

INTERACTION BETWEEN DISSOLVED ORGANIC MATTER AND
ENDOCRINE DISRUPTORS IN LANDFILL LEACHATE



张彩香 著
王焰新

垃圾渗滤液中溶解有机质 与内分泌干扰物相互作用研究

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Caixiang Zhang & Yanxin Wang

张彩香 王焰新 著

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Preface

Disposal of huge amount of municipal wastes produced by 1.3 billion Chinese people in the process of fast industrialization and urbanization presents a major challenge for environmental management. In most areas, the tradition of uncontrolled garbage landfilling or dumping in a nearby space is still in practice, and industrial, municipal, domestic and hospital wastes are dumped together. During our work on groundwater geochemistry, the historic record and recent report of groundwater contamination close to landfill sites have retained our great attention to the impact of landfill leachate on the subsurface environment.

The chemical composition of landfill leachate is highly variable both spatially and temporally, due to differences in garbage sources, local climate, landfill age and composition. As potential sources of groundwater pollution, the refractory organic substances in landfill leachate were the focus of our study. We realized that dissolved organic matter (DOM) and environmental endocrine disruptors (EEDs) are two major groups of refractory organic pollutants in landfill leachate that are hardly biodegradable. Their cost-effective removal has become a great challenge for environmental engineering studies, while their interaction a hot and frontier topic for environmental science. With the support of National Natural Science Foundation of China (No.40830748 and No.40972156), as reported in this book, basic research work has been done by us in recent years.

The goal of this book was to characterize DOM and EEDs in leachates from three landfills and to understand the interaction mechanisms between DOM and EEDs to develop new processes for EEDs removal as well as to provide background data for understanding the transport of landfill leachate organic pollutants in the subsurface environment. The chemical compositions of leachate DOM from three landfills in Hubei province of central China were investigated. The DOM fractions isolated from landfill leachate by ultrafiltrate and XAD resin separation were

characterized using different analysis methods such as DOC, DON, UV, FTIR, ICP-AES, HPLC, Fluorescence spectra, ^1H NMR and GPC. Trace organic pollutants in leachate and target compounds such as NPs, PAEs, BPA and estrogens were analyzed by GC/MS and GC \times GC/ToFMS to understand the fate of EEDs in the environment. The compositions or structures of leachate DOM were analyzed and their possible sources identified using Py/GC/MS. And the adsorption mechanisms between DOM and EEDs and the feasibility of treating PAEs by adsorption were studied. Experiments were made to remove BPA, E_2 and E_1 under ultraviolet (UV) light irradiation with the catalyzer of TiO_2 and to understand the effects of DOM on the removal efficiency. Besides, a new process to degrade EEDs using photocatalytic oxidation was proposed and the effect of DOM on EEDs removal experimentally was tested.

The book was written in English and translated into Chinese by Dr. Caixiang Zhang as a result of her Ph.D thesis work at China University of Geosciences (CUG) and post-doc research work at the United States Geological Survey (USGS, Reston, VA). As her Ph.D supervisor and her colleague now at CUG, I was involved in working out research plan, evaluating the results and revising the book text. We appreciate the firm support of Wuhan Environmental Sanitation Science Research & Design Institute, Bureau of Environmental Protection of Wuhan Municipal Government, and the great help of Dr. Isabelle Cozzarelli and Dr. Robert Egenhouse of USGS.

Yanxin Wang, Ph.D
Professor of Hydrogeology
China University of Geosciences

前 言

在我国快速工业化、城镇化进程中，13 亿人民生活水平得以不断提高，但产生的巨量生活垃圾的处置问题对环境管理提出了严峻挑战。在大多数地区，至今仍沿袭就近空地填埋甚至随意堆放垃圾之陋习，工业、市政、家庭和医疗废物被堆置于一体。众多垃圾填埋场附近地下水污染的历史记录与现实结果，使得我们近年来在从事地下水地球化学研究过程中，越来越关注垃圾渗滤液及其对地下水的影响。

垃圾渗滤液的物质成分呈现强烈的时空变异性，所含有机和无机污染物浓度因垃圾来源、当地气候、填埋龄和填埋废物组成等多因素的变化而变化。作为周边地下水污染源的垃圾渗滤液中难降解有机物成为我们近期关注的焦点。我们认识到，溶解性有机物（DOM）和内分泌干扰物（EEDs）是渗滤液中两大类不易被现有微生物降解的有机污染物，如何有效去除之是环境工程研究面临的重大挑战，而其间的相互作用则成为环境科学研究的热点和前沿课题。在国家自然科学基金 No.40830748 和 No.40972156 的支持下，在过去的几年中，我们围绕本书所述的内容开展了基础性研究工作。

