fluids, and potential gradient. It is need to clarify the large-scale eoenvironmental structure. Then, consequently, the remediation schedule can be controlled well.

Result of electrokinetic(EK) process to treat benzene in soil, using DI water, SDS and NaCl as processing fluid, the removal rate were 17.3 %, 26~37.6 % and 23.9~33.9 %, efficiency of degradation were 45.6 %, 50.8~62.2 % and 62.2~73.7 %. Because the NaCl as strong electrolyte,

increased ion migration effect and enhance the performance of EK efficiency. The results of potential gradient influences were enhanced briefly, while 1 V/cm to 2 V/cm. However, high voltage cause the electrode to corrode rapidly. The results indicated to lack of influences in benzene efficacy while EK process treat co-contaminated soil content benzene and copper. Nevertheless, the electrolysis reaction led to the soil alkalize and composite metal complexes caused blocking. The Cu removal rate about 38.9 % barely after 20 days treatment. Next, enhance the removal effect by extending processing time or to enhancing the potential gradient to enhance the removal effect.

Recently, designed and constructed the rigid box. This research conducted the centrifuging experiment above EK simulated test, dye and copper simulated transportation underground. The performance of copper transport for 133 days and 16 m(length) x 8 m(width) x 8 m(depth) after 2 L soil centrifuged 30 min in 80 G gravity field. It observed that copper transported deeper (Z), and high head transport to low head(X) at sand matrix. The EK process overcome the movement of sinking and raising to shallow layer. Therefore, using the centrifuge to simulate underground transmission test to solve numerical simulation result can not be verified



[139] 建構電容去離子系統整合模組處理含砷地下水之先驅試驗

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中文摘要

本研究計畫之目的在於考量電容去離子技術(capacitive deionization, CDI)於地下水整治之實場應用時可能遭遇之干擾與困難，建構電容去離子技術系統整合模組，進行 CDI 技術處理含砷地下水之先驅試驗。工作內容包含(1)含砷地下水之水質分析，(2)結合 CDI 技術與微過濾薄膜技術(microfiltration, MF)，建構電容去離子技術系統整合模組(MF-CDI)，(3)以 MF-CDI 系統模組進行實驗室規模模場試驗，評估移除水體砷污染之成效，並探討地下水中之溶解性離子對於 CDI 技術以電吸附機制移除水體中砷污染時，可能造成之干擾行為。同時，以表面修飾技術增加活性碳電極對砷的吸附容量。

水質分析結果指出，地下水中富含多種陰陽離子，而總砷濃度為 0.13 mg/L。模組試驗結果則顯示，CDI 模組僅需施加一低電壓(1.2 V)，最佳之砷去除率可達 76%，使出流水砷濃度符合飲用水水源標準及農業灌溉用水水源標準(0.05 mg/L)。同時，CDI 模組可同時去除水體中其它帶電荷離子，總溶解固體濃度(total dissolved solids, TDS)之最佳去除率可達 67%。另外，由於地下水體中陰離子的存在(如硝酸根離子)，會與砷產生競爭性的電吸附行為，故需進一步加強 CDI 模組對於砷的去除能力。本研究將陰離子交換樹脂塗均勻的批覆於活性碳電極表面，除可提升 CDI 模組對砷的電吸附容量外，亦可有效改善活性碳電極的親水性，並增加其電化學穩定性。綜合評估本研究所架設之 MF-CDI 系統模組，於實務應用上適合以抽取處理法(pump and treat, P&T)將地下水抽至地表，MF-CDI 系統模組則作為地表處理設備，進行地下水砷污染之移除作

業。依據實驗結果，CDI 單元處理含砷地下水之能耗為 0.495 kWh/m³，電力消耗低為其主要優勢，與現有之水處理技術相比，具有操作成本的優勢，具進一步發展實地模場試驗之潛力。

Abstract

The objective of this study is to develop an integrated module system by coupling microfiltration (MF) and CDI technology for remediation of arsenic contaminated groundwater. In addition, the effects of non-dissolved matter (suspended solids, microbial, organic matters, etc.) and dissolved substances (such as alkali metal ions, alkaline-earth metal ions, salt, heavy metals, manganese ions and iron ions) in natural groundwater on the CDI performance have been studied in this study. Furthermore, surface modification of porous carbon electrode could be conducted to improve the electrosorption performance and selective removal of arsenic over others substrates (i.e., sodium chloride and heavy metal ions).

An integrated module system of MF-CDI has been developed in the present work. MF unit is a pretreatment process for removing non-dissolved matters from the practical groundwater. As evidenced by the single-pass CDI experiments, an efficiency of 76% for arsenic removal can be achieved at an applied voltage of 1.2 V. Notably, negatively charged species (e.g., Cl⁻, NO₃⁻, SO₄²⁻) could compete with arsenic to be eleroadsorbed onto the anode in the CDI cell. In order to improve arsenic removal from aqueous solutions, the activated carbon electrodes were coated with anion-exchange resin layer. The surface-modified activated carbon electrode has improved hydrophilic properties, good capacitive behaviors, and larger salt adsorption capacity. As



evidenced, the electrosorption capacity of surface modified activated carbon electrodes is calculated to be 0.0057 mg/g. Consequently, we have demonstrated that integrated MF-CDI system has high potential for applications for arsenic-contaminated groundwater and removal capacity of activated carbon electrodes can be significantly enhanced by coating an anion-exchange resin layer on the electrode surface.



[140] 研發穩定型奈米釋氧顆粒以應用於受柴油污染土壤之 生物復育整治

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中文摘要

本計畫的主要目的在於統整柴油污染場址生物整治之必要因素，創新開發具有整合多種生物刺激功能之「穩定型奈米金屬釋氧顆粒」添加劑，探討此添加劑對於柴油污染土壤及地下水生物降解之成效，嘗試提出未來可廣泛應用於柴油污染場址之釋氧顆粒，並搭配分子生物技術能有效監測土壤柴油降解微生物降解效能，以期研發低成本高效益的生物復育方式。

目前已備製多種過氧化鈣(Calcium peroxide, CaO_2)，以動態光散射儀(dynamic light scattering, DLS)量測平均粒徑，其顆粒分布範圍主要在 10-1,000 nm 之間，PDI 值為 0.267，顯示透過研磨並添加分散劑後過氧化鈣顆粒可以有有效的分散並不再聚集，其中以 Wet-grinded- CaO_2 平均粒徑為最小(123.2 nm)。在柴油降解微生物方面，已篩選出一些具柴油降解能力之混菌，以 Basicmedium 添加柴油(1,000 ppm)35°C 培養 14 天，與國內文獻報導之最佳柴油分解菌 *Gordonia alkanivorans*(CC-JG39)相比較，去除效率分別為 71.9% (effective microorganisms, EM) 及 61.8%(CC-JG39)。土壤降解初步結果，以復育土所馴養微生物亦有柴油降解的情形，顯示原生菌群中已具有可分解柴油之微生物，經馴養後可經由降解實驗驗證其降解能力。在分子生物監測技術之建立上，利用聚合酵素鏈鎖反應(polymerase chain reaction, PCR)偵測使用的 EM 菌確實存在特定柴油降解基因，進一步配合變性梯度明膠電泳(denaturing gradient gel electrophoresis, DGGE)進行菌群結構分析，菌種豐富度隨復育天數上升之而後因主要碳源之柴油濃度下降後而菌種隨之下降。藉本土菌篩選出具有柴油降解之特殊菌群，

並配合穩性性奈米過氧化鈣的處理，以及整合分子生物資訊的對應關係，希冀未來可提供學界、產業界與土壤及地下水整治的新策略。

Abstract

There were some problems in bioremediating the petroleum hydrocarbon contaminated soils, such as low contaminant degradation rate and limited degradation amounts. The objective of this project is to establish a cost-effectiveness technique for enhancing the efficiency of bioremediation by developing novel stabilized oxygen-releasing nanoparticles (SORNPs), which would mitigate the deficiency of microbial demands. On the other hand, genetic tool would also be developed to evaluate potentials of microorganisms in the biodegradation process.

We have synthesized several oxygen-releasing calcium peroxide (CaO_2) particles by wet synthesis methods and grinding method (both wet or dry). Their particle sizes were ranged from 10-1,000 nm according to the measurement by dynamic light scattering (DLS) and transmission electron microscopy (TEM). The Wet-grinded CaO_2 particle has the smallest in size (123.2 nm) and was most stable. The diesel degradation percentage of our mix culture (Effective Microorganisms, EM) was 71.9% compared to the 61.8% of the pure culture (CC-JG39) which the sampling point was at day 14 and the degradation experiments were performed at 35°C using basic medium with 1,000 ppm of diesel as the main carbon source. The microorganisms in the mix culture also presented diesel degrading abilities in the treated soil. All these results indicated the



possible presence of diesel degrading microorganisms in the mix culture. We further proved the existence of diesel degrading related genes and microorganisms in our mix culture using gene specific primers and denaturing gradient gel electrophoresis (DGGE). The DGGE data suggested the species in the consortium increased with the increase of carbon source during remediation and decreased with the depletion of carbon source. Our results demonstrated that the screened microbial consortium showing diesel degradation property could have great interest to academic and industry when combining its usage with our stable CaO_2 nanoparticles in terms of diesel degradation in soil and under water remediation.



[141] 臭氧注氣法處理飽和層及未飽和層柴油污染物試驗

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中文摘要

柴油污染場址因物質的低揮發特性，整治工法難以物理方式執行，如飽和層使用的空氣注入法(Air sparging, AS)，以及適合未飽和層的土壤氣體抽除法(Soil vapor extraction, SVE)。因此化學氧化法較能快速有效率的降解柴油污染物，但以現地整治方式，對於未飽和層液體氧化劑在添加注入時，常會因優勢流或短流現象，以及接觸氧化反應的非均勻性，無法有效的完全去除柴油污染物。而化學氧化法中使用的臭氧氣體，可以針對飽和層地下水中柴油污染物降解去除，也較能充滿在未飽和層土壤孔隙之間，增加臭氧氧化污染物的機率。雖然臭氧氧化處理費用較液體氧化劑昂貴，但具有同時處理飽和層及未飽和層柴油污染物的效果，因此在現地整治工法中，不失一個良好的選擇。

本研究目前製備飽和層及未飽和層同時污染柴油的小型模場，利用臭氧注氣法(Ozone sparging)方式探討化學氧化能力。研究初始以連續式臭氧注氣系統探討降解成效與最佳操作條件，結果顯示當空氣流量設定為 10 L/min 時，可得到最佳化臭氧產率 2,888 mg/min。依柴油降解效率選擇每批次 1 小時臭氧注氣方式，進行多批次試驗同時處理飽和層及未飽和層中之柴油污染物。當處理含柴油污染濃度 4,100 mg/kg 土壤時，注入臭氧第 4 小時後土壤柴油濃度即可低於土壤污染管制標準 1,000 mg/kg 以下，但仍有柴油殘餘濃度約 600-700 mg/kg 難以氧化降解，大部分屬於高碳數或支鏈碳氫化合物組成。隨著離臭氧注氣井篩距離半徑越遠時，降解效率也明顯降低，當以臭氧氧化含柴油污染濃度 24,200 mg/kg 土壤時，此現象越為明顯。當以臭氧注氣方式處理含柴油污染濃度 300 mg/L 地下水時，注入臭氧 1 小時後地下水柴油濃度即可低於地下水

污染管制標準 10 mg/L，柴油降解效率可達 95% 以上。臭氧注氣系統的空氣流量 5-18 L/min 所產生之臭氧尾氣濃度皆能低於空氣品質標準 0.06 ppm，並不會造成人體健康影響及空氣污染。研究結果亦顯示，模場的毛細管層相較飽和層及通氣層的鐵片鏽蝕情形最為顯著，顯示接觸臭氧的時間較長越容易造成鏽蝕現象。

Abstract

With characteristics of its low volatility, the diesel contaminated sites suggest poor results of using physical approaches such as Air Sparging (AS) for saturated zones or Soil Vapor Extraction (SVE) for vadose zones. Therefore, chemical oxidation has being widely utilized to serve as an effective and efficient tool to degrade diesel pollutants. Nevertheless, some in-situ practices like complementing liquidized oxidants as dosage shows unsatisfied results due to its prevailing, short-cut flow or inhomogeneous contact between oxidants and target pollutants in vadose zones. The application of Ozone, as one of the chemical oxidation measures, could aim at removal of diesel contaminant in saturated zone, and its relatively high mobility in vadose zone also contributes the possibility of oxidizing the contaminants. The Ozone application can simultaneously remove diesel contaminants either at saturated or vadose zones shall be a feasible undertaking even it is expansive compared with other in-situ alternatives.

A pilot plant featured both saturated and vadose zones contaminated by diesel was prepared for the study. Application of ozone sparging was then introduced to investigate the performance of oxidation. Firstly, the best degradation and optimum parameters of operation by conducting continuous ozone sparging was



determined, the best ozone yield rate 2,888 mg/min was obtained while using air flow rate at 10 mL/min in this study instrument. The experiment was then using one hour per batch ozone sparging to remove diesel from saturated or vadose zones. The contaminated soil, with diesel concentration 4,100 mg/kg, could be degraded by ozone sparging to below 1,000 mg/kg which is the soil pollution control standard for diesel in Taiwan. However, the residual diesel with concentration 600-700 mg/kg was difficult to degrade, those was identified as high molecular and branch chain petroleum hydrocarbons, this phenomenon was obvious in longer distance from ozone sparging screen and high diesel concentration 24,200 mg/kg was selected in the experiment. Using ozone sparging for one hour to degrade contaminated groundwater with 300 mg/L diesel, the removal efficiency could reach 95% above, and the diesel concentration could be below 10 mg/L which is the groundwater pollution control standard in Taiwan. The ozone sparging system was operated with air flow rate between 5 to 18 L/min, the off-gas ozone was determined to be below air quality standard 0.06 ppm. In addition, corrosion was observed in capillary layer due to longer contact time with ozone.



[142] 強化土壤氣體現場篩測方法調查石油碳氫化合物儲槽設施及 污染場址

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中文摘要

造成石化污染事件的污染來源多以加油站之地下儲槽及地面上之大型儲槽為多，而油槽之洩漏對環境之衝擊以地面上之大型儲槽最直接及嚴重，因其造成之空氣、土壤甚至地下水之污染是直接快速的，故需立即反應並處理，否則後果及處理費用難以估計，另外在地下儲槽方面，例如加油站必須在地面下構築密閉油槽，然而臺灣地區地震頻繁和地下管線鏽蝕等潛在問題，均可能在加油站油品儲存和輸送過程中污染土壤及地下水。

隨著分析儀器的進步與發展，偵測油品洩漏所使用之分析技術與儀器設備也日趨成熟，但其需借重站方工作人員平時對測漏管等測漏設備，以測爆器進行土壤氣體與油氣篩測，而環保人員在污染查察上，對所選定加油站進行勘查污染防治與監測設施，了解地下水使用情形，進行浮油量測，分別進行測漏管檢測、土壤氣體採樣、土壤氣體氣相層析分析、地下水位確認、及污染潛勢篩選。

本專案研究目的為提升地下儲槽土壤氣體監測井(或稱測漏管)污染預防措施之功能性，及強化土壤氣體現場篩測方法，以精石化業者管理者及環保人員的污染防治與監測設施勘查流程。本研究主要分為實驗室試驗以及加油站實場測試調查。

實驗室評估進行吸附材質 Solid phase microextraction(SPME)、Sorbent Tubes Anasorb CSC[®]及 ULTRA sampler sorbe[®]的測試。脫附條件實驗設計主要探討各種吸附材質與目標化合物之間的脫附效益，藉以評估吸附材質之最佳脫附條件。試驗係以 50 mL 中油 95 無鉛油品進行模擬洩漏於土壤中，再以吸附材質進行吸附 1 小時(SPME)及 24 小

時 (Sorbent Tubes Anasorb CSC[®] 與 ULTRA sampler sorbe[®])，待吸附時間結束後再分別以不同的脫附條件進行脫附。其中 SPME 適用最佳吸附時間為 9 小時，最佳脫附條件為在 200°C 下脫附 0.5min；而 Sorbent Tubes Anasorb CSC[®] 與 ULTRA sampler sorbe[®]最佳吸附時間為 72 小時，最佳脫附條件則是 150°C，進行平衡頂空裝置的前處理流程可達到最佳脫附效果。

吸附時間實驗設計主要探討汽油洩漏至土壤中再揮發至空氣中被不同的吸附材質吸附的時間差異與濃度變化，藉以評估吸附材質之被動性採樣之可行性。試驗同樣以 50 mL 中油 95 無鉛汽油進行模擬洩漏，模擬情境分別為：剛洩漏的情況及洩漏後已擴散後兩種情境。結果發現 SPME 在汽油剛洩漏之環境下吸附 9 小時內即可對目標化合物達到吸附之最大量，Sorbent Tubes Anasorb CSC[®]及 ULTRA sampler sorbe[®]在汽油剛洩漏之環境與汽油已洩漏後已擴散之環境皆於 72 小時達到吸附最大量。

第二階段工作則是利用實驗室試驗之數據，以此為基準使用於實際加油站污染場址進行技術之評估。本計畫場址選定 4 站分別為南部場址 A、北部場址 B 與北部場址 C、南部場址 D 共 4 站，皆為汽油洩漏污染場址，實驗結果首先係以加油站標準採樣流程進行，後再將進行本試驗之吸附材質進行吸附分析。以手持式 PID 與 FID 進行土壤氣體監測井篩測，然後以 TOF-MS 進行土壤氣體分析，再進行各種吸附材質吸附效能試驗。每一加油站共進行五座土壤氣體監測井之測試，由於 TOF-MS 因為只要有水氣就不能進行分析受場地限制較大，所以在操作上較無法便捷。在

進行吸附材質吸附試驗中，SPME 於實場試驗中，大多的測試點都能夠檢測出污染物，尤其是 MTBE 是最容易檢測到的目標化合物，而 Sorbent Tubes 則只有檢測到 MTBE，但其含量均遠大於 SPME 之吸附量，在四個污染場址之檢測數據較低。在測試結果中依據測得目標污染物之種類，可以發現測試之靈敏度為：在 Sample Bag 中以 TOF-MS 分析(在表格中標示為 TOF-MS) > SPME > Sorbent Tubes Anasorb CSC[®] > Tedlar[®] Sample Bag 經由 GC-MS 分析(在表格中標示為 Tedlar[®] Sample Bag) > ULTRA sampler sorbe[®]。

Sorbent Tubes Anasorb CSC[®] 與 ULTRA sampler sorbe[®] 在實驗室中皆為可控條件(如無日照、濕度干擾等)，故測值會相對較高，加油站實場測試中，因日照、溫度與測漏管中濕度皆不相同，場址污染現況、水文地質條件及場址是否進行整治均會影響被動式吸附作用，但其成本較低，可建議業者多使用。就成本考量而言 SPME 較貴但可重複使用，根據便利性及經濟效益考量，SPME 及 Sorbent Tubes Anasorb CSC[®] 是目前建議作為土壤氣體監測井被動式採樣之最佳吸附材質。

Abstract

To unambiguously characterize spilled fuel products and to link them to the known sources are extremely important for environmental damage assessment, understanding the fate and behavior and predicting the potential long-term impact of spilled fuels on the environment, selecting appropriate spill response and taking effective clean-up measures. These data, in combination with historic, geological, environmental, and any other related information on the contaminated site can, in many cases, help to support pollution control and remediation design. Thus, design and development of fast, sensitive, economic and accurate analytical methods for screening of target pollutants (i.e., volatile organic compounds, VOCs) in soil gas

monitoring wells become very important.

The objective of this research was to develop a fast and reliable method for quantification of concentrations of soil gas in gas stations and storage tank facilities to assess potential subsurface contamination. Specific objectives were to test the efficacy of retracted solid phase microextraction (SPME) fiber, commercial available sorbents such as Sorbent Tubes Anasorb CSC[®] and ULTRA sampler sorbe[®]. Commonly detected VOCs such as methyl tert butyl ether (MTBE), benzene, toluene, ethylbenzene, xylenes, substituted benzenes, and diaromatics were selected as the target compounds in gas stations and above/underground storage facilities.

Passive sampling of air and soil gas involves the deployment of an adsorbent that collecting compounds in the vapor state over time. Conventionally discussions of passive sampling in procedural documents are often limited in scope and fail to recognize the quantitative capabilities and benefits of passive sampling. It is proposed that passive sampling method can provide samples of soil gas, sub-slab soil gas, and air for volatile and semivolatile organic compounds under varied conditions of contaminated sites.

Gasoline contaminated soil was prepared to verify desorption efficiency of different sorbents while sorbing target compounds. The effects of sampling time, temperature, concentration levels, retraction depth, and the contribution of extraction of SPME needle assembly was tested. Sorption of gasoline contaminated vapor was allowed to contact SPME for one hour. Contact time of 24 hours was set for Sorbent Tubes Anasorb CSC[®] and ULTRA sampler sorbe[®]. The ultimate desorption condition for SPME was found to be 30 seconds at 200°C prior to gas chromatograph/mass spectrometer (GC-MS) analysis. The suitable desorption temperature for Sorbent Tubes Anasorb CSC[®] and ULTRA sampler sorbe[®] was



150°C.

Gasoline contaminated soil was prepared for verifying sorption efficiency of different sorbents. SPME reached highest sorption capacity after 9 hour in the newly spilled soils. However, longer time of 12 hour was required to reach the highest sorption capacity for extended contaminated soil. Sorption onto Tubes Anasorb CSC[®] and ULTRA sampler sorbe[®] will require contact time of 72 hour to reach highest capacity.

Field study was conducted to evaluate the performance and applicability of passive soil gas absorbent kits under different hydrogeological conditions in gas stations and storage tank facilities. Four gasoline contaminated stations were selected for field test. Two of them were operated by Formosa Petroleum Company and two operated by Chinese Petroleum Company. Prior to evaluate the efficacy of retracted SPME fiber, commercial available sorbents such as Sorbent Tubes Anasorb CSC[®] and ULTRA sampler sorbe[®], soil gas in all of the soil monitoring wells in each station were analyzed by portable gas chromatograph/photo ionization detector (GC/PID) and gas chromatograph/flame ionization detector (GC/FID). Five soil gas monitoring wells were selected in each gas station for further study. The results indicated that SPME can sorb more gas components in soil monitoring wells than other sorbents applied. Time of flight mass spectrometer (TOF-MS) did offer precise analysis of soil gas components. However interference such as humidity and other contaminants from the contaminated sites and relative high cost of the instrument may limit its applicability. In terms of time, data accuracy, and cost, it is recommended that SPME and Sorbent Tubes Anasorb CSC[®] may serve as the better choice in passive sorption of soil gas in the field. In particular, SPME and Sorbent Tubes Anasorb CSC[®] serve as precaution tools for contamination

prevention in gas stations.

[143] 結合生物毒性測試及環境代謝體學進行高雄港底泥生態風險評估

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中文摘要

陸源性受污染的水源進入到港區，使得水域中的底泥成為污染物長期累積的儲存庫，因此底泥在生態環境中化學物質的水地化循環中扮演重要的角色。而高雄港上游河流的廢水每天大量地將污染物輸進高雄港。為了研究高雄港底泥的生態風險，我們應用環境代謝組學的方法，來研究海洋端足類 *Hyalella azteca* 的暴露在不同環境因素下，其影響的生理和代謝途徑。從不同位置收集到高雄港的底泥，包括愛河(LR)，第五船渠(CR)，前鎮河(JR)，以及鹽水溪(SR)四河的流入口。這些河流流經高度的民生活動和工業區域。另外，高雄港 1 號入港口(E1)作為一個參考測站。我們分別針對五個樣點進行包括物化分析、重金屬及 PAH 等分析。顯示 E1 底泥的粒徑較大，屬於沙質，而重金屬和 PAH 等污染物均為較低，其餘樣點並無一致的污染物趨勢。成熟雌性端足類暴露在不同的底泥 10 日後，以核磁共振光譜學和多變量統計進行其生物體的代謝組學分析。偏最小二乘判別分析(PLS-DA)的結果顯示端足類萃取物顯著地分成 2 組：(HE, LR, CR)和 (JR, SR)，再將 VIP>0.9 及 ROC curve 的 AUC>0.9 的代謝物，共有 homocystine, isocaproate, levulinate, methylmalonate, methylsuccinate, N-acetylglutamate, oxalacetate, pimelate, proline, suberate, theophylline, threonine, trimethylamine N-oxide, tryptophan, valerate, valine, valproate 等代謝物為可能的生物標記。結果表明，核磁共振的代謝組學研究方法可用於鑑定被污染物污染的生物體反應的有效方法，且能篩選出可能的代謝物生物標記。本計畫同時亦利用此平台，以銅對端足類測試其毒性，以及尋找其影響的代謝物，發現端足類暴露於高濃度的銅離子環境下，valine 及 isocaproate 很顯著地表現，

顯現未來將可陸續依此平台來進行不同單一或多種重金屬影響下的代謝反應，開發可當檢測的生物標記。

Abstract

Aquatic sediment is a long-term sink of all pollutants, therefore it has played an important role in the biohydrogeochemical cycle of chemical species in the ecological environment. Inflow of waste water from upstream rivers bring large flux of pollutants entering the Kaohsiung Harbor daily. In order to reveal the ecological risk of Kaohsiung Harbor sediments, we have applied an ecological metabolomic approach to investigate environmental factors pertinent to physiological and metabolic pathways of a marine amphipod *Hyalella azteca*, at the molecular levels, after exposure to sediments collected from different location in the Kaohsiung Harbor including the stream inlet of four rivers of Love River (LR), Canon River (CR), Jen-Gen River (JR), and Salt River (SR). These rivers are flowing through region of high human and industry activities. Additional, an harbor entrance 1 (E1) was selected as a reference site. We analysed the sediment particle sizes, heavy metals and PAHs. In E1, the particle size was the largest belonging to sand, and the heavy metals and PAHs were the lowest in the sampling sites. In addition, there was no consistent trend of pollutant concentrations in the other sampling sites. Adult female *Hyalella azteca* was exposed to different sediments in seawater. After 10-day exposure, the metabolomic analysis of *Hyalella azteca* was carried out using ¹H NMR spectroscopy and multivariate statistical analyses. Results of partial least square discriminant analysis (PLS-DA) revealed significant separation between extracts of *Hyalella azteca* as 2 groups: (E1, LR, CR), and (JR, SR).



