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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

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目 录

Content

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 behaviror 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 containments (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 behaviror 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 reprented 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 ingradients 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