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沉积物中有机污染物多残留同时分析技术及其
应用于九龙江河口复合污染特征研究

Development of Simultaneous Determination Method for Multi-categorized
Organic Pollutants in Sediment and Its Application to the Study of
Combined Pollution Characteristics of
the Jiulong River Estuary

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摘 要.....	I
Abstract.....	IV
第 1 章 绪 论.....	1
1.1 引言.....	1
1.2 环境中 5 类典型有机污染物的来源及其危害.....	1
1.2.1 多环芳烃.....	1
1.2.2 多氯联苯.....	2
1.2.3 多溴联苯醚.....	3
1.2.4 农药.....	3
1.2.5 抗生素.....	4
1.3 有机污染物进入沉积物的迁移途径.....	4
1.4 沉积物中 5 类典型有机污染物研究进展.....	5
1.4.1 仪器检测方法研究进展.....	5
1.4.2 样品前处理方法研究进展.....	8
1.4.3 不同区域沉积物中 5 类典型有机污染物的污染状况.....	10
1.5 污染物来源解析技术.....	11
1.5.1 分子比值法.....	11
1.5.2 “指纹”图谱法.....	12
1.5.3 多元变量统计分析法.....	13
1.6 沉积物中有机污染物生态风险评价.....	13
1.6.1 沉积物质量标准在生态风险评价中的应用.....	13
1.6.2 污染物生物毒性数据在生态风险评价中的应用.....	14
1.7 课题的提出.....	15
1.8 研究内容和技术路线.....	18
参考文献.....	18
第 2 章 沉积物中 76 种有机污染物的 GC-MS/MS 同时分析方法研究	28

2.1 引言.....	28
2.2 实验仪器和材料.....	28
2.2.1 仪器设备.....	28
2.2.2 材料与试剂.....	29
2.2.3 试剂处理及配制.....	30
2.2.4 数据分析.....	30
2.3 实验方法.....	30
2.3.1 GC-MS/MS 仪器条件	30
2.3.2 样品前处理方法.....	30
2.4 结果与讨论.....	31
2.4.1 GC-MS/MS 仪器方法的优化	31
2.4.2 样品前处理方法优化.....	38
2.4.3 分析方法的质量控制.....	41
2.5 本章小结.....	46
参考文献.....	46
第 3 章 沉积物中 46 种有机污染物的 LC-MS/MS 同时分析方法研究	
.....	48
3.1 引言.....	48
3.2 实验仪器和材料.....	48
3.2.1 仪器设备.....	48
3.2.2 材料与试剂.....	48
3.2.3 试剂处理及配制.....	49
3.2.4 数据分析.....	50
3.3 实验方法.....	50
3.3.1 LC-MS/MS 仪器条件	50
3.3.2 样品前处理方法.....	55
3.4 结果与讨论.....	55
3.4.1 LC-MS/MS 仪器方法建立优化	55
3.4.2 样品前处理方法优化.....	59
3.4.3 方法质量控制.....	65

3.5 本章小结.....	68
参考文献.....	68
第 4 章 九龙江河口沉积物中有机污染物复合污染特征	70
4.1 引言.....	70
4.2 实验设备和材料.....	70
4.3 样品采集与处理.....	70
4.3.1 采样点设置.....	70
4.3.2 样品采集保存及处理.....	70
4.3.3 样品分析.....	71
4.3.4 样品分析过程质量控制.....	72
4.3.5 总有机碳测定及定年.....	72
4.4 样品分析过程质量控制.....	72
4.5 目标化合物检出情况及其复合污染特征.....	73
4.5.1 多环芳烃检出情况及污染特征.....	73
4.5.2 多氯联苯检出情况及污染特征.....	77
4.5.3 农药检出情况及污染特征.....	81
4.5.4 抗生素检出情况及污染特征.....	90
4.6 本章小结.....	95
参考文献.....	96
第 5 章 九龙江河口沉积物中有机污染物来源解析	99
5.1 引言.....	99
5.2 数据分析.....	99
5.3 来源解析.....	99
5.3.1 多环芳烃的来源解析.....	99
5.3.2 多氯联苯的来源解析.....	104
5.3.3 DDTs 的来源解析	107
5.3.4 BHCs 的来源解析.....	109
5.4 本章小结.....	111
参考文献.....	112