Metabolites whose VIP scores and AUC >0.9 were homocystine, isocaproate, levulinate, methylmalonate, methylsuccinate, N-acetylglutamate, oxalacetate, pimelate, proline, suberate, theophylline, threonine, trimethylamine N-oxide, tryptophan, valerate, valine, valproate. Results demonstrated that NMR-based metabolomics can be an efficient method for characterizing metabolic responses related to heavy metal contamination derived from polluted area, for discovery of metabolite biomarkers exposed to whole sediment test. We also used this platform to perform on toxicity test of copper on the amphipod and the effects on metabolites changes. The future work will be continued to discover the metabolite biomarkers related to different single or multiple heavy metal influences.

[144] 開發高效能螯合與還原毒性汞之菌株及量產移汞蛋白質-metallothionein

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中文摘要

土壤和水是地球上最重要的自然資源，然而，在過去數十年中，由於工業化、人口的大量增加和城市化，環境重金屬污染問題日益嚴重。其中，汞因其具高毒性及生物累積等特性，可能對生物體及環境造成影響或危害，且具有高風險，因此汞污染需優先被進行整治。利用生物復育程序(Bioremediation)進行環境污染整治是屬於對環境最友善的技術，而且也具有包括經濟效益所需花費少，容易操作且較易受社會大眾接受等優點。但由於汞與土壤形成之錯合物溶解度非常低，不容易被生物所利用，因此藉由使用螯合劑輔助使土壤中汞錯合物由固相轉移至液相，使生物能更有效處理污染物為有效可行之方法，本研究團隊於去年研究計畫已有初步成果。在期中報告的研究執行內容與成果我們著重在利用基因工程方式建構強化先前研究內容菌種，開發具有潛力之汞抗性基因重組菌株，欲強化其產生之汞抗性蛋白並探討未來應用模場整治可行性。

本次的期末報告，我們設計了新的穿梭載體 pJBR 系列，使用持續性啟動子 J23100(不需使用誘導物)、核糖體結合位 B0034 以及 rrnB T1 終止位構成，並且能讓 MT-1 和 EGFP 的融合蛋白質順利的表現，之後，我們利用生物反應器(Bioreactor)測試了轉型 pJBME 質體的 *Pseudomonas* A46 菌株在靜止細胞培養液和生長細胞培養液中固定汞的效果，在靜止細胞培養液中此株菌並沒有特別的提升固定汞能力，但是在生長細胞培養液中，細胞中固汞量有明顯增加。本計畫成功開發抗汞並固定汞之基因工程菌，與去年計畫淋洗法共同應用，未來則能在環境復育上開闢新的前景。

Abstract

Soil and water are the most important natural resources on earth. However, environmental pollution of heavy metal is escalating due to industrialization, huge population and urbanization. Mercury has been reported as highly toxic and need priority treat. Bioremediation is economy and environmental friendly approaches and also acceptable by general public. However, due to very low solubility of mercury compounds. It's not easy to be used by microbes. Therefore, using chelating agent to make mercury compound in soil transferred from solid phase to liquid phase is an effective way for bioremediation. We have isolated various strains of microorganisms from the previous study funded by "Soil and Groundwater Remediation Fund Management Board, Environmental Protection Administration, Executive Yuan" – "Screening and study of indigenous microorganisms from mercury contaminated soil for bioremediation application". These indigenous microorganisms will be excellent candidates to develop bioremediation approach for mercury contaminated area in situ.

In the final report, we design a novel shuttle vector – pJBR family, which consist of promoter J23100 and RBS B0034 and rrnB T1 terminator. This vector is very successful to let MT-1-EGFP fusion protein express in *Pseudomonas* A46. We also use the Bioreactor to test the mercury resistant ability of the *Pseudomonas* A46 which transfect with pJBME in the resting medium and growth medium. However, the resting medium cells didn't show the enhancement ability of mercury resistance, but the growth cells indeed arise the mercury accumulation in the cell pellet. So that our plant is confirm to success, and we can also combine with the previous ground wash study method to



fulfill the bioremediation application, it has a very good prospect in the future.

[145] 醇類增加有機物揮發應用於受柴油污染場址之研究

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中文摘要

空氣注入法與土壤蒸氣萃取法均為土壤地下水受到有機物污染時常見的處理方法，但可惜的是受限於有機物的揮發速率，常需要花費許多時間才能達到整治目標，若能有效增加有機物之揮發量，則能提高空氣注入法與土壤蒸氣萃取法之處理效率，本計畫延續去年以醇類加入增加高揮發性有機物之研究成果，今年改以揮發較低的柴油組成物為揮發測試對象，研究可分成兩部分，一部分以柴油組成中個別有機物進行揮發測試，了解加入醇類後對這些有機物揮發所產生之影響，第二部分為直接以柴油樣品進行測試，評估加入醇類後揮發量增加比例。

在本研究中選擇三種醇類包括正戊醇、正己醇與正庚醇進行實驗，醇類濃度目前設定為 2、6、10ppm 三種濃度，個別測試揮發的化合物包括 C9~C14 的烷類，另一部分則直接以市售柴油進行測試，實驗時間依據有機物的性質設定為 3 小時至 63 小時不等，揮發出的有機物以商用吸附管吸收，再以二硫化碳萃取後注入氣相層析儀分析揮發出的質量，再與未加入醇類時進行比較。

研究結果顯示加入醇類確實可使所選擇有機物的揮發效率增加，但由於柴油組成之污染物具低水解度在設定條件下已形成非水相液體(NAPL)，因此揮發量增加的比例大部分低於兩倍，且由於形成 NAPL 有機物較難混合均勻，因此實驗將產生較大的偏差，當以未加入土壤、加入一般有機質的蘆竹土與加入高有機質的彰化土進行比較，土壤有機質仍會對有機物在土壤中的傳輸產生抑制，但抑制效果不如高揮發性有機物明顯，在揮發增加比例變化趨勢方面，由於污染物已呈現 NAPL 形式，因此無法完全呈

現穩定的趨勢，整體而言加入醇類仍可視為改善空氣注入法效率的方法之一。

Abstract

Air sparging (AS) and soil vapor extraction (SVE) are widely used to remediate contaminated soil and groundwater for the contamination of organic compounds. When the target contaminants are low volatile organic compounds, it would be a very long schedule to finish the remediation process. If a method was developed to enhance volatilization of organic compounds, it would improve the removal efficiency of organic contaminant. This study continued the previous project and, diesel fuel with the lower volatility was selected to examine the increase in volatilization of organic compounds by adding alcohol to groundwater. The volatilization experiment in this study was divided into two parts, including individual organic compounds and diesel fuel sample. The increase in volatile amount was evaluated as presence of alcohols in the soil-water system.

These alcohols need the properties of relatively lower water solubilities and higher volatility. Three kinds of alcohols n-pentanol, n-hexanol and n-heptanol were selected to carry out the experiments. The target organic compounds including C9~C14 alkane and diesel fuel was used to examine the result. The concentrations of alcohols with 2, 6, and 10ppm were added in the solution mixing with a target organic compound. The released VOCs were adsorbed by using a commercial adsorption tube. CS₂ was used to extract the target organic compound. Furthermore, the extractive solution was injected in GC to analyze the volatile amount of target organic compound. The changes in volatile amounts of organic compounds in alcohol solution were examined.



The obtained result including the presence of alcohols could enhance the volatile amounts of test organic contaminants. However, the target organic compounds have formed NAPL caused the lower efficiency in volatilization enhancement. Some of potential bias was ascribed to poor uniform mixing under NAPL condition. Although soil organic matter could reduce transport of organic contaminants in soil, the reduced amounts for the low volatile organic compounds are far lower than those for the high volatile organic compounds. It is difficult to quantify the change in volatile amounts of target organic contaminants under the NAPL condition. The developed method can be used to improve the efficiency of AS in the further.



pH、Eh、有機物含量、反應天數等等的變化條件下，以 pH 值的影響為最大，從 pH 6.0 到 pH9.0 之間， H^+ 的濃度降低了 103 倍，而 Eh 值僅有 100 mV 的變化（從 150 mV 下降至 50 mV）。而有機物的角色則主要是影響物種變化與分佈的情形。

Abstract

As semiconductor technology is improved with the progress of time, the manufacturing processes has embraced a boom in the use of trace elements to improve the performance of thin film growth. The manufacturing processes released intermediate byproducts and residual chemicals into waste water and caused the increasing hazardous risks to human health. The trace metal of selenium (Se), is rarely recognized and the related regulations has not developed completely. The risk level of Se depends on the mobility, toxicity and bioavailability in the environments. Bioavailability is dependent on solubility and species, which also controls Se toxicity through the ecosystem. Se exists in multiple oxidation states, with each state having different fates within the environment. Selenides and elemental Se are considered to be relatively less mobile or bioavailable, but the gaseous H_2Se is the most toxic in Se species. Selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}) are more soluble than the reduced and elemental Se species. Selenate is the most soluble Se species and is readily taken up by plants. The organic Se is less toxic than inorganic Se. Therefore, the speciation of Se should be considered in evaluating environmental risk assessments of Se-bearing wastes, forecasting Se bioaccumulation, and understanding Se distribution and transformation in the ecosystems.

According to our incubation results, the incubation pH would cause the decrease of oxidation-reduction potential (ORP) in the systems. The commercial Aldrich humic acid (AHA) that was mixed with the sediment samples has relatively

great molecular structures and is hard to be decomposed. Therefore, ORP of the system with 5 % AHA addition slightly decreased with increasing incubation time. In addition, AHA could affect the reduction reactions. At pH 6.0, 7.5, and 9.0, the total organic carbon contents were decreased about 66.5~6.3%, 27.5~2.1%, and 21.3~11.6%, respectively. The dissolved Se contents were increased with incubation time, and the maximum amounts were 29, 48, and 92 $\mu g L^{-1}$ for pH 6.0, 7.5, and 9.0 systems. In terms of AHA addition, Se dissolution decreased with increasing AHA, agreeing with our previous results that indicated the positive correlation between element retention and organic matter content in the Wu River sediments (Hsu et al., 2016). However, the Fe dissolution increased with increasing AHA addition, suggesting that AHA complexed with Fe to release it but inhibited Se dissolution. The correlation coefficient and linear regression analysis indicated that ORP was highly correlated with the dissolved Fe and Se contents.

[147] 二仁溪污染底泥整治模場試驗計畫

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中文摘要

臺灣地區之底泥污染情況相當嚴重，多項疏水性有機污染物以及重金屬污染監測濃度在全世界之監測濃度均名列前茅，大部分有機污染物之監測濃度已經屢次超過法規限值，且因絕大部分持久性有機污染物皆具有較高疏水性，容易吸附於小粒徑底泥顆粒或是富含有機成分之輕質底泥，故容易沉積於淺層底泥為底棲生物與浮游生物所接觸與攝食，進而損害生態系與人體健康福祉。為有效去除表層底泥中之疏水性鹵化有機污染物，本研究應用以下技術進行疏水性氯化有機物污染底泥整治技術研發，利用高溫之水在油中乳化液進入孔隙中直接接觸疏水性有機污染物，藉高溫加速脫附與擴散之特性將污染物有效傳輸至油相中；再利用上層底泥造成降溫完成相反轉與形成超小油顆粒之技術，快速有效地將污染物傳輸至底泥上方加以去除；並且利用已經完成整治並達標之淺層底泥作為現成加蓋材料，進行生物主動式加蓋(Bioactive capping)；於完成加蓋後，可利用下方底泥中經過熱篩而佔優勢之產氫微生物成為優勢菌群進行殘餘乳化液之發酵產氫，上方底泥中之厭氧還原脫鹵菌群利用氫氣進行有效且持續之生物降解作用，形成有效之主動式生物屏障(active biobarrier)。本計畫依據原進度完成各項工作，唯有實際底泥管柱試驗仍在進行中，目前結果顯示底泥中微生物可有效降解 Aroclor 1254 但對六氯苯之降解較為有限；依田口實驗設計法進行批次降解試驗顯示 Aroclor 1254 生物降解之顯著控制因子為溫度與 pH 值，溫度較低似乎降解較佳，pH 值在中性及偏鹼區域降解較佳；六氯苯生物降解之顯著控制因子為溫度與乳化液，溫度較高降解較佳，乳化液濃度愈高似乎降解愈差。以相反轉法進行底泥中污染物回收測試結果顯示單次操作可去除約

58.2% Aroclor 1254 與 56.5% 之六氯苯，並且的確可以達到篩選特定菌群之目的，管柱實驗初步顯示經過回收後之上層底泥可能確實具有降解疏水性污染物能力，在 35 天之內在表層與中層底泥中微生物將殘餘之 Aroclor 1254 及六氯苯繼續降解約 30%。這些結果顯示以結合相反轉法與再利用加蓋法進行疏水性污染底泥之整治有極高可行性。

Abstract

Sediment contamination in Taiwan is an imperative environmental problem. Concentration levels of some hydrophobic organic compounds (HOCs) and heavy metals are ranked at the front all over the world. For example, the sediments in a seawater lagoon at An-Sun site in Tainan is heavily contaminated by dioxin, pentachlorophenol, and mercury while the sediment in Er-Ren River is highly contaminated by polychlorinated biphenyls, polybrominated diphenyl ethers, phthalate esters, polycyclic aromatic hydrocarbons, and heavy metals. Monitoring results often showed that some HOCs already exceeded the regulated levels. These HOCs are easily accumulated at the surface sediment because finer particles which have slower settling velocities after resuspension tend to deposition on the top of the sediments and they offer larger surface area for HOCs to adsorb on. Thus, HOCs are easy for benthic organisms to access and uptake and can be biomagnified through trophic levels. At the end, these HOCs would impact ecosystem integrity and human health. To remove HOCs at shallow sediments, in this research, we proposed to employ four technologies and the inherent properties of HOCs, i.e., (1) higher contact opportunity between hot water-in-oil emulsion and HOCs in sediments, (2) more efficient desorption and diffusion of HOCs at higher temperature, (3)



utilization of the cleaned sediment material as an active capping materials, and (4) higher hydrogen generation rate at the heat treated microorganisms at lower region of the sediment to enhance reductive dechlorination at the upper region of the sediments. Up to now, the scheduled milestones have been finished except the column study is ongoing. Batch biodegradation test showed that the controlling factors for Aroclor 1254 and hexachlorobenzene (HCB) biodegradation were temperature and pH, and temperature and emulsion concentration, respectively. Single operation of phase inversion recovery can achieve removal rates for Aroclor 1254 and HCB were as high as 58 and 57%, respectively. The result suggested that it is highly feasible to couple phase inversion and recycled sediment capping to remediate sediment contaminated by HOCs.

[148] 現地電解整治受氯乙炔污染地下水之模場試驗

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中文摘要

本研究提出現地電解整治工法的概念，整合太陽能供電系統與電解處理系統，開發綠色整治工法應用於地下水氯乙炔污染場址之整治。研析太陽能應用於環境污染整治之潛力，實驗裝置以太陽能為電力來源，太陽能板發電，儲存於電池，以直流電輸出，電化學反應器以電壓控制，觸發電化學反應產生氫氧自由基，可快速氧化降解整治井中氯乙炔污染物，達到地下水污染整治之成效。本研究規劃模場試驗確立現地電解整治系統的操作條件，展示現地電解整治工法應用於地下水氯乙炔污染場址之可行性。本專案模場試驗場址位於高雄市小港區伍桐股份有限公司地下水污染控制場址，利用現地電解整治工法降低地下水中氯乙炔濃度，本案例落實綠色及永續整治概念，操作以太陽能為動力之電解系統，可降低污染整治的長期操作費用，並兼具節能減碳的成效，未來可進一步開發太陽能應用於環境污染整治的工具。

現階段執行進度已完成實驗室電解實驗，比對氯乙炔經由曝氣作用與電解機制移除的效果，確認未添加電解質直接電解地下水的可行性，建立現地電解系統電壓操作條件。現地模場試驗已完成單井流速流向測定、鑽設1口簡易井(整治井)、鑽設1口標準井(背景監測井)、現地電解整治設備製作與系統安裝等工作，現地電解整治系統正常操作約1個月，整治井氯乙炔濃度迅速降至地下水管制標準以下(ND值)，成效監測井氯乙炔濃度略有上下浮動，目前亦降至地下水管制標準以下(ND值)。現階段整治成效明顯，後續持續操作現地電解整治系統，依成效評估結果適時調整操作方式。

Abstract

This study proposed the concept of in-situ electrolysis remedy scheme to integrate solar energy power supply system with electrolytic treatment system. The proposed remedy scheme, one of green remediation methods, was applied to the cleanup of groundwater contaminated with vinyl chloride. For applying solar energy on environmental cleanup, experimental apparatus is designed using solar energy as power source. Solar energy was collected from the solar plate unit, stored in a battery, and transferred as a DC current. The electrochemical reactor received the electrical current, initiated serial electrochemical reactions, generated the OH radicals, degraded chlorinated pollutants, and remediated contaminated groundwater. The objective of the pilot study is focused on confirming the operation control of the in-situ electrolysis (ISE) remediation system and illustrating the feasibility of ISE application on a vinyl chloride-contaminated groundwater case. The selected study site is a groundwater contaminated site with vinyl chloride located at Kaohsiung, Taiwan. This study tried to remediate residual vinyl chloride with in-situ electrolysis remedy scheme, and the concept of green and sustainable remediation was implemented by the designed solar-driven energy system. The benefits of employing the proposed remedy scheme include energy saving, green-house gas (GHG) reduction, treatment cost cutback, and thus the application of the solar-driven electrolysis system can be prevailed in the near future.

Lab electrolysis experiments were completed at present. The effects of vinyl chloride (VC) removal through bubble stripping and/or electrolysis were compared under the control of operating potentials. The feasibility of electrolyzing field VC-contaminated groundwater samples without the addition of



electrolytes were examined in lab experiments. Based on the results of lab electrolysis experiments, the optimal operating control was applied to the operation of the in-situ electrolysis remediation system. Pilot-scale experiments including the measurement of flow direction and flow velocity in one monitoring well, the establishments of a remediation well and an efficiency monitoring well, the manufacture of the in-situ electrolysis remediation system and the setup. Pilot-scale experiment has been conducted for about one month, the VC concentrations dropped rapidly to the undetected level in the remediation well and also reduced up and down to the undetected level in the efficiency monitoring well. The remediation efficiency is remarkable at present, and the future work is to keep operating the in-situ electrolysis remediation system and to adjust the operating control according to the outcome of remediation efficiency evaluation.

[149] 整合電動力與植生復育技術整治重金屬污染土壤

章日行

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中文摘要

本計畫擬整合循環式電動力 CEEK 技術及植生復育技術整治重金屬鉛污染土壤。依據過去的模場試驗成果顯示，CEEK 能夠於短時間內快速去除土壤中的重金屬，殘留於土壤的重金屬可經由植生復育技術運用植物根系激素析出，再運用 CEEK 快速去除土壤中的重金屬，後續再利用植生復育技術析出殘留於土壤的重金屬，經兩技術交替運用使土壤重金屬濃度有效降低，並進一步探討相關處理效率、問題及成本，並評估本技術對於鉛污染土壤的處理效益。

本計畫實驗按照計畫書執行內容進行，目前已完成污染土壤的基本物化特性分析、模場試驗裝置、重金屬的移除效率及栽種玉米以進行後續植生復育試驗，試驗結果可以歸納如下：

- 本電動力系統 CEEK 經不斷改良下，系統具有簡便、組裝容易、運送輕便及可重複使用性，有利未來廣泛推展與實際進行。
- 本試驗經由不透水夾層的持續改善及測試，除了可大幅減少操作液的損失，也可降低污染物垂直移動所造成電鍍成效不彰的情況。
- 循環式電動力技術及植生復育整合下，其鉛污染土壤之最高濃度可從 $5,650 \text{ mg kg}^{-1}\text{P}$ 降至約 $2,083 \text{ mg kg}^{-1}\text{P}$ ，去除效率最高可約達到 63%。
- 經電動力法整治後其土壤 pH 值及土壤有機質未有顯著改變，仍可栽種玉米作物，土壤並未產生毒化現象。
- 整合電動力法及植生復育之整治下，鉛金屬鍵結型態以鐵錳氧化態濃度最高，且鍵結型態顯著改變的現象並不明顯。

Abstract

In practice, for the contaminated sites to complete removal efficiency of heavy metals and maintain soil fertility, this study intends to using electrokinetics and phytoremediation to clean heavy-metal contaminated soils. Based CEEK mode test results show that CEEK could quickly remove heavy metals in soil for a short time in the past, and the residues heavy metal in soil could be precipitated via phytoremediation technique. At the same time, using the CEEK rapid remove the heavy metals in the soil, then the phytoremediation technique to precipitated the residues heavy metal in soil again. By using two techniques alternate until the concentrations of heavy metals in soil reaches the crops monitoring benchmark, and to further explore the treatment efficiency, problems and operation cost. The execution of experimental program according to the previous plans, the analysis of physical-chemical characterization of contaminated soil, mode experimental equipment, removal efficiency of heavy metal and planting corn for subsequent phytoremediation regulation have been obtained. Several conclusions and suggestions can be drawn:

After continuous improvement, the CEEK system possesses some features such as: more concise, easy construction, easy transport, and reusable. These features are beneficial to promote in the future.

The impermeable interlayer has been continuous improved and tested which can reduce the loss of operation solution and to enhance the effectiveness of cathode plating.

After the CEEK and phytoremediation treatment, the average Pb concentration in the contaminated



soil could be decreased from $5,650 \text{ mg kg}^{-1}$ to $2,083 \text{ mg kg}^{-1}$ and the removal efficiency could be achieved to 63%.

The pH value and organic matter in the soil change insignificantly after electrokinetics operation. The corn plant was still planted and poisoning phenomenon not occurred.

The Fe-Mn Oxides bound was highest concentration and the patterns distribution influence between electrokinetics and phytoremediton techniques insignificantly.

[150] 土壤地下水地圖網頁線上資料分析及互動式模擬平台開發

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中文摘要

快速與正確判斷、評估與預測地下水污染傳輸機制，為污染場址管理、污染事件應變以及場址整治成功的關鍵因素之一。本計畫將延續前一期計畫成果，建置以物理模式為基礎的線上分析平台，結合環保署既有土壤地下水管理資訊系統與外部單位開放資料，達到與使用者互動、即時與快速分析觀測資料空間分布與污染團遷移的目的。分析平台將考量跨作業系統、跨網頁平台操作，使相關領域調查及研究人員能在網路連結情形下，使用辦公室或行動裝置，進行線上分析評估與模擬。為提高分析成果的空間資訊理解與評估，平台將使用 Google 地圖模組做為平台基礎架構，結合政府單位開放資料，開發資料庫介接模組、大數據資料傳輸技術、空間資料統計分析、污染團遷移物理模式分析模組及視覺展示等。在此架構下，使用者能藉由地圖資訊做為條件門檻，查詢分析與調查區位既有資料；亦可依據潛在土壤地下水污染場址通報資訊，即時以物理模式推估污染團的歷史遷移與空間分布。成果將有效率地結合既有土壤地下水管理系統與其他相關部門與機構開放資料，協助土壤地下水領域產、官、學、研相關工作推動與執行。

Abstract

Efficient identification, assessment, and prediction of groundwater flow and contaminant transport behaviors have become the key process for site management, strategy design of emergency events, and site remediation. This study aims to develop an interactive online map platform for spatial data analysis and flow and transport modeling in soil groundwater systems. The physical-based analysis and modeling was expected to integrate available data in soil groundwater management (SGM) system and other government open sources. In this study, the platform was developed to compatible with different operation systems and web platform and was allowed to operate with office and mobile devices. To improve the usefulness and understanding of analysis and modeling results for users, the map platform uses the Google map for results visualizations. The users can consider map information as the criteria for data mining and spatial data analysis. Additionally, the map information also provides the base map for physical-based interactive flow and transport modeling. With the available SGM data and other data sources, the data analysis and flow and transport modeling integrated in the developed platform are expected to be efficient for most cases proposed by fields of soil groundwater contamination in industries and government and research agencies.



[151] 土壤污染現地寬頻電性量測技術研發

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中文摘要

近年來環境地球物理探測在土壤污染的快速探測與評估中獲得越來越廣泛的應用，常見土壤污染物改變土壤孔隙水特性，甚而形成額外獨立相，即所謂的非水相液體(Non-Aqueous Phase Liquid)。因土壤電學特性改變而影響電流或電磁波在污染區域內傳輸產生異常，為地球物理探測的電學方法應用提供了探測前提。由於污染土壤為三相或四相的複和材料，其電學性質與土壤含水量、孔隙率、污染含量之關係相當複雜，有必要在相當寬的頻率範圍內來探討污染土壤的電學性質。本研究提出創新的時域反射技術多重反射訊號分析(TDR RRA)方法，經室內試驗與現地試驗驗證可獲得10MHz-1GHz寬頻的全電學性質(複介電度實部與虛部)，對材料電學性質量測有很大突破。該量測系統具備容易組裝、標定及操作的特性，有助於探討各種污染物及不同土壤組成與含水量的電學特性，據以作為電學探測結果解讀與量化分析的依據。RRA在特定情況之量測可靠度較不佳，後續可加裝人工阻抗模組以產生一訊號穩定且無頻散現象之穩定R1，並可延伸至與CPT貫入試驗結合，可應用於現地調查及監測。長期而言，現地污染探測需更完善寬頻電學量測技術，結合基於中高頻波傳方法與低頻電路方法，研發適合實驗室與現地試驗之試體感測器及現地貫入式探測器以達到此目標。

Abstract

Recent implementation of environmental geophysical exploration technique in rapid detection and evaluation of soil contamination is widely involved. Typical soil contaminants tend to alter the pore fluid properties and some even form an individual phase, namely non-aqueous phase liquid (NAPL). Due to the variation

of soil electrical properties, the transmission path of electrical currents or electromagnetic waves may be affected within the contaminated region, which in turn provided the detection basis of the electrical and electromagnetism methods in geophysical exploration methods. As contaminated soils consisted of composite materials of three or four phases, the relationship between their electrical properties and their water content, porosity, contaminant concentration are relatively complex. The demand for a wide electrical spectral range has hence arisen for contaminated soil detection. This study proposed an innovative Time-domain reflectometry (TDR) Remaining Reflection Analysis (RRA) method, in order to measure a broadband complex dielectric spectrum (including both real and imaginary parts of complex dielectric permittivity, CDP) within 10MHz - 1GHz frequency range and to perform a more complete electrical characterization of contaminated soil. The robustness, in-situ applicability, and performance of the proposed RRA method is verified using series of laboratorial and in-situ experiments, involving various contaminants. The measurement system of RRA can be setup, calibrated and operated easily, which assisted in investigating the electrical characteristics of various contaminants and soil composition. This provided useful insights into the interpretation of in-situ electrical exploration data results. However, RRA encountered some limitations in materials of highly dispersive or low dielectric permittivity. This limitation may be resolved by adding an impedance block prior to the sensing section and provide a steady, non-dispersive R1. The TDR RRA sensing probe can even be adapted to CPT probe for field investigation and monitoring. In the long run, a more



comprehensive broadband electrical measurement technique, which involves wave based and circuit based methods, is required for the ultimate goal of in-situ soil contamination exploration. Specimen probes and in-situ penetrating probes can also be designed and integrated with the aforementioned technique for laboratorial and in-situ experiments.

