

学校编码: 10384

密级_____

学号: 33320131151734

廈門大學

硕士学位论文

城市化河口沉积物中四季铵盐化合物的时
空分布和初步生态风险评估

Spatial-temporal Distribution and Ecological Risk
Assessment of Quaternary Ammonium Compounds in
Urban Estuarine Sediments

王翠翠

指导教师姓名: 陈猛/李骁麟 副教授

专业名称: 环境科学

论文提交日期: 2016年5月

论文答辩时间: 2016年5月

2016年5月

厦门大学学位论文原创性声明

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

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

声明人(签名):

年 月 日

厦门大学学位论文著作权使用声明

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

本学位论文属于：

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

2.不保密，适用上述授权。

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

声明人（签名）：

年 月 日

目 录

摘要.....	I
Abstract.....	III
图表目录.....	VI
缩略词表.....	X
第一章 绪论	1
1.1 选题依据和研究背景.....	1
1.2 四季铵盐化合物 (QACs) 概述.....	2
1.2.1 理化性质.....	2
1.2.2 环境毒性.....	4
1.2.3 环境行为.....	5
1.3 QACs 的环境污染现状.....	6
1.3.1 污水处理厂废水和淤泥中 QACs 的研究现状.....	6
1.3.2 水体及沉积物中 QACs 的研究现状.....	7
1.4 污染物沉积记录研究.....	9
1.5 生态风险评价现状.....	10
1.5.1 生态风险评价.....	10
1.5.2 沉积物中有机物生态风险评价.....	12
1.5.3 珠江口生态风险评价现状.....	12
1.6 研究目的、内容和意义.....	14
1.6.1 研究目的和内容.....	14
1.6.2 研究意义.....	15
第二章 研究区域与研究方法	16
2.1 研究区域背景和自然环境概况.....	16
2.1.1 珠江口概况.....	16

2.1.2 东京湾概况.....	17
2.2 样品采集.....	18
2.3 样品分析.....	19
2.3.1 试剂与仪器.....	19
2.3.1.1 试剂材料.....	19
2.3.1.2 仪器设备.....	20
2.3.2 样品前处理.....	20
2.3.3 HPLC-MS/MS 分析条件	21
2.3.3.1 高效液相色谱条件.....	22
2.3.3.2 质谱条件.....	22
2.3.4 质量控制和定量方法.....	24
2.3.4.1 质量控制.....	24
2.3.4.2 定量方法.....	25
2.4 TOC 测定.....	26
2.5 沉积物定年.....	27
2.6 储量估算方法.....	28
2.7 生态风险评价方法.....	29
第三章 珠江口表层沉积物中 QACs 的空间分布.....	30
3.1 珠江口表层沉积物中 QACs 的分布.....	30
3.2 与其他地区的比较.....	31
3.3 表层沉积物中 QACs 的组成变化.....	33
3.4 对比珠江口表层沉积物中其他传统和新型有机污染物浓度和分布.....	35
3.5 珠江口表层沉积物中 QACs 和其他主要有机污染物储量估算.....	45
3.6 沉积物中 DADMACs 的示踪作用	48
3.6.1 QACs 与 TOC 的相关关系.....	48
3.6.2 DADMACs 示踪其他污染物的源	50
3.7 本章小结.....	52
第四章 珠江口和东京湾沉积物柱状样中 QACs 的沉积记录.....	54
4.1 沉积物柱状样定年结果.....	54

4.1.1 沉积柱 A04 定年结果.....	54
4.1.2 沉积柱 ST7 定年结果.....	55
4.2 珠江口沉积柱样品中 QACs 的沉积记录.....	56
4.2.1 沉积物柱状样中 QACs 的污染特征.....	56
4.2.2 沉积物柱状样中 QACs 的垂直分布特征及污染历史分析.....	58
4.2.3 沉积物柱状样中 QACs 的组成特征.....	60
4.3 东京湾沉积柱样品中 QACs 的沉积记录.....	61
4.3.1 沉积物柱状样中 QACs 的污染特征.....	61
4.3.2 沉积物柱状样中 QACs 的垂直分布特征及污染历史分析.....	64
4.3.3 沉积物柱状样中 QACs 的组成特征.....	66
4.4 本章小结.....	68
第五章 珠江口表层沉积物中 QACs 等主要有机污染物初步生态风险评估	69
5.1 沉积物中有机污染物初步生态风险评估.....	69
5.1.1 沉积物中不同有机污染物的生态风险评估.....	71
5.1.2 珠江口表层沉积物生态风险评估综合分析.....	73
5.2 本章小结.....	75
第六章 总结与展望	76
6.1 主要结论.....	76
6.2 主要创新点.....	77
6.3 展望.....	77
参考文献	79
附录	89
致谢	90

