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RADIOANALYTICAL CHEMISTRY IN SUPPORT OF THE NATURALLY OCCURRING RADIOACTIVE MATERIAL (NORM) INDUSTRIES IN SOUTH AFRICA

Immanda Louw

A Thesis submitted to the Faculty of Science, University of the Witwatersrand, in fulfillment of the requirements for the degree of Doctor of Philosophy

Johannesburg, 2018

DECLARATION

I declare that the contents of this thesis represent my own unaided work and that the thesis has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the University of the Witwatersrand.

NAME: Immanda Louw

_____

Signature of Candidate

_____ day of _____ 20____

ABSTRACT/SUMMARY

Humans are exposed to ionizing radiation from a number of sources of which the largest proportion (about 75%) comes from natural sources. Exploitation of Uranium- and Thorium bearing mineral resources may result in elevated concentrations of the naturally occurring radionuclides (^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{210}Pb, ^{210}Po, ^{235}U, ^{231}Pa, ^{227}Ac, ^{232}Th, ^{228}Ra, ^{228}Th) in products, residues, waste and the environment at industries involved with processing of these raw materials. This can result in exposure to the public via a number of pathways.

In South Africa the main industries of concern include the building-, coal-, phosphate-, and mineral sands industry, as well as gold mining. The industry operator is responsible for radiation protection of both people and the environment in relation to all industrial and mining activities. The radiological impact of all operations in South Africa is monitored as part of the license obligations, imposed by the South African Nuclear Energy Act and enforced by the South African National Nuclear Regulator (NNR).

Accurate and sensitive measurements are required to provide data for Naturally Occurring Radioactive Material (NORM) industries to prove compliance with regulations in order to minimize the radiological impact on humans and the environment. In this study the application of radiometric techniques in support of environmental monitoring programmes of NORM industries, were demonstrated. Suitable radiometric techniques were evaluated and implemented in the laboratory.

Radio-analytical data for environmental media from various NORM industries were collected and evaluated. Results of more than 1000 samples analysed over a period of 5-7 years were used in this study. Although the focus of the presented work was on the analytical techniques, measurement and the results obtained, is also gave some indication of the radiological impact of NORM industries in South Africa, how they contribute to radioactivity in the environment and how this can be accurately measured and assessed.

The method performance parameters indicated suitability of the implemented methods for quantification of naturally occurring radionuclides in water, food and solids at levels well below internationally accepted limits.

It was demonstrated how incorrect and insensitive analytical methodology could result in incorrect conclusions, usually leading to over-estimation of the dose and impact of the industry. For analysis of foodstuff it was shown that measurement of ashed samples greatly improved the limit of detection (LOD) of the instrumental techniques. However, to prevent overestimation of dose due to a high LOD, nuclides such as ^{230}Th and ^{210}Po had to be analysed by radiochemical separation after microwave digestion.

The radiochemical methods were adequate for determination of individual nuclides of

interest at a level of 0.005-0.01 $Bq.L^{-1}$ with a precision and accuracy of better than 20%, which met the demand for more sensitive radiometric techniques for lower maximum limits in radioprotection regulations. Since equilibrium between the nuclides within the natural decay series may be disturbed as a consequence of physical and chemical processes in the extraction of minerals and concentrates from ores, it was important to analyse the individual radionuclides of these series and not only the parent nuclides.

Analytical data for environmental samples obtained from routine monitoring programmes of NORM industries were used to evaluate the potential impact of the industries in South Africa by application in several case studies. The ERICA tool was used to assess the radiological risk to biota, but the main emphasize was on the impact to humans. For this purpose the pathways of internal ingestion and external gamma dose radiation were considered, as well as some secondary pathways such as consumption of meat and milk of cattle grazing on contaminated crops.

The results presented for solids gave an indication of the distribution of radionuclides associated with solids from different NORM industries in SA. In general, results obtained were comparable to similar studies undertaken in other countries. As long as activity concentrations remained below 500 $Bq.kg^{-1}$, the reference dose level of 1 mSv per year was not exceeded. Higher activity concentrations observed in solid samples from some industries was found to be of limited concern to the public.

Based on the results presented for selected samples of building materials and constituents used in the manufacture of cement, it was concluded that the building industry can be exempted from nuclear regulatory control in South Africa, even though some raw material (slag, fly ash) exceeded the recommended exemption levels for exposure. The results presented for selected samples from the phosphate industry also suggested that it was unlikely for any member of the public to receive a significant dose from the use of phosphate rocks for fertilizer production.

Essential basic data were provided for environmental radiological risk analysis for Coal Fired Power Plants which are not currently regulated in South Africa. Since the activity concentrations in fly ash and coal samples were all lower than the 500 $Bq.kg^{-1}$ exemption limit set by the NNR, it was found not to be a source of alarm. Natural radioactivity in coal samples was not significantly higher than in soils and rocks and of the same order of magnitude as in other parts of the world, whereas fly ash showed some enrichment, again similar to the trend observed in worldwide studies on coal and ashes. Utilization of fly-ash as an additive in cement should be possible without any special restrictions based on the regulations dealing with building material in the European directive.

