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廈門大學

博士後研究工作報告

廈門市城市土壤與塵土、SY 電廠海域及九龍江河口
紅樹林區汞的形態分布特徵

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工作完成日期 : 2009 年 9 月

報告提交日期 : 2009 年 9 月

廈 門 大 學

2009 年 9 月

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红树林区汞的形态分布特征

**The distribution characteristics of mercury species in topsoil
and dust of Xiamen city, the seawater and sediment of
Xiamen western sea area adjacent to SY power plant, and
the mangrove ecosystem at Jiulong estuary**

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流动站(一级学科)名称 : 海洋科学

专 业(二级学科)名称 : 海洋化学

研究工作起始时间 : 2007年9月

研究工作期满时间 : 2009年9月

厦 门 大 学

2009年9月

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目 录

摘 要	I
Abstract	IV
第 1 章 绪 论	1
1.1 汞的污染来源与毒性	1
1.2 不同生态体系中汞的赋存形态的国内外研究现状	2
1.2.1 大气	2
1.2.2 水体	3
1.2.3 土壤和沉积物	5
1.3 环境中甲基汞浓度与环境参数的关系	6
1.4 本课题的提出	7
1.5 本课题的主要内容	9
第 1 章参考文献	10
第 2 章 环境样品中总汞测定方法的建立——吹扫-金柱捕集-热脱附 (双柱)-冷原子荧光光谱法	17
2.1 引言	17
2.2 实验部分	17
2.2.1 主要仪器与试剂	17
2.2.2 双金柱热脱附-原子荧光检测系统	17
2.2.3 实验方法	19
2.3 结果与讨论	20
2.3.1 吹扫时间和吹扫流速的影响	20
2.3.2 尾吹气流速的影响	21
2.3.3 脱附效率	22
2.3.4 吹扫空白、试剂空白和检测限	22
2.3.5 检测系统准确性的验证	23
2.4 本章小结	25
第 2 章参考文献	25

第3章 环境样品中甲基汞分析方法的建立——蒸馏-衍生-Tenax 柱富集-热脱附-GC 分离-热解-原子荧光光谱法.....	26
3.1 引言	26
3.2 实验部分	26
3.2.1 主要仪器与试剂.....	26
3.2.2 热脱附-GC 分离-热解-原子荧光检测系统	27
3.2.3 实验方法	29
3.3 结果与讨论.....	32
3.3.1 实验条件的选择.....	32
3.3.2 色谱图和工作曲线.....	32
3.3.3 仪器检测限.....	32
3.3.4 基底加标回收率.....	33
3.4 本章小结.....	33
第3章参考文献.....	33
第4章 厦门市城市土壤和尘土中总汞和甲基汞的分布特征	35
4.1 引言.....	35
4.2 实验材料与方法.....	35
4.2.1 采样和样品制备.....	35
4.2.2 总汞和甲基汞的测定.....	37
4.2.3 环境参数的测定.....	37
4.2.4 样品分析过程的质量控制.....	37
4.2.5 统计分析.....	37
4.3 结果与讨论.....	37
4.3.1 总汞在表层土壤和尘土中的浓度及分布.....	37
4.3.2 表层土壤和尘土中甲基汞的浓度和分布.....	42
4.3.3 总汞和甲基汞与环境参数的关系.....	47
4.4 本章小结.....	48
第4章参考文献.....	48
第5章 厦门西海域燃煤电厂海区海水和沉积物中汞的形态分布	52

5.1 引言	52
5.2 实验材料和方法	52
5.2.1 样品的采集	52
5.2.2 总汞和甲基汞的测定	53
5.2.3 环境参数的测定	54
5.2.4 样品分析过程的质量控制	54
5.2.5 统计分析	54
5.3 结果与讨论	54
5.3.1 海水中的汞	54
5.3.2 沉积物中的汞	57
5.4 本章小结	60
第 5 章参考文献	61
第 6 章 九龙江河口红树林生态系统中总汞和甲基汞的分布特征及其来源分析	63
6.1 引言	63
6.2 实验材料与方法	63
6.2.1 样品采集	63
6.2.2 总汞和甲基汞的测定	65
6.2.3 环境参数的测定	65
6.2.4 样品分析过程的质量控制	65
6.2.5 统计分析	65
6.3 结果与讨论	65
6.3.1 沉积物中总汞和甲基汞分布特征	65
6.3.2 秋茄各植物组织中总汞和甲基汞的分布特征	76
6.3.3 招潮蟹和弹涂鱼中的总汞和甲基汞	82
6.4 本章小结	83
第 6 章参考文献	83
成果、不足、展望	86
博士后期间发表的论文	88