本书的主要研究目标是表征渗滤液中 DOM 和 EEDs，研究其相互作用机理，为合理选择渗滤液处理工艺、探讨渗滤液有机污染物在地下水系统中的迁移转化规律提供科学基础。通过调查三个代表性填埋场，对于渗滤液中 DOM 化学成分进行了表征，即综合各种分离手段（如超滤和 XAD 树脂分离）和表征手段（如元素分析、FTIR、UV、NMR、Py/GC/MS、GPC、HPLC、GC/MS 和 FL 等），全面系统地了解垃圾渗滤液中 DOM 的组成与分子结构特征；运用 GC/MS 和 GC × GC/ToFMS，全面调查渗滤液中的有机污染物质，尤其是 EEDs，并建立定量分析目标化合物壬基酚（NPs）、邻苯二甲酸酯类（PAEs）、双酚 A

和激素类的方法，探索其在环境中的最终归宿；运用热解-GC/MS 进一步地表征渗滤液 DOM 组成与结构，对其进行源解析；为揭示渗滤液 DOM 与 EEDs 的吸附机理，探索运用 DOM 作为吸附剂去除 PAEs 的可能性。最后，探讨了在二氧化钛催化-紫外光辐射作用下，DOM 对双酚 A、雌二醇和雌酮光降解的影响，提出了一种处理 EEDs 的光催化氧化新工艺，考察 DOM 对 EEDs 去除的影响。

本书原稿为英文，由张彩香执笔并译成中文，是她在中国地质大学开展博士学位论文研究和在美国地质调查局从事博士后研究工作的主要成果总结。作为其导师和现在的同事，我参与了研究方案制定、研究结果讨论、文字修改等工作。研究工作得到武汉市环境卫生研究设计院、武汉市环境保护局和美国地质调查局 Isabelle Cozzarelli 博士和 Robert Egenhouse 博士的帮助和支持，特此致谢！

王焰新

2009年12月18日于南望山麓

ABSTRACT

Sanitary landfilling remains the predominant approach for municipal solid waste (MSW) disposal in many countries. Large amount of landfill leachate with fluctuating and complex compositions and high concentrations of refractory organic pollutants and toxic substances has been generated in the process of landfilling. The residual COD in the leachate after conventional treatments is generally around 500 mg/L. Until now there has been no practically applicable technology to effectively remove COD from landfill leachate existed. It was discharged into the environment without meeting national solid waste landfill pollution control standards such as GB16889-1997 in China, let alone the discharge standards for hazardous substances that can not be indicated effectively using parameters of total organic pollutants such as COD. Even if the contents of toxic substances such as environmental endocrine disruptors (EEDs) are as low as ng/L level, they may have carcinogenic, teratogenic and mutational effects on human organisms including reproductive organs, endocrine, nervous and immune systems. Thus, with the development of analytical methods and the increase of environmental awareness, great attention has been paid to toxic substances in landfill leachate in recent years.

Dissolved organic matter (DOM) is the main composition as well as a major source of residual COD in landfill leachate. DOM plays a significant role on the fate and transformation of pollutants in the environmental systems. Therefore, characterization of DOM in landfill leachate is significant.

Landfill leachate samples were collected from three landfills (labeled as R-landfill, J-landfill, H-landfill respectively). R and J landfill are in Wuhan. R Landfill has a history of 5 years in operation, while landfill J has been closed for about 5 years. H-landfill lies in Yichang city, a smaller city 300 km away from Wuhan. Representative compounds of EEDs such as bisphenol A (BPA), estradiol (E_2), estrone (E_1), and phthalate esters (PAEs) were chosen according to the characteristics of occurrence of DOM and organic pollution in leachate. The effect of DOM on solid/liquid two-phase fraction of EEDs adsorption mechanism and photodegradation processes of EEDs were studied. The main results are as follows:

(a) DOM in landfill leachate was characterized systematically. Leachate DOM was characterized by fractionation using ultrafiltration (UF) and XAD resin and analyzed both qualitatively and quantitatively by combining different analysis methods such as UV, fluorescence, GPC, HPLC, FTIR spectroscopy, element analysis, 1H NMR and pyrolysis-gas chromatography/mass spectrometry (Py/GC/MS). The results showed that the compositions of DOM depend on landfill age, waste content in landfill and rainfall in landfill region. Fulvic acid was dominant in all samples. High H/C and N/C in leachate DOM (especial in R-landfill)

indicated the dominant biochemical process. In the older J-landfill, the amount of carbohydrates and proteins determined by Py/GC/MS analysis was lower, and concentrated high aromatic structure of DOM may be the main reason for the difficulty of removing residual COD.