The results for environmental media showed elevated concentrations compared to the baseline data in some areas. Measured soil concentrations from all areas were similar to background, whereas some sediment samples showed enhanced concentrations. On average the concentrations in sediment and tailings samples from the specific gold mine area investigated did not exceed the 500 $Bq.kg^{-1}$ exemption level and no urgent countermeasures are required. The radiological impact may become important if new uses for these areas are considered.

The bottled water analysed was radiologically safe and posed no significant hazard to the consumer. For the majority of environmental water sources sampled by the Department Water and Sanitation (DWS) the screening results indicated good or ideal quality water, with only some radioactive "hot spots" indicated; for which future monitoring should include nuclide specific analysis. Dose assessment based on nuclide specific analysis of environmental surface- and groundwater showed that the radiological quality of most of the sources was good resulting in a dose of less than 1 $mSv.a^{-1}$ if consumed. Water from some sites exceeded the NNR dose constraint of 0.25 $mSv.a^{-1}$ and might have health effects to the most sensitive age group (infant) if used for domestic purposes.

The quality of water from mining- and NORM industries varied, with fairly high activities measured in some surface water samples from the gold mine areas, indicating a possible radiological health risk from ingestion of this water which was clearly impacted by process water. However, for the majority of sources from other industries the results indicate insignificant levels of public exposure and suggest only limited radiological impact of the industrial activities on communities in the area. In water impacted by mines the ratio of $^{234}U/^{238}U$ was found to be equal to one, whereas in environmental groundwater the concentration of ^{234}U was found to be higher than ^{238}U up to a factor three. Measurement of only ^{238}U was shown to result in an underestimation of the total U activity in these water samples with observed disequilibrium. However, for surface water sources from the DWS study future radiological assessment may only require determination of the chemical concentration of uranium, based on the correlation found between the U concentration and gross alpha activity.

With single exceptions, the results did not indicate a significant impact of the industrial activities on food grown in any of the areas. The estimated dose for adults was well below the "single facility" dose constraint of 0.25 $mSv.a^{-1}$. For many samples where the dose limit was exceeded it could be explained by either poor sensitivity of the analytical technique resulting in high LODs, assumption of equilibrium for some nuclides with high dose conversion coefficients which were not measured (*e.g.* ^{230}Th and ^{210}Po) or unrealistic high consumption rates used for the dose estimation. The high concentrations measured in some samples cannot be ignored since it might indicate contamination in some areas. More work has to be done to determine the impact of the specific NORM industries. The activity concentrations of ^{210}Po in food confirmed that ingestion of food is an important route

for intake of this nuclide.

The choice of parameters used in dose assessment models can have a huge impact on results. Discrepancies were observed between measured and modelled values. The parameters suggested for use by the NNR for assessments were in most cases found to be conservative, resulting in overestimation of dose. Unfortunately, overestimation due to conservative assumptions is usually not communicated to the public, leading to unnecessary concern. It was therefore recommended that site-specific parameters are collected whenever possible. The ability of the radio analytical laboratory to provide accurate and reliable data at the required sensitivity level in a timely fashion is essential for this purpose.

NORM industries in South Africa are well regulated; operating under a Certificate of Registration issued by the NNR, and optimizing practises to keep dose As Low as Reasonably Achievable (ALARA). Industries are assuming responsibility and control releases to the environment. The results presented suggested that members of the public were unlikely to receive any significant dose from any of the NORM industries. The high concentrations measured in some of the products confirmed the need for continuous control and monitoring of the industry, especially where by-products are utilized elsewhere. To prevent unnecessary concern by the public it is important that enough scientific data are published and available in the public domain. Access to data similar as presented in this thesis will help to provide clarity and transparency. Finally it was emphasized that no evaluation should be based on results from a single grab sample, but that an effort should be made to obtain samples representative of a long period.

DEDICATION

This thesis is dedicated to my wonderful children, Milanda, Ivan and Karyn.

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ABBREVIATIONS AND ACRONYMS

AAS	Atomic Absorption Spectroscopy
ACI	Activity Concentration Index
AED	Annual Effective Dose
ALARA	As low as reasonably achievable
ALI	Annual limit of intake
ALMERA	Analytical Laboratories for the Measurement of Environmental Radioactivity
AMD	Acid Mine Drainage
BCG	Biota Concentration Guidelines
BF	Bio-accumulation factor
BM	Building Material
BSS	Basic Safety Standard
Bq	Becquerel
CAC	Codex Alimentarius Commission
CF	Concentration factor
CoR	Certificate of Registration
CPP	Coal-fired power plant
CR	Concentration Ratio
D	Absorbed Dose rate
DAP	Di-ammonium Phosphate
DCF	Dose Conversion Factor
DCL	Derived concentration limits
DCRL	Derived consideration reference levels
DNC	Delayed Neutron Counting
DOH	Department of Health
DWS	Department Water Affairs and Sanitation
EC	European Commission
EMCL	Environmental Media Concentration Limits
EDTA	Ethylene-diamine-tetra-acetic acid
EIA	Environmental Impact Assessment
EU	European Union

