学校编码：10384 密级_____
学号：22420070153562

厦门大学

博 士 学 位 论 文

福建近海重金属分布特征、形态分析与地球化学过程

Study on Distribution、Speciation and Geochemical Processes of heavy metals in Fujian Province

林 彩

指导教师姓名：李文权 教授
专 业 名 称：海 洋 化 学
论文提交日期：2012 年 12 月
论文答辩时间：2012 年 12 月

2012年12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

Contents

摘要

海洋中重金属具有来源广、毒性大、潜伏期长且能沿食物链富集等特点，一直是海洋环境研究的焦点。本论文以福建近海为研究区域，通过对该海域完整统一的水体、沉积物重金属的调查，研究其分布特征及来源，并结合实验模拟及多年实测数据的拟合，探讨影响其分布的因素以及迁移过程。此外，选择厦门湾表层沉积物为研究对象，分析重金属的形态在其迁移过程中的作用。

主要研究结果如下：

1. 基于 2006 年~2007 年间实施的第二次大规模、长时间的全国性近海海洋综合调查与评价（国家“908”专项和福建省“908”专项）的数据资料，发现：①福建近海表层海水重金属含量在夏、冬、春、秋四季均低于国家一类海水水质标准，铜 (Cu)、镉 (Cd)、铬 (Cr)、汞 (Hg)、砷 (As) 基本呈现近岸高外海低的分布特征，锌 (Zn) 的分布特征不明显，铅 (Pb) 受到大气沉降因素的影响，其高值出现在偏离近岸的海域。②福建近海表层沉积物重金属的平均含量均低于国家一类海洋沉积物质量标准，基本呈现近岸高外海低的分布特征，As 在兴化湾以南的近岸海域存在低值区，Cr 在厦门湾以南海域呈现从北向南递增的分布特征。③福建省潮间带沉积物重金属的平均含量亦符合国家一类海洋沉积物质量标准，但以各重金属含量而言，则主要受 Pb、Cd 及 Hg 污染。

2. 运用 SPSS 13.0 软件分析福建近海海水及沉积物中重金属的来源。结果表明：①福建近海表层海水重金属主要来源于径流输入、工业排污以及大气沉降等，其中径流输入的贡献率四季均在 30%~40%之间，工业排污、大气沉降等的贡献率均在 10%~20%之间，此外，在夏季、秋季还存在水体中有机物质吸附解吸带来的影响。②福建近海表层沉积物重金属主要来自有机物质降解、工业生活排污以及沉积环境本身特性的影响，其贡献率分别为 45.5%、15.0%及 11.1%。Cu、Zn、Hg、As 主要来源于有机物质降解；Cr 主要来源于工业、生活污水的排放；Pb 主要来源于有机物质的降解及工业、生活污水的排放，且两种来源的影响程度基本一致；Cd 则同时受到上述三个主成分的影响，且影响程度大致相同，有机物质降解的影响略低。③福建省潮间带沉积物重金属主要来自于陆源径流的输入、工业生活排污以及沉积环境本身特性的影响，其贡献率分别为 47.5%、20.8%

及 15.1%。Cu、Zn、Cd、Hg、As 主要来源于陆源径流的输入；Cd 同时还受到潮间带沉积环境的影响；Pb、Cr 则主要来源于工业、生活污水的排放。

3. 厦门湾九龙江口淡水端及大嶝岛附近海水端样品的单因子模拟实验结果表明厦门湾水体中各重金属 (Cu、Pb、Zn、Cd、Cr) 含量均与盐度、pH、悬浮物 (Suspended Matter, SPM) 及总有机碳 (Total Organic Carbon, TOC) 含量存在显著的相关关系，该海域水体的表层重金属在从河口向外海扩散过程中，这四个因子均是影响重金属含量的重要因素：①随盐度的增加，各重金属含量均有不同程度地降低，尤其是 Cu、Zn 和 Cd，盐度增加到 31.5391 时，含量仅约为淡水端含量的 60%。②随 pH 的增加，各重金属含量亦有不同程度地降低，尤其是 Zn 和 Cd，pH 增加到 8.30 时，含量仅分别为淡水端含量的 20%及 40%左右。③随 SPM 含量的增加，除 Cr 外，各重金属含量均有不同程度地增加，尤其是 Zn 和 Pb，SPM 增加到 427.3 mg/L 时，含量分别约为淡水端含量的 45 倍及 8 倍；SPM 与 Cr 之间存在显著的线性负相关关系，随 SPM 含量的增加，Cr 含量略有下降，但降幅不大，SPM 增加到 427.3 mg/L 时，Cr 含量约为淡水端的 80%。④随 TOC 含量的增加，各重金属含量均有不同程度的增加，尤其是 Cu、Zn 和 Cr。

4. 厦门湾九龙江口淡水端及大嶝岛附近海水端样品的混合实验结果表明在天然水体多因素的共同作用下，重金属与盐度、pH、SPM 及 TOC 等环境因子之间仍存在相关性，但受其影响的程度与单个因素影响不同，表明厦门湾表层海水重金属在天然水体，从河口向外海扩散过程中，其含量受环境因子的影响作用是较为复杂的，迁移过程的规律具有复杂性。

