SPECIATION OF MERCURY IN DIFFERENT ENVIRONMENTAL COMPARTMENTS. DESIGN, DEVELOPMENT AND OPTIMIZATION OF ANALYTICAL METHODS AND PROCEDURES.

Julien Lusilao Makiese

A dissertation submitted to the faculty of science, University of Witwatersrand, in fulfilment of the requirements for the degree of Master of Science.

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Declaration

I declare that this dissertation is my own, unaided work. It is being submitted for the degree of Master of Science in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

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(Signature of Candidate)

_____ Day of _____2009

Abstract

The widespread use of organometallic compounds and their subsequent release into the environment has created a great environmental concern about the toxicity and effects of these pollutants. Mercury pollution is a growing concern worldwide because its can reach high concentrations in various environmental media and thus adversely affect humans, wildlife and ecosystem functioning.

Mercury is present in the environment in different molecular forms with specific biogeochemical transformation and ecotoxicity. Inorganic Hg^{2+} is the main form in water and sediment samples. Concentration levels of organomercury species is very low (usually ng L-1) in aquatic environments but the toxic effect of these compounds can be significant due to their tendency for bioaccumulation and biomagnification in the food chain.

The development of a sensitive, reliable, simple, and cost effective procedure for speciation analysis of mercury in different environmental compartments is currently one of the principal research challenges in environmental analytical chemistry. To this end, this study aimed to develop and optimize analytical methods and procedures for the determination of total mercury and the speciation of inorganic and organic forms of mercury. The hyphenation of gas chromatography and inductively coupled plasma mass spectrometry (GC-ICP-MS) was achieved and used successfully.

Rapid and efficient sample preparation procedures based on microwave-assisted extraction for solid samples were developed. The optimized analytical methods and procedures were validated by the analysis of environmental certified reference materials (CRM 015-050 sediment for Hg_{TOT} and CRM 463 tuna fish for Hg_{TOT} and MeHg).

The developed methodologies were finally applied to real environmental samples, namely soil, sediment, water, fish and human hair, collected in some South African regions affected by environmental pollution due to reprocessing of old tailings dumps and chlor-alakali facilities. The study included collection of ancillary data (pH, redox potential) which are critically important for mercury monitoring program. Predictive models of mercury speciation in water samples based on thermodynamic solution equilibria were also established.

Dedication

To Mickel-Ange Lusilao

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TABLE OF CONTENTS

CONTENTS **Page**

List of Figures

List of tables

ABBREVIATIONS

AAS: atomic absorption spectrometry

AFS: atomic fluorescence spectrometry

BCR: Community Bureau of Reference

CE: Capillary electrophoresis

CNRS: Centre national de recherché scientifique

CRM: certified reference material

CV: cold vapor

CVG: chemical vapor generation

CVT: cold vapor technique

CZE: capillary zone electrophoresis

Eth: Ethylation

FOREGS: Forum of the European Geological Surveys

GC: gas chromatography

GC-ICP-MS: gas chromatography- inductively coupled plasma-mass Spectrometry

GPS: Global Positioning System

HG: hydride generation

$HgEt_2$: Diethylmercury

Hg-P: particulate-bound mercury

HPLC: high-performance liquid chromatography

ICP-MS: inductively coupled plasma-mass spectrometry

IDMS: isotope dilution mass spectrometry

IHg: inorganic mercury

IPCS: International Programme on Chemical Safety

LC: liquid chromatography

LCABIE: Laboratoire de chimie analytique bio-inorganique et environment

LOAEL: lowest-adverse-affect-effect-level

LOD: Limit of detection

LOQ: Limit of quantitation

MAE: microwave-assisted extraction

MCL: maximum contaminant level

MeHg: monomethylmercury

MeHgEt: Methylethylmercury

MIP-AES: microwave-induced plasma atomic emission spectrometry

MRC SA: Medical Research Council South Africa

MS: mass spectrometry

$NaBEt_4$: sodium tetraethylborate

NOAEL: no-adverse-affect-effect-level

QC: quality control

RfD: reference dose

RGHg: reactive gaseous mercury

RSD: Relative standard deviation

SA: South Africa

SABS: South African Bureau of Standards

SAWQG: South African Water Quality Guidelines

SEM: secondary electron multiplier

SFE: supercritical fluid chromatography

TDI: tolerable daily intake

TMAH: Tetramethylammonium hydroxide

USEPA: United States Environmental Protection Agency

WHO: World Health Organization