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[152] 以不同熱處理技術應用多氯聯苯污染場址之可行性評估

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中文摘要

多氯聯苯 (Polychlorinated Biphenyls, PCBs) 屬持久性有機污染物 (POPs)，因氯原子取代位置和數量的不同共有 209 種同系物。由於其良好的阻燃性、低電導率、抗熱解能力和化學穩定性，曾被廣泛用於變壓器和電容器絕緣油、油墨添加劑、燃料分散劑以及農藥延效劑等。PCBs 在使用過程中經由各種途徑進入土壤，造成土壤污染。PCBs 在土壤中的分佈超過其進入環境總量的 99%，在工業污染區的土壤中其含量可高達十幾個 mg/kg。國內由於過去所使用的大型變壓器和電容器設備老化，出現不同程度的 PCBs 洩漏事件，給當地土壤帶來嚴重污染。由於 PCBs 具有高分子穩定性，低水溶性和高吸附特性，導致土壤基質中多氯聯苯的去除極其困難。本研究以典型電力電容器污染土壤為對象，透過本研究群自主研發的三種熱處理技術模組(熱脫附/氧化系統、熱裂解系統及超臨界流體氧化 (SCWO) 系統)進行比較，就不同操作參數條件(包含排氣組成、操作溫度、操作壓力及停留時間等)對 PCBs 及戴奧辛類化合物(dioxin-like compounds)之去除效率進行系統性的評估。本研究執行成果可提供國內受 PCBs 或 dioxin 污染土壤處理技術的新選擇。

實驗室批次熱裂解試驗結果顯示污染土壤中戴奧辛及 PCBs 的去除效率隨熱裂解模組操作溫度的提高而上升。操作於 600°C，土壤中各污染物之殘餘濃度皆可符合法規標準。在超臨界流體氧化技術試驗結果方面，污染土壤中戴奧辛及 PCBs 的去除效率隨 SCWO 操作溫度、壓力、氧化劑濃度 (H₂O₂) 及反應時間的增加而提升。使用 100% 過剩氧量，反應溫度為 380 °C，壓力為 22MPa 及停留時間為 30 分鐘條件下，對戴奧辛及 PCBs 的破壞效率皆

可達 99.9% 以上，土壤中各污染物之殘餘濃度皆可符合法規標準。由於超臨界流系統可直接進行污染物破壞，使戴奧辛污染土壤整治技術達到低碳、低處理成本及低環境負荷的目標，故 SCWO 處理技術處理受戴奧辛及 PCBs 污染土壤符合最佳可行控制技術(BAT)及最佳環境實踐(BEP)之目標。

Abstract

Polychlorinated biphenyls (PCBs) are a class of persistent organic pollutants (POPs) and there are 209 PCB congeners as a function of chlorine numbers and chlorinated position. In recent years, the issue of PCB-contaminated soils has aroused wide public concern. PCBs are extremely hard to remove from soil matrix due to their high molecular stability, low solubility in water and high tendency to adsorb on particulate phase. In this study, super-critical water oxidation (SCWO) technology is self-developed for the remediation of soil contaminated with PCBs and dioxin-like compounds. For efficient contaminant removal, operating parameters including temperature, pressure, reaction time and oxidative additives ratio are tested. The fruitful results obtained in this study will support the novel technology for remediation of the PCB-contaminated soil.

Before pilot-scale test, lab-scale batch tests are conducted to evaluate the effects of operating parameters including temperatures and additives on PCB destruction efficiency. The results obtained from lab-scale tests indicate that removal efficiencies of contaminants are significantly increased with increasing operating temperatures. However, operating the thermal treatment system at a temperature higher than 600°C may be needed to make sure that PCDD/F and PCBs concentrations are lower than the



limits, i.e., 1000 ng-TEQ/kg and 0.09 mg/kg, respectively. Preliminary results for SCWO indicate that the removal efficiencies of PCDD/Fs and PCBs achieved increase with increasing operating temperatures, pressure, and the oxidant (H_2O_2) added. The destruction efficiencies of PCDD/Fs and PCBs achieved for the contaminated soil are more than 99.9% with 100% of stoichiometric demand, 380°C operating temperature, 22 MPa operating pressure and 30 min. retention time. The target pollutants in the remediated soil treated with above operating parameters of SCWO system meet the regulation of Taiwan EPA. SCWO designed in this study is a powerful and environment-friendly remediation technology for PCDD/F and PCB removal from the soil contaminated with PCBs or dioxin.



[153] 以污染整治後閒置公有(營)土地做為區域排水滯洪規劃再利用之 評估模式

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中文摘要

滯洪設施有助於削減尖峰流量、降低渠道水位及延長洪峰到達時間，減少洪災發生，是治水的重要設施之一。然而，滯洪設施屬於具有公益性之公共設施，其涉及用地取得及補償之問題，以致推動常面臨困難。究其因發現主要係透過與地主簽訂契約，允許洪水漫淹該區，以達到治理目標，並對提供滯蓄洪空間之土地給予土地所有權人或相關權利人適當金額之補償之方法，但易面臨私地主之協議困難，配合度不高，尤其涉及民眾用地之生計需求，而難以推動。相對而言，污染整治後閒置公有(營)土地基於公共利益之考量下，可適度檢討提供作為公共設施使用，尤其針對既有公有(營)閒置土地，因其閒置往往是原訂用途廢止或周邊發展不佳所致，如確實未來無使用需求，則可透過撥用、租用等方式永久性或暫時性的供作滯洪設施使用，以達到防洪、防災之需求，發揮該閒置土地之再利用。

本研究經由國內、外文獻回顧，完成彙整污染整治重要性與相關影響之因素，其中包含閒置土地做為滯洪規劃國內外案例之探討，以及都市防洪防災與滯洪規劃相關文獻之彙整，並蒐集我國閒置公有(營)土地之現況資料，藉以透過模糊德爾菲法(FDM)之專家評估導向，完成指標架構體系之篩選與建立，續以分析網絡程序法導入灰色概念(Grey-ANP)建立出一套適用於評估污染整治閒置土地做為滯洪規畫再利用之指標系統，其中包含四大構面與13項評估指標項目，以此計算出各項指標權重值與優先排序之成果，加以運用指標系統進行案例地區臺南市敬惠工業場址之實例分析與應用，最後據以提出推動污染整治相關策略與建議。

依據本研究成果，污染整治推動過

程亦可依據各項權重值高低，反向進行污染場址重點整治項目的排列，亦可作為土污基金分配運用的考量基準，以有效防止污染整治區域擴大與棕地或污染整治後的土地持續閒置與荒廢，藉以做為國內提升整治後閒置土地活化再利用的同時，亦能兼具有滯洪防災規劃效益，以此達到增加現有防洪空間，亦可擬定相關策略建議作為污染整治基金運用，以及作為鼓勵政府與民間辦理之參考。

Abstract

Flood detention facilities help reduce peak flow, reduce channel levels and extend peak arrival times to reduce flooding, which is one of the important facilities for water management. However, flood detention facilities are public welfare public facilities which involve problems of obtaining and compensating for the use of land so that the promotion often faces difficulties. It is mainly because of the discovery that it is mainly through the contract with the landlord to allow flooding of the area to flood the area in order to achieve the goal of governance and to compensate the land owner or the relevant obligee for the amount of land provided with the stranded flood space, Private Landlord agreement difficult, with a low degree of coordination, especially for people's livelihood needs, and difficult to promote.

In this study, through reviewing the literature both at home and abroad, the paper summarizes the importance of the pollution remediation and related factors, including the discussion of the cases of idle land as a domestic and international case of flood detention planning, the compilation of relevant documents on urban flood control and disaster

prevention and detention planning, Idle the information of the public (battalion) land so as to complete the selection and establishment of the indicator architecture system through the fuzzy expert evaluation of the Delphi method (FDM), and continue the analysis of the network program method by introducing the Gray-ANP The set is suitable for assessing the remediation of idle land as pollution remediation indicator system, which contains the four major facets and 13 assessment indicators project, in order to calculate the weight of each indicator and the priority of the results, to be used indicators The system analyzes and applies the case of Tainan Hui industrial site in the case area, and finally puts forward some strategies and suggestions to promote pollution remediation.

According to the results of this study, the process of pollution remediation can also be based on the value of the weight value, reverse the arrangement of key remediation projects contaminated sites can also be used as the basis for the allocation of the soil fund to effectively prevent the expansion of pollution remediation and Brownfield or remediation of contaminated land continued to be idle and abandoned, so as to improve the rehabilitated idle land after the re-use of the same time, but also both flood control and disaster planning benefits, so as to increase the existing flood control space can also be drawn up Strategy recommendations as a pollution control fund to use, and as a reference to encourage government and private management.



[154] 以氧化銅活化過二硫酸鹽降解地下水有機污染物之研究

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中文摘要

有效整治受有機物污染之土壤及地下水為建立永續水資源之重要議題。現地化學氧化法(In-Situ Chemical Oxidation, ISCO)係直接注入氧化劑於土壤或地下水體以達到污染物降解的氧化方法，因不須將地下水抽至地面成本較低，目前被廣泛應用於土壤及地下水污染整治上。硫酸鹽屬於較新穎的氧化劑，包含過單硫酸鹽(PMS, HSO_5^-)和過二硫酸鹽(PDS, $\text{S}_2\text{O}_8^{2-}$)兩類，與其他氧化劑相比，可適用在較廣 pH 範圍及長途運輸，亦可有自由基的產生。常見的過硫酸鹽的氧化降解機制，主要活化過硫酸鹽後產生的自由基與有機物污染物結合進行反應。然而，自由基的反應機制，會受到自然水體中的鹵素、天然有機物及其他水質參數的影響，可能間接產生毒性更強的副產物。本研究計畫使用氧化銅(CuO)為活化劑，對過二硫酸鹽進行活化，降解常見之地下水有機污染物，研究結果顯示氧化銅活化二硫酸鹽在中性條件下為一非自由基之反應，反應機制為 PDS 先吸附於氧化銅表面，此吸附之 PDS 以氧化銅作為電子傳遞媒介，進行污染物氧化反應，值得注意的是實驗結果顯示污染物不須強烈吸附於氧化銅表面，此反應即可進行，且在未添加氧化銅的條件下，PDS 不具降解污染物之能力。鹵素離子的存在不影響 2,4-二氯酚之降解，並可透過增加氧化銅劑量解決天然有機物的干擾。此處理程序對於添加於真實地下水的有機污染物也具有良好的降解效果。

Abstract

Remediation of soil and groundwater contaminated by organic pollutants is a key component to develop a sustainable water supply. In-situ chemical oxidation (ISCO) is a method that directly introduces the oxidant into soil or groundwater to degrade organic contaminants. Because of its relatively low cost due to the elimination of pumping, ISCO has been widely considered in real practices. Persulfates, including peroxymonosulfate (PMS, HSO_5^-) and peroxydisulfate (PDS, $\text{S}_2\text{O}_8^{2-}$), are novel oxidants considered in ISCO. They possess a long lifetime in the aquifer and can be activated to form radicals to effectively degrade organic contaminants. The presence of halide ions and natural organic matter (NOM), however, may react with these radicals to produce unwanted toxic by-products. We propose to use CuO as an activator to activate PDS to degrade common organic pollutants found in contaminated groundwater. Our results showed that PDS activation is a non-radical process at neutral pH conditions. The degradation mechanisms involve: 1. adsorption of PDS on the CuO surface and 2. Adsorbed PDS utilizes CuO as an electron shuttle to oxidize the target organic contaminants. Experimental results demonstrated that the organic contaminants do not need to strongly adsorb on the CuO surface for the reaction to proceed and that the degradation did not proceed in the absence of CuO . The presence of halogen ions did not affect the degradation of 2,4-dichlorophenol and the interference caused by the presence of NOM can be resolved by increasing CuO dosage. The test using real groundwater showed good degradation efficiencies.

[155] 以植物微生物燃料電池技術復育受六價鉻污染土地的研究

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中文摘要

土壤重金屬污染是一個全球性的污染問題，其中六價鉻(Cr(VI))為一種廣泛存在的重金屬污染物，在臺灣的一些土壤污染列管場址就含有Cr(VI)，其毒性及遷移性都遠大於三價鉻(Cr(III))。Cr(VI) 污染的大量存在會對人體健康和生態安全產生潛在的危害，並且是一種致癌物。

微生物燃料電池為一新興的環境生物技術，由微生物和電極系統組成，最近開發出耦合植物及微生物電化學技術的植物微生物燃料電池系統，利用植物根系分泌物，提供根系的微生物包含產電菌作為碳源，促進微生物胞外電子傳遞，結合電極系統，可以收集能源。

本研究計畫之目的在於評估以植物微生物燃料電池技術復育 Cr(VI)污染土壤，提升對 Cr(VI)的去除效果，同時並能產能。目前研究進度，先構建基於蘆葦及狼尾草等植物微生物燃料電池系統，並利用蘆葦與狼尾草對不同濃度的 Cr(VI)污染土壤，分別是 0 mg/kg, 50 mg/kg, 200 mg/kg 與 500 mg/kg 的樣品在溫室進行實驗。透過不同濃度的試驗，以求得最佳處理參數。之後進行機理的探討，植物吸收及微生物電化學系統對 Cr(VI) 在電極上的還原及沉積的協同作用，達到促進 Cr(VI)在土壤中的去除效果及產能。這些參數將有助於我們進行受污染實場的試驗。

由實驗的結果顯示，實驗的土樣經過植物微生物燃料電池的運行，由酸性土壤提升至中性土。土壤導電度也下降超過 100 μ s/cm。土壤六價鉻最大平均的去除率超過 99%。土壤總鉻也是隨著系統的運行逐漸下降。運行過程中，使用石墨碳氈為電極的實驗組在外接 1K Ω 電阻下可在當日平均產生平均 469.21mV 的輸出電壓。應用在實際污染土壤，53 天後，系統可去除 67.07% 的土壤六價鉻，以及產生 64.70mV 的輸

出電壓。

經由實驗結果，可確定植物微生物燃料電池進行去除 Cr(VI)的機制以電化學過程為主。此外，Cr(VI)在系統中的還原作用可沉澱在電極上。去鉻微生物與植物的吸附作用也會有去除 Cr(VI)與總鉻的反應。從直接與間接效應來衡量，不管是處理污染物、無二次污染、綠化、使用太陽能、產生綠色能源與生態保育等觀點，植物微生物燃料電池進行土壤復育具有多功能的作用。

Abstract

Heavy metals contaminated soil is a global pollution problem. Cr(VI) is a widely reported heavy metal contaminant and it has much higher toxicity and mobility than Cr(III). Some regulatory sites in Taiwan contain Cr(VI). Widespread Cr(VI) contamination will pose a serious threat to the health of human and ecosystem. It is also a carcinogen.

The microbial fuel cells (MFC) is an emerging environmental biotechnology. It is composed of microorganisms and electrodes system. When microorganisms metabolize organic pollutants, extracellular electron transfer (EET) to the electrode will occur, and therefore, can simultaneously achieve pollutant treatment and electricity collection.

In this proposal, we intend to evaluate the use of PMFC for bioremediation of Cr(VI)-contaminated soil and also produce energy at the same time. We will build a PMFC based on *Phragmites australis* and *Pennisetum alopecuroides* under different Cr(VI) concentrations samples, 0 mg/kg, 50 mg/kg, 200 mg/kg and 500 mg/kg in the green house. By different concentrations in research, we will evaluate the best treating performance. Furthermore, we will explore mechanisms of PMFC: We will use *Phragmites australis*'s and *Pennisetum alopecuroides*'s ability to uptake Cr(VI)



and also use MFCsystem to reduce Cr(VI) to Cr(III) and precipitate Cr(III) on the electrode. We hope the integrated mechanisms can enhance Cr(VI) removal in contaminated soil and produce energy. The research in this proposal can improve the current knowledge of treatment techniques in Cr(VI) removal, providing useful information in actual Cr(VI) contaminated sites.

According to this experiment, PMFCmakes acid soil to neutral soil. In addition, PMFCcould decreaseelectric conductivity of soil more than $100\mu\text{s}/\text{cm}$. Third, the maximum removal of Cr(VI) in soil is 99%. Moreover, total Cr also is decreased withtime. After 53days, maximum average output voltage of PMFCsystems with graphite carbon felt couldachieve 469.21mV. According to actual contaminated soil experiment, PMFCcould remove 67.07% Cr(VI) in contaminated soil and produce 64.70mV output voltage.

From the results, the major mechanism of Cr(VI) removals is the bioelectrochemical process. In addition, redox reactions in PMFCpromote Cr(VI) precipitate on the electrode. Furthermore, Cr-reducing microorganisms and plant uptake improve Cr(VI) andtotal Cr removals. Finally, from the direct and indirect benefits, PMFCfor soil remediation possess multiple functions: treating pollutants, no secondary pollution, greening, utilizing sunlight energy, generating green energy, and ecological conservation, etc.

[156] 以養份最佳化促進能源作物植生復育重金屬污染土壤效能之研究

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中文摘要

植生復育(Phytoremediation)是利用植物來移除污染物的技術。因此本計畫擬利用本土種植物進行綠色復育試驗研究,以取得現地已污染含有重金屬鎘、鉻、銅的土壤作為植物種植的介質來源,目前規畫以本土常見與具有能源潛力作物,如狼尾草、臺灣藜進行重金屬吸附試驗,待植物收成後除移除,亦可能作為生質能源作物料源來源。

從目前來看狼尾草所獲得的生物量最大,其次為臺灣藜,狼尾草所獲得的生物量為臺灣藜的 3.53-4.28 倍。在以不同養份處理量來看,狼尾草在施加不同比例養份,其生物量將較對照組提升 1.29-2.21 倍。而臺灣藜在施加不同比例養份,其生物量將較對照組提升 1.26-2.28 倍。

而不同養份處理的環境下,狼尾草植體重金屬銅的濃度,對照組為 42.10 mg/kg,隨著養份的增加,重金屬吸收為 68.63~82.19 mg/kg,臺灣藜植體重金屬銅的濃度,對照組為 265.30 mg/kg,隨著養份的增加,重金屬吸收為 337.45~377.64 mg/kg。狼尾草植體重金屬鉻的濃度,對照組為 14.65 mg/kg,隨著養份的增加,重金屬吸收為 38.20~44.36 mg/kg,臺灣藜植體重金屬鉻的濃度,對照組為 41.95 mg/kg,隨著養份的增加,重金屬吸收為 55.20~64.15 mg/kg。狼尾草植體重金屬鎘的濃度,對照組為 2.57mg/kg,隨著養份的增加,重金屬吸收為 3.93~4.81 mg/kg,臺灣藜植體重金屬鎘的濃度,對照組為 13.43 mg/kg,隨著養份的增加,重金屬吸收為 17.27~20.11 mg/kg。

而不同養份添加 EDTA 後的環境下,狼尾草植體重金屬銅的濃度,隨著養份的增加,重金屬吸收為 83.59~127.32 mg/kg,臺灣藜植體重金屬銅的濃度,隨著養份的增加,重金屬吸收為 416.55~447.77 mg/kg。添加 EDSS

後的環境下,狼尾草植體重金屬銅的濃度,隨著養份的增加,重金屬吸收為 78.67~99.26 mg/kg,臺灣藜植體重金屬銅的濃度,隨著養份的增加,重金屬吸收為 351.54~437.79 mg/kg。

而不同養份施用量,對於植體吸收三種重金屬的效果都有上升趨勢,在重金屬鎘的效果較其他兩種重金屬銅及鉻來的較高。雖然對於植體內重金屬濃度效果較不顯著,但因生物量的增加,對於重金屬移除的總量將有助益。另以具有能源潛力的作物進行植生復育,對於環境永續上將具有一定的效益。

Abstract

Phytoremediation is a technique that uses plants to remove contaminants. Therefore, this project plans to use the local plant for green rehabilitation test study to obtain the pollution of the land containing heavy metals cadmium, chromium, copper soil as a medium for plant cultivation, the current planning to local common and energy potential crops, such as Pennisetum, Taiwan Chenopodium for heavy metal adsorption test, after removal of plants, but also as a source of energy for the source of raw materials.

The biomass obtained from Pennisetum was the highest, followed by Taiwan quinoa, and the biomass obtained from Pennisetum was 3.53-4.28 times of Taiwan. In terms of different nutrient treatments, the biomass of Pennisetum was increased by 1.29-2.21 times compared with the control group. While Taiwan's quinoa in the application of different proportions of nutrients, the biomass will be higher than the control group 1.26-2.28 times.

The concentration of heavy metal copper in the control group was 42.10 mg / kg, and the absorption of heavy metals was 68.63 ~ 82.19 mg / kg with the



increase of nutrient content. The contents of heavy metal copper And 265.30 mg / kg in the control group. With the increase of nutrient content, the absorption of heavy metals was 337.45 ~ 377.64 mg / kg. The concentration of heavy metal chromium in the control group was 14.65 mg / kg, with the increase of nutrient content, the absorption of heavy metals was 38.20 ~ 44.36 mg / kg, the concentration of heavy metal chromium in Taiwan quinoa plant was 41.95 mg / kg, with the increase of nutrients, heavy metal absorption of 55.20 ~ 64.15 mg / kg. The concentration of heavy metal cadmium in the control group was 2.57 mg / kg, and the concentration of heavy metal was 3.93 ~ 4.81 mg / kg with the increase of nutrient content. The concentration of heavy metal cadmium in Taiwan quinoa was 13.43 mg / kg, with the increase of nutrients, heavy metal absorption of 17.27 ~ 20.11 mg / kg.

The concentration of heavy metal copper in *Pennisetum americana* was 83.59 ~ 127.32 mg / kg with the increase of nutrient content, and the concentration of heavy metal copper in Taiwan quinoa was increased with the increase of nutrient content. The increase of heavy metal absorption is 416.55 ~ 447.77 mg / kg. In the environment of adding EDDS, the concentration of heavy metal copper in *Pennisetum purpureum* was 78.67 ~ 99.26 mg / kg with the increase of nutrient content. The concentration of heavy metal copper in Taiwan quinoa plant increased with the increase of nutrient, Heavy metal absorption was 351.54 ~ 437.79 mg / kg.

The effect of different nutrient application on the absorption of three heavy metals in the plant is increasing, and the effect of heavy metal cadmium is higher than that of the other two heavy metals. Although the effect on the concentration of heavy metals in the plant is less significant, the total amount of heavy metal removal will be helpful due to the increase in biomass. Another with the potential of energy crops for plant regeneration, for the environment will

have a certain degree of sustainable benefits.

[157] 利用低能耗可見光催化劑進行SVE尾氣之降解

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中文摘要

當土壤受到油氣污染時多以氣體抽除法進行整治，該法為防止土壤氣體污染氣體直接排放進入大氣環境，抽出之氣體經由管線至尾氣處理設備，經光催化處理後排放，以確保排放符合氣體標準，該尾氣處理方式需要添加光觸媒催化劑。因此，本計畫擬發展利用可見光催化劑直接於現場將SVE法尾氣進行催化降解，不需再利用活性碳吸附，由於使用可見光催化劑，因此較一般光催化劑節省能源，可降低尾氣處理之成本。

目前本研究結果顯示在其光催化加濕前處理甲苯則是以1wt% La/TiO₂較佳可降解甲苯氣達32.1%，於濕度60%時30分鐘內1wt% La/ TiO₂塗部於玻璃皿上降解甲苯效果達22.8%，綜合加濕前後來看，La/TiO₂的穩定性比市售光催化來得好。附載不同載體的條件下，玻璃球的失重率低，但玻璃纖維布表面的附著二氧化鈦較為明顯，進而使用玻璃球與玻璃纖維布做降解甲苯速率之測試，在紫外光UVA(波長320~400nm)條件下，測試結果顯示玻璃球之最佳速率為15%，反觀三片光催化玻璃纖維布可達94.84%，在可見光條件下，光催化玻璃球則無效果，光催化玻璃纖維布可達54.32%，綜合上述濕度及載體條件，採用環境濕度60及3片1 wt% La/TiO₂塗佈於玻璃纖維布置於本研究開發光催化模組。

另在成本分析的觀點上，本研究所合成之鑷摻雜二氧化鈦前驅物平均每毫升的成本約為3.76元；商業型二氧化鈦-P25每克僅需5.8元，而製作單片光催化載體約為625.85元。雖然本研究所製備之材料比起商業型二氧化鈦價差約107倍，無論在紫外光或是可見光的條件下，甲苯的降解效果著實比商業型二氧化鈦更佳，且塗佈於玻纖布將能大幅提升光催化的降解效率，本研究結果

顯示可降低處理SVE尾氣之成本。

Abstract

Soil vapour extraction (SVE) is the most frequently used technology, being applied in the remediation of groundwater contaminated by petroleum hydrocarbon. In order to prevent the emission of contaminated gas, volatile pollutants and gas were adsorbed by activated carbon at tail gas treatment unit before their release in the atmosphere. In this study, we propose a low cost and no sophisticated processing method for treating vapor extraction tail gas by utilizing visible light-induced photocatalyst. In first half year, the BTEX removal efficiency will be evaluated to determine the photocatalyst with the best performance. In the following half year, the novel hollow fiber module will be developed and also evaluated the performance in treating the SVE tail gas in the contaminated site operated by Sinotech Environmental Technology, Ltd. (STEL)

Two kinds of substrate including glass ball and glass fiber cloth were employed to load La-doped TiO₂ photocatalysts. It was found that the degradation efficiency of toluene for glass fiber cloth can reach up to 94.84% under UV light (320~400nm), which is much higher than that of glass ball (15%). Moreover, the degradation efficiency of toluene for glass fiber cloth can reach up to 54.32% under visible light. However, glass balls loaded La-doped TiO₂ have no any photocatalytic performance to remove toluene. According the above experimental results, the operating conditions including 60% RH and glass fiber cloth loaded 1 wt% La-doped TiO₂ are applied to develop the photocatalytic module for degradation of toluene. The result showed that photocatalytic removal efficiency of toluene could reach up to 94.84%. The rate is low, but the



adhesion and titanium dioxide on the surface of the glass fiber cloth is more obvious, and then use the glass ball with glass fiber cloth to do test of degradation rate of toluene.