致谢	89
个人简历	91
联系地址	91

厦门大学博硕士论文摘要库

Table of Contents

Abstract (in Chinese)	I
Abstract (in English)	IV
Chapter 1 Preface	1
1.1 Source and toxicity of mercury	1
1.2 Research on mercury species in different ecosystem	2
1.2.1 Atmosphere	2
1.2.2 Water	3
1.2.3 Soil and sediment	5
1.3 Correlation between methyl mercury and parameters in environment	6
1.4 Objectives and interests of this research	7
1.5 Research contents	9
Cited references for chapter 1	10
Chapter 2 Determination method for total mercury in environmental samples using purge-trap, dual-trap amalgamation, and cold vapor atomic fluorescence spectrometry	17
2.1 Introduction	17
2.2 Experimentation	17
2.2.1 Instruments and reagents	17
2.2.2 Determination system equipped with dual-trap amalgamation and cold vapor atomic fluorescence spectrometer	17
2.2.3 Experimental method	19
2.3 Results and discussion	20
2.3.1 Effect of purging time and flow rates	20
2.3.2 Effect of tail gas flow rates	21
2.3.3 Desorption efficiencies	22
2.3.4 Bubbler blank, reagent blank and detection limit	22
2.3.5 Validation of the determination system	23

2.4 Summary for chapter 2.....	25
Cited references for chapter 2.....	25
Chapter 3 Determination method for methyl mercury in environmental samples using distillation, derivation, preconcentration by Tenax, thermal desorption, GC separation, pyrogenation and cold vapor atomic fluorescence spectrometer.....	26
3.1 Introduction.....	26
3.2 Experimentation.....	26
3.2.1 Instruments and reagents.....	26
3.2.2 Determination system equipped with the devices of thermal desorption, GC separation, pyrogenation and cold vapor atomic fluorescence spectrometer.....	27
3.2.3 Experimental method.....	29
3.3 Results and discussion.....	32
3.3.1 Optimization of the experimental parameters.....	32
3.3.2 Chromatogram and calibration curves.....	32
3.3.3 Instrumental detection limit.....	32
3.3.4 Matrix recoveries.....	33
3.4 Summary for chapter 3.....	33
Cited references for chapter 3.....	33
Chapter 4 Distribution characteristics of total mercury and methyl mercury in the topsoil and dust of Xiamen.....	35
4.1 Introduction.....	35
4.2 Materials and methods.....	35
4.2.1 Sampling and sample processing.....	35
4.2.2 Determination of total and methyl mercury.....	37
4.2.3 Determination of environmental parameters.....	37
4.2.4 Quality control of sample analysis.....	37

Table of Contents

4.2.5 Statistical analysis	37
4.3 Results and discussion	37
4.3.1 Total mercury concentrations and distribution in the topsoil and dust	37
4.3.2 Methyl mercury concentrations and distribution in the topsoil and dust...	42
4.3.3 Relationships of total mercury, methyl mercury and environmental parameters	47
4.4 Summary for chapter 4.....	48
Cited references for chapter 4.....	48
Chapter 5 Mercury species in seawater and sediment of Xiamen western sea area adjacent to a coal-fired power plant.....	52
5.1 Introduction.....	52
5.2 Materials and methods	52
5.2.1 Sampling	52
5.2.2 Determination of total and methyl mercury	53
5.2.3 Determination of environmental parameters	54
5.2.4 Quality control of sample analysis.....	54
5.2.5 Statistical analysis	54
5.3 Results and discussion	54
5.3.1 Mercury in seawater.....	54
5.3.2 Mercury in sediment	57
5.4 Summary for chapter 5.....	60
Cited references for chapter 5.....	61
Chapter 6 Distribution characteristics and source of mercury and methyl mercury in the mangrove ecosystem located in Jiulong estuary	63
6.1 Introduction.....	63
6.2 Materials and methods	63
6.2.1 Sampling	63
6.2.2 Determination of total and methyl mercury	65

Table of Contents

6.2.3 Determination of environmental parameters	65
6.2.4 Quality control of sample analysis.....	65
6.2.5 Statistical analysis	65
6.3 Results and discussion	65
6.3.1 Distribution characteristics of total and methyl mercury in sediment	65
6.3.2 Distribution characteristics of total and methyl mercury in different plant tissues of <i>Kandelia candel</i>	76
6.3.3 Total and methyl mercury in <i>Uca formosensis</i> and <i>Periophthalmus cantonensis</i>	82
6.4 Summary for chapter 6.....	83
Cited references for chapter 6.....	83
Achievements, shortages and perspectives	86
Published articles during postdoctoral time	88
Acknowledgements.....	89
Resume.....	91
Address	91