第 6 章 九龙江河口沉积物中有机污染物初步生态风险评价	115
6.1 引言	115
6.2 沉积物中有机污染物的生态风险评价	115
6.2.1 生态风险评价方法	115
6.2.2 多环芳烃的生态风险评价	116
6.2.3 多氯联苯的生态风险评价	117
6.2.4 DDTs 的生态风险评价	118
6.2.5 BHCs 的生态风险评价	119
6.2.6 表层沉积物中其它农药的生态风险评价	121
6.2.7 表层沉积物中抗生素污染生态风险评价	122
6.3 本章小结	123
参考文献	124
第 7 章 结语与展望	126
7.1 本研究的贡献	126
7.2 本研究的不足	126
7.3 研究展望	126
致 谢	128
附 录	129
攻读硕士研究生期间发表的论文	158

Contents List

Abstract (in Chinese)	I
Abstract (in English).....	IV
Chapter 1 Preface.....	1
1.1 Introduction	1
1.2 Sources and hazardous of five categories of typical organic pollutants in the environment	1
1.2.1 PAHs	1
1.2.2 PCBs	2
1.2.3 PBDEs.....	3
1.2.4 Pesticides.....	3
1.2.5 Antibiotics	4
1.3 Transference pathways of organic pollutants into sediment	4
1.4 Review on reaserches of the five categories of typical organic pollutants in sediment	5
1.4.1 Instrumental analysis	5
1.4.2 Sample preparation	8
1.4.3 Pollution status in different areas.....	10
1.5 Sources apportionment techniques	11
1.5.1 Diagnostic ratios	11
1.5.2 Fingerprint chromatogram	12
1.5.3 Multivariate analysis.....	13
1.6 Ecological risk assessment of organic pollutants in sediment	13
1.8.1 Application of sediment quality guidelines.....	13
1.8.2 Application of biological toxicity datas	14
1.7 Objective of this research	15
1.8 Research contents and technical approaches	18
References	18
Chapter 2 Development of a multi-residue method for the determination of 76 organic pollutants in sediment using GC-MS/MS.....	28
2.1 Introduction	28

2.2 Equipments and materials	28
2.2.1 Instruments and equipments.....	28
2.2.2 Materials and reagents	29
2.2.3 Preparation for reagents	30
2.2.4 Data analysis	30
2.3 Experimental methods	30
2.3.1 Instrumental parameters for GC-MS/MS.....	30
2.3.2 Sample preparation	30
2.4 Results and discussion	31
2.4.1 Optimization of GC-MS/MS parameters	31
2.4.2 Optimization of sample preparation.....	38
2.4.3 QA/QC	41
2.5 Summary	41
References	46
Chapter 3 Development of a multi-residue method for the determination of 46 organic pollutants in sediment using LC-MS/MS	48
3.1 Introduction	48
3.2 Equipments and materials	48
3.2.1 Instruments and equipments.....	48
3.2.2 Materials and reagents	48
3.2.3 Preparation for reagents	49
3.2.4 Data analysis	50
3.3 Experimental methods	50
3.3.1 Instrumental parameters for LC-MS/MS	50
3.3.2 Sample preparation	55
3.4 Results and discussion	55
3.4.1 Optimization of LC-MS/MS parameters	55
3.4.2 Optimization of sample preparation.....	59
3.4.3 QA/QC	65
3.5 Summary	68
References	68
Chapter 4 Combined pollution characteristics of 122 organic compounds in sediment from the Jiulong River Estuary	70

4.1 Introduction	70
4.2 Equipments and materials	70
4.3 Sampling and pretreatment	70
4.3.1 Sampling station.....	70
4.3.2 Sampling, storage and pretreatment.....	70
4.3.3 Sample analysis.....	71
4.3.4 QA/QC for sample analysis	72
4.3.5 Determination of TOC and dating of sediment core	72
4.4 QA/QC	72
4.5 Pollution status of target compounds and its combined pollution characteristics	73
4.5.1 Pollution status and characteristics of PAHs	73
4.5.2 Pollution status and characteristics of PCBs	77
4.5.3 Pollution status and characteristics of pesticides.....	81
4.5.4 Pollution status and characteristics of antibiotics.....	90
4.6 Summary	95
References	96
Chapter 5 Sources apportionment of organic pollutants in sediments from the Jiulong River Estuary.....	99
5.1 Introduction	99
5.2 Data analysis	99
5.3 Sources apportionment	99
5.3.1 Sources apportionment of PAHs.....	99
5.3.2 Sources apportionment of PCBs.....	104
5.3.3 Sources apportionment of DDTs.....	107
5.3.4 Sources apportionment of BHCs	109
5.4 Summary	111
References	112
Chapter 6 Preliminary ecological risk assessment of organic pollutants in sediments from the Jiulong River Estuary.....	115
6.1 Introduction	115
6.2 Ecological risk assessment of organic pollutants in sediments	115
6.2.1 Method for the ecological risk assessment	115