In addition, the preparation cost of photocatalytic module was also calculated. In details, the average cost for per milliliter of the raw chemicals is about 3.76 NTC per milliliter. However, commercial P25 costs only 5.8 NTC per gram. After assembling module with glass fiber cloth loaded 1 wt%La-doped TiO_2 , the photocatalytic performance can be enhanced drastically. This study will provide a promising and significant approach to remediate soil exhaust through SVE.

[158] 利用層狀複合金屬氫氧化物即時合成特性去除地下水中

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中文摘要

在過去地下水中的鉻酸鹽一直無法找到適當的現地處理方法，因此大部分地下水中鉻酸鹽是以抽出處理的方式將污染物去除，但抽出處理需耗費高處理成本，因此在本研究中期望發展出一種成本低且可以現地處理地下水中鉻酸鹽的技術。層狀複合金屬氫氧化物一種新興的材料，在過去較少被用於吸附污染，但其具有表面帶正電的特性，因此可有效吸附陰離子污染物，且合成之成本遠較陰離子交換樹脂便宜。除此之外，層狀複合金屬氫氧化物尚具備即時合成與記憶效應等特性，可以被應用於現地處理地下水中之鉻酸鹽，因此本計畫中將以此為基礎發展出現地處理地下水中鉻酸鹽之方法，同時測試吸附後鉻酸鹽在不同條件下的脫附狀況。

層狀複合金屬氫氧化物的主要成分為二價與三價金屬離子以及陰離子，在本研究中考慮使用常見的 Mg^{2+} 與 Al^{3+} 為陽離子金屬， NO_3^- 、 CO_3^{2-} 或 Cl^- 做為可能測試之陰離子，利用即時合成之特性，在控制不同的溶液pH值下，將 Mg^{2+} 與 Al^{3+} 配置莫耳比3:1之濃度配合陰離子加入溶液中與不同濃度之鉻酸鹽混合，測試在不同時間下鉻酸鹽濃度變化，計算出吸附速率與最大吸附量。對於記憶效應方面，先以水熱合成法製作出層狀複合金屬氫氧化物，再將合成材料放在不同溫度下鍛燒，冷卻後將產品與鉻酸鹽混合攪拌，在不同時間下測定鉻酸鹽濃度變化，同樣計算出吸附速率與最大吸附容量。脫附實驗則是將已吸附鉻酸鹽之材料加入土壤與水混合系統，並於不同pH下進行脫附實驗，觀察脫附狀況，最後評估此方法在現場應用之可行性。

本研究目前所獲得的結果顯示，由XRD圖譜顯示以有效合成LDHs，且在

表面性質分析中可以證實記憶效應的存在，LDHs由於表面帶正電荷可以吸附水中帶負電的鉻酸鹽，未鍛燒的LDHs對鉻酸鹽的最大吸附量可達192 mg/L，鍛燒後LDHs之吸附量超過308mg/g，即時合成對高濃度鉻酸鹽去除率可達70%，溶液的pH值增加將使鉻酸鹽去除效率增加，LDHs對於鉻酸鹽的吸附量已接近離子交換樹脂，但成本卻遠低於離子交換樹脂，除此之外，經過脫附實驗後顯示，吸附於LDHs之鉻酸鹽不易被脫附，因此可考慮應用於實場。

Abstract

In the past years, the most common method for chromate remediation in groundwater was the pump-and-treat process. The process is high cost in operation. Thus, the objective of this study is to develop a new method with low operation cost to remove chromate in groundwater in situ. The Mg-Al layered double hydroxides (LDHs) is a new adsorbent in the recent years. The LDHs with exchangeable anions can effectively adsorb chromate in the groundwater. The operation cost for LDHs is quite lower than that for anion exchange resin. In addition, the characteristics of LDHs possessing structural memory and synthesized in situ facilitate removing chromate in groundwater in-situ. The LDHs are intended to apply in adsorbing chromate in groundwater. Moreover, the desorption for chromate adsorption on LDHs under various environmental conditions are also investigated.

The LDHs consist of metal ions with two and three valence electrons, and anions including NO_3^- 、 CO_3^{2-} or Cl^- . In this study, Mg^{2+} and Al^{3+} with molar ratio 3:1 and anions are added to solution containing chromate under the various pH



values to synthesize LDHs. The adsorption rates and adsorption amounts for chromate are evaluated. For the structural memory effect, the LDHs can be synthesized using hydrothermal method, and then calcine them under different temperatures. The calcined LDHs mixed with chromate solution. The changes in chromate concentration in given period are analyzed. The adsorption rates and adsorption amounts for chromate can be estimated in the process. For the desorption experiments, the LDHs adsorbing chromate are added in a soilwater system. The pH values of solutions are controlled ranged from 5 to 9. The released amounts of chromate from adsorbents can be measured.

The obtained results indicated that LDHs with positive charge could adsorb chromate in the solution. The structural memory LDHs can be demonstrated using XRD patterns. The maximum adsorption capacity of chromate on LDHs is 192 mg/g. The adsorption amount of chromate in the structural memory experiment is more than 291 mg/g. LDHs synthesized in situ to remove chromate in the solution generated 70% of removal efficiency. The removal efficiency increased with the increasing pH of solution. According to cost and desorption, LDHs can be applied to remove dichromate in groundwater.

[159] 受戴奧辛及汞污染底泥之生態風險評估-以安順場址為例

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中文摘要

戴奧辛及汞係難分解且高毒性之持久性有機污染物，對於生態環境與人體健康危害甚鉅。本計畫針對臺灣台南前台鹼安順廠已關廠之鹼氣與五氯酚工廠，擇其海水貯水池中的底泥進行生態風險評估，及建置概念性場址模型，使風險評估者或其他利害關係人能夠更深入瞭解本案場。

本計畫之風險評估系統，係篩選自美國、加拿大、英國與澳洲等各國針對其污染場址所訂定之生態風險評估指引，賴以建立本計畫使用之生態風險評估架構。首先，先進行安順污染場址的資料蒐集與補充調查，再將資料彙整歸類，以建置安順場址之概念性場址模型及污染傳輸路徑圖。

本計畫團隊目前蒐集資料，包含：SCI 國際期刊論文、美國環保署 (USEPA)、英國環境署 (Environment Agency)、加拿大環境部長理事會 (Canadian Council of Ministers of the Environment)、澳洲環保議會 (National Environment Protection Council)、Contaminated Site Clean-Up Information (CLU-IN)、美國材料與試驗協會 (American Society for Testing and Materials, ASTM)、我國環保署專案計畫，以及國內論文期刊等資料庫之文章、技術報告、指引等共 325 篇文獻，經歸納後決定專注於 USEPA、ASTM 及重點國際期刊論文等相關指引；尤其是美國環保署 (1998) 「Guidelines for Ecological Risk Assessment」及特別針對超級基金場址提出一套評估指引「Ecological Risk Assessment Guidance for Superfund: Process for Designing and Conducting Ecological Risk Assessments」。

本團隊已針對底泥污染與評估終點進行本場址初步生態風險評估的計算(以民國 99 年調查計畫報告之底泥及魚蝦蟹數據為基準)，且進行定性定量

之探討，評估項目包含：污染程度校正值 (modified degree of contamination, mCd)、污染指數 (pollution index, PI)、地質累積指數 (geoaccumulation index, I-geo)、潛在生態風險指數 (potential ecological risk index, RI)、風險商數 (risk quotient, RQ) 以及生物濃縮因子 (bioconcentration factor, BCF) 等等。

評估結果顯示，由污染程度校正值 (mCd)、污染指數 (PI) 可知，在算術平均值之結果分別為 40.44 及 56.01，均屬於最高等級的污染程度。然而，在幾何平均值的計算下，mCd 為 8.10，屬於分類等級 4 的污染程度，但 PI 為 11.23 仍大於 PI 指標之上限值。因此，整體而言，海水貯水池的底泥污染仍是屬於最高等級之污染程度。另一用於評估底泥中重金屬(汞)污染之地質累積指數 (I-geo) 計算之結果顯示，在算術平均值計算下，I-geo 值為 5.50 屬於最高等級 6 的極度污染；而在幾何平均值計算下，其結果為 3.19 屬於等級 4 的嚴重污染；因此可知，底泥中汞之污染仍屬高污染。再者，由潛在生態風險指數 (RI) 與風險商數 (RQ) 初步計算之結果，在算術平均下，戴奧辛及汞之 RI 分別為 958.25 和 2724.18，均屬於最高等級的非常高風險；而在幾何平均下，汞之 RI 為 546.42 係屬於 300 至 600 之間的較高風險，戴奧辛之 RI 則較低為 190.67 係介於 150 至 300 之間的中度風險 (moderate risk)。對於 RQ 而言，分別在算術平均與幾何平均值下之結果為，汞分別為 1481.27 和 297.12，而戴奧辛分別為 1025.14 和 203.98；其不論是算術平均或幾何平均之戴奧辛及汞，計算出來的 RQ 均是大於 1；因此，顯示海水貯水池之底泥中戴奧辛及汞，對於水生生態環境所造成的風險很高。

而生存在海水貯水池中的水生生物種類其生物濃縮因子 (BCF) 顯示戴奧辛具有非常高之生物濃縮潛勢；整體魚



蟹中戴奧辛之 BCF 值(2.70E+3 至 1.09E+5)較汞的 BCF 值(25.33 至 189.67)高出數百倍，且戴奧辛的 BCF 均超過指標之最高上限值 5000，表示對於生物種而言戴奧辛為非常生物累積；而汞在生物體中積累的潛勢相對較低，因此，相較於戴奧辛，汞則屬於較低之生物濃縮潛勢；而水生魚蟹中則以海鱧體內的戴奧辛及汞之 BCF 最高；其次為紅帶海鯉、大鱗梭與鋸齒青蟬等。綜合而言，安順場址內海水貯水池之底泥，其各別受戴奧辛及汞污染程度與潛在風險都屬於最高等級。

本計畫由前述 5 個底泥風險評估計算因子推估案場海水貯水池之底泥整治目標，結果顯示，底泥可接受之戴奧辛濃度介於 0.85 至 136.40 ng-TEQ/kg 之間；而底泥中可接受之汞濃度則介於 0.02 至 3.26 mg/kg 之間；前述 5 項底泥風險評估指標中，又以 RQ 及 PI 兩指標影響最巨。對於水生生物體可被接受之風險而言，僅有 BCF 一項指標可為參考；依據 BCF 反推所得之生物體可接受之戴奧辛濃度為 2 ng-TEQ/kg，而生物體中可接受之汞濃度則為 30 mg/kg。

綜合結果顯示，分布於工廠排水口處及往鹿耳門溪出海處這兩處之底泥，具有高濃度之戴奧辛及汞污染，因此，可優先對此區域加密調查且進行工程控制或整治技術評估；對於海水池中水生生物而言，雖然其體內汞濃度均在標準之內，但是其體內戴奧辛濃度仍具相當風險，因此建議該採取行政禁制或工程方面之防治行動，以控制污染的擴散及避免再次危害至人體與環境。綜合而言，本計畫提供相關風險管理及整治技術建議，可採行風險基準矯正行動，包含行政禁制、工程控制及整治技術等等。其中，行政禁制方案包含：場址周邊設置圍籬，並架設監視系統監控，禁止捕獵並張貼公告，撲殺焚化受污染魚蟹等等；工程控制方案包含：設置圍堤避免陸域污染土壤進入水域，且關斷海水閘門，進行底泥濬泥作業，並設置廢水淨

水廠，處理抽出污染底泥之廢水等等。整治技術方案可採行美國環境保護署提出之底泥整治建議，其技術包含：不採取行動、現地整治、監測式自然復育、現地封蓋及疏濬或挖掘等等整治技術方案；此外，亦可以擷取各整治技術之優勢並相互補足其缺失，使用複合式整治技術進行整治，以有效提高去除率且降低各區域之潛在風險及整治成本。

後續，若進一步深入執行本場址海水池底泥整治目標之評估，建議應進行更準確的生態風險估算及健康風險評估，且持續評估戴奧辛及汞在水和底泥中的形態及傳輸機制，使海水池的風險評估更具代表性。以風險結果推算其合適之整治目標，再對於技術可行性及經濟可行性進行細部評估，以訂定更詳細之風險管理規劃及對策，且執行最佳風險基準矯治行動，以達到整治目標及早日解除場址管制之總體效益。

Abstract

On July 20, 2011, Taiwan-EPA posted The Technical Guideline of Health Risk Assessment for the Environmental Protection in Taiwan. However, the Health Risk Assessment Guideline fell short of providing the Ecological Risk Assessment methodology. In order to enhance our health risk assessment protocol, the Project Team had researched the ecological risk assessment tools and methodologies from countries that had advanced experience in ecological risk assessments, including United States, Canada, England and Australia. The Project Team integrated the selected tools and methodologies into a tool and methodology that are more suitable for us in Taiwan. The integrated tool and methodology were tested through assessing the ecological risk at the An-Shun Site to establish the CSM and the frame work for our ecological risk assessment in Taiwan. Based on the results from refinement processes of the tool and methodology, the Project Team has reached the project goals for developing

our own ecological risk assessment tool and protocol. The ecological risk assessment results will also be used for risk communication before the risk based site remedial actions can be proposed.

Guidelines for site ecological risk assessment from the United States, England, Canada, and Australia were the basis for developing the risk assessment system for this project. The risk assessment system provided the framework for future ecological risk assessment. In order to refine the ecological risk assessment system, the Project Team started with collecting site information from the An-Shun facility and conducting additional site investigation to fill the information gaps. All the relevant information and site previous and current conditions were organized and built into a database with different categories in supporting the ecological risk assessment. Upon the completion of data and information collection, the Project Team established the physical model of the An-Shun site. The transfer paths of chemical of concerns (COCs) and potential risk exposure routes were identified for the ecological risk assessment at the site.

In addition to the guidelines for ecological risk assessment from various countries, the Project Team had collected and reviewed over 325 relevant documents including:

- SCI journal articles,
- Technical reports from USEPA, Environment Agency of England, Canadian Council of Ministers of the Environment, National Environment Protection Council of Australia, Contaminated Site Clean-Up Information (CLU-IN), and American Society for Testing and Materials (ASTM),
- Taiwan EPA's research project reports,
- Journal articles published in Taiwan, and
- Technical reports, dissertations and research

After completing the literature review phase of the project, the Project Team would propose to focus on the

methodologies provided by USEPA and ASTM especially from the "Guidelines for Ecological Risk Assessment, 1998" and "Ecological Risk Assessment Guidance for Superfund: Process for Designing and Conducting Ecological Risk Assessments." Regarding the risk assessment of the key COCs at the An-Shun site, literatures for Mercury were relatively more than the literatures for Dioxins. With limited ecological risk assessment for Dioxins, the Project Team focused on the knowledge provided by professor Antonio Marcomin of the University Ca' Foscari of Venice in Italy. Future research topics and suggestions to overcome the limitation in the area Dioxins' risk assessment are also suggested in this final project report.

As of today, the Project Team has completed the estimations of the risk posted by the COCs in sediments of the An-Shun site according to the above mentioned sediments and bio-tissues collected in 2000. These calculation include:

- Modified degree of contamination, mCd,
- Pollution index, PI,
- Geoaccumulation index, I-geo,
- Potential ecological risk index, RI,
- Risk quotient, RQ, and
- Bioconcentration factor, BCF.

The preliminary results from mCd, PI, and I-geo indicated that the elevated Dioxins and Mercury concentrations in sediment of the An-Shun site posted high risk for biological receivers. The preliminary results for RI and RQ also showed the high risk of the ecological system at the site from the Dioxins and Mercury in the sediments of both saltwater basins. Based on the calculations of BCF for both Dioxins and Mercury, it appeared that Dioxins had very high potential of bioaccumulation than the Mercury. Among the all bio-receivers, the *Elops machnata* had the highest BCF. Detailed discussion of all the qualitative and quantitative assessment are presented in the main text of this report.

In summary, the Dioxins and Mercury in sediments in sea water basins



of the An-Shun site posted very high risk for bio-receivers and the ecological system. The combined impact of the Dioxins and Mercury has not yet been assessed. More updated assessments as required by the Tier II and or Tier III (if necessary) are warranted, and should base on the most updated sediments and bio-tissues data. Finally, the Project Team has provided suggestions and recommendations for the site correction measures.

[160] 河川底泥金屬生物有效性的評估方法

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中文摘要

臺灣溪流環境水流湍急，造成棲地環境物化特性的快速變動，許多污染物被沖刷而蓄積在水體底層表面。底泥為許多底棲生物棲息之場所，亦為流水體潛在污染來源，其中有許多包括物化交互作用、硫化物和生物等因子都會影響污染物的生物可利用性。本研究將嘗試結合化學評估和生物毒性測試來預測底泥和孔隙水中金屬的生物可利用性。除了利用會影響平衡分配的酸揮發性硫化物及同時提取金屬分析判斷臺灣南部武洛溪及牛稠溪之底泥金屬生物毒性，主要目的還希望能探討不同萃取模式(全量金屬及稀釋酸萃取)及擴散梯度薄膜裝置等多面向來判斷底泥金屬之生物可利用性，並搭配底棲端足蟲 *Hyalella azteca* (10天及28天全底泥急慢性及48小時孔隙水毒性)試驗進行水生生態系統危害程度(Tiers evaluations)評估，另外也利用潛在生態風險指數(potential risk index)來判斷各樣站底泥金屬在不同季節之風險等級。

本研究透過底泥基本物化性質可得知牛稠溪以砂粒為主，而武洛溪則以粉粒比例較高。總有機碳介於0.38%~4.27%，其中以樣站N₂最低，樣站WR4最高。利用不同底泥品質指標(臺灣底泥品質指標上下限值、TEL/PEL、共識法底泥品質基準)判斷底泥污染程度之結果顯示，武洛溪高於上限值之比例大於牛稠溪，其中又以武洛溪W4高於三種指標上限值，及污染最為嚴重。以平衡模式法進行評估結果顯示，武洛溪W4經三種指標(以 $\Sigma\text{SEM}/\text{AVS} > 9$ 、 $\Sigma\text{SEM}-\text{AVS} > 2\mu\text{mol/g}$ 及 $\Sigma\text{SEM}-\text{AVS}/\text{foc} > 130\mu\text{mol/g}$)，底泥金屬含量皆會對水生生物及人體健康造成不利影響，為本研究底泥金屬毒性最高之樣站；而底泥金屬影響程度最低樣站為N₅及W₂，在三種指標均未超過閾值。擴散梯度薄膜技術結果顯示，放置現地96h之

DGT 與實驗室之吸附具有顯著相關。序列萃取搭配RAC計算之結果顯示武洛溪(W₁~W₅)樣站無風險或低風險之比例介於62.5(W₂)~87.5%(W₃)；其中以金屬Mn評估之風險值最高。牛稠溪流流域之風險比例介於為50.0~87.5%，以Mn及Zn產生之風險值最高。潛在生態危害風險指數評估結果顯示，單一及多重底泥金屬污染評估結果均顯示武洛溪較牛稠溪相對污染嚴重之流域。

全底泥毒性試驗急毒性顯果顯示，以W₁存活最佳，枯水期N₃、N₄及W₃與豐水期於試驗終點並未觀察到任何存活個體；慢毒性試驗結果顯示樣品暴露之個體體長及重量均低於控制組，且藉由統計分析結果顯示均具有顯著性差異，顯示樣站污染物對生物體體長與體重均具有明顯抑制效應。孔隙水急慢性試驗結果顯示，武洛溪各樣站平均存活率低於牛稠溪，顯示因雨量或地區變化所存在溶解性污染物對底棲無脊椎動物具急毒性效應。

根據統計分析結果顯示，Cu濃度對於底泥慢毒性試驗之成長效應(體長)具有顯著性相關($p < 0.05$)；重量則與孔隙水中Cd、Co、Cu及Ni濃度具有顯著性相關($p < 0.05$)，顯示生物體長時間暴露於溶解性污染物儘管並未直接產生生物死亡，但可能抑制其成長。此外，根據DGT濃度與生物體累積之金屬濃度進行線性迴歸結果顯示，吸附於DGT之Cu與Mn金屬與端足蟲生物體累積濃度呈正相關。

綜合各種以化學為基礎的潛在金屬生物利用性預測生物毒性之能力差異很大。並沒有一種方法足以完全預測其生物毒性，但初估能力排序依序為DGT>全量消化(總金屬濃度)>孔隙水>序列萃取>稀釋酸>SEM-AVS模式。本研究數據未來能提供底泥金屬污染生物有效性評估，其對管理者在品質準則施行及風險定量上是非常重要的。



Abstract

Sediment not only provides habitat for benthic organisms, it is also a potential source of contamination of streams and therefore has a significant influence on the aquatic environment. Many contaminants are washed into and stored in bottom waters and subsequently change the physical and chemical characteristics of the habitat. Sediments are complex, within which many processes (physical/chemical interactions, acid volatile sulfide [AVS] interaction, and biological) occur that affect contaminant bioavailability.

A combination of chemical assessment and biological toxicity testing was conducted to predict the toxicity of metals in sediments or pore water. Equilibrium partitioning models using AVS were applied simultaneously with extracted metals analyses to evaluate the bioavailability of sediment metals that exhibit toxic effects from the Niuchou and Wuluo Rivers. Their bioavailabilities were compared in multiple approaches to determine which DGT-metal fluxes were useful for predicting the acute and chronic toxicities of multiple metals in selected sediments. That acid extracting metal (AEM) measurements provide more information on labile and biologically available sediment phases also remains unclear. Therefore, their toxic effects were evaluated using the amphipod *Hyaella azteca* (10-day and 28-day for whole sediments and 96-hr for pore waters) to assess their hazard (Tier 1, Tier 2, and Tier 3) to aquatic ecosystems. The potential risk index was applied to clarify the degree of ecological risk in the tested sediments.

In this study, a basic physico-chemical assessment showed that sediments in the Niuchou River were mainly composed of sand while in the Wuluo River consisted of a higher proportion of silt. Total organic carbon ranged from 0.38% to 4.27%, with the lowest found at site N2 and the highest at site WR5. The degree of contamination,

based on different sediment quality indicators (Taiwan sediment quality guidelines, TEL / PEL, CBSQGs), indicated that metals in sediments exceeded upper guideline limits more often in the Wuluo River than in the Niuchou River. Among sampling sites, W4 in Wuluo exceeded all three guideline limits, which indicated more serious pollution. Three indicators ($\Sigma\text{SEM} / \text{AVS} > 9$, $\Sigma\text{SEM} - \text{AVS} > 2 \mu\text{mol/g}$, and $\Sigma\text{SEM} - \text{AVS} / \text{foc} > 130 \mu\text{mol/g}$) implied that metals in W4 sediments exerted the highest toxicity and therefore had the greatest adverse impacts on aquatic life. The lowest impacts from metals were at sites N5 and W2, and did not exceed all three indicators. Our results showed that diffusion gradient thin films (DGT) under a 96-hr in situ field exposure were significantly correlated with adsorbed mass in laboratory tests. A combination of the sequence extraction technique and risk assessment code calculation (RAC) showed that the risk in the Wuluo River was in the range of 62.5 (W2) ~ 87.5% (W3) and the highest risk was from Mn. The risk for the Niuchou River was between 50.0 ~ 87.5%, with higher risk values being found for Mn and Zn. The potential ecological risk index showed that serious sediment contamination in the Wuluo River was from either single or multiple sediment indicators.

Whole sediment acute toxicity tests showed that survival at site N1 was highest and that there were no survivors at sites N3, N4, and W3 by the end of the trial. Chronic toxicity testing showed that the growth (body length and weight) of *H. azteca* was lower than in controls and that there were statistically significant differences among samples, indicating that the contaminants had significant inhibitory effect on growth. Average survival (pore water) in the Wuluo River was lower than in the Niuchou River, indicating that the presence of dissolved contaminants may have acute effects on benthic invertebrates.

Cu concentration was significantly

correlated ($p < 0.05$) with the growth (body length) of exposed biota in sediment toxicity tests. Body weights were significantly correlated with Cd, Co, Cu, and Ni concentrations in porewater ($p < 0.05$), indicating that dissolved contaminants over extended periods of time may inhibit growth but not cause death directly. In addition, this relationship was observed for DGT measurements of Cu and Mn accumulating in *H. azteca*.

In summary, the ability of different chemistry-based measures to predict potential metal bioavailability to *H. azteca* varied considerably. None of the methods appeared to be particularly precise; however, our preliminary conclusion is that they followed the descending order of DGT > total metal concentrations > porewater concentration > sequential extraction > dilution acid concentration > SEM-AVS mode. Useful information could be provided to regulators when using this contamination evaluation during the process of quantifying risk and implementing related guidelines.