摘要

汞是一种全球循环的持久性有毒污染物，主要人为来源为燃煤释放。全球燃煤释汞半数以上来自亚洲，而亚洲又以中国为最，占全球释汞量三分之一左右。有关环境中汞及其化合物的研究，已成为专家们的研究热点，但多集中于欧美等发达国家，国内研究甚少。开展近岸典型生态系统中汞的形态分布研究，尤为必要。本文在搭建了总汞和甲基汞测定系统的基础上，以厦门市城市土壤和尘土、厦门 SY 电厂海域和九龙江河口红树林生态系统为研究区域，研究其中汞的形态分布特征，主要内容和结果如下：

(1) 基于美国环境保护局 (U.S. Environmental Protection Agency, USEPA) 1631 方法，自制双柱热脱附装置，以国产 AF-610B 型原子荧光仪为检测器，搭建吹扫-金柱捕集-热脱附(双柱)-冷原子荧光法测定环境样品中总汞的测定系统。对吹扫流速、吹扫时间和尾吹流速等实验参数进行了优化。自制双柱热脱附装置的脱附效率为 99%-100%。在最优化测定条件下，仪器检测限约为 5.0 pg，海水的方法检测限低于 0.50 ng/L，土壤、沉积物和红树样等固体样品的方法检测限低于 1.0 ng/g。采用基底加标回收率法和参考样，验证了该系统的准确可靠性。结果表明该系统测定海水、土壤、沉积物和红树植物组织等样品的基底加标回收率均符合 USEPA 的限定范围，土壤参考样 (ESS-4) 和近海海洋沉积物参考样 (GBW07314) 的测定结果在参考值的可控范围内。该系统可满足总汞测定的要求。

(2) 基于 USEPA 1630 方法和美国地质调查局 (U.S. Geological Survey, USGS) 颁布的甲基汞测定方法，在实验室搭建了蒸馏-衍生-Tenax 柱富集-热脱附-GC 分离-热解-原子荧光法测定甲基汞的分析系统。该系统由自制热脱附装置、GC 柱温箱、自制热解装置和 AF-610B 原子荧光仪组成。热脱附装置脱附效率约为 100%。该系统的仪器检测限约为 5.0 pg (以 Hg 计)，线性范围为 $12-4.9 \times 10^2$ pg (以 Hg 计)。采用基底加标回收率法验证了该系统的准确可靠性，结果表明该系统测定土壤和沉积物样的基底加标回收率符合 USEPA 的限定范围。

(3) 研究了厦门市城市土壤和尘土中总汞和甲基汞的分布特征。在厦门市不同功能区设置 20 个采样站位，在每个站位采集表层土壤和尘土样。厦门市表

层土壤中总汞浓度在 0.071-1.2 mg/kg 范围内, 平均值为 0.46 mg/kg, 中值为 0.46 mg/kg。尘土中总汞浓度介于 0.034 至 1.4 mg/kg 之间, 平均值为 0.28 mg/kg, 中值为 0.16 mg/kg。尘土中总汞浓度小于 0.31 mg/kg 的站位中, 表层土壤和尘土的总汞显著正相关 ($r = 0.597, n = 16, P = 0.014$)。表层土壤中甲基汞浓度 (以 Hg 计) 介于 0.14 -5.7 $\mu\text{g}/\text{kg}$ 之间, 平均值为 1.2 $\mu\text{g}/\text{kg}$, 中值为 0.74 $\mu\text{g}/\text{kg}$ 。土壤中甲基汞占总汞比例在 0.069%-0.74% 范围内变化, 平均值为 0.28%, 中值为 0.26%。尘土中甲基汞浓度 (以 Hg 计) 为 0.092-2.3 $\mu\text{g}/\text{kg}$, 平均值为 0.55 $\mu\text{g}/\text{kg}$, 中值为 0.49 $\mu\text{g}/\text{kg}$ 。尘土中甲基汞占总汞的比例和表层土壤中的处于同一水平。表层土壤和尘土中甲基汞浓度均与相应站位的总汞浓度和有机质有关, 与土地使用功能无关。