6.2.2 Ecological risk assessment of PAHs	116
6.2.3 Ecological risk assessment of PCBs	117
6.2.4 Ecological risk assessment of DDTs.....	118
6.2.5 Ecological risk assessment of BHCs.....	119
6.2.6 Ecological risk assessment of other pesticides in surface sediments	121
6.2.7 Ecological risk assessment of antibiotics in surface sediments	122
6.3 Summary	123
References	124
Chapter 7 Conclusions	126
7.1 Contributions	126
7.2 Shortages	126
7.3 Perspectives	126
Acknowledgements.....	128
Appendix.....	129
Manuscripts during master graduate study	158

廈門大學博碩士論文摘要

摘要

我国沿海社会经济相对发达,河口区域承载着流域各类生产、生活活动排放的大量有机污染物。沉积物作为水环境的重要组成部分,既是污染物的主要归宿,又是污染物迁移的载体和二次污染来源。河口沉积物中频繁检出的多环芳烃(PAHs)、多氯联苯(PCBs)、多溴联苯醚(PBDEs)、农药和抗生素等有机污染物严重威胁着河口生态环境。本论文以PAHs、PCBs、PBDEs、农药和抗生素5类122种有机污染物为目标物,运用色谱-串联质谱技术建立了其在沉积物中的分组同时分析方法,并且应用于福建九龙江河口表层和柱状沉积物样品的分析,对污染物进行了污染特征、来源解析和初步生态风险评价研究。

主要研究内容和结果如下:

1. 沉积物中16种PAHs、27种PCBs、6种PBDEs和27种农药的GC-MS/MS同时分析方法

通过对气相色谱-串联质谱联用(GC-MS/MS)仪器条件(母离子、子离子、碰撞能和升温程序等)和样品前处理条件(固相萃取柱类型/规格/组合方式、洗脱溶剂种类及体积、萃取溶剂体积和铜粉的影响等)的优化,建立了沉积物中16种PAHs、27种PCBs、6种PBDEs和27种农药在选择性反应监测模式(SRM)下的同时分析方法。各目标化合物方法检出限(MDL)在 0.01 ng g^{-1} ~ 12.9 ng g^{-1} 之间。采用内标法进行定量, 0.50 ng g^{-1} 、 2.0 ng g^{-1} 和 10.0 ng g^{-1} 三个不同浓度水平的沉积物基底加标回收率和相对标准偏差(RSD)分别为68.6%~125.2% (1.1%~23.3%, $n=5$)、45.3%~128.1% (2.1%~19.3%, $n=5$)和43.8%~136.0% (1.4%~16.4%, $n=3$)。

2. 沉积物中13种农药和33种抗生素的LC-MS/MS同时分析方法

通过对液相色谱-串联质谱联用(LC-MS/MS)仪器条件(母离子、子离子、碰撞能、碰撞池加速电压、离子源参数和梯度洗脱程序等)和样品前处理条件(固相萃取柱类型/规格/组合方式、洗脱溶剂体积、萃取溶剂种类及体积、萃取方式、萃取液稀释体积、 Na_2EDTA 添加量和针头式滤膜等)的优化,建立了13种农药和33种抗生素在多反应监测模式(MRM)下的同时分析方法。各目标

化合物 MDL 在 0.01 ng g^{-1} ~ 12.6 ng g^{-1} 之间。采用基底匹配工作曲线进行定量, 2.0 ng g^{-1} 、 5.0 ng g^{-1} 、 10.0 ng g^{-1} 和 25.0 ng g^{-1} 四个浓度水平下的沉积物基底加标回收率及 RSD ($n=5$) 分别为 32.6%~126.6% (1.5%~16.9%)、36.5%~102.9% (1.0%~10.2%)、38.7%~102.3% (2.4%~18.4%) 和 37.3%~104.3% (1.0%~10.9%)。