(b) The distribution of organic pollutants in leachate was investigated comprehensively and a suitable method for EEDs was established. A comprehensive determination of the composition of organic pollutants including surfactants, plasticizers, pharmaceuticals, pesticides, hormones, and oil was obtained by using GC/MS analysis. Based on the investigation, the methods of simultaneously determining BPA, E₁, E₂, sterols and phthalates as targets compounds in leachate were developed. Concentrations of pollutants were usually low during the whole processes except for BPA and DEHP, which were up to 127.66 µg/L and 232.5 µg/L respectively. The concentrations were correlated with landfill ages, waste compositions and sampling seasons. The results indicate that conventional treatment processes can not meet the demand of discharge, and advanced treatment methods were required. In addition, more than 20 types of sterols in landfill leachate were identified for the first time in China. Different biomarker index showed that leachate poses a long-term threat to the aquatic environment. Finally, over 178 NP compounds and 27 main NP isomers were found in tNP by using SDE-GC×GC/ToFMS analysis.

(c) The mechanism of adsorption between DOM and EEDs was studied to explore the possibility of removing EEDs by adsorption. Sorption experiments and the interaction between targets EEDs, including BPA, E₂, E₁, and DOM from leachate were investigated using FTIR, ¹H NMR and ESR. The adsorption isotherms fit the Freundlich equation well. The results suggested that multiple binding mechanisms might occur simultaneously in the adsorption process such as ionic bonds, hydrogen bonds and charge-transfer bonds. Adsorption can be applied to remove hydrophobic pollutants ($\lg K_{ow} > 4.5$) from water by DOM as a complexing agent during complexation-flocculation process.

(d) A new process to degrade EEDs using photocatalytic oxidation was proposed and experimentally tested. The direct and indirect photolysis of BPA, E₂ and E₁ was investigated in the absence and presence of DOM from three landfills. EEDs degradation by direct photolysis under sunlight irradiation was significantly slower than that in the presence of DOM. However, distinct differences in indirect EEDs photolysis by DOM from direct photolysis were observed primarily due to competitive light absorption and quenching of EEDs. Photodegradation rate constant are relative to DOM source or molecular structure. The pathway of photodegradation of EEDs was proposed and the estrogenic activity of E₂ degradation products was discussed. On this basis, a multi-variable model of photodegradating EEDs was established and a new process to degrade EEDs using photocatalytic oxidation proposed, which might be applicable for treating other types of wastewater with high concentrations of refractory organic matters. The process therefore has great potential of application in environmental studies.

List of Acronyms and Abbreviations

^1H , ^{13}C NMR	Proton and carbon nuclear magnetic resonance spectra
AP ₂ EO	4-alkylphenol di-
APEOs	Alkylphenol polyethoxylates
BBP	Butyl benzyl phthalate
BOD	Biochemical oxygen demand
BPA	2,2'-bis-(4-hydroxyphenyl) propane
BSTFA	Bis(trimethylsilyl)trifluoroacetamide
CDOM	Chromaphoric dissolved organic matter
COD	Chemical oxygen demand
DBP	Di-butyl benzyl phthalate
DCM	Dichloromethane
DEET	N,N-diethyltoluamide
DEHP	Di-ethyl hexyl phthalate
DEP	Diethyl phthalate
DHA	Dissolved humic acid
DI	Deionized
DMP	Dimethyl phthalate
DnOP	Di-n-octyl phthalate
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
DON	Dissolved organic nitrogen
E ₁	Estrone
E ₂	17 β -estradiol
E ₃	Estriol
EE ₂	17 α -ethynylestradiol
EEDs	Environmental endocrine disruptors
ESR	Electron spin resonance
FAs	Fulvic acids
FL	Fluorescence spectroscopy
FTIR	Fourier transform infrared spectroscopy
GC/MS	Gas chromatography–mass spectrometry
GPC	Gel permeation chromatography
HAs	Humic acids
HHW	Household hazardous wastes

HMW	High molecular weight
HiA	Hydrophilic acids
HiN/B	hydrophilic neutrals and bases
HoA	Hydrophobic acids
HoN/B	hydrophobic neutrals and bases
HPI	Hydrophilics
HPLC	High-performance liquid chromatography
HPO	Hydrophobics
K_{ow}	Water and octanol
LC/MS	Liquid chromatography–mass spectrometry
LLE	Liquid–liquid extraction
LMW	Low molecular weight
MBR	Membrane bioreactor
MCPP	Mecoprop
MSW	Municipal solid waste
MW	Molecular weight
NP	4-nonylphenol
NP ₁ EO	Monoethoxylates
NP ₂ EO	4-nonylphenol di-
PAEs	Phthalic acid esters
PAH	Polyhydroxy-aromatics hydrocarbon
pc	Polar compounds
Py/GC/MS	Pyrolysis–gas chromatography/mass spectrometry
ROS	Refractory organic substances
RIC	Reconstructed ion current
RID	Refractive index detector
SEC	Size Exclusion Chromatography
SPE	Solid-phase extraction
SS	Suspended solid
TFUF	Tangential flow ultrafiltration
TIC	Total ion current
TMAH	Tetramethylammonium hydroxide
TOC	Total organic carbon
UCM	Unresolved Complex Mixture
UF	Ultrafiltrate
UV	Ultraviolet
WWTPs	Wastewater treatment plants
XOCs	Xenobiotic organic compounds

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