5. 回归分析厦门湾多年的实测数据，发现得到的 Cu、Cd、Cr 回归方程能较好地模拟整个福建近海的实际情况，这三种重金属元素与盐度、pH、SPM 之间存在良好的相关关系；Zn 由于存在其它多个输入来源，无法模拟整个福建近海的实际情况，需要根据整个福建近海的实测数据进行模拟；Pb 由于受到大气沉降等的影响，与上述环境因子之间的规律性不明显。

6. 2011 年开展的厦门湾表层沉积物重金属形态分析研究结果表明：厦门湾表层沉积物中 Cu 以残渣态为主，Fe/Mn 氧化物结合态亦较高；Pb 以 Fe/Mn 氧化物结合态为主；Zn、Cr 的优势形态均为残渣态；Cd 则以可交换态和碳酸盐结合态为主。其迁移顺序为 Cd>Pb>Cu>Zn>Cr；受人为污染程度的顺序则为

Cd>Pb>Cu>Zn>Cr。

关键词：重金属；分布特征；形态分析；迁移过程

Abstract

Heavy metals are always one of the focuses in marine environmental researches due to their wide sources, high toxicity and enrichment along food chain. Based on the surveys of seawater and sediment in Fujian Province, the contributions and sources of heavy metals were studied and the influence effects were indicated combined with the experimental simulations and years of measured data. In addition, morphology analysis was used to explore the roles of different fractions of heavy metals in migration process in Xiamen Bay sediment.

The main results were as following:

1. Based on the national and provincial marine environmental surveys from 2006 to 2007, three results were got: ①Heavy metals in surface seawater of Fujian Province were all lower than the first category of national seawater quality in four seasons. The concentrations of Cu, Cd, Cr, Hg and As were high in costal water and low in offshore area, but Pb was highest in area deviated from costal water due to the atmospheric deposition effect. There was no rule for the contribution of Zn. ②The average concentrations of heavy metals in subtidal zone sediment in Fujian Province were all lower than the first catrgory of national sediment quality. The concentrations of heavy metals were high in costal area and low in offshore. In addition, there was a low value area of As located to the south of Xinghua Bay and the concentration of Cr increased from north to south in southern area of Xiamen Bay. ③The intertidal zone sediment in Fujian Province was mainly polluted by Pb, Cd and Hg, but the average concentrations of heavy metals were all accordance with the first category of national sediment quality.

2. By soft of SPSS 13.0, three results of heavy metal sources in seawater and sediment of Fujian Province were got: ①The heavy metal in surface seawater was mainly from runoff input, industrial sewage and atmospheric deposition. The ratio of these three sources were about 30%~40%, 10%~20% and 10%~20% respectively in four seasons. Furthermore, the heavy metal was also from desorption of organic

matter in summer and autumn. ②The heavy metal in subtidal zone sediment was mainly from desorption of organic matter, industrial sewage and the characteristics of sedimentary environment, which were 45.5%, 15.0% and 11.1% respectively. Cu, Zn, Hg, and As were mainly from the first source; Cr from the second one; Pb equally affected by the first and second; and Cd influenced by these three factors. ③The heavy metal in intertidal zone sediment was mainly from runoff input, industrial sewage and the characteristics of sedimentary environment, which were 47.5%, 20.8% and 15.1% respectively. Cu, Zn, Hg, and As were mainly from the first source; Cd from the first and second; Pb and Cr were both affected by the second one.

3. The single element simulation experiments of freshwater end in Jiulongjiang estuary and seawater end in Dadeng island in Xiamen Bay were indicated the heavy metals including Cu, Pb, Zn, Cd and Cr were all significantly correlated with salinity, pH, SPM and TOC, so these four factors were the main influencing factors of heavy metals during the spread process from estuary to open sea. ①The concentration of heavy metals decreased with the increase of salinity especially when the salinity was 35, the concentrations of Cu, Zn and Cd were about 60% of those in freshwater end. ②The concentration of heavy metals decreased with the increase of pH especially when the pH was 8.30, the concentrations of Zn and Cd were only 20% and 40% of those in freshwater end. ③The concentration of heavy metals except Cr increased with the increase of SPM especially when the SPM was 400 mg/L, the concentrations of Zn and Pb in seawater end were about 45-fold and 8-fold in freshwater end. However, the concentration of Cr was significantly negatively correlated with SPM. The reduction degree of Cr was not high when the SPM increased. The concentrations of Cr were about 80% of that in freshwater end when SPM was 400 mg/L. ④The concentration of heavy metals especially Cu, Zn and Cr increased with the increase of TOC.

4. The mixing simulation experiment showed in natural water, the heavy metals was still correlated with salinity, pH, SPM and TOC, but the degree of influences was different from that in single element simulation experiments, indicating the environmental influences on heavy metals were complicated in nature water.