[161] 建立微流道平台以快篩底泥重金屬污染的細胞毒性效應

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中文摘要

隨著工業及經濟蓬勃發展，環境中污染源增加且複雜化，透過食物鏈影響著生態系及人體健康。許多重金屬會被吸附或成為低溶解度之樣態累積於底泥中，微生物、底棲動物、魚類均可能經由暴露或攝食行為，將重金屬累積於體內而產生毒性反應。底泥作為環境最終受體，是眾多污染物(如芳香烴有機化合物、重金屬及農藥等)之蓄積庫，因此，評估底泥污染物之生物有效性及危害效應，為國內外極其重要之環境污染監測與防治議題。

水環境中重金屬存在樣態、氧化還原電位、酸鹼值及含氧量多寡、金屬及有機物間之親和性及底泥礦物組成等，均會影響底泥重金屬之生物有效性及毒害效應。然而，目前重金屬檢測多於環境中採樣後，經由一連串前處理過程再行分析，而如何快速、精準且即時偵測現地環境中重金屬濃度及對生物之毒性，是未來各式儀器方法與生物毒性評估發展之方向。

生物毒性評估可以老鼠、魚類、線蟲、細菌或細胞株等作為模式生物。老鼠之研究模式及方法學已十分成熟，可應用於多數生物毒理試驗；魚類優勢在於能與水體或底泥接觸，直接或間接暴露污染源，且能獲得污染物於生長發育、畸形或器官損傷等毒性反應資訊；細菌培養容易且快速，能以基因轉殖之方式放入報導基因(如螢光或冷光基因)，並以報導基因之表現量即時偵測環境中特定污染物之濃度；細胞株則多分離自哺乳動物(多為人、大鼠或小鼠)，且有不同器官(如肝臟、腎臟、肺臟及結腸等)來源之細胞株，可快速偵測污染物對高等生物及不同器官之毒性效應。

傳統細胞株多以靜態培養之方式

培養於培養皿中，然而，大多數細胞在生物體內應處於有體液或血液循環之狀態下，本計畫研究團隊先前研究發現，細胞在前述兩種不同培養狀態下對環境刺激之反應不盡相同(Lo et al., 2013)。因此，本計畫將以微流道晶片平台模擬生物體內流體環境，建立評估環境中重金屬生物毒性評估之平台。並將進一步自人造底泥萃取表層水及孔隙水，並以該平台評估重金屬在不同環境基質下之生物毒性與暴露濃度間之相關性。本計畫建置之方法與策略，可快速且有效地預測底泥重金屬經由不同途徑進入人體後之生物有效性及危害潛勢，研究成果將可協助提供環保署在底泥品質管理或污染危害風險方面之參考數據，或針對現行方法不足之處提供相關修正建議。

Abstract

The contaminants are increasing and the varieties become more complicated in the environment along the development of industry and economics. The contaminants impact eco-system and human health via food chain. Many heavy metals are absorbed or precipitate in the sediments. Microorganisms, benthic animals, and fish, are likely to accumulate heavy metals in the body from direct exposure or feeding behavior, resulting in toxicity. Sediments are the reservoir of many contaminants, i.e. heavy metals. Therefore, evaluation of the bioavailability and toxicity of sediments is an important issue.

Many instruments and methods are developed for fast, accurate, and timely detection of the concentrations of heavy metals in the environment. However, different valence number and complex form of metals, pH and oxygen content of water, different affinity between metals and organic matters, and mineral

compositions of sediments, all make metals become different degrees of toxicity to organisms. Therefore, it is necessary to develop methods for fast and accurate eco-toxicological assessment of soil contaminated with heavy metals. Many organisms, including mouse/rat, fish, nematode, bacteria, and cell lines, are used for toxicological assessments. The advantages are listed below. The study models and methods of mouse/rat are developed and the whole genome sequence is known. Besides, many mutants could be applied in the study. Fish could expose directly to the contaminants since it is grown in the water and contacts sediments directly. The further information from how the toxins affect the growth, development, or organ damage could be obtained. Bacteria are easy to be cultured. The reporter genes could be transformed into bacteria for monitoring the concentrations of toxins. Most cell lines are isolated from mammals, and obtained from different organ sources, including liver, colon, nerve, lung and etc. Therefore, cell lines could be used to study how toxins damage the organs of higher mammals. Most importantly, the readout is very fast.

Cells are usually cultured in the dish in vitro. However, cells in vivo are in the environment circulating with body fluid or blood. In our previous study, we found cells responded differently to environmental stimuli in two culture conditions (Lo et al., 2013). In this proposal, we will develop a microfluidic chip to mimic in vivo environment and evaluate the cytotoxicity of heavy metals under this condition. Further, we will correlate the cytotoxicity and metal concentrations extracted from the formulated sediments. The establishment of this method can evaluate how the contaminants will damages to human being quickly. The results derived from this project will provide the data for the Environmental Protection Administration for evaluation about sediments quality or regulation of pollution hazard risks in the

future.



[162] 研發光觸媒覆膜材料以提高光纖光催化處理地下水中 三氯乙烯之應用性

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中文摘要

本研究研發覆膜液作為光纖表面與光觸媒之結合媒介，探討不同覆鍍模式及配方對光傳輸距離及側光光強度、反射率及穿透率變化、光纖表面覆鍍觸媒分佈性與結構性、光纖光降解及光催化效率、並以最佳配方進行不同光照強度之光催化效率探討，以及後續光催化產生氫氧自由基效率評估與COFB透水性反應牆之土壤砂箱試驗。本研究規劃主要以聚乙烯醇(Polyvinyl alcohol, PVA)、無機樹脂、氟樹脂3種覆膜液種類作為覆膜基底，並以覆膜基底與稀釋劑不同比例進行試驗，探討不同基底/稀釋劑-水比例，分別為25:75與50:50，後續再添加PTFE溶液(20、40、80 mL/L)，混和攪拌均勻後，即為光纖外層之覆膜材料。

研究首先以PVA膠體進行不同PTFE添加劑量與稀釋比例試驗，研究結果顯示，添加PTFE溶液確實會提升光源於光纖內部傳輸之反射率，並且經過不同PVA與水之摻雜比例，將會得到不同的每段光照強度，這也證明膠體物質較高的情況下，附著於光纖上之PTFE含量將會相對增加。但由後續光降解的實驗結果得知，當在50:50摻雜比例條件下，添加較高劑量的PTFE溶液，將會不利於光源傳輸，導致光纖後端之TCE去除效率較低。因此，在SEM&EDS儀器分析方面，藉由分層與混合支覆鍍模式，探討光纖表面觸媒分佈性與元素含量百分比，研究結果得知，隨著觸媒及PTFE摻雜比例提升，將有助於觸媒覆鍍於光纖表面含量增加，光纖表面所佔之Ti及F元素比例隨著添加量增加而相對提升。而分層與混合覆鍍結果可以發現，分層覆鍍可使觸媒達到較均勻的分佈性。研究再進一步以不同覆鍍模式、不同覆膜液種類、以及不同

覆膜液觸媒添加劑量條件下，實驗結果得知，以分層覆鍍之無機樹脂，稀釋比例25:75以及0.5 wt% TiO₂會得到最佳光源延伸性，可有效地將光源延伸至6-8 cm。另一方面，在穿透率與反射率試驗也有相同結果，當觸媒添加劑量由0.5增加至5 wt%將不利於光源傳輸。

在光纖光降解與光催化效果方面，研究以不同覆膜液種類與配方進行TCE去除效率之探討，實驗結果得知，以新穎覆膜液進行光纖覆鍍，確實可有效提升光催化效率，而覆膜配方以分層較混合為佳。另一方面，在不同覆膜液稀釋比例方面，以25:75覆膜比例，並以分層的覆膜方式進行光催化處理效率最佳，其中以無機樹脂覆膜液光催化效果優於其他2種覆膜液。在不同光照強度方面，若增加光照強度確實可有效提升光源傳輸距離，並增加光纖光催化之距離。

實驗最後以最佳覆膜條件進行COFB透水性反應牆之砂箱試驗，結果顯示，TCE與TOC之去除效率會隨著經過COFB處理而提升，並且氯離子(Cl⁻)生成將隨著TCE之去除率提高而增加，此實驗結果也再次證明光催化將更有效的將TCE降解為最終產物。本研究並進行初步之處理成本效益評估。

Abstract

In this study, the coating liquid was used as the bonding medium between optical fiber's surface and photocatalysts. The effects of different coating methods and formula on the light transmission distance and side light intensity, reflectivity and transmittance of optical fibers were discussed. The photodegradation and photocatalytic efficiency of the optical fiber were studied, and the photocatalytic efficiency of

different light intensities was discussed with the best formulation, as well as the evaluation of the free radicals formation and the soil sandbox test with COFB permeable reaction wall. In this study, three kinds of plastic film types, such as polyvinyl alcohol (PVA), inorganic resin and fluororesin, were used as the coating substrate. The different substrates/diluents were tested with different ratio of film base and diluent-water ratio of 25:75 and 50:50, respectively, followed by the addition of PTFE solution (20,40,80 mL/L), after stirring evenly, which were used as the coating material for photocatalyst coated fiber preparation.

The results show that the addition of PTFE solution does improve the reflectivity of the light source in the fiber, and after different PVA and water doping ratios. Study of applying different light intensities show that higher concentration of colloidal substances attached to fiber on the PTFE content resulted in higher light intensity transmission. However, it was found that the addition of higher dose of PTFE solution at 50:50 doping ratio would be detrimental to the light source transmission, resulting in lower efficiency of TCE removal at the end of the fiber. Therefore, in the SEM & EDS analyses, the distribution of photocatalysts on the surface of optical fibers and the percentages of the elements' content were discussed by the stratified and mixed support platings. The results show that with the increase of photocatalyst and PTFE doping ratio, the contents of Ti and F on the surface of the optical fibers increased with the increase of the amount of the photocatalysts. Comparing with stratified and mixed coating, it was found that layered coating achieved a more uniform distribution of photocatalysts. The experimental results also show that with the inorganic resin, the dilution ratio of 25:75 and the content of 0.5 wt% TiO_2 of the inorganic resin with different coating conditions, different coating types, different coating liquid types and different coating liquid catalyst,

got the best light source extensibility and effectively extended the light source up to 8 cm. On the other hand, the same results were obtained for the transmittance and reflectance test. The photocatalyst additive dose increased from 0.5 to 5 wt% would be detrimental to the light source transmission.

In the aspect of fiber photodegradation and photocatalytic effects, the removal efficiency of TCE was studied with different coating types and formulations. The experimental results show that the photocatalytic efficiency can be improved by using the new coating liquid. The coating formulation is preferably mixed with layers. On the other hand, in the case of different coating liquid dilution ratio, the photocatalytic efficiency was the best at 25:75 coating ratio, and the photocatalytic effect was better than others. In the test with different light intensities, the best formulation enhanced the light transmission distance. As the light intensity increased, the effective photocatalization of optical fibers increased.

The results also show the concentrations of TCE and TOC decreased after passing through the COFB in the soil box. The chloride ion (Cl^-) formed after the COFB treatment implies that photocatalysis effectively degraded TCE. The cost-effectiveness assessment of the treatment was also conducted in this study.



[163] 重金屬污染農地土壤水力漩流分離系統建置暨 產製功能性材料技術研發

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中文摘要

本計畫選取桃園市、彰化縣、台南市等三處污染農地土壤進行採樣當研究標的，以『重金屬污染農地土壤水力漩流分離系統建置暨產製功能性材料技術研發』為主題，研究工作內容包含進行土壤採樣、基本特性分析、重金屬、粒徑分布及毒性特性溶出程序(TCLP)。研究以水力漩流分離器(Hydrocyclone)分離重金屬含量較高之細顆粒、重金屬含量少之粗顆粒，達分級之效。此外，更以 FLUENT 軟體模擬流況，結合分析數據及流況模擬，了解水力漩流行為，回饋改善操作條件。惟水力漩流分離土壤顆粒雖然有效，但分析耗時，時間效率差，應做積極改善。因此，本研究擬建置設計自動化水力漩流分離系統。應用流速流量分析數據回饋及即時錐形尾部(Apex)之 underflow 排出顆粒監測分析、漩渦管(Vortex Finder)之 overflow 排出顆粒監測分析回饋，修正水力漩流分離系統，達成客製化目標。

其後，針對重金屬含量高之細顆粒土壤(考量酸洗/萃洗衍生土壤重金屬移動性增加問題)，以鐵氧化物覆膜於經水力漩流分離之土壤細顆粒殘餘物(功能性材料)，鐵氧化物覆膜改質被覆物質的表面特性，增進應用性。除控制殘留金屬外，製成之鐵氧化物覆膜資材亦再回用於廢污處理(加值化再利用途徑)，達成以廢(土壤細顆粒廢棄物)治廢(有機、無機廢污)之目標。為了解功能性材料對於重金屬離子之影響，本研究了解功能性材料對銅離子之吸附能力，並求得吸附量隨時間的變化關係。此外，功能性材料亦具催化 H_2O_2 降解除草劑(拉草)之效應，於本研究中改變實驗條件予以討論。期製做功能性產品，建立鐵氧化物覆膜經水力漩流分離之細顆粒土壤產品產製技術。

Abstract

In this work, functional materials production and hydrocyclone separation for heavy metal contaminated farmland soils are studied. The contaminated farmland soils are collected from three places including Taoyuan city, Changhua county and Tainan city. The basic characteristics such as pH value, heavy metal content and toxic characteristic leaching procedure (TCLP) are conducted to examine the properties of the contaminated farmland soils. In addition, the separation processes, hydrocyclone treatment, is designed to separate coarse and fine-grained particles by high settling velocity of particles. Ideally, hydrocyclone separator could be applied to reduce contaminated soil volume and concentrated the pollutants into fine particles as overflow stream during hydrocyclone operation. The coarse particle possess less contaminant, it might be help to achieve the reduction in volume of contaminated farmland soils. Furthermore, the FLUENT flow simulations are help to calculate the cut-off size and fractional efficiencies in hydrocyclone separators. The demonstration of liquid-solid flow and the simulation results are feedback to the hydrocyclone operating parameters.

However, the operating conditions are governing the hydrocyclone dimensions and inlet velocity. To modify the optimum operating factors needs the inlet velocity information and the particles distribution in overflow and underflow streams. Thus, this work sets up an auto-control system, which collects the velocity meter and particle distribution analysis mechane data at realtime. After calculating, the auto-control system could change the inlet velocity to get customized particle cutting size. It is more suitable for



hydrocyclone system operation.

In spite of the traditional chemical washing/extraction processes are used for the concentrated polluted fine particles treatment, it is found that the pollutant's leachability increases after chemical washing/extraction. The treated particles might have higher leachability compare to untreated particles, and it needs to clarify the problem and pay more attention to it. This work proposes iron oxide coating treatment on concentrated polluted fine particles to form functional materials. This surface coating material, iron oxide (goethite (α -FeOOH)), own the heavy metal adsorption properties and have the ability to catalyze hydrogen peroxide for the destruction of organic pollutants. Hence, the copper ions adsorption experiments and herbicide (Alachlor) destruction with the existence of hydrogen peroxide are also conducted in the work.



[164] 烏河流域底泥砷型態分布與環境因子之關係

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中文摘要

台中之筏子溪 (F1~F6)、烏溪 (W1~W6) 及台中榮總、澄清醫院、精密科學園區、台中工業區、台中科學園區二期之放流口 (S1~S5) 等 17 處從 2014 年 03 月到 2015 年 08 月的 pH、電導度其數值變化並未隨著時間有趨勢性的改變。氧化還原電位排除 2015 年 06 月烏溪樣品中極高的數值，筏子溪在整治的情況是高於烏溪樣品的。筏子溪樣品總有機碳濃度平均高於烏溪樣品，推測烏溪的河面較大，流速較快導致有機物無法沉積。無定型鐵鋁濃度分佈亦與總有機碳分析之結果比較類似。水樣總砷濃度平均約為 $1.39 \mu\text{g L}^{-1}$ ，是遠低於監測標準值的，且差異性並不大。而有幾個底泥樣品的總砷濃度高出底泥品質指標下限值，表示水體的流動會稀釋總砷濃度，但底泥在水體流動下會持續的累積總砷濃度，導致砷濃度不斷放大。筏子溪樣品 F6 為筏子溪中底泥總砷濃度最高的，可能從上游累積至下游 F6；烏溪樣品以 W5 的底泥總砷濃為最高，可能因 W5 為 S5 的下游累積的，而 S5 的底泥總砷濃度為樣品中平均底泥總砷濃度最高的，導致 W5 的底泥總砷濃度也較高。筏子溪底泥樣品 F1 圖譜 LCF 結果顯示，此區域的底泥砷的來源主要為地質環境的砷，其他為移動性較高吸附型態的砷。烏溪底泥樣品的砷，主要為吸附型態的砷。S5 可能是中科排放出的砷與此處底泥吸附錯合，表示其底泥中的砷可能往下游移動，因此 W5 為台 S5 的下游，底泥砷濃度相對高，表示 W5 底泥砷濃度可能由 S5 累積而來。由 Pearson 相關性分析結果顯示底泥砷濃度與河水 As 濃度及無定型 Fe 氧化物濃度之間亦具有顯著相關，烏溪下游各採樣點與中科廢水排放口的底泥、河水中砷濃度與無定型 Fe 氧化物濃度較上游筏子溪

高，且底泥砷濃度與河水砷、底泥無定型 Fe 氧化物是有相關，並將 W2、W4、W5、W6 與 S5 分為同一群，明顯受水體砷濃度影響。而其餘的環境因子與水體、底泥中的砷濃度間並未呈現顯著相關。孵育實驗結果顯示，孵育系統 pH 5.5 與 7.5 的鐵溶出量與砷的溶出曲線是有顯著相關的，且兩者溶出時間趨勢相似。其中，砷最高溶出量出現時間點隨著添加葡萄糖濃度而變化，添加葡萄糖濃度愈高時，出現砷最高溶出量時間愈久，pH 5.5 孵育系統明顯有此趨勢。孵育系統 pH 7.5 在孵育第 14 天後，又觀察到砷有再次溶出的現象，而且 pH 9.5 系統也有此類似趨勢出現。pH 9.5 下添加三種葡萄糖濃度的孵育系統，因鐵氧化物在高 pH 值系統下以沉澱態為主，使得 pH 9.5 系統的鐵溶出量極低，砷的溶出主要應是底泥表面吸附被釋出，因此 pH 9.5 系統沒有像 pH 5.5 與 7.5 系統有明顯的沉澱態鐵與砷溶解的變化情形。本研究成果顯示主要控制底泥砷濃度的環境因子為水體砷濃度與無定型鐵氧化物含量。

Abstract

The Arsenic (As) release from the semiconductor industry might result in a significant biomagnification effect even a very small amount. The pH and EC in the sampling sites at the Fazih River (F1~F6), the Wu River (W1~W5) as well as the effluent outlet of hospitals, the Taichung Industrial Park, the Taichung Precision Machinery Innovation Technology Park, and the Central Taiwan Science Park (S1~S5) have not shown a clear change during the period of March 2014 to August 2015. Except the extremely high ORP value in samples collected from the Wu River in June 2015, the ORP in the Fazih River is generally higher than that in the Wu River. In terms of the amount of TOC,

that in the Fazhi River is averagely higher than the Wu River, possibly due to the greater flow rate in the Wu River that hinders the TOC accumulation in sediments. The distribution of amorphous Fe and Al follows the similar pattern of TOC. The average concentration of As in water samples is $1.39 \mu\text{g L}^{-1}$, below the regulated limit. However, As concentrations in few sediment samples are greater than the lower limit of the sediment quality index, suggesting a continuous accumulation of As in sediments. Results of linear combination fitting (LCF) for the As X-ray absorption spectroscopy (XAS) data indicate that As originated from the intrinsic geological environments dominates the As inventory in the upstream of the Fazhi River (F1). However, the major species for other sediment samples is As sorbed on minerals, which shows a greater mobility than As precipitates. Sediments at W5 received the effluents from the Central Taiwan Science Park (S5), resulting in a greater amount of As accumulation. Only a portion of As analyses in terms of quantification and qualification have been done currently. Finishing analyses including As XAS for the rest samples will be the key emphasis afterward. In addition, the redundancy analysis will be used to determine the relationship between As accumulation and environmental factors. Pearson correlation matrix and principal component analysis data showed that As concentrations in sediments had a significant correlation to As concentrations of water and amorphous Fe oxides, and As concentrations in sediments, waters and amorphous Fe oxides from the Wu River and the Central Taiwan Science Park were higher than those from the Fazhi River. In the incubation experiments, the trends of the dissolved As concentration were similar with the dissolved Fe concentrations in the systems incubated at pH 5.5 and 7.5. Besides, it was observed that the dissolved As concentrations in pH 7.5 systems were increased again in 14 days incubation, and there were the similar trends in pH 9.5

systems. However, the iron oxide was mainly precipitated under pH 9.5 system, and thus the dissolved Fe amounts were low. The adsorbed As was released from the sediments in pH 9.5 incubation systems. This study pointed that As concentrations of water and amorphous Fe oxides were the major factors to control the As concentration in sediments.



[165] 植生復育潛力植物芒草之分子選育及重金屬吸附能力評估

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中文摘要

C4植物芒草因極高的光合效率與生物量具有生質能源的潛能，這個原生的雜草是組成臺灣的草原生態系重要的物種，從低海拔的荒廢地、高鹽及高重金屬的棲地、中海拔的邊坡一直到高山的草原，都有優勢的族群分布，然而這個臺灣的草卻已經是歐洲的寶，透過國際合作，歐盟正式將臺灣的芒草種源引入歐洲，作為生質能源發電的原料；在美國芒草被列為生產生質酒精的物種之一。在環境永續的考量上種植芒草還有定沙、防止地層下陷等優點，近年來研究亦顯示芒屬植物在土壤整治的植生復育技術上對眾多重金屬吸附亦有良好的效果，再加上臺灣的芒屬植物為多年生植物且多樣性高，且具有栽培容易，生長快速，適應性強及粗放管理之特性，因此應亦具有高度潛力作為植生復育之選項植物之一，本計畫利用次世代定序選殖出10組微衛星DNA基因座之分子標誌物，並利用五節芒以及白背芒檢測檢測多型性，顯示10組微衛星DNA基因座具有中到高度的多型性，其對偶基因數目介於6-17，異型合子觀測值介於0.174-0.935，異型合子期望值介於0.260-0.905，多型性則介於0.255-0.898，本研究所選用的五節芒三個品系(Line1、Line3以及Line4)具有不同之基因型。五節芒三個品系利用污染地以及非污染地土壤進行盆栽栽種試驗，經過3個月結果顯示三個品系的生長狀況良好，其中試驗組Line1品系不論在地上部以及地下部皆具較高生物量。植株重金屬分析顯示五節芒三個品系其地下部重金屬鋅以及銅濃度皆高於地上部，說明五節芒對重金屬的吸收是以根部為主，且對重金屬鋅的吸收能力大於銅，其中Line1品系吸收能力最高。進一步分析顯示

Line1品系對重金屬鋅以及銅具有較高的生物累積因子BF、生物濃縮系數BCF以及轉移系數TF值，且重金屬鋅的轉移系數TF值顯著大於銅。植物組織的實際吸收量顯示五節芒三個品系中不論對重金屬鋅或銅的吸收能力為Line1>Line4>Line3，綜合上述結果顯示在未來應用於現場時本研究中五節芒Line1品系應是較好的選項，此外亦可藉由螯合劑的添加，增加土壤中重金屬之移除能力以及植物對於重金屬的吸收量。最後本研究針對五節芒特用分子標記開發，將可用於鑑定並找尋未來可用於現場植生復育之芒草品系或品種，此外亦可做未來種原鑑定與臺灣種原保護的使用。

Abstract

Featured with high photosynthetic efficiencies and biomass, *Miscanthus*, a C4 plants, has become a potential biofuel crop. *Miscanthus* is native to East Asia with high species diversity, including *M. sinensis* Anders. That is widespread in the Chinese mainland and Japan. *Miscanthus* taxa of Taiwan are ecologically diverse, including at wastelands, at saline-alkali habitats, at heavy metal areas, at slopes of intermediate altitude, and at grasslands of high mountains. The European *Miscanthus* Improvement Project, which is sponsored by the European Union, identified *Miscanthus* as a potential biofuel crop for renewable energy. Via international collaboration, *Miscanthus* seeds were exported officially from East Asia including Taiwan to EU. *Miscanthus* has been used for combustion in Europe to reduce the usage of charcoal in the fossil-fuel power; in America, *Miscanthus* is used for producing ethanol. Compared to fossil fuel, that simply emit greenhouse gases, *Miscanthus* plants fix carbon dioxide from atmosphere and carbon

elements from soil, and transfer to biomass. Recently, studies also show that *Miscanthus* plant accumulated the large quantities of heavy metal, and could also be used in phytoremediation of contaminated areas. The *Miscanthus* species is a perennial plant with a high species and genetic diversity in Taiwan, easy cultivation, fast growth, and strong ability of adaptation to environments. Therefore it should be a good candidate used in phytoremediation. In total, 10 novel microsatellites were developed from *M. floridulus* by next-generation sequencing technology. Ten microsatellite markers that successfully PCR amplified showed medium to high polymorphisms when tested on *M. floridulus* and *M. floridulus* var. *papillayus*. The number of alleles, observed and expected heterozygosities, and polymorphism information content (PIC) values across loci varied with a range of 6 to 17, 0.174 to 0.935, 0.260 to 0.905 and 0.255 to 0.898, respectively. The combinations of 10 microsatellite loci were able to discriminate effectively among three lines of *M. floridulus*. These three lines of *M. floridulus* were planted in three pots with contaminated soil and one pot with uncontaminated soil, respectively. After three months of the growth, the three lines grew well in the contaminated soil, and higher levels of biomass for above- and under-ground parts were indicated in Line 1. The higher levels of Zn and Cu in under-ground part were showed than above-

ground part for three lines. These results indicated the a good metal accumulation ability in roots, higher level of Zn accumulation was indicated than Cu, and Line 1 had a better Zn and Cu accumulation ability than others. We also evaluated bioaccumulation factor, bioconcentration factor and translocation factor of Zn and Cu for three lines. The accumulation amount of Zn and Cu for three lines of *M. floridulus* is Line1> Line4> Line3. The Line1 of *M. floridulus* is suitable for phytoremediation. Chelating Agents addition increased the uptake of heavy metals by plants, and the removable ability of heavy metal in the future. This study developed high efficient method to screen suitable *M. floridulus* germplasm used in phytoremediation. The development and application of molecular markers for *Miscanthus* can be useful to identification and protection of *Miscanthus* germplasms in Taiwan.