Content

Abstract (In Chinese)	I
Abstract (In English)	III
List of Figures and Tables	VIII
List of Abbreviations	X
Chapter 1 Preface	1
1.1 The selected topic basis and research background	1
1.2 Overview of Quaternary Ammonium Compounds (QACs)	2
1.2.1 Physical and chemical properties	2
1.2.2 Environmental toxicity	4
1.2.3 Environmental behavior	5
1.3 Review on the QACs research processes in environment	6
1.3.1 Research status of QACs in wastewater and sludge	6
1.3.2 Research status of QACs in water and sediment	7
1.4 Sedimentary records overview	9
1.5 Status quo of ecological risk assessment	10
1.5.1 Ecological risk assessment	10
1.5.2 Ecological risk assessment in sediments	12
1.5.3 Status quo of ecological risk assessment in the PRE	12
1.6 Research purposes, contents and significance	14
1.6.1 Research purposes and contents	14
1.6.2 Research significance	15
Chapter 2 Sampling and measurement methods	16
2.1 General situation of research areas	16
2.1.1 Introduction of the PRE	16

2.1.2 Introduction of Tokyo Bay	17
2.2 Sample collection.....	18
2.3 Sample analysis.....	19
2.3.1 Experimental materials, chemicals and instruments.....	19
2.3.1.1 Material and chemicals	19
2.3.1.2 Instruments.....	20
2.3.2 Sample preparation and pretreatment	20
2.3.3 HPLC-MS/MS conditions.....	21
2.3.3.1 Chromatography conditions.....	22
2.3.3.2 Mass spectrum conditions.....	22
2.3.4 Quality control and quantitative method.....	24
2.3.4.1 Quality control	24
2.3.4.2 Quantitative method.....	25
2.4 The determination of TOC	26
2.5 Sediment dating	27
2.6 Estimation method of mass inventory.....	28
2.7 Ecological risk assessment method.....	29
Chapter 3 Spatial distribution of QACs in surface sediments	30
3.1 Occurrence of QACs in surface sediments of the PRE.....	30
3.2 Compared with other areas	31
3.3 Composition change of QACs in sediments	33
3.4 Occurrence of legacy and emerging contaminants in the PRE.....	35
3.5 Mass inventory of QACs and other contaminants in the PRE.....	45
3.6 Tracer actions of DADMACs in sediments	48
3.6.1 Relationship of QACs and TOC	48
3.6.2 DADMACs as the tracer of other containments.....	50
3.7 Summary in this chapter	52
Chapter 4 Sedimentary record of QACs in sediment cores from the PRE and Tokyo Bay	54

4.1 Dating results of sediment cores	54
4.1.1 Result of core A04	54
4.1.2 Result of core ST7	55
4.2 Sedimentary record of QACs in sediment core from the PRE	56
4.2.1 Pollution feature of QACs in sediment core	56
4.2.2 Vertical distribution and pollution history of QACs	58
4.2.3 Compositions of QACs in sediment core.....	60
4.3 Sedimentary record of QACs in sediment core from Tokyo Bay	61
4.3.1 Pollution feature of QACs in sediment core	61
4.3.2 Vertical distribution and pollution history of QACs	64
4.3.3 Compositions of QACs in sediment core.....	66
4.4 Summary in this chapter	68
Chapter 5 Ecological risk assessment of QACs and other organic contaminants in sediments from the PRE	69
5.1 Risk assessment of organic contaminants in sediments from the PRE.....	69
5.1.1 Risk assessment of different contaminants in sediments	71
5.1.2 The comprehensive risk assessment for the sediments	73
5.2 Summary in this chapter	75
Chapter 6 Conclusion and prospection	76
6.1 Conclusion	76
6.2 Innovation	77
6.3 Prospection.....	77
References.....	79
Appendix	89
Acknowledgement	90