EPA	United States Environmental Protection Agency
ERICA	Environmental Risks from Ionizing Contaminants
ESL	Ecological screening levels
ESP	Electrostatic precipitator
EU	European Union
EU-BSS	European Union Basic Safety Standards
EXC	Extraction Chromatography
F_f	Transfer coefficient animal products
F_m	Transfer coefficient milk
FAO	Food and Agriculture Organization
FCV	Free Column Volume
FLM	Fluorometry
FW	Fresh weight
FWHM	Full Width at Half Maximum height
GA	Gross Alpha
GB	Gross Beta
GDARD	Gauteng Department of Agricultural and rural development
GEMS	Global Environmental Monitoring System
GFPC	Gas-flow Proportional Counting
GI	Gastro-intestinal
GSR	General Safety Requirement
GL	Guidance Level
H_{ex}	External Hazard Index
H_{in}	Internal Hazard Index
HE	High Energy
HMC	Heavy Minerals Concentrate
HPA	Health Protection Agency
HPGe	High Purity Germanium
I_γ	Gamma Index
IAEA	International Atomic Energy Agency
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICRP	International Commission on Radiological Protection
INAA	Instrumental Neutron Activation Analysis

ISO	International standards organization
IWQS	Institute for water quality studies
K_d	Partition Coefficient
K’	Capacity factor
KNP	Kruger National Park
KPA	Kinetic Phosphorescence Analysis
LabSOCS	Laboratory Sourceless Calibration Software
LE	Low energy
LLE	Liquid Liquid Extraction
LLRD	Long-lived radioactive dust
LOD	Limit of Detection
LSC	Liquid Scintillation Counting
MAC	Maximum acceptable concentrations
MAP	Mono-ammonium phosphate
MAPEP	Mixed Analyte Performance Evaluation Program
MC-ICP-MS	Multi-Collector Inductively Coupled Plasma Mass Spectrometry
MCL	Maximum Contaminant Level
MDA	Minimum detectable activity
MRA	Mine Residue Areas
mSv	Milli-Sievert
NAA	Neutron Activation Analysis
NBS	National Bureau of Standards
NECSA	South African Nuclear Energy Corporation
NEMA	National Environmental Management Act
NIST	National Institute of Standards and Technology
NNR	South African National Nuclear regulator
NORM	Naturally Occurring Radioactive Material
NPL	National Physics Laboratory
NRMP	National Radioactivity Monitoring Programme
NRPB	National Radiological Protection Board (UK)
NWA	National Water Act
OHS	Occupational Health and Safety
PERALS	Photon/electron rejecting alpha liquid scintillation

PROCORAD	Association for the promotion of quality control in radiotoxicological analysis
PFA	Pulverized Fly Ash
PIPS	Passivated Implanted Planar Silicon
PG	Phosphogypsum
PTFE	polytetrafluoroethylene
R^2	Linearity
RA	RadioAnalysis
RA_{eq}	Radium equivalent activity
RAP	Reference animals and plants
RDL	Reference dose limit
REE	Rare earth elements
RINGAS	Routine Instrumental Neutron and Gamma Analysis System
RO	Reference Organism
ROI	Region of Interest
RPS	Radiation Protection Specialist
RSD	Relative standard deviation
RQ	Risk Quotient
SA	South Africa
SAFARI	SA fundamental Atomic Research Installation
SANAS	South Africa National Accreditation System
SANBWA	South African Bottled Water Association
SANS	South African National Standard
SARPA	South African Radiation Protection Association
SDA	Spreadsheet for data analysis
SDWA	Safe Drinking Water Act
SF-ICP-MS	Sector Field Inductively Coupled Plasma Mass Spectrometry
SHEQ	Safety Health Environment and Quality
SLT	Sample Lifetime
SPC	Statistical process control
SRM	Standard reference material
SSB	Silicon Surface Barrier
SSP	Single super phosphate
Sv	Sievert

TBP	Tri-n-butyl phosphate
TDS	Total dissolved solids
TECDOC	Technical Document
TENORM	Technologically Enhanced Naturally Occurring Radioactive Materials
TEVA	Tetravalent Actinide resin
TF	Transfer Factor
TID	Total Indicative Dose
TOPO	trioctyl phosphineoxide
TSF	Tailings Storage Facility
TSP	Total suspended particles
TWQR	Target Water Quality Range
TRU	TransUranium resin
UTEVA	Uranium and Tetravalent Actinide resin
UNSCEAR	United Nations Scientific Committee on the Effects of Atomic Radiation
WCA	Wonderfonteinspruit Catchment Area
WFS	Wonderfonteinspruit
WHO	World Health Organization
WRC	Water Research Commission
QC	Quality Control

LIST OF PUBLICATIONS AND PRESENTATIONS

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