[166] 發展毒性監測及預報平台-使用高通量生物篩選工具

預測土壤中環境荷爾蒙污染物

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中文摘要

美國環保署於2012年開始運作 Endocrine Disruptor Screening Program (EDSP)，計劃篩選85,000種新化合物確認是否有內分泌干擾效應，達成毒性預報的目標。生物分析法為一種被廣泛應用於污染物之篩檢工具，其快速且操作容易，可分析複雜化學混合物中的總毒性效應。因此，本研究目的為建立高通量篩選工具(HTS assays)，包含致癌性篩選平台(p53 bioassay)、綜合毒性篩選平台(ATP biosassay)、芳香族化合物毒性篩選平台(Ad-DR bioassay)及雌激素毒性篩選平台(T47D-KBluc assay)，可分析土樣品中環境化學品之毒性，並進一步進行風險評估。本研究土壤樣品位於高雄市某受重油品污染之區域，已完成30件次化學法分析與140件次四種HTS分析測定。本研究結果顯示，污染程度較高之土壤樣本其有機相平均細胞存活率為83%，顯著低於其他三種土壤樣本(低污染、輕微污染與背景土樣)，且與BTEX化合物均呈現負相關，但未達顯著；無論在有機相或無機相受污染土壤樣本所誘發之DNA損傷顯著高於背景土樣($p=0.002$)；戴奧辛與Non-Dioxin AhR濃度範圍分別為ND~1.50 pg BEQ/g d.w.與ND~29.7 pg BEQ/g d.w.，3種BTEX(苯、乙本與二甲苯)均與Non-Dioxin AhR數據呈現顯著正相關($p<0.05$)，在TPH方面則有邊緣顯著之現象($p=0.071$)；僅於有機相中檢測出微量之雌激素效應，部分樣本其濃度均低於本研究偵測極限。本研究已建立毒性預報系統流程圖，並遵循污染物指紋鑑定之概念，建立受油品污染土樣之生物指紋圖，後續應用本系統針對未知樣本測試時，可快速評估該地是否遭受油品污染之情形。

Abstract

The Environmental Protection Agency (EPA) began the implementation of Endocrine Disruptor Screening Program (EDSP) in 2012 which aims to screen 85,000 new compounds for potential endocrine disrupting effects and tox-cast targets. Bioassays are becoming increasingly attractive screening tools due to the relative speed and ease of analysis, and can provide an integrated measure of toxicity potency in complex chemical mixtures. Therefore, the aim of this study is to establish high-throughput screening assays (HTS assays) including the carcinogenicity pathway (p53 bioassay), cytotoxicity (ATP biosassay), aryl hydrocarbon receptor pathway (Ad-DR bioassay) and the estrogen receptor pathway (T47D-kbLuc assay) to screen for toxicity of environmental chemicals and to do further risk assessment in soil samples. Thirty (30) and One hundred forty (140) samples were analyzed on GC/FID and four HTS assays, respectively which were located in a heavy oil pollutant area in Kaohsiung city. Compared to other samples in our study, our results showed low cell survival rate (83%) in samples heavily polluted with oil. In addition, Negative correlations of cell survival rate and BTEX pollutants were observed in whole samples. Significant increase in DNA induced damage were incurred in pollution soils either in the organic or inorganic extraction fractions. The range of dioxin and Non-Dioxin AhR luciferase responses are ND~1.50 pg BEQ/g d.w and ND~29.7 pg BEQ/g d.w. which was observed with positive correlation and marginal positive correlation with three BTEX compounds namely: benzene, ethyl benzene and dimethylbenzene and TPH. Notably, very low estrogenic activity was observed in



organic fraction and most sample concentrations were lower than limit of detection. In conclusion, the toxicity report system based on four HTS assays have been established and to be able to make a bioassay fingerprinting of soil heavily contaminated with oil to further assess and evaluate on unknown soil samples.

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[167] 結合臭氧與過氧化氫處理飽和層及未飽和層柴油污染物試驗

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中文摘要

本研究模擬飽和層及未飽和層同時受柴油污染的試驗，採用飽和層的臭氧注氣(ozone sparging)方式，同時結合過氧化氫注入未飽和層中，以探討兩者接觸時的化學氧化能力。並探討柴油污染物化學當量所需的臭氧劑量、過氧化氫濃度、pH值，探討氫氧自由基的形成情形。本研究最終探討臭氧劑量結合過氧化氫濃度的最佳搭配，能夠用最低的注氣量與最短的時間，達到最佳的柴油污染物去除效果。

本研究第一批試驗所使用土壤柴油初始濃度為24,200 mg/kg，地下水柴油初始濃度300 mg/L，臭氧流率為2,888 mg/min，僅使用臭氧而無過氧化氫添加，批次注氣1個小時後地下水柴油即已完全降解，累積批次注氣12個小時後土壤柴油降解效率為37%，累積批次注氣24個小時後土壤柴油降解效率為58%；第二批試驗所使用土壤柴油初始濃度為32,131 mg/kg，使用過氧化氫濃度為7%，添加量為7% H₂O₂: soil = 1 : 100 (w/w)，臭氧流率為2,888 mg/min，累積批次注氣12個小時後土壤柴油降解效率為63%，累積批次注氣24個小時後柴油降解效率為78%；第三批試驗所使用土壤柴油初始濃度為17,115 mg/kg，使用過氧化氫濃度為7%，添加量為7% H₂O₂: soil = 2 : 100 (w/w)，累積批次注氣12個小時後土壤柴油降解效率為64%；第四批試驗所使用土壤柴油初始濃度為14,286 mg/kg，使用過氧化氫濃度為10%，添加量為10% H₂O₂: soil = 2 : 100 (w/w)，累積批次注氣12個小時後土壤柴油降解效率為37%，高過氧化氫濃度效果反而較不顯著；第五批試驗所使用土壤柴油初始濃度為24,223 mg/kg，過氧化氫濃度為4%，添加量為4% H₂O₂: soil = 2 : 100 (w/w)，累積批次注氣12個小時後土壤柴油降解效率僅為15%，低

過氧化氫濃度顯示氧化能力不足。

本研究利用建立的過臭氧反應設備，變動操作參數如過氧化氫濃度與比例，研究成果發現，過臭氧反應系統更有效率的處理場址中飽和層及未飽和層的高濃度柴油污染物，使用過氧化氫7%，與土壤的比例2%的操作條件下，即可得到最佳且經濟的效果，此成果應該可提供國內廠商利用過臭氧氧化法進行實場的應用。

Abstract

Simulations of saturated and vadose zones were simultaneously contaminated by diesel oil in this study. Using ozone sparging and injecting hydrogen peroxide into the vadose zones to explore the chemical oxidation ability. This study also investigated the chemical equivalent amount of ozone required for diesel oil, hydrogen peroxide concentration, and pH value for exploring the formation of hydroxyl free radicals. The optimal quantity of ozone sparging combined with hydrogen peroxide, with the lowest ozone sparging and the shortest time, to achieve the best diesel removal efficiency was investigated.

In the first stage, the initial diesel concentration in soil was 24,200 mg/kg, the initial diesel concentration in groundwater was 300 mg/L, and the ozone flow rate was 2,888 mg/min. Ozone was used only without hydrogen peroxide addition in this stage. After one hour ozone sparging into the groundwater, diesel had been completely degraded, and then cumulative batch ozone sparging for 12 hours, the diesel in soil was degraded by 37%, cumulative batch ozone sparging for 24 hours, the diesel in soil was degraded by 58%. In the second stage, the initial diesel concentration in soil was 32,131 mg/kg, the concentration of hydrogen peroxide is

7%, and the addition was 7% H_2O_2 : soil = 1: 100 (w/w), the ozone flow rate is 2,888 mg/min, The degradation efficiency of diesel in soil was 63% after 12 hours of ozone sparging, and 78% after 24 hours of cumulative batch ozone sparging. In the third stage, the initial diesel concentration in soil was 17,115 mg/kg, the concentration of hydrogen peroxide is 7%, and the addition was 7% H_2O_2 : soil = 2: 100 (w/w), the cumulative efficiency of diesel in soil was 64% after 12 hours of cumulative batch sparging. In the fourth stage, the initial diesel concentration in soil was 14,286 mg/kg, the concentration of hydrogen peroxide was 10%, and the addition was 10% H_2O_2 : soil = 2: 100 (w/w), the degradation efficiency of diesel in soil was 37% after 12 hours of cumulative batch sparging, and the effect of higher hydrogen peroxide concentration was less significant degradation. In the fifth batch, The concentration of H_2O_2 : soil = 2: 100 (w/w), the biodegradation efficiency of diesel in soil was only 15% after 12 hours of cumulative batch sparging, and the concentration of hydrogen peroxide was 4%, the result showed insufficient oxidation capacity was possessed in low hydrogen peroxide concentration.

Peroxone system and equipment were established in this study, by changing operating parameters such as hydrogen peroxide concentration and proportion, the result indicated that the peroxone reaction system could more efficiently degrade high concentration of diesel in the saturated and unsaturated zones. The use of hydrogen peroxide 7%, with the weight ratio of 2% as the operating conditions approached the optimal and economical results, the operating conditions should be able to provide domestic manufacturers to use the peroxone oxidation method for field applications.



[168] 結合電動力技術與地工離心機提升污染物/整治試劑傳輸效能及長期傳輸行為實驗模擬之研究

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中文摘要

本年度(106 年)將利用電動力法之電解驅動力,探討將標的物(污染物/整治試劑)移動至可處理範圍/污染熱區之成效,以克服污染物及整治試劑無法準確投藥解決病灶之問題,同時利用地工離心機於高重力 G 值運轉下產生之尺度效應(scaling effect),在極短時間內準確模擬標的物長期傳輸或於大空間實場之傳輸行為,將可掌握標的物傳輸途徑,藉以提升整治效能及降低投藥成本,更能保護土壤資源,以邁向綠色整治之目標。

本計畫之標的物為生物製劑(EOS/ECOcLean,5%)與重金屬銅(1100 mg/kg),以標的物進行重力傳輸試驗、電動力傳輸試驗及地工離心機模擬傳輸試驗為三大主軸,經過水力坡降 1:50、14 天之重力傳輸試驗可求得水力傳導係數(k)分別為 EOS: $6.89 \times 10^{-5} \text{ cm/s}$;ECOcLean: $4.13 \times 10^{-5} \text{ cm/s}$ 及銅 $7.92 \times 10^{-5} \text{ cm/s}$ 。另結果顯示,EOS、ECOcLean 和 Cu 的垂直平均轉移效率分別為 5%,11%和 82.7%;在垂直剖面上,EOS 累積在上層,ECOcLean 累積在中層,乃因 ECOcLean 的密度高於 EOS。然而銅之溶水性較高,故易受重力流遷移影響而累積在底層。在水平剖面上,EOS 和 ECOcLean 的濃度比銅分佈均勻。

三維電動力傳輸試驗中以 EOS 為標的物進行為期 28 天之監測,電位坡降 1 V/cm 之條件下水力傳導係數(k)為 $3.11 \times 10^{-4} \text{ cm}^2/\text{s}$,約為重力傳輸試驗 k 值之 4.6 倍;電位坡降 1.5 V/cm 之條件下 k 值為 $6.11 \times 10^{-4} \text{ cm}^2/\text{s}$,約為重力傳輸試驗 k 值之 4.6 倍。以 ECOcLean 為標的物進行為期 28 天之監測,電位坡降 1 V/cm 之條件下水力傳導係數(k)為 $9.21 \times 10^{-4} \text{ cm}^2/\text{s}$,約為重力傳輸試驗 k 值

之 22 倍;電位坡降 1.5 V/cm 之條件下 k 值為 $14.2 \times 10^{-4} \text{ cm}^2/\text{s}$,約為重力傳輸試驗 k 值之 34 倍。以 Cu 為標的物進行為期 28 天之監測,電位坡降 1 V/cm 之條件下水力傳導係數(k)為 $6.91 \times 10^{-4} \text{ cm}^2/\text{s}$,約為重力傳輸試驗 k 值之 8.7 倍;電位坡降 1.5 V/cm 之條件下 k 值為 $12.5 \times 10^{-4} \text{ cm}^2/\text{s}$,約為重力傳輸試驗 k 值之 15.8 倍,故電動力有效提升 EOS,ECOcLean,及 Cu 之遷移。

地工離心機以 25G 重力加速度進行 32 分鐘與 64 分鐘之運轉,相當於實場整治時間 14 天與 28 天。根據地工離心機於模擬重力傳輸及 1G 環境下電動力滲透係數(k)比較下,可獲得實場尺度之兩週及四週傳輸結果,結果顯示在電位坡降 1V/cm 條件下,兩週後 EOS 之整治熱點尚未擴散出去,但濃度前鋒已達 10.58 m 處,四週後整治熱點擴散至 2.3m 處,而濃度前鋒卻僅達 7.82 m 處;對 Ecoclean 而言,兩週後之整治熱點擴散至 15.61m,因受限於模擬槽尺寸,濃度前鋒應已超過 111.5 m,四週後整治熱點擴散至 44.6m 處,而濃度前鋒亦遠超過 111.5

m;對 Cu 而言,兩週後之整治熱點擴散至 32.19m,因受限於模擬槽尺寸,濃度前鋒應已超過 43.5 m,四週後整治熱點及濃度前鋒均遠超過 111.5 m 處。而當電位坡降增加至 1.5V/cm,兩週後 EOS 之整治熱點尚未擴散出去,而濃度前鋒已擴散至 21.16 m,四週後整治熱點擴散至 4.6m 處,而濃度前鋒當然已超過 15.64 m 處;對 Ecoclean 而言,兩週後之整治熱點擴散至 24.08m,因受限於模擬槽尺寸,濃度前鋒應已超過 172 m,四週後整治熱點擴散至 68.8m 處,而濃度前鋒亦遠超過 172m;對 Cu 而言,兩週後之整治熱點擴散至 58.48m 處,因受限於模擬槽尺寸,濃度前鋒應已超過 79

m, 四週後整治熱點及濃度前鋒均遠超過 79 m。

本計畫結果證實利用地工離心模擬現場標的物於重力下之移動行為, 再於實驗室尺度利用 1G 環境滲透係數(k) 分別於重力及電場之比較, 即可模擬出電動力技術應用於實場時標的物移動之預期效應, 將有效助於現場整治工法整治成效及整治時間之規劃評估。

Abstract

The project of 2017 is aimed to investigate the behavior of target compounds (contaminants and biological agents) transferring to the hot spot by electrical driving force. The long-term transportation path in field will be clarified by geo-environmental centrifuge experiment conducted with high gravitational acceleration (G). To have a good knowledge of transportation path of target compounds, it is help for enhancing remediation efficacy, decreasing cost, and conserving soil resource. It will be a big step to achieve green remediation.

Three kind of experiments, including gravity transfer, electrokinetic (EK) transfer, and geo-environmental centrifuge tests, were conducted. The contaminant of copper (1100 mg/kg) and biological agents of EOS and ECOclean (5%) were selected as target compounds. Results of gravity transfer experiments with hydraulic gradient of 1:50 showed that the hydraulic conductivity was 2.07×10^{-5} cm/s, 1.24×10^{-5} cm/s, and 2.38×10^{-5} cm/s for EOS, ECOclean, and Cu in the investigated systems, respectively. The vertical average transfer efficiency of EOS, ECOclean and Cu was 5%, 11%, and 82.7%. In vertical profile, the EOS was accumulated at the top layer and ECOclean was accumulated at the middle layer because the density of ECOclean was higher than that of EOS. However, copper was found to accumulated at the bottom layer because the high water solubility of copper resulted in migrating with gravity flow to the bottom layer. In horizontal profile, the concentration of EOS and ECOclean was

more homogeneous distributed than copper.

The three-dimensional EK transfer experiments were conducted with potential gradient of 1 V/cm and 1.5 V/cm for 28 days for target compounds, respectively. For EOS, the hydraulic conductivity was 3.11×10^{-4} cm/s and 6.11×10^{-4} cm/s which was 4.6 times higher than gravity transfer system. For ECOclean, the hydraulic conductivity was 9.21×10^{-4} cm/s and 14.2×10^{-4} cm/s, which was 22 times and 34 times greater than gravity transfer system, respectively. For Cu, the hydraulic conductivity was 6.91×10^{-4} cm/s and 12.5×10^{-4} cm/s, which was 8.7 times and 15.8 times greater than gravity transfer system, respectively. It indicated that the migration of EOS, ECOclean, and Cu was effectively enhanced by electrokinetic driving force.

The geo-environmental centrifuge tests were conducted with gravitational acceleration of 25G for 32 min and 64 min, which was corresponding to 14 days and 28 days transfer in prototype. As applied potential gradient of 1 V/cm in field, results showed that the concentration front of EOS was achieved to 10.58 m and 7.82 m after

14 days and 28 days, respectively. For ECOclean, the hot spot was found at 15.61m and 44.6 m after 14 days and 28 days, respectively. The concentration front of ECOclean was transported to 111.5 m or greater after 14 days. For Cu, the hot spot was found at 32.19m and greater than 43.5 m after 14 days and 28 days, respectively. As applied potential gradient of 1.5 V/cm in field, results showed that the concentration front of EOS was achieved to 21.16 m and 15.64m m after 14 days and 28 days, respectively. For ECOclean, the hot spot was found at 24.08 m and 68.8 m after 14 days and 28 days, respectively. The concentration front of ECOclean was transported to 172 m or greater after 14 days. For Cu, the hot spot was found at 58.46 m and greater than 79 m after 14 days and 28 days, respectively.

The gravitational transportation of target compounds predicted by geo-



environmental centrifuge tests was successfully confirmed in this study. By multiplying the ratio of the hydraulic conductivity in system with EK to that in system without EK, the transportation behavior can be predicted. It will be helpful for prediction of remediation performance and remediation time.

[169] 開發加強式生物刺激還原法整治鉻污染地下水

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中文摘要

工業發展過程中需大量使用鉻重金屬，但由於管理不慎與偷排廢水等情形，導致土壤與地下水鉻污染層出不窮，環境中鉻常以三價鉻(Cr^{3+})和六價鉻(Cr^{6+})形式存在，六價鉻則對人體具有高毒性與高致癌性，生物復育法是利用生物材料，例如細菌、真菌或酵素使環境中污染物轉變成低毒性或無毒性的方法，許多環境中微生物帶有六價鉻還原能力，這些微生物體內酵素能將高毒性的六價鉻還原成三價鉻，一般微生物降解污染物速率通常是非常緩慢的，因此利用適合的方式強化微生物處理污染物的能力是值得研究的議題。目前加強式生物復育法可分為兩大類，一、生物刺激法(Biostimulation)；二、生物強化法(Bioaugmentation)。期中報告部分研究執行內容與成果顯示，使用生物刺激法添加NB作為營養物質可促進現地地下水微生物生長，增加六價鉻還原效率，此外，將生物強化法結合生物刺激法可大幅增加六價鉻還原效率，使整體整治時間降低並達到更好的整治成效。次世代定序菌相分析結果顯示鉻污染地下水經整治處理後鉻還原相關菌屬Bacillus、Acinetobacter和Delftia等比例大幅增加，由此結果推測本研究使用之整治策略可使地下水中鉻還原相關微生物大量增生，加速六價鉻還原，未來可將本研究成果應用於現地模場試驗，以推廣生物整治技術應用。

Abstract

Chromium is a heavy metal which is used in large quantities in the process of industrial development. Due to the bad management and illegally discharge of waste water, more and more soil and groundwater are contaminated by the chromium. In the environment, chromium usually is dissociated into trivalent and hexavalent chromium ions, the latter one is highly toxic and highly carcinogenic to the human body. Bioremediation is a waste management technique that involves the use of organisms to neutralize pollutants from a contaminated site. Many microorganisms have an ability to reduce the hexavalent chromium ions into the low toxic trivalent form by the self-express enzymes. Using microorganisms to neutralize pollutants is mild and environmental friendly, so that, it is worthy of study to find a proper way to enhance microbial treatment. In our report, adding NB medium for biostimulation can promote the local groundwater microbial growth, in hence, improving the hexavalent chromium reduce efficiency. Besides, bioaugmentation combined with biostimulation can also increase largely hexavalent chromium reduce efficiency, therefore, the overall remediation time is down and achieve to better remediation effectiveness. The results of Next Generation Sequencing show that ratio of Bacillus, Acinetobacter and Delftia in chromium contaminated groundwater increased after NB medium treat. In the future, this research result can be applied to in-situ bioremediation to promote the application of bioremediation technology.



[170] 開發油品污染場址中土壤與底泥之生物指標化合物之 鑑定與量化應用技術

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中文摘要

油品中生物指標化合物具有高度抗風化與污染源有直接連結性之原生物質，環境中含有之生物指標化合物因為年代久遠或因濃度太低導致非常難以鑑定而且大部份生物指標化合物並無商用化標準品使得定量技術更為複雜。本研究目的為開發生物指標化合物類污染物程序與提升鑑定與量化技術之精準度，建置有效之鑑定與量化技術。本年度計畫已經完成實驗系統設計及執行，建置了微量生物指標化合物淨化技術並依據 CG4 潤滑油為基礎樣本鑑定出 37 種 terpene 生物指標化合物及完成定性及定量。期中也依據我們研究團隊的期初研究成果發表了一篇論文 (SCI 2.522/2017)，本期末也完成一篇論文並於投稿程序中。期末依據進度進行河川底泥、溪口底泥、漁港區底泥、加油站土壤、大型儲槽區土壤等取得之現地樣本來進行應用與驗證並擬延續過往之長年研究成果，建立環境法醫程序以鑑定土壤及底泥是否受到油品污染物準確度的技術，並以現地樣本來驗證成果來鑑定出低濃度之油品生物指標化合物，此類主要生物指標化合物類為汽油、柴油、潤滑油等油品含有之 adamantanes (金剛烷類 C10 到 C12)、BSs (bicyclic sesquiterpanes, 雙環倍半萜類 C14 到 C16)、terpanes (萜烷類 C18 到 C36) 及 steranes (甾烷類 C28 到 C30) 等。本研究成果除了可用於未來研擬現有法規所規範之污染物種以外之政策參考，也可配合整治產業建置污染場址之整治效果評估制度。

Abstract

Fossil oil products are the anthropogenic materials that containing various kinds of weathering resisting biomarker compounds. However, identification technologies are not easy due to the long history or low concentrations of the biomarkers in the environments. Mostly, there are no full scale of commercialized biomarker standards in the market and that makes difficulty in identification process. The objective of the study for the year is to establish an effective and an accurate biomarker identification technology. To date, we have planned, established and conducted a new cleanup process and identified those biomarkers with micro concentrations in the studied based CG4 lubricant sample. Based on our yearly research and the preliminarily study of the project, we had publish a SCI (IF 2.522/2017) paper and another written paper is in the process of submission. To date we have verified the midterm results by the taken environmental samples which includes sediments in the revivers and soils in the contaminated sites. In the final report, we identify those related biomarker compounds in the oil products, which include adamantanes (C10 to C12), BSs (bicyclic sesquiterpanes C14 to C16), terpanes (C18 to C36) and steranes (C28 to C30). In the future, the results of this study can be used as a reference of policy making to develop newer regulations other than the currents. The results can also be used to establish an evaluation system for a treatment efficiency in the contamination site.

[171] 新式高通量雙離子多層式油水分離模組應用於非水相液體回收

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中文摘要

本研究目的係將雙離子親水性表面抗油污薄膜修飾技術應用於編織型多孔洞材料上以達成Light Non-aqueous Phase Liquid (LNAPL)分離與回收。將超親水兩性雙離子矽烷sulfobetaine silane (SBSi) 經縮合反應修飾於適當孔徑的金屬材不鏽鋼編織網/玻璃纖維上，然而，矽烷分子普遍存在易水解與縮合反應，在溶液中形成聚集與失活，這會降低矽烷材料在表面的接枝與修飾能力，所以，本期中報告的內容係調整SBSi的修飾條件，已達濾網的最佳油水分離功能。實驗中以X射線光電子能譜儀、全反射式霍氏轉換紅外光譜儀進行表面元素與官能基的鑑定分析；以接觸角測定器進行表面能變化的分析；以橢圓儀鑑定修飾薄膜厚度，將修飾效率與效能最佳化。實驗條件中，以水的含量、pH值、反應溫度與時間作為最佳化的參數。初步結果證實經SBSi修飾後17 μm孔徑的濾膜通透的柴油混和濾液的分離率可達99.5%以上，而常壓下的海水通透濾可達 $6.5 \times 10^7 \text{ L/m}^2 \cdot \text{h} \cdot \text{bar}$ 。經實驗更證實了修飾物在UV照射、高熱環境下仍有良好的穩定度。而藉由調控孔徑與模組化設計的油水分離設備，經計算可以達到每小時11公噸的處理量。本計畫將進一步最佳化SBSi修飾的濾網，結合API油水分離器中形成一個模組，以分離廢液中固體雜質與成為自動化，以應用於加油站...等之小型油水分離器。總結，此雙離子油水分離器對LNAPL油污染的水質具有高分離率、高水量通透濾、高修飾穩定性以及環境無污染等優點。本計畫最終將設計一低耗能、高效率且可模組化的LNAPL油水分離設備，對於LNAPL影響的環保議題提出有效的解決方案。

Abstract

In this midterm report, we prepared and optimized an oil-water filtration mesh, which was modified with superhydrophilic zwitterionic sulfobetaine silane (SBSi) for high throughput oil-water separation. Identification of SBSi-coated meshes was performed by X-ray photoelectron spectroscopy and attenuated total reflection-Fourier transform infrared spectroscopy. Surface energy and thickness observation were carried out with contact angle goniometer and ellipsometry. The disadvantages of the silanes for surface modification is that silane tends to aggregate in solution and form large sphere to precipitate onto surfaces. This is mainly due to fast hydrolysis and condensation of silane functional groups, which leads to deterioration of efficiency of surface modification. The silane is susceptible to the experimental conditions, such as the pH, water content, experimental temperature and time. The optimal oil recovery rate for the oil-water mixtures reached >99.5% when using the SBSi-coated meshes with a pore size of 17 μm. More importantly, the water flux with modified meshes achieved $6.5 \times 10^7 \text{ L/m}^2 \cdot \text{h} \cdot \text{bar}$, enabling gravity-driven and energy-saving separation. The stability test showing great stability of the covalent coating of SBSi under explosion of UV wavelength 365 nm for 144 hours and so period of time put in 60°C oven. The effectiveness of the zwitterionic meshes for the oil-water separation is due to the superhydrophilicity of SBSi coatings to avoid the penetration of organic fluids through the meshes. As a result, we apply the modified meshes to further accomplish the design of the zwitterionic oil-water separation device incorporated with a API device by optimizing and automizing the configuration for addressing the LNAPL pollution in the water body. The device in



this study will be implemented in the gas station for in-field application. Consequently, we aim to develop the module of the zwitterionic oil-water separation device for removing LNAPLs in an effective, low-cost and high-performance way.