摘要

四季铵盐化合物 (QACs) 是一类主要的阳离子表面活性剂, 广泛使用于衣物柔顺剂、消毒剂、个人护理品等产品中。QACs 易吸附于沉积物上且不易降解, 欧美国家于上世纪八十年代已经禁止部分难降解 QACs 的使用, 而亚洲国家仍在大量使用 QACs 作为商业产品的主要有效成分。在城市化河口环境中关于 QACs 的分布特征和环境行为的研究还很少。本研究进一步优化了 QACs 在沉积物的痕量分析方法, 选取珠江口这一典型城市化河口区域, 研究其表层沉积物中 QACs 的分布特征和环境行为, 并对比分析珠江口沉积物中其他污染物 (207 种) 的浓度和储量; 通过解析珠江口和东京湾沉积柱中 QACs 的沉积记录, 反演其在不同区域的污染输入历史; 最后对珠江口沉积物中 QACs 和其他主要有机污染物进行初步生态风险评估, 主要研究结果如下:

1. QACs 在珠江口是一种普遍存在的污染物, 其中, 苄基烷基双甲基季铵盐 (BACs) 的浓度范围是 10.2-1345 ng/g, 双烷基双甲基季铵盐 (DADMACs) 的浓度范围为 39.6-10917 ng/g, 在世界范围内属于中等水平, QACs 的含量整体在珠江口呈现出从河口上游到下游逐渐减少的趋势, 最高浓度集中在虎门上游广州附近; QACs 在整个研究区域内沉积物中组成特征保持一致, 并且和广州城市污水处理厂污泥检测结果一致, 表明城市污水排污是珠江口沉积物中 QACs 的主要污染源, 并且 QACs 在释放到河口环境中呈现保守的环境行为; 对比其他污染物浓度和储量发现, 珠江口表层沉积物中主要的有机污染物是 QACs, 浓度比多环芳烃 (PAHs)、有机磷阻燃剂 (OPFRs)、香料 (Fragrances)、紫外滤光化合物 (UV-Filters) 和壬基酚 (NP) 等主要有机污染物要高 1-2 个数量级, QACs 储量已经占到珠江口各类有机污染物总储量的一半以上; 用 DADMACs 来示踪城市排污对各类有机污染物的贡献发现, PAHs、PCBs、OPFRs、NP、Triclosan、Pesticides 主要的源是城市排污, 而 Fragrances 和 UV-Filters 可能存在其他污染源。

2. 在浓度方面, 珠江口柱状样中 BACs 和 DADMACs 的垂直分布曲线具有良好的一致性, 从 20 世纪 50 年代开始上升, 在 1965 年和 1989 年附近出现两个峰值, 基本与我国经济社会发展相吻合; 东京湾柱状样 BACs 和 DADMACs 整体上均呈现出先增加后减小的趋势, 在 20 世纪 70 年代取得极大值, 之后开始减

小,证明东京湾地区 20 世纪 70 年代开始的实行的一系列环保措施取得了较好的效果。在组成方面,珠江口 BACs 组成在 1981 年之前和 1981 年之后变化较大,DADMACs 组成主要是 DADMAC18:18、DADMAC16:18 和 DADMAC16:16,分别占 61%、26%和 10%;东京湾沉积柱中 BAC18 所占比例从 1930s 开始减小,BAC12、BAC14 和 BAC16 则不断增加,DADMACs 组成在整根沉积柱中保持一致,DADMAC18:18 占总 DADMACs 的 86%。珠江口和东京湾地区 BACs 和 DADMACs 分布曲线和组成的不同可能是由于中国和日本两个国家所使用含 QACs 产品量和配方的不同。

3.采用商值法对珠江口 QACs 等主要有机污染物进行生态风险评估发现,QACs 存在较低的风险,主要存在潜在风险的物质是 DDE 和 PAHs,另外两类 UV-Filters (EHMC 和 4-MBC) 和 NP 也具有较高风险,风险较高的区域主要是虎门上游和澳门沿岸地区,需要采取相关风险减排措施。