3. 九龙江河口沉积物中 5 类 122 种有机污染物的复合污染特征

运用上述建立的分析方法, 研究了九龙江河口表层和柱状沉积物中 5 类典型有机污染物的复合污染特征。结果显示: (1) 目标物检出种类方面, 除 PBDEs 其余 4 类在沉积物中均有检出, 表层沉积物中 PAHs、PCBs、农药和抗生素检出总量分别为 92.7 ng g^{-1} ~ 355.3 ng g^{-1} 、 0.07 ng g^{-1} ~ 0.73 ng g^{-1} 、 7.7 ng g^{-1} ~ 132.2 ng g^{-1} 和 2.3 ng g^{-1} ~ 39.6 ng g^{-1} , 柱状沉积物各层位样品中 PAHs、PCBs、农药和抗生素检出总量分别为 128.7 ng g^{-1} ~ 232.9 ng g^{-1} 、 0.04 ng g^{-1} ~ 0.52 ng g^{-1} 、 33.3 ng g^{-1} ~ 63.4 ng g^{-1} 和 13.1 ng g^{-1} ~ 51.7 ng g^{-1} ; (2) 表层沉积物中检出污染物的空间分布特征显示, 陆源污染物经九龙江径流输入是大部分有机污染物的主要来源; (3) 柱状沉积物中检出沉积物的时间特征方面, PAHs 总量呈先下降后上升趋势; PCBs 总量呈缓慢上升趋势; 农药方面, 三氯杀螨醇呈下降趋势, 吡虫啉和啉虫脒呈上升趋势, 其余均无明显变化趋势; 4 类抗生素无明显变化趋势。

4. 九龙江河口沉积物中有机污染物的来源解析

PAHs 的分子比值法来源解析结果表明, 研究区域表层沉积物和柱状沉积物中 PAHs 主要来源为煤、生物质燃烧和石油燃烧的混合源; 主成分分析/多元线性回归 (PCA/MLR) 分析 1981~2012 年期间污染源历史贡献率也表明煤、生物质燃烧 (50.2%)、交通污染源 (33.0%) 和焦炉 (16.8%) 是研究区域 3 个主要的 PAHs 输入源。对表层沉积物中 PCBs 进行主成分分析和柱状沉积物中 PCBs 进行聚类分析, 结果均显示其主要来源于废旧电力设备中 PCBs #1 产品的泄漏。运用比值分析法对 DDT 与其降解产物进行源解析, 结果表明九龙江河口沉积物中 DDTs 主要来源于早期环境残留, 同时有一定量新 DDTs 自九龙江径流输入。BHCs 组成及同分异构体比值分析显示, 九龙江河口沉积物中 BHCs 主要来源于早期 BHCs 工业品和林丹的残留, 1993~2003 年期间研究区域有大量林丹输入。

5. 九龙江河口沉积物中有机物污染的初步生态风险评价

初步生态风险评价显示：九龙江河口沉积物中 PAHs 和 PCBs 生态风险处于较低水平，发生负面生态效应的可能性低；农药方面，DDTs、三氯杀螨醇、毒死蜱、苯醚甲环唑和丙环唑的生态风险处于中、高水平，可能造成负面生态效应；抗生素方面，金霉素具有高生态风险，其次磺胺嘧啶、氧氟沙星、红霉素和四环素具有中等生态风险。

关键词：沉积物；有机污染物；固相萃取；气相色谱-串联质谱；高效液相色谱-串联质谱；九龙江河口；复合污染特征；来源解析；生态风险评价

Abstract

Over the past decades, with the rapid economic development in Chinese coastal area, thousands of industrial, agricultural and domestic chemical pollutants are being imported into aquatic environment through direct use, atmospheric deposition, riverine runoff *etc.*. Sediments, acting both as a pollutant reservoir and as a potential secondary pollution source, are very important to water quality and aquatic ecosystem health. The frequently detected organic pollutants are polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), pesticides, and antibiotics *etc.*. In this study, accurate and sensitive multi-residue analytical methods for simultaneous determination of 122 target organic compounds in sediment were developed and applied to sediment samples from the Jiulong River Estuary. Organic combined pollution characteristics and ecology risk assessment were discussed. The main research contents and results are as the following:

1. Development of simultaneous determination method for 17 PAHs, 27 PCBs, 6 PBDEs and 27 pesticides in sediment using gas chromatography-tandem mass spectrometry