[172] 廢機油優勢分解菌篩選配合土堆法提昇含油污染場址的整治效能評估

賴文亮

大仁科技大學環境與職業安全衛生系

中文摘要

本研究採取屏東縣公告土壤污染整治場址5 個分區的土壤樣品，發現每公克可生長於water agar 或1/5、1/10 營養培養基的菌落數約介於10⁶-10⁷ CFU 之間，較有機質豐富之土壤少2 次方以上。以16S rDNA 方法完成14 株菌的菌種鑑定，分別屬於Acinetobacter sp. (靜止桿菌屬，G(-)，1 號與9 號菌株)、Pseudomonas sp.(假單孢菌屬，G(-)，2 號與11 號菌株)、Rhodococcus (紅球菌屬，G(+)，3 號菌株)、Stenotrophomonas sp.(寡養單胞菌屬，G(-)，4 號與5 號菌株)、Ochrobactrum sp. (蒼白桿菌屬，G(-)，6 號菌株)、Cupriavidus sp.(貪銅菌屬，G(-)，7 號菌株)、芽孢桿菌屬(Bacillus sp. G(+)，8 號菌株)、伯克氏菌屬(Burkholderia sp. G(-)，10號與14 號菌株)、金黃桿菌屬(Chryseobacterium sp. G(-)，12 號與13 號菌株)等。

篩選14 株菌株在含少量鹽類培養基中添加1%廢機油作為唯一碳源，發現皆可利用機油當作碳源生長，其中02、04、05、12 號菌株皆有能力使廢機油產生明顯乳化現象；10 號菌可明顯使乾淨機油乳化成小球體；12 號菌株對乾淨機油具有明顯分解能力；14 號菌可能具有較強吸附廢機油的能力。三次土堆實驗均添加黃豆粉與米糠，其中因其含總石油碳氫化合物 (Total petroleum hydrocarbon, TPH)(背景值)，在第一次誦驗無法得知添加養分與膨鬆劑是否具有加速TPH 的分解；第二次土堆法，在實驗進行3 個月後，每2 星期添加一次混合菌株(02、04、05、10、12 與14 號)，再經6 週後採樣分析，發現混合菌株具有加速分解TPH 的能力；第三次土堆法，採每2 星期添加混合菌(02、04、05、10、12 與14 號)一次，共添加了6 次，於3 個月後檢驗TPH 含

量變化，相較無添加養分與膨鬆劑的對照組其TPH 殘餘量相當，很難判斷添加混合菌株分解TPH 效力。但若以單獨菌株(02、04、05 與12 號)200 mL 菌液(108-109 CFU/mL)每2 星期添加於1 公斤土壤樣品之誦驗，6 週後可觀察到4 株菌株皆具有分解TPH 的效果。依目前結果顯示，污染場址現地篩選出的菌株對機油具分解能力，但受限時間及經費，後續仍需要更多的基礎研究，包括各別菌株基本生理特性、對不同油品的分解能力、菌株不同組合對分解TPH 是否具有協同作用等，才可瞭解混合菌株應如何添加才可達到最大的TPH 分解效率。

Abstract

In this study, five blocks in soil pollution remediation sites declared by Pingtung government had been taken with soil samples, it was found that the number of colonies in water agar or 1/5 and 1/10 nutrient medium was about 10⁶-10⁷ CFU, which was less than 2 times values in the soil rich in organic matter. The strains of 14 strains were identified by 16S rDNA method, belonging to Acinetobacter sp. (G(-), No 1 and 9 strains), Pseudomonas sp. (G(-), No 2 and 11 strains), Rhodococcus (G(+), strain No 3), Stenotrophomonas sp. (G(-), No 4 and 5 strains), Ochrobactrum sp. (G (-), No 6 strains), Cupriavidus sp. (G(-), Strain No 7), Bacillus spp. (G(+), No 8), Burkholderia sp. (G(-), No 10 and 14th strains), Chryseobacterium sp. (G(-), No 12 and 13 strains). Whole indentified strains were selected to add with 1% of waste oil as sole carbon source in a small amount of saline medium, and then could grow and use the engine oil as the carbon source. Among them, No 2, 4, 5, and 12 strains has the ability to make the waste engine oil to produce the obvious



emulsification phenomenon. No 10 strain can obviously make clean oil emulsification into pellets No 12 strain has obvious decomposition ability to clean oil, and No 14 strain could have the strong ability of absorbing waste oil. Three times of biopile tests were added with soybean powder and rice bran rich with total petroleum hydrocarbon (TPH) of the background value. The first test could not know whether the addition of nutrients and the expansion of the swelling agent is accelerated TPH decomposition. Second biopile test, three months after the experiment, a mixed strain (No 2, 4, 5, 10, 12 and 14) every 2 weeks was added, and then after 6 weeks of sampling analysis, revealing that the mixed strains have the ability to accelerate the decomposition of TPH. For the third biopile test, the addition of mixed bacteria every 2 weeks (No 2, 4, 5, 10, 12 and 14), a total of 6 times in 3 months, there had insignificant difference of TPH decrease compared with no added nutrients and the control group, indicating that it is difficult to determine the ability of mixed strains on TPH decomposition. If a single strain (No 2, 4, 5 and 12) of 200 mL with 108-109 CFU/mL was added to the test of 1 kg of soil samples every 2 weeks. Four strains were observed to have the effect on TPH decomposition after 6 weeks experiment. According to the current results, the screened strains from the contaminated site in this study are capable of decomposing the engine oil, but the limitation on time and outlay, more basic research, including the basic physiological characteristics of individual strains, the decomposition ability of different oil products and the synergistic effect of different combinations of strains on decomposition TPH, should be further conducted in designed experiments for understanding how the mixed strains should effectively achieve the maximum TPH decomposition

[173] 整治場址及離場處理場污染土壤總石油碳氫化合物

快速篩檢方法效能評估

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中文摘要

如何在發現油品污染初期，判斷洩漏來源並加以截斷，並減少實驗室分析成本，大幅縮短調查工作的時間，乃是非常關鍵的議題，本研究目的為提升總石油碳氫化合物 (total petroleum hydrocarbon, TPH) 現場篩測儀器之功能性，並了解其可能分析方法限制性，以強化現場篩測方法與傳統TPH分析結果之相容性。

工作項目主要分為兩個部分：實驗室測試及污染場址測試，實驗室測試首先針對一系列自行配置柴油污染土壤以RemScan進行污染土壤TPH分析，其TPH濃度範圍介於1060至52800 mg/kg，此一系列柴油污染土壤對應RemScan分析測值之相關係數為 $R^2=0.9696$ ，顯示不同濃度梯度之柴油污染土壤與RemScan TPH測值具高相關性。並將此一系列柴油污染土壤其檢測結果以GC/MS進行TPH分析，其TPH濃度介於770至59066 mg/kg，此一系列柴油污染土壤對應GC/MS TPH分析之相關係數為 $R^2=0.9930$ ，顯示不同濃度梯度之柴油污染土壤與TPH測值具極高相關性。在比對此一系列柴油污染土壤濃度測值時，可以發現在污染土壤TPH濃度小於10000 mg/kg時，RemScan數值較傳統TPH分析方法為高，但在污染土壤TPH濃度大於10000 mg/kg時，RemScan數值則較傳統TPH分析方法為低。

為探討不同污染土壤其污染時間長短對偵測之影響，因此以RemScan檢測新近石化污染土壤及受長期風化作用之石化污染土壤，測試不同污染年代的石化污染土壤，及評估TPH濃度高低對RemScan檢測之影響，並比較與傳統分析方法數據之差異性。在本研究中RemScan測值與GC/MS分析測值準確度以相對誤差來表示，在檢測8個樣品

中有6個樣品得其測值，其兩種方法相對誤差介於3.37-20.4%。

污染場址測試選擇不同油品污染之場址，進行RemScan現場測試工作，並比較與傳統TPH分析方法數據之差異性，了解儀器偵測濃度線性範圍。針對污染場址中污染土壤樣品源自不同油品(如汽油加柴油、柴油加潤滑油)，挑選三個石化污染場址土壤樣品進行試驗，發現二處石化污染場址RemScan之測值均高於GC/MS分析。針對土壤樣品前處理發現土壤樣品以60°C烘乾及自然風乾前處理所得之RemScan測值較接近，但自然風乾前處理需時72小時之等待時間，可能不符合現場及即時性之需求，因此若含水率過高之樣品將建議使用40°C或60°C烘乾，但經烘乾或風乾後碳數範圍屬於前端之化合物則會溢散，故此儀器不適合分析含有汽油之樣品。

在污染場址測試並於南部某台塑加油站污染場址進行18個污染土壤樣品RemScan測定，部分樣品無測值，6個樣品之RemScan之TPHd所測讀值均高於GC/MS測值，RemScan之測值與GC/MS分析檢測數據的相對誤差屬可接受範圍，5個樣品之RemScan之TPHd所測讀值低於GC/MS測值。在南部某中油加油站污染場址進行18個污染土壤樣品測定，多數樣品無測值，發現3個樣品RemScan之TPHd測值高於GC/MS測值。

土壤樣品中存在RemScan無法分析之樣品，評估應為土壤質地影響RemScan無法進行檢測，發現可分析之土壤樣本主要分佈於砂土(sand)、壤質砂土(loamy sand)、砂質壤土(sandy loam)及壤土(loam)；不可分析之土壤樣本則主要分佈於黏土(clay)、坩質黏土(silty clay)、坩質黏壤土(silty clay loam)、黏質



壤土(clay loam)、砂質黏壤土(sandy clay loam)。於實驗同時亦發現土壤有機碳之含量會對RemScan檢測造成影響，有機碳含量從3.15% - 6.28%影響TPH測值數值為220.0 – 4140 mg/kg。

根據原廠之檢驗證明得知，RemScan之最低偵測極限為250 mg/kg，實際針對不同土壤可能有所變異。RemScan分析檢測數據僅需不到30秒即可得其測值，每小時可收集超過30筆之數據，可進行持續性操作。操作不需使用任何耗材，僅需維持電池電量供RemScan檢測分析。RemScan檢測僅使用紅外光照射樣品表面，樣品表面反射吸收之紅外光進入儀器偵檢器後獲得讀值，分析過程並無添加任何藥劑，故並無以化學性或物理性破壞樣品，檢測後樣品並可用於傳統TPH分析萃取使用。限制性為RemScan使用需避免含水率過高之因素，於含水率大於8%無法檢測，含水率低於8%亦能檢測，故樣品需風乾亦或是烘乾。因其紅外光射出區域僅直徑1 cm，測試需充分拌勻，並且需要夯實使其表面平坦，建議檢測時需進行5重複，以確保儀器檢測之可信度及準確性。根據原廠聲明，RemScan可檢測所有土壤質地之土樣，但須選擇不同土壤質地(砂土、黏土及坩土)之土壤為標準土進行校準，及建立其污染土壤檢量線方可使用，故欲分析之土壤需先判斷其土壤質地後方能進行模式選擇，爾後進行污染土壤測定。本研究發現適用於砂土及壤土，其適用之土壤質地尚需更多實際操作以累積數據。

Abstract

Total petroleum hydrocarbons (TPH) is a term used to describe a large family of several hundred chemical compounds that originally come from crude oil. The typical range from C6–C40 consist of fractions and classes. The fractions range from gasoline, through kerosene, diesel, jet fuel and crude oil. TPH analyses are required by regulatory agencies to evaluate subsurface contamination. These

analyses are needed to assess the subsurface contamination stemming from leaking underground fuel tanks, spills, and product delivery lines. Evaluating the extent of contamination by TPH requires the following considerations in the field: type of hydrocarbon contamination, age of the hydrocarbon, type of matrix (water, soil, sludge), and distribution of hydrocarbon. Limitations of the TPH analytical method chosen from an environmental perspective not only total petroleum measurement is a requirement, but the compound classes and sometimes the individual components need reporting. This is due to the toxicity differences between the classes and individual compounds. In addition it is also very useful to know what fraction of petroleum is present, in the case of site investigation, under remediation processes or site closure.

The objective of this project is to evaluate individual field measurement devices in laboratory and field studies. Quantitative results of TPH instrument (i.e., RemScan[®] developed by Ziltek) were generated from laboratory and contaminated sites to draw conclusions regarding technology performance. In details, the tasks of laboratory measurement and field test were to: (1) determine the method detection limit, (2) evaluate the accuracy and precision of TPH measurement for a variety of contaminated soil samples, (3) evaluate the effect of interferences on TPH measurement, (4) evaluate the effect of soil moisture content on TPH measurement, (5) measure the time required for TPH measurement, and (6) estimate costs associated with TPH measurement.

A series of diesel contaminated soils were prepared to verify correlation of TPH concentration gradient versus response of RemScan analysis in the laboratory. The TPH ranged from 1060 to 52800 mg/kg by RemScan analysis. Correlation was considered acceptable. Conventional TPH analysis was also performed by gas

chromatograph/mass spectrometer (GC/MS). Concentrations of TPH ranged from 770 to 59066 mg/kg. When soil contains TPH less than 16000 mg/kg, it was observed that values of RemScan was normally higher than GC/MS analysis. However, when soils with TPH content higher than 16000 mg/kg, RemScan illustrated compatible results with GC/MS analysis. It was proposed that concentration of TPH at 10000 mg/kg may be the cutting point for better results.

Weathered diesel contaminated soils were analyzed by both methods. Relative error ranged between 3.37 to 20.4% in 6 samples. Weathering effect of diesel contaminated soil did not affect the detection of TPH by field measurement device. However, 2 soil samples with texture of loamy sand cannot be detected by RemScan. Apparently physical characteristics of soil may affect application of RemScan in field work. Due to the limitation of instrument allowing sample with water content less than 8%, methods of sample pretreatment were assessed. The results indicated that oven dry at 40 or 60°C is proper prior to RemScan analysis.

Environmental samples were collected from three contaminated sites with mixture of diesel, gasoline, or lubricating oil. Among three samples tested in contaminated sites, RemScan demonstrated higher TPH values than conventional TPH method. Twenty four samples were collected from two gas stations which were operated by Formosa Petrochemical Corporation and CPC Corporation, respectively. Four samples from Formosa Petrochemical Corporation owned gas station indicated higher value by RemScan analysis. Also two samples from CPC Corporation owned gas station indicated higher value by RemScan analysis.

Overall RemScan is a hand-held portable instrument that can be operated stand alone without the need for electricity or computer equipment. It is suitable for a

full 8-hour day of infield use with only one battery swap. Also RemScan is easy to use and can be operated by relatively unskilled personnel in the field (i.e. <2 hours of training). No extra certification is required. It takes less than 30 seconds to collect a measurement from an air-dried sample with RemScan. For air-dried soil samples (<5% free moisture content by weight), the total sample measurement time, including preparation of a flat surface, is less than 2 minutes. Under this scenario, the instrument can collect more than 30 TPH measurements per hour. Operation does not require any consumables or hazardous chemicals. Calibrating the instrument takes less than 3 minutes after every hour of continuous use. The RemScan method is non-destructive in the sense that the measured soil can be left in, or returned to, its original location without significantly altering its physical and chemical properties. Certainly variety of soil texture and soil moisture are the limitation to its function. However, it offered compatible result of TPH analysis.



[174] 應用多硫化物整治重金屬污染地下水技術之建立--適用之重金屬、地下水特性、操作參數及衍生物穩定性之研究

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中文摘要

地下水重金屬污染是目前國內在污染場址整治上經常面臨且較棘手的問題。重金屬具有無法分解的特性，因此對於重金屬污染地下水之改善，所能應用之技術相當有限。鉻、鎳、銅、鋅、鉛等重金屬污染之地下水，抽出或現地化學還原、穩定法是目前較可行的整治技術之一。對於小規模而高濃度的污染場址，採用地下水抽出再配合化學還原、沉澱方法具有可行性。對於污染源不明確、污染擴散範圍大之場址，採用現地化學還原穩定法可能較具有經濟效率。目前國內對於地下水重金屬污染的化學還原、穩定技術研究相對較少，技術的開發及本土操作參數的建立仍有待努力。此外，化學還原穩定技術在現地應用時，衍生物在地下環境中之長期穩定性，有必要針對國內地下水環境特性進行研究確認。多硫化物還原穩定法近年在國外應用於處理鉻鐵礦砂殘渣及六價鉻污染場址證實對六價鉻的還原及穩定具有顯著的成效。近年在國內有污染場址嘗試應用，但因缺少本土之操作技術，目前還未有成功案例。因此本研究將針對多硫化物還原穩定法，探討其適用條件，並建立適用於本土地下水特性之應用技術。多硫化物之製備主要以混合硫磺及生石灰加熱熬煮所製成，其主要成分以五硫化鈣為主，目前國內外文獻或場址試驗所採用之多硫化物多仰賴美國進口。因此，本研究內容包括：1.建立多硫化物之製備技術，以提供穩定品質之多硫化物，以取代藥劑之進口需求，降低整治技術成本。2.建立水質參數包括：pH、溶氧、氧化還原電位等對多硫化物還原、穩定鉻、鎳、銅、鋅、鉛等重金屬之相關性，藉此了解

多硫化物還原穩定法所適用之重金屬，並建立各種金屬最佳之施用條件。3.探討台中地區地下水質特性對多硫化物處理重金屬效率之影響，並建立最佳之操作參數。4.以管柱模型試驗，建立現地處理之施用方法。5.以台中地區地下水質特性，探討多硫化物還原、穩定衍生物在地下環境中長期之穩定性。透過本研究將建立製備多硫化物之方法，並建立自製多硫化物應用於抽出或現地重金屬污染地下水整治之最佳操作條件，開發重金屬污染地下水之整治技術。

Abstract

In currently, remediation of groundwater contaminated by heavy metals face the more difficult issues. Heavy metals cannot degradation, therefore for improving the heavy metal contamination of groundwater, the application of technology that can be quite limited. Remediation of heavy metals contaminated-groundwater, chemical reduction method is one of the more feasible remediation technology. For small-scale and high concentrations of groundwater contaminated sites, remediation by using groundwater pump and treat coupled with chemical reduction precipitation method is feasible. For sources of uncertainty, a large spread of contamination range of sites, using chemical reduction method in situ may be more economically efficient. In contrast, few studies focused on the heavy metal contamination of groundwater chemical reduction technology. Development of technology and the establishment of local operational parameters still to be done. In addition, the application of in situ chemical reduction stabilization, the stability of derivatives in the underground

environment of long-term, it need studies to confirm. The research literature confirmed that polysulfide has a significant effect on hexavalent chromium reduction. In Taiwan, in recent years, there are contaminated sites try to apply polysulfide, but the lack of local technical operations, has not yet been success. Therefore, this study will focus on polysulfide reduction method to investigate the conditions of application, and the establishment of local groundwater characteristics suitable for application of the technology. Preparation of polysulfide by mixing of sulfur and lime, made of boiled heating, the main ingredient is calcium polysulfide. Currently, polysulfide used in literature or test site all imported from the United States. Therefore, this study include: 1. To establish the technology of preparation of polysulfide, to provide a stable quality as much as polysulfide, to replace the agent import demand, which reduces the cost of remediation technology. 2. Research on the influence of water quality parameters including: pH, dissolved oxygen, redox potential, etc. on the polysulfide reduction efficiency. Thereby, establish the optimum application conditions and the applicable of heavy metals. 3. For groundwater quality characteristics of Taichung area, to investigate the effect on polysulfide reduction efficiency, and to establish the optimal operating parameters. 4. By using the column tests to establish the method of in situ treatment. 5. By using groundwater of Taichung area, to investigate the stability of the polysulfide derivatives in the underground environment of long-term. Through this study we will establish the process for preparing polysulfide, and the optimum operating condition of polysulfide reduction method.



[175] 應用含硫活性碳以活性覆蓋法針對含汞底泥進行溶出抑制研究 席行正

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中文摘要

汞因為具有高毒性、揮發性、生物累積性，被認為是最具生物毒性的金屬。在水相中及土壤底泥環境中汞多為二價汞之形式存在。底泥環境因為存在厭氣狀態，有利底泥厭氧微生物經由生物甲基化反應產生甲基汞，為最具毒性與生物累積性的汞物種。汞污染之底泥因此具有很高的生態風險潛勢，更被相關部門視為重要的整治項目。現行整治汞污染底泥的方法主要以開挖法、熱處理法、傳統覆蓋法，或監控生物降解為主，但部分方法因為成本過高、或環境衝擊大等因素，或僅適用低污染底泥，在應用上有許多限制。利用活性碳之活性覆蓋法之新興整治工法，因施工成本低、低環境破壞，可吸附新沉降污染物等優點，具有相當大的潛力。

本研究為加速於未來利用活性覆蓋法整治含汞底泥之實場化，從活性碳材開發、水相吸附試驗、底泥競爭吸附試驗，到汞溶出抑制試驗，逐步探討活性碳在底泥相中對汞的吸附與抑制汞釋出效能。本研究之底泥選用桃園灌溉渠道之底泥並進行汞添加，而吸附材料則使用高品質椰子殼活性碳，並成功熱硫化處理製備成含硫量約 4.096wt% 之含硫活性碳並豐富含硫官能基如：C-SO₃、C₂S(=O)₂、C₂S=O、C-S-S-C、C-S-C 及 C-SH。從水相吸附動力學實驗中，AC 及 SAC 皆在吸附時間前 6 個小時即有良好之去除率，且在約 16 小時達到平衡。其吸附動力學模式由 pseudo-first-order kinetic model 模擬較為適切。AC 及 SAC 一階動力吸附方程之吸附常數分別為 2.994x10⁻³min⁻¹ 及 3.224x10⁻³min⁻¹。等溫吸附實驗發現 SAC 比起 AC 對於二價汞及甲基汞具有較佳之親和性，SAC 與 AC 對於二價汞及甲基汞之 KD 值分別為 9.4256×10⁴(R²=0.9958)、7.661×10⁵(R²=0.8336)，與 3.6942×10⁴

(R²=0.9579)、2.2541×10⁵(R²=0.9825)。在底泥競爭吸附實驗中，AC 對比 SAC 對於汞具有較佳之抑制溶出能力。利用微型系統之汞溶出抑制試驗發現，活性覆蓋層對於甲基汞之溶出抑制效果較總汞顯著。對於高汞濃度之污染底泥 (~250 mg/kg)，本研究之各式覆蓋層 (SAC+膨潤土、SAC+TY03 底泥、AC+膨潤土) 均對甲基汞具有良好溶出抑制能力並能控制甲基汞表水中之甲基汞濃度在大部分時間中小於 5 ng/L。在本研究中之活性碳材 AC 與 SAC 在所有實驗(水相等溫吸附實驗、底泥競爭吸附實驗，汞溶出抑制實驗)中皆具有良好之抑制汞溶出之能力，並具有應用於活性覆蓋法整治含汞底泥之可行性。

Abstract

With high toxicity, volatility, and bioaccumulation ability, mercury has been considered one of the most toxic heavy metal in the environment. Mercury exists in the form of double valent mercury in aqueous phase and sediment environment. In sediment environment, it is often anoxic and facilitates biomethylation reactions of mercury, resulting in increasing concentration of methylmercury, which is known as the most toxic form of mercury due to its highest bioaccumulation ability and toxicity. Mercury-contaminated sediment environment is therefore regarded as a highly potential source of generating methylmercury, and remediation of which is often needed to be dealt with in a high priority. The conventional remediation methods such as dredging, capping, or monitored natural recovery, have limited use due to their high cost, great environmental impact, or otherwise being time-consuming or ineffective. Therefore, emerging technologies for mercury-contaminated

sediment are needed. Active capping is one of the technologies with many advantages such as cost-effectiveness, low environmental impacts, persistency, and ability to adsorb new deposited contaminants. Despite active capping has been considered as a high potential remediation method, relative research is limited other than adsorption isotherm batch experiments in aqueous phase.

In order to promote the speed of scaling up active capping method to remediate mercury-contaminated sediment, the proposed one-year research has gone through batch experiments, sediment competition adsorption tests, and microcosm tests to evaluate the adsorption/immobilization capability of activated carbon adsorbents on both mercury and methylmercury. The sediment used in this study was collected in Taoyuan and spiked with various concentrations of mercury solution. High-quality coconut shell activated carbon used in this research was successfully sulfurized to prepare effective mercury adsorber with 4.096 wt% of sulfur, with various of sulfur functional groups such as: C-SO₃·C₂S(=O)₂, C₂S=O, C-S-S-C, C-S-C, and C-SH. In kinetic adsorption batch experiment, AC and SAC obtained high removal efficiency of mercury in 6 hours and obtain equilibrium in 16 hours. The correlation using first-order pseudo kinetic model best fitted the adsorption curve of AC and SAC, with constant of 2.994×10⁻³ min⁻¹ and 3.224×10⁻³ min⁻¹, respectively. In Isotherm batch experiments, SAC had high affinity to mercury and methylmercury, with KD value of 9.4256×10⁴ (R²=0.9958) and 7.661×10⁵ (R²=0.8336), respectively, compare to KD value of AC at 3.6942×10⁴ (R²=0.9579) and 2.2541×10⁵ (R²=0.9825). In sediment competition adsorption tests, AC had greater performance of inhibiting leaching of Hg in porewater phase, as compared with SAC. In microcosm tests, active caps composed with SAC+bentonite, SAC+TY03 sediment, and AC+bentonite

had good performance of inhibiting methylmercury from leaching into overlying water form, and can control methylmercury concentration lower than 5 ng/L for most of the test period. In this research, batch experiments, sediment competition adsorption tests, and microcosm tests all suggest that AC and SAC have high performance of inhibition of mercury leaching into water phase; therefore activated carbons may be feasible to apply as active caps to remediate mercury contaminated sediment.