本研究首次对珠江口 QACs 等主要有机污染物进行了综合的调查及初步生态风险评估,另外,首次对典型城市化河口地区 QACs 的沉积记录进行了研究,为相关部门制定环保政策提供了理论依据。

关键词: 四季铵盐; 持久性有机污染物; 空间分布; 沉积记录; 生态风险评估; 珠江口; 东京湾

Abstract

Quaternary ammonium compounds (QACs) are one of the major classes of cationic surfactants used as the ingredients in fabric softeners, disinfectants, personal care products and so on. QACs tend to adsorb strongly on sludge and sediment due to their physicochemical properties, therefore QACs tend to be persistent in the nature environment. European countries carried out a voluntary phase-out of Dialkyldimethyl ammonium compounds (DADMACs) applied in fabric softener since 1980s due to its highly persistent behavior in the sewage treatment. However, Asian countries are still use them as the active ingredients in commercial products. At present, the occurrence and distribution character of QACs in urban estuarine environment were rarely studied. In this study, we develop the analytical method for trace level QACs in sediments, and study the origin of occurrence of QACs in the PRE, one of the most urbanized estuary in China. Comparison of QACs and other traditional and emerging organic contaminants (n=207) was done in the PRE surface sediments, and mass inventories were calculated to evaluate their relative abundance. The sedimentary records of QACs from the PRE and Tokyo Bay was analyzed in order to establish the historical records of the pollution discharge. Preliminary environmental risk assessment for the chemicals in the PRE were performed by the calculation of Hazard Quotient (HQ). Main results are showing as follows:

1. QACs are ubiquitous contaminant in urban estuarine sediment of the PRE, and the concentrations of benzalkonium chloride (BACs) and DADMACs are 10.2-1345 ng/g and 39.6-10917 ng/g, respectively. Compared with other areas from the world, QACs concentrations in the PRE are moderated. In terms of the spatial distribution pattern in the PRE, the concentrations of QACs decreased from the upstream to downstream in the estuary and the highest concentrations occurred near Guangzhou, the biggest city in the PRE. The composition pattern of the QACs was found to be uniform in the sediments analyzed throughout the PRE, and the average composition

pattern was identical to that determined in the sewage sludge from Guangzhou, indicating the major contribution from the municipal wastewater input of QACs to the sediments and a conservative behavior in environment for QACs. In the PRE, the most predominant compounds are QACs, which was one or two orders of magnitude higher than Polycyclic aromatic hydrocarbons (PAHs), Organophosphate flame retardants (OPFRs), Fragrances, UV-Filters and Nonylphenol (NP). All the organic chemicals detected in the surface PRE sediments accounted for a total mass over 300 tons, and QACs accounted for the highest fraction in the surface sediments (>50%). The correlation of DADMACs with other containments analyzed in the same set of the sediments indicated that sewage discharges are a common source for many of these chemicals (PAHs, PCBs, OPFRs, NP, Triclosan and Pesticides), although other sources are more important for UV-Filters and Fragrances.

2. The distributions of BACs and DADMACs in the sediment core collected from the PRE showed significant correlation. Levels of BACs and DADMACs increased gradually from the beginning of the 1950s, and reached two peaks in the 1960s and 1980s respectively. It is consistent with China's economic and social development on the whole. The vertical distributions of BACs and DADMACs in Tokyo Bay showed one peak around 1970s. Concentrations of BACs and DADMACs measured in this core increased from the beginning of the early 1930s, reached a maximum in the 1970s, and then decreased steadily. The declining environmental concentrations of BACs and DADMACs in Tokyo Bay attest to the effectiveness of emission controls during the 1970s. For the individual QAC homologues from the PRE, individual BAC compositions before 1981 and after 1981 are quite different, the composition of DADMAC congeners were uniform at the whole sediment core, and DADMAC18:18, DADMAC16:18 and DADMAC16:16 represented 61%, 26% and 10% respectively. In the core from Tokyo Bay, the relative abundance of BAC18 dropped markedly since 1930s, while BAC12, BAC14 and BAC16 increased over time. DADMAC composition were relatively stable and DADMAC18:18 represents an average level of 86%. The differences of concentration and composition profiles of BACs and DADMACs in sediment cores from the PRE and Tokyo Bay reflecting the different ingredients applied

in the commercial products.