(4) 研究了厦门 SY 电厂海域海水和沉积物中汞的形态。设置了 18 个采样点, 调查研究邻近电厂区域海水和沉积物中汞的形态分布特征, 探讨电厂脱硫海水对海域中汞的分布影响。海水中溶解态汞浓度介于 0.70-4.6 ng/L, 平均值为 1.5 ng/L, 中值为 1.1 ng/L; 颗粒态汞为 ND (未检出) -91 ng/L, 平均值为 10 ng/L, 中值为 1.3 ng/L, 总汞在 1.5-93 ng/L 之间, 平均值为 12 ng/L, 中值为 2.8 ng/L。高浓度 (>70 ng/L) 的总汞和颗粒态汞仅在电厂的排水口附近出现。海水中汞的最主要存在形态为颗粒态汞, 沉积物中的总汞浓度在 0.055-0.20 $\mu\text{g}/\text{g}$ 之间变化, 平均值为 0.13 $\mu\text{g}/\text{g}$, 中值为 0.12 $\mu\text{g}/\text{g}$ 。研究区域中沉积物中甲基汞浓度较低, 介于 0.017-0.26 ng/g (以 Hg 计) 之间, 平均值为 0.087 ng/g, 中值为 0.081 ng/g。沉积物中甲基汞占总汞比例也较低, 平均值为 0.069%, 中值为 0.069%。沉积物中总汞和甲基汞与有机碳显著相关。

(5) 研究了九龙江河口红树林生态系统中汞的形态分布特征。在九龙江口浮宫镇红树林保护区内设置了 3 个采样点, 并在红树林光滩、九龙江流域和九龙江河口分别设置 1 个对照点, 用以研究红树林沉积物中汞的分布特征及红树植物组织中汞的分布特征。红树林沉积物中总汞含量基本不随采样深度的变化而变化, 枯水期介于 0.12-0.17 $\mu\text{g}/\text{g}$ 之间, 丰水期介于 0.11-0.14 $\mu\text{g}/\text{g}$ 之间, 均低于我国的海洋沉积物一级标准 (0.20 $\mu\text{g}/\text{g}$), 说明该红树林生态系统并未受到明显的汞污染。但红树林沉积物中总汞浓度远高于九龙江口和九龙江流域所设对照点沉积物中的含量, 显示汞更易被富集在红树林沉积物中。沉积物中甲基汞含量随采

样深度的增加呈现先增后降的趋势, 在 10-25 cm 深处出现峰值; 枯水期甲基汞浓度 (以 Hg 计) 介于 0.15-1.8 ng/g 之间, 丰水期介于 0.081-0.58 ng/g 之间。红树林沉积物中甲基汞浓度大于红树林光滩、九龙江口和九龙江流域所设对照点沉积物中的浓度, 约为九龙江口甲基汞含量的 4-8 倍, 九龙江流域沉积物中的 12-24 倍。红树林沉积物中甲基汞占总汞比例随采样深度的变化趋势与甲基汞浓度的变化趋势相同, 峰值亦出现在 10-25 cm 深处; 枯水期各站位的平均值为 0.48%, 丰水期为 0.30%, 枯水期时明显高于丰水期, 远大于九龙江流域和西海域沉积物中甲基汞占总汞的比例。红树林沉积物中甲基汞浓度与其中的硫化物含量成对数曲线关系, 与有机质呈先增后降的二次曲线关系, 与沉积物的 pH 成负相关关系。

对成熟林分秋茄 (*Kandelia candel*) 和秋茄幼苗分不同组织采样, 研究了其中汞的分布特征, 发现无论是成熟林分还是秋茄幼苗, 总汞在各部位中的分布趋势相同, 均为叶>>皮>根>木质部, 叶中总汞含量远高于其他植物组织中的含量, 成熟林分秋茄叶中总汞含量为 35-98 ng/g, 秋茄幼苗叶中总汞含量为 22-61 ng/g。各组织中主干木质部中甲基汞浓度最大, 为 0.22 ng/g (以 Hg 计), 占总汞比例为 6.4%, 其次是红树叶, 最小的是侧根和主干皮。丰枯水期招潮蟹 (*Uca formosensis*) 和弹涂鱼 (*Periophthalmus cantonensis*) 体内总汞含量远低于世界卫生组织 (World Health Organization, WHO) 规定的安全限量值 0.5 $\mu\text{g/g}$ (以 Hg 计), 招潮蟹中甲基汞占总汞比例, 枯水期的样品为 $24\pm 12\%$ ($n=4$), 丰水期的为 $49\pm 16\%$ ($n=2$); 弹涂鱼枯水期的为 $69\pm 24\%$ ($n=4$), 丰水期的为 43% ($n=1$), 招潮蟹和弹涂鱼对沉积物中的甲基汞有明显的富集作用。