An accurate and sensitive method for simultaneous determination of above 76 weak-polar target compounds in sediment was developed using ultrasound for extraction, SPE for cleanup and GC-MS/MS for detection. The effect of extraction solvent, SPE clean-up procedures (SPE cartridges, elution solvent and volumes, and sulfur removal *etc.*), GC conditions and MS parameters (parent ions, daughter ions, and collision energy) were investigated. Under optimized conditions, recoveries and RSD at 0.50 ng g⁻¹, 2.0 ng g⁻¹, and 10.0 ng g⁻¹ spiking levels were 68.6%~125.2% (1.1%~23.3%, *n* = 5), 45.3%~128.1% (2.1%~19.3%, *n* = 5) and 43.8%~136.0% (1.4%~16.4%, *n* = 3), respectively. Method detection limits were in the range of 0.01 ng g⁻¹ ~12.9 ng g⁻¹ (dry weight) for all 76 target analytes.

2. Development of simultaneous determination method for 13 pesticides and 33 antibiotics in sediment using liquid chromatography-tandem mass spectrometry

A reliable method was developed for the simultaneous extraction and determination of 13 strong-polar pesticides and 33 ionic antibiotics in sediments using ultrasonic-assisted extraction (USE) followed by solid phase extraction (SPE) clean-up

and liquid chromatography-tandem mass spectrometry (LC-MS/MS) analysis. The extraction solvent, SPE clean-up procedures (SPE cartridges, dilution volumes, and Na₂EDTA addition *etc.*), LC gradient program, and MS parameters (parent ions, daughter ions, collision energy, and cell accelerator voltage) were optimized. Quantification was performed by matrix-matched calibration curves. Recoveries and RSD ($n = 5$) at 2.0 ng g⁻¹, 5.0 ng g⁻¹, 10.0 ng g⁻¹ and 25.0 ng g⁻¹ spiking levels were 32.6%~126.6% (1.5%~16.9%), 36.5%~102.9% (1.0%~10.2%), 38.7%~102.3% (2.4%~18.4%) and 37.3%~104.3% (1.0%~10.9%), respectively. Method detection limits were in the range of 0.01 ng g⁻¹~12.6 ng g⁻¹ (dry weight) for all 46 target analytes.

3. Combined pollution characteristics of 122 organic pollutants in sediments from the Jiulong River Estuary

The combined pollution characteristics of 122 organic pollutants in surface sediments and sediment core from the Jiulong River Estuary were investigated using above established determination methods. Results indicated that PAHs, PCBs, and organochlorine pesticides (OCPs) were the most frequently detected contaminants, then currently used pesticides and antibiotics, PBDEs are not detected. The total contents of PAHs, PCBs, pesticides, and antibiotics in surface sediments varied from 92.7 ng g⁻¹~355.3 ng g⁻¹, 0.07 ng g⁻¹~0.73 ng g⁻¹, 7.7 ng g⁻¹~132.2 ng g⁻¹ and 2.3 ng g⁻¹~39.6 ng g⁻¹, respectively. While in sediment core subsamples, 128.7 ng g⁻¹~232.9 ng g⁻¹ for PAHs, 0.04 ng g⁻¹~0.52 ng g⁻¹ for PCBs, 33.3 ng g⁻¹~63.4 ng g⁻¹ for pesticides and 13.1 ng g⁻¹~51.7 ng g⁻¹ for antibiotics. Most detected pollutants showed a decrease spatial trend along river downstream towards estuary, which suggested that terrestrial input were the primary pollution sources. Temporal distribution also indicated terrestrial pollution sources and no noticeable change during 1981~2012.

4. Sources apportionment of PAHs, PCBs, DDTs, and BHCs in sediments from the Jiulong River Estuary

Isomeric ratios indicated that PAHs in surface sediment were contributed by a mixture source of liquid fossil fuel and coal/grass/wood combustion. Principal component analysis/multiple linear regression (PCA/MLR) results revealed that PAHs contribution rate of 3 main sources to PAHs in sediment core subsamples were 50.2% by coal/grass/wood combustion, 33.0% by vehicles and gasoline emissions and 16.8% by coke oven during 1981~2012. PCA results for surface sediments and hierarchical cluster analysis (HCA) for sediment core subsamples both suggested that PCBs were originated from commercial mixtures PCBs #1. The ratios of (DDD + DDE)/ΣDDTs

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