3. An environmental risk assessment for QACs and other selected chemicals in the PRE were performed by the calculation of HQ. The results show that QACs has a low ecological risk, while PAHs and dichlorodiphenyl dichloroethylene have the highest HQ values in the sediments. NP and two UV-Filters (2-ethyl-hexyl-4-trimethoxycinnamate and 4-methylbenzylidene camphor) also posed a significant threat to benthic species. The areas showing the highest potential risk for the benthic organisms are the upper Humen area, followed by the coast of Macau.

In this study, we conducted a comprehensive investigation on the occurrence and ecological risk assessment of QACs and other major organic containments from the PRE surface sediments for the first time. In addition, the sedimentary records of QACs in the urbanized estuarine regions was studied firstly. These results provide important information on current and historical contamination in the PRE and Tokyo Bay, and help to develop relevant environmental policies.

Keywords: Quaternary ammonium compounds; Persistent organic pollutant; Spatial distribution; Sedimentary record; Ecological risk assessment; Pearl River estuary; Tokyo bay

图表目录

图1-1 QACs及其同系物的结构	2
图1-2 QACs应用领域的分布	3
图1-3 美国生态风险评估流程图	11
图2-1 珠江口沉积物采样站位图	18
图2-2 东京湾沉积物采样站位图	19
图2-3 沉积物样品中QACs的前处理流程图	21
图2-4 QACs标准品的MRM谱图	24
图3-1 珠江口表层沉积物中QACs的空间分布	31
图3-2 珠江口沉积物和广州污水厂污泥中QACs组成分布	34
图3-3 珠江口沉积物中BACs和DADMACs的关系	35
图3-4 珠江口表层沉积物中有机污染物的空间分布	38
图3-5 沉积物中不同有机污染物的储量	48
图3-6 珠江口表层沉积物总有机碳分布	49
图3-7 珠江口表层沉积物中QACs与TOC的相关关系	50
图3-8 珠江口表层沉积物中DADMACs与其他有机污染物的关系	51
图4-1 沉积柱A04 ^{137}Cs 的剖面图	54
图4-2 沉积柱ST7 $^{210}\text{Pb}_{\text{ex}}$ 的剖面图	55
图4-3 珠江口沉积物柱状样中QACs含量的垂直变化	58
图4-4 珠江口沉积物柱状样中BACs的组成	60
图4-5 珠江口沉积物柱状样中DADMACs的组成	61
图4-6 东京湾沉积物柱状样中QACs含量的垂直变化	64
图4-7 东京湾流域人口数量和流入污染物负荷量的变化	65
图4-8 东京湾沉积物柱状样中BACs的组成	67
图4-9 东京湾沉积物柱状样中DADMACs的组成	67
图5-1 沉积物中目标物的风险商范围	74
图5-2 珠江口表层沉积物中累积风险空间分布	75

表1-1 QACs的物理化学性质	4
表1-2 污水和污泥中QACs研究现状	7
表1-3 水体和沉积物中QACs研究现状	8
表1-4 珠江口沉积物生态风险研究现状	13
表2-1 QACs高效液相色谱梯度洗脱程序	22
表2-2 离子源参数	22
表2-3 MRM监测模式参数	23
表2-4 目标物的工作曲线	26
表3-1 世界不同地区表层沉积物中QACs的浓度分布	33
表3-2 珠江口表层沉积物样品的经纬度、TOC和目标物浓度	41
表3-3 珠江口表层沉积物中不同有机污染物的储量	45
表4-1 珠江口沉积物柱状样品中QACs同系物的浓度	57
表4-2 东京湾沉积物柱状样品中QACs同系物的浓度	63
表5-1 环境风险评价所用毒性数据表	70
表5-2 珠江口沉积物中目标物的风险商	73

Degree papers are in the “[Xiamen University Electronic Theses and Dissertations Database](#)”.

Fulltexts are available in the following ways:

1. If your library is a CALIS member libraries, please log on <http://etd.calis.edu.cn/> and submit requests online, or consult the interlibrary loan department in your library.
2. For users of non-CALIS member libraries, please mail to etd@xmu.edu.cn for delivery details.