关键词: 总汞; 甲基汞; 土壤; 尘土; 海水; 沉积物; 红树林生态系统; 秋茄

Abstract

Mercury (Hg) is one of the most toxic heavy metals commonly found in the global environment. The main anthropogenic emission source of Hg is the coal combustion. The Asian countries contributed more than half amount to the global Hg anthropogenic source, and China about one third. Hg and mercurial compounds need great attention and study, to better understand their potential impacts on the environment and public health. However, most of the studies on Hg have been done by the scientists in western countries, and few were reported from Chinese. It is necessary to study Hg in typical ecosystems in Chinese coastal areas. The total Hg and methyl Hg determination systems were established in this study, and the study of the distribution characteristics of Hg species in topsoil and dust of Xiamen city, the seawater and sediment of Xiamen western sea area adjacent to a coal-fired power plant, and the mangrove ecosystem at Jiulong estuary had been carried out. The main results are listed as follows.

(1) Based on U.S. Environmental Protection Agency (USEPA) Method 1631, a detection system was established for total Hg in water, sediment, soil and biota samples with the devices of purge-trap, and cold vapor atomic fluorescence spectrometry (CVAFS). The system equipped with a lab-made dual-trap thermal desorption set-up and an AF-610B CVAFS instrument. The parameters including flow rates of purging gas and tail gas, as well as the purging time, were optimized. The desorption efficiencies of the dual-trap thermal desorption were ranged from 99% to 100%. Under the optimized conditions, the instrumental detection limit was 5.0 pg, and the method detection limits for seawater and solid sample (soil, sediment and plant sample) were less than 0.50 ng/L and 1.0 ng/g, respectively. The matrix recoveries were in the ranges regulated by USEPA Method 1631, and the results of a soil certified reference material (CRM) (ESS-4) and a sediment CRM (GBW07314) were within the 95% confidence interval values.

(2) Based on USEPA Method 1630 and U.S. Geological Survey (USGS) method, a detection system was established with the devices of distillation (or digestion),

aqueous ethylation, purge-trap, and CVAFS, for the determination of methyl Hg in soil, sediment and biota samples. The system included a home-made thermal desorption set-up, a GC-oven, a home-made pyrogenation set-up and an AF-610B CVAFS. The desorption efficiencies were about 100%. The instrumental detection limit was 5.0 pg as Hg, and linear range was between 12 and 4.9×10^2 pg as Hg. The matrix recoveries were in the range regulated by USEPA Method 1630.

(3) A study was carried out to investigate the levels and distributions of Hg species, including total Hg and methyl Hg, in the topsoil and dust collected from twenty sampling stations locating in different land function areas of Xiamen. Total Hg concentrations in the topsoil ranged from 0.071 to 1.2 mg/kg, with a mean of 0.46 mg/kg and a median of 0.46 mg/kg. Total Hg concentrations in the dust were in the range of 0.034 to 1.4 mg/kg, with a mean of 0.28 mg/kg and a median of 0.16 mg/kg. For the stations where the total Hg of dust was less than 0.31 mg/kg, the concentrations of total Hg in the topsoil were significantly correlated to those in the corresponding dust ($r = 0.597$, $n = 16$, $P = 0.014$). Methyl Hg concentrations in topsoil were between 0.14 and 5.7 $\mu\text{g}/\text{kg}$ as Hg, and the mean was 1.2 $\mu\text{g}/\text{kg}$ and median 0.74 $\mu\text{g}/\text{kg}$. The ratios of methyl Hg/total Hg in the topsoil ranged from 0.069% to 0.74%, with a mean of 0.28% and a median of 0.26%. The range, mean and median methyl Hg in the dust were 0.092-2.3 $\mu\text{g}/\text{kg}$ as Hg, 0.55 $\mu\text{g}/\text{kg}$ and 0.49 $\mu\text{g}/\text{kg}$, respectively. The ratios of methyl Hg/total Hg in the dust were at the same level as those in the topsoil. Methyl Hg concentrations in both topsoil and dust were linked to corresponding total Hg and soil organic matters. Neither total Hg nor methyl Hg in the topsoil and dust was obviously linked to the land function.

(4) The levels and spatial distributions of Hg species including dissolved, particle and total Hg in seawater, and total and methyl Hg in sediment of Xiamen western sea area adjacent to a coal-fired power plant had been investigated. The influence of the waste seawater discharged from the seawater desulphurization (De-SO₂) system in the power plant had been discussed. The dissolved, particulate and total Hg in the seawater from 18 sampling sites were in the range of 0.70-4.6 ng/L (mean 1.5 ng/L;

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