[176] 應用粒徑篩選及植生復育整治重金屬鉛銅污染土壤

章日行

朝陽科技大學環境工程與管理系

中文摘要

本計畫擬整合粒徑篩選及植生復育技術整治重金屬鉛銅污染土壤，以乾式篩選及濕式篩選進行土壤顆粒分離，並分析不同粒徑中土壤重金屬的濃度及重金屬型態分佈，此方式不僅不會造成土壤性質的改變，是一種務實簡單的操作方法，更是值得現地推廣的應用技術，能進而達到有效整治的目標。本研究以實場鉛、銅污染農地的現地土壤進行乾式與濕式篩選試驗，並透過玉米植生復育的盆栽栽種驗證及復育，進而探討兩者模式下的整治效果。本計畫實驗按照計畫書執行內容進行，研究結果可以歸納如下：

- 污染土壤鉛金屬於植生復育八週整治後，以根部吸收最為顯著，最高平均可吸收濃度約為774 mg kg⁻¹，其次為葉子吸收濃度為124 mg kg⁻¹，最低為莖部76 mg kg⁻¹。
- 鉛污染土壤經植生復育後重金屬鍵結型態以鐵錳氧化態含量最多，依序為碳酸鹽態、有機物態、可交換態及殘餘態，與未處理前之鍵結型態沒有顯著差異。
- 乾式粒徑篩選可獲得鉛污染土壤不同粒徑土壤之比例、重金屬濃度及重金屬鍵結型態，同時將大顆粒(2.83 mm以上)土壤移除及填入乾淨砂土混合稀釋後，能快速使鉛污染濃度降至管制標準的要求。
- 鉛污染土壤透過乾式篩選及砂石混合稀釋後，不僅降低其污染濃度，亦能進行後續植生復育整治，其作物生長不受影響，且1噸砂石所需成本僅為乾淨土壤約1/10，顯示此方法對鉛污染土壤處理的可行性及實用性。
- 濕式篩選方法能有效分離不同粒徑之銅污染土壤，其粒徑越小濃度越

高，將高濃度小顆粒(矽粒及粘粒)土壤移除後填入少數乾淨土壤混合稀釋，能有效降低其污染濃度。

- 透過將銅污染土壤小顆粒移除的方式，可大幅減少傳統客排土法所需要的土方量，亦能大幅降低鉛污染濃度，解決未來土壤供應不求的問題，故銅污染土壤以濕篩粒徑篩選搭配植生復育進行整治應為適當之方法。
- 本研究透過乾式及濕式粒徑篩選的方式分選其不同粒徑，具工法簡單、操作容易，再透過植生復育的驗證及復育下，可快速降低污染濃度及節省操作成本，提供未來不同污染物選擇整治技術的重要參考。

Abstract

This study is to integrate the particle-size screening and phytoremediation to remove lead and copper in soils. The soil particle separation was carried out by dry screening and wet screening, and the concentration and distribution of heavy metals in different particle diameters was analyzed. In this study, dry and wet screening experiments were carried out in the field soils of lead and copper contaminated farmland. The remediation effect of the two models was explored and verified by phytoremediation experiment. Several conclusions and suggestions can be drawn:

- The average absorbable concentration of the root about 774 mg kg⁻¹, leaf was about 124 mg kg⁻¹ and the lowest was stem after eight weeks cultivate.
- The state of heavy metal bonding in lead-contaminated soil was the highest in iron-manganese oxidation state, followed by carbonate state, organic state, exchangeable state and residual state.
- Dry-type particle size screening could

obtain lead-contaminated soil with different particle size of soil, concentration and bonding type of heavy metal. While large particles (up 2.83 mm) soil remove and filling dry sand mixed dilution, could quickly reduce the lead concentration to reach the requirements of regulatory standards.

- Lead contaminated soil through dry screening and dry sand mixed dilute not only reduce its pollution concentration, but also to follow-up reforestation remediation. The cost of one ton dry sand about 1/10% to the clean soil, showing the feasibility and practicability of this method for lead contaminated soil treatment.
- Wet screening method could effectively separate the different size of copper contaminated soil, the smaller particle with high concentration. The smaller particles soil removed and filling a few clean soils mixed dilute could effectively reduce pollution concentration.
- Through the removal of smaller particles of copper pollution could significantly reduce the amount of earthwork required by traditional passenger, but also reduce the concentration of pollution and to agree the regulatory standards.
- This study is simple and easy to operate by dry and wet particle size screening. It can quickly reduce the pollution concentration and save the operation cost and through the verification and rehabilitation of the plant regeneration.



[177] 二仁溪污染底泥整治模場試驗計畫
(結合相反轉法與再利用加蓋法技術研發2/2)

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中文摘要

臺灣地區之底泥污染情況相當嚴重，多項疏水性有機污染物以及重金屬污染監測濃度在全世界之監測濃度均名列前茅，如中國石油化學工業開發(股)公司台南安順場址海水池底泥中之戴奧辛、五氯酚與汞以及二仁溪底泥中之 PCBs、多溴聯苯醚、多環芳香烴類、聯苯二甲酸酯類塑化劑以及重金屬等。由於部分污染物之監測濃度已經屢次超過法規規範值，且因絕大部分污染物是附著於較小粒徑之底泥顆粒，在水體經過反覆擾動後再沉降之過程中，小粒徑底泥顆粒之沉降速度明顯較慢，故容易沉積於淺層底泥，且容易為底棲生物與浮游生物所接觸與攝食，且因這些疏水性鹵化有機物不易代謝降解，一旦進入生物體內將導致食物鏈中污染物隨營養層次向上傳遞而形成生物放大(biomagnification)現象，損害生態系與人體健康福祉。為有效去除表層底泥中之疏水性鹵化有機污染物，本研究主要應用四項技術及污染物之物化特性進行疏水性鹵化有機物污染底泥整治技術研發，即(1)利用高溫之水在油中乳化液進入孔隙中直接接觸疏水性有機污染物增加接觸機會，藉著高溫使污染物之脫附與擴散加快之特性可將其有效傳輸至油相中；(2)再利用上層底泥造成降溫完成相反轉與形成超小油顆粒之技術，快速有效地將污染物傳輸至底泥上方以去除污染物；(3)利用已經完成整治並達標之淺層底泥作為現成加蓋材料，進行直接壓實之生物主動式加蓋(Bioactive capping)；(4)於完成加蓋後，可利用下方底泥中經過熱篩而佔優勢之產氫微生物成為優勢菌群進行殘餘乳化液之發酵產氫，上方底泥中之厭氧還原脫鹵菌群利用氫氣進行有效且持續之生物降解作用，將由下層底泥中擴

散進入上層底泥之鹵化污染物持續降解，形成有效之主動式生物屏障(active biobarrier)。本計畫原本為2年期計畫之第2年計畫，截至目前為止，符合進度要求，初步結論為歷年來二仁溪匯流處 PCBs 濃度似乎未見降低，不同深度樣品中有 73% 超出底泥品質指標下限值；相反轉單次操作可回收約 62% 之風化之 Aroclor 1254，風化污染物組之回收去除程度明顯優於添加污染物組，可能與乳化液現地相反轉可大幅提高與風化之疏水性有機污染物接觸所致，且高溫可能極有助於污染物之質傳，HCB 整體去除及降解情況均優於 Aroclor 1254。無論 HCB 或是 Aroclor1254，只要是風化之污染物，以現地相反轉乳化液回收結合生物分解可以達到 98% 以上之整體去除率，此可能為文獻中最佳之結果。本研究之結果應可確認此技術在遭受疏水性有機物污染底泥之現地整治具有高度可行性。

Abstract

Sediment contamination in Taiwan is an imperative environmental problem. Concentration levels of some hydrophobic organic compounds (HOCs) and heavy metals are ranked at the front all over the world. For example, the sediments in a seawater lagoon at An-Sun site in Tainan is heavily contaminated by dioxin, pentachlorophenol, and mercury while the sediment in Er-Ren River is highly contaminated by polychlorinated biphenyls, polybrominated diphenyl ethers, phthalate esters, polycyclic aromatic hydrocarbons, and heavy metals. Monitoring results often showed that some HOCs already exceeded the regulated levels. These HOCs easily accumulated at the surface sediment because finer particles tend to deposit on top of the

sediments and they offer larger surface area for HOCs to adsorb on. Thus, HOCs are easy for benthic organisms to access and uptake and can be biomagnified through trophic levels. At the end, these HOCs would affect ecosystem integrity and human health. To remove HOCs in shallow sediments, we proposed a study to employ four technologies and the inherent properties of HOCs. Major mechanisms are as follows: (1) higher contact opportunity between hot water-in-oil emulsion and HOCs in sediments, (2) more efficient desorption and diffusion of HOCs at higher temperature, (3) phase inversion at the cooler upper region of sediments to facilitate oil droplet transportation in pores, (4) utilization of the cleaned sediment material as an active capping materials, (5) higher hydrogen generation rate at the heat-treated lower region of the sediment, and (6) enhanced reductive dechlorination of halo-respirers at the upper region of the sediments. This study has shown that single inverse phase operation can remove 62% of weathered Aroclor 1254 and the following biodegradation generally is decreasing. For weather HCB and Aroclor1254, the overall removal could reach higher than 98% in 70 days. These results strongly support that this new technology has high feasibility to be implemented in full-scale field remediation.



[178] 以高分子聚合物 γ -PGA處理受含氯有機物污染地下水之 現地模場試驗

高志明

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中文摘要

本計畫以三氯乙烯(trichloroethylene, TCE)為目標污染物, 研究發展處理重質非水相溶液(dense non-aqueous phase liquids, DNAPL)污染地下水之整治技術。由於DNAPL污染場址之整治是屬於長期性的工作, 因此生物整治技術是較為經濟可行的整治方式。惟DNAPL之生物降解需長期注入主要基質, 但基質之注入往往造成地下水阻塞及酸化問題。聚麩胺酸(γ -PGA)是一種經由生化作用合成之高分子聚合物, 由於具有保濕性、無毒性、金屬螯合性、生物可分解性及生體相容性等特性, 已在各工業領域上有廣泛之運用性。因此 γ -PGA具有發展做為加強含氯有機物污染地下水之厭氧生物整治基質之優勢和潛力。本計畫主要之目的為評估以 γ -PGA為基質, 以整治受TCE污染地下水之可行性。本計畫工作項目包括(1) γ -PGA基本特性分析, 以評估 γ -PGA之物化和生物特性;(2)厭氧批次生物降解試驗, 以評估 γ -PGA加強TCE還原脫氯之可行性;(3)管柱試驗以模擬現地應用之成效並以管柱試驗獲得現地應用之設計參數; 及(4)現地模場試驗, 以獲得實場應用之成果並驗證實驗室數據。本計畫完成 γ -PGA基本特性分析、厭氧批次生物降解試驗、管柱試驗以及模場試驗場址。 γ -PGA基本特性分析之結果顯示 γ -PGA之二個主要粒徑包含437 nm及5,423 nm, 因此在奈米到微米之間。此粒徑大小可使 γ -PGA有效分佈到粗細顆粒間(包括黏土到砂粒), 達到均勻分佈及增加生物可及性目標。此外, γ -PGA之介達電位為-36 mV, 此負電位可使 γ -PGA向下游傳輸, 不會被主要代負電的土壤顆粒吸附在注入點附近。厭氧微生物批次實驗結果顯示, 實

驗中以 γ -PGA為主要基質時, TCE具有最佳之降解效率。TCE濃度由初始濃度之4.23 mg/L在42天內可持續穩定降解至0.26 mg/L, 反應至84天濃度剩餘0.01 mg/L, 降解效率高達99%, 已低於地下水污染管制標準0.05 mg/L。然而, 實驗中以乳化油為主要基質時, pH在第28天後迅速下降至5.95, pH值並在84天後降為5.66, 呈現酸化之情形。而 γ -PGA組之pH值在第84天仍在7.32, 維持良好之中性環境。 γ -PGA之總有機碳(total organic carbon, TOC)初始濃度為1,977 mg/L, 在第84天後降為量646 mg/L, 生物利用率為67.3%。乳化油組之TOC初始濃度為841 mg/L, 在第84天後為492 mg/L, 生物利用率為41%。此外, 由變性梯度膠體電泳(denaturing gradient gel electrophoresis, DGGE)菌相分析結果可知, γ -PGA可使環境中之菌相群集豐富度增加, 且各組別以即時定量聚合酶連鎖反應(real-time polymerase chain reaction, real-time PCR)分析初始脫氯菌(Dehalococcoides spp., DHC)菌量約為104 gene copies/g soil, γ -PGA組於84天增加到 1.49×10^6 gene copies/g, 生長效果較乳化油於84天之 9.4×10^4 gene copies/g soil為佳。由管柱試驗結果得知, 添加 γ -PGA於管柱中做為碳源時, 反應期間並未監測到出流水質酸化問題, pH值可維持在中性(6.5-7.5之間), 而氧化還原電位(oxidation-reduction potential, ORP)亦因 γ -PGA之注入, 使環境由氧化態轉變為還原態(ORP為-142 mV), 顯示 γ -PGA可有效做為微生物碳源。管柱試驗結果顯示管柱出流水TCE濃度於操作40天後, 可由初始之1.51 mg/L降為0.05 mg/L以下, 出流端3初期DHC菌量在約 10^3 gene copies/g, 於120天增加到 1.02×10^6 gene copies/g, 由批

次及管柱實驗結果可知，添加 γ -PGA 基質可促進現地脫氯菌生長，並能加強現地厭氧還原脫氯效果。現地模場評估結果顯示，本場址地下水 TCE 濃度介於 0.04 至 0.15 mg/L 之間，水力傳導係數為 7.269×10^{-4} cm/s，地下水流速為 41.2cm/day，地下水流向由西南向東北流動。W1 上游井做為 γ -PGA 灌注井，W3、W4、W5 三口下游井做為監測井，現地試驗於注藥後 W1 井 TCE 濃度 11 周內為 0.089 mg/L 改善 0.007 mg/L。監測井結果顯示，W3 井 TCE 濃度 5 周內由 0.149 mg/L 改善至 0.035 mg/L。另，初期各井脫氯菌量在約 103 gene copies/L，經灌注基質後各井位均有變化趨勢，後期第 75 天脫氯菌量維持在 $1.1 \times 10^5 \sim 4.6 \times 10^7$ gene copies/L；W2 井無灌注基質，脫氯菌量介於 $1.67 \times 10^3 \sim 4.52 \times 10^3$ gene copies/L。實驗結果證實上游注藥井降解效果顯著，亦形成透水性生物整治牆，符合現地、被動及生物整治概念之綠色整治技術。由基質成本計算，相較其他須添加緩衝溶液基質，以每公斤 NT 30 至 50 元 γ -PGA 釋碳基質較為優勢。本計畫執行成果顯示：(1)以 γ -PGA 為基質，可加速 TCE 之還原脫氯效率，並縮短整治期程；(2) γ -PGA 基質黏度低，可提升藥劑傳輸之能力；(3) γ -PGA 具有緩衝 pH 之效果，解決以往生物基質會造成水質酸化之問題，維持良好之中性環境；(4) γ -PGA 可有效促進厭氧分解反應，維持厭氧環境和菌種豐富度；(5) γ -PGA 釋碳基質可避免其他釋碳基質造成地下水體 pH 值酸化問題，亦較其他基質具有較佳之傳輸性及可維持高濃度之生物可利用碳性質。實場數據顯示 γ -PGA 可有效促進現場 TCE 之生物降解，使 γ -PGA 之基質系統成為一種更具經濟效益及環境友善之綠色整治工法。

Abstract

Soil and groundwater at many existing and former industrial areas and disposal sites are contaminated by halogenated organic compounds that were

released into the environment. When they are released into the subsurface, they tend to adsorb onto the soils and cause the appearance of DNAPL (dense-non-aqueous phase liquid) pool. In situ bioremediation of DNAPLs sites need to inject carbon substrates into the subsurface, which would cause the acidification and odor problems of the subsurface environment. This would deteriorate the groundwater quality and cause the increase in maintenance cost. The objective of this proposed study is to evaluate the feasibility of applying the poly-(γ -glutamic acid) (γ -PGA) as the primary substrate to enhance the TCE reductive dechlorination. The γ -PGA is a biopolymer synthesized by biochemical processes. Due to its characteristics of moisture resistance, no toxicity, and chelating ability with metals, it has been widely applied by the industry. The one-year project includes four major tasks: (1) analysis of basic physical, chemical, and biological characteristics of γ -PGA, (2) performance of anaerobic microcosm experiments, (3) conduction of anaerobic column experiments, and (4) in situ pilot-scale study. This project results from the particle size distribution of γ -PGA show that two major diameters of γ -PGA were observed, which were around 437 nm and 5,423 nm. Thus, the diameter of γ -PGA globule was in nano to micro-scale ranges. These two different size ranges of γ -PGA globule allowed it to distribute evenly in soil particles. The average zeta potentials of γ -PGA was -36 mV. This result implies that γ -PGA globule was in a reduced state, and the reduced zeta potential would result in the increase in the repulsion and friction force between γ -PGA globule and soil particles. This would promote γ -PGA to migrate to farther downgradient area, and thus, the influence zone can be enlarged. The microcosm study was conducted to evaluate the feasibility and effectiveness of using γ -PGA for the enhancement of TCE dechlorination. Results show that the addition of γ -PGA created anaerobic conditions and also caused a rapid increase in the total organic carbon



concentration (about 1,977 mg/L). This led to a more thorough biodegradation of TCE through reductive dechlorinating mechanisms. Up to 99% of TCE (with initial concentration of 4.23 mg/L) was degraded after 84 days of operation. Acidification was prevented due to the release of amine functional groups could react with water and form ammonia, which resulted in alkaline conditions due to its basic characteristic. Thus, pH was maintained in neutral conditions, which benefited the growth of *Dehalococcoides* spp. (DHC). Increase in DHC population indicates that the supplement of γ -PGA enhanced the growth of DHC (increased from 1×10^4 to 1.49×10^6 gene copies/g soil) after 84 days of operation, and thus, the TCE dechlorination rate was enhanced. Microbial analyses reveal that dechlorinating bacteria existed in soils, which contributed to TCE dechlorination. The increased ethene concentrations indicate the complete TCE dechlorination with γ -PGA addition. The column experiments were performed to evaluate the effectiveness of using the γ -PGA as the primary substrates for TCE control and biodegradation. Results from the column study show that the TCE concentration in the column effluent dropped from the initial concentration of 1.51 mg/L to below 0.05 mg/L after 40 days of operation. TCE biodegradation byproducts (dichloroethylene and vinyl chloride) were also observed. The results indicate that the addition of γ -PGA could effectively enhance the TCE dechlorination. The produced byproducts were further degraded and accumulation of byproducts was not observed. In this study, Increase in DHC population indicates that the supplement of effluent 3 enhanced the growth of DHC (increased from 1×10^3 to 1.02×10^6 gene copies/g) after 120 days of operation, and thus, a DNAPL-contaminated site (Yun-Kun TCE-contaminated site) is selected to apply γ -PGA as the primary substrate for field application. The TCE concentrations

in groundwater at the selected site ranged from 0.04 to 0.15 mg/L. The site hydraulic conductivity and groundwater flow velocity are 7.269×10^{-4} cm/s and 62.8 cm/d, respectively. The groundwater flows to the northeastern direction. One upgradient well and three downgradient wells are selected as the substrate injection and monitoring wells, respectively. Moreover, an upgradient well with TCE contamination is used as a control well for comparison. Results from the contaminated site show that the TCE concentration in the degradation dropped from the initial concentration of 0.089 mg/L to below 0.007 mg/L after 11 weeks of operation in W1 wells Perfusion matrix, Results from the Monitoring wells study show that the TCE concentration in the degradation dropped from the initial concentration of 0.149 mg/L to below 0.035 mg/L after 5 weeks of operation in W3 wells. In addition, the initial amount of each well is about 10^3 gene copies/L, Increase in DHC population indicates that the supplement of γ -PGA enhanced the growth of DHC (increased from 1.1×10^5 to 4.6×10^7 gene copies/L) after 75 days of operation, and thus, W2 wells without perfusion matrix, DHC between 1.67×10^3 to 4.52×10^3 gene copies/L. The results show that the degradation effect of upstream injection is significant and the formation of permeable biological treatment wall is realized. The technology of conforming to the concept of local, passive and biological remediation includes the local biological rehabilitation combined with the permeable reaction wall. Calculated from the matrix cost, compared to other need to add buffer solution matrix, γ -PGA to NT 30 to 50 yuan per kilogram carbon matrix is more advantage. The major conclusions include the following: (1) γ -PGA can be applied as a primary substrate and create a reduced condition, which enhances the in situ reductive dechlorination of TCE, (2) γ -PGA has a low globule diameter, which allows it to migrate to the farther downgradient without causing a clogging



problem, (3) γ -PGA has a pH buffering capacity, which prevents the groundwater acidification problem after supplement, (4) γ -PGA could be used as the carbon source and improve the microbial diversity, and (5) γ -PGA carbon-depleting matrix can avoid the problem of acidification of groundwater by other carbon-releasing matrix, and it has better transportability and high bio-usable carbon properties than other nature. Results of this study will aid in designing an in situ bioremediation system containing γ -PGA substrate for remedial application. The proposed treatment scheme would be expected to provide a more cost-effective alternative to remediate chlorinated-solvent contaminated aquifers.



[179] 環境友善型聚麩胺酸清洗受重金屬污染土壤之模場試驗

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中文摘要

在臺灣，土壤受到重金屬之污染已成為一嚴重之問題，尤其是農地的污染，往往導致其生產作物亦受到污染，對食品安全造成極大的威脅。本研究選擇一受中高濃度銅、鋅、鎳、鉻污染之農地，以氫型聚麩胺酸(polyglutamic acid, H- γ -PGA)清洗受重金屬污染之土壤。研究將先進行批次實驗，評估不同清洗條件對土壤重金屬移除之影響，再以最佳可行操作條件進行現地模場試驗，並做適度的參數調整，以提供現場整治之參考。本研究之主要目的為(1)評估不同操作參數(洗劑濃度、土水比、清洗時間等)對H- γ -PGA 去除重金屬之影響；及(2)評估H- γ -PGA 清洗對土壤性質及土壤肥力之影響。本場址面積為3,158 m²，本團隊以15 m × 15 m 網格進行現地細密調查結果顯示，各項重金屬污染最高濃度分別為Cu：784 mg/kg、Cr：256 mg/kg、Zn：1,050 mg/kg 及Ni：195 mg/kg，高污染區域集中於1892-19 及1892-20 兩靠近溝渠之點位，顯示該農地之污染可能來自溝渠。XRF 分析結果與王水消化總量之間的相關性，結果發現對於銅、鉻、鋅及鎳的決定係數(R²)分別達0.9969、0.9972、0.986 及0.9943，未來進行現地整治時，可利用XRF分析，輔以本研究建立的公式迅速評估現地整治成效。PGA 清洗土壤中Cr、Ni、Cu 及Zn 等金屬之試驗結果顯示，PGA 對各種目標金屬皆有去除能力，PGA 濃度升高，Cu、Cr、Zn 及Ni 去除效果亦增進。田口實驗結果顯示，不同操作因子對重金屬去除之影響為PGA 濃度>水土比>清洗時間>轉速，最佳操作條件為PGA 3.5%、水/土比15/1、清洗時間60分鐘及轉速200 rpm。在此操作條件下，主要污染物Cu 去除率最高可達50.7%。若以PGA清洗三次，Cu 去除率可提升至74.3%。研究結果顯示，經PGA 清洗

後，各項重金屬濃度皆有下降，雖未低於管制標準，但對於超標倍數最高的銅已大幅降低其濃度，有助於翻轉稀釋法之成功率，毋需將高污染土壤外運處理。土壤經PGA 清洗後，pH 值接近中性、氮含量提高至114 mg/kg，且土壤菌相變化不大，顯示PGA 相當具環境友善性。本研究結果，將可提供受污染場址進行整治之參考。

Abstract

In Taiwan, soil contaminated by heavy metals has become a serious problem. The contamination of agricultural lands results in the polluted produce, causing a great threat to food safety. In this study, a farmland contaminated by heavy metals (Cu, Zn, Ni, and Cr) was selected to evaluate the performance of H-type polyglutamic acid (H- γ -PGA) on the removal of heavy metals in soil washing. Batch experiments were conducted first to assess the effect of different washing conditions on the removal of heavy metals in laboratory. In situ pilot study will be then performed by using the optimum operating parameter obtained from the batch experiments. The main objectives of this study are to (1) evaluate the effect of different operating conditions (washing agent concentration, water/soil ratio, washing time) on the removal of heavy metals by H- γ -PGA; and (2) assess the effect of H- γ -PGA on the soil property and fertility. The area of the site was 3,158 m² and soil sampling was conducted using a 15 m × 15 m grid soil sampling procedure. The results show that the highest heavy metal concentrations at this site were Cu: 784 mg/kg, Cr, 256 mg/kg, Zn: 1,050 mg/kg, and Ni: 195 mg/kg. The most seriously polluted area located at two sampling points near a trench, 1892-19 and 1892-20, indicating that water from the ditch may be the



source of the heavy metals. The analytical results of soil between X-ray Fluorescence (XRF) and aqua regia digestion had a good relationship. Therefore, XRF analysis can be used during site remediation to evaluate the remedial performance in the future. The results of soil washing experiments show that PGA was capable of removing the target metals. The removal efficiency of heavy metals increased with increasing PGA concentrations. The results of Taguchi Method show that factors that affected the removal efficiency of heavy metals was of the order PGA concentration > water/soil ratio > washing time > rotational speed. The optimal operating parameters for heavy metal removal were: PGA 3.5%, water/soil ratio 15/1, washing time 60 min, and rotational speed 100 rpm. Under the optimal conditions, up to 50.7% of the major target metal, Cu was removed. When the soil was washed 3 times by PGA, the removal efficiency of Cu was improved to 74.3%. Although heavy metal concentrations in soil did not meet the soil control standards, Cu concentrations were reduced significantly. The washed soil could be further treated by the turn-over dilution method to achieve the success in remediation. Therefore, off-site treatment of soil was not needed. After the treatment, pH of soil was around neutral, total nitrogen content increased to 114 mg/kg, and the change in soil bacterial community was moderate, indicating that PGA is an environmental friendly washing reagent. The results of this study can provide valuable information for site remediation in the future.

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多重索引 Index

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重金屬

Heavy Metals

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