

Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.



MASSEY UNIVERSITY
TE KUNENGA KI PŪREHUROA
UNIVERSITY OF NEW ZEALAND

CONTRIBUTIONS TO CONTAMINATION DYNAMICS, ASSESSMENT AND REMEDIATION OF THE ENVIRONMENT

by

Professor Ravendra Naidu

PhD, DSc (*Honorary*), FSSSA, FASA, FAAAS, FNZSSS, C Chem

Application for the degree of

DOCTOR OF SCIENCE

DSc

from

Massey University, Palmerston North
New Zealand

May 2015

Volume 1 of 2

© Massey University, 2014. All rights reserved. No part of this publication may be reproduced without the written permission of the copyright holder

ABSTRACT

Environmental contamination is a massive problem for Australia and, indeed, globally. It has serious impacts on:

- human health;
- the health and sustainability of our natural environment; and
- the economy.

Historical environmental contamination will be a toxic legacy for Australians for decades to come. There are over 160,000 potentially contaminated sites in Australia. Remediation is currently costing companies and owners of contaminated sites in excess of \$3 billion per annum, with the number of sites remediated being less than 5%. Cases of poisoning by substances such as arsenic, lead, asbestos, pesticides etc. are in the news almost daily, while large areas of valuable land (for example in China) cannot be used because of past contamination.

Surface and subsurface soil and its groundwater environment is a complex and heterogeneous system. Once contaminants have come into contact with these systems, assessment and remediation is difficult and extremely challenging. Australia has not yet developed the affordable solutions, the preventative technologies and advanced regulatory frameworks to address this huge problem and curb its spread.

Professor Naidu, a PhD graduate of Massey University, recognised environmental contamination as a major challenge confronting the community, owners of contaminated sites and regulatory bodies as early as the 1990s – before Australia even had its National Environment Protection Measure in place. Recognising the gap in knowledge on contaminants, he commenced a research and technology development program providing initial leadership in Australia and later internationally by heading Commission 3.5 (2002 to 2010) which focuses on Soil Degradation and Reclamation. He also raised in excess of \$500 million to establish a Co-operative Research Centre for Contamination Assessment and Remediation of the Environment (CRC CARE) – the only National

Centre of Excellence that focuses on contamination and remediation. The research undertaken within this Centre is prioritised through extensive consultation and participation by end-users.

Since commencing research on contaminants, Professor Naidu has enhanced our understanding of risks posed by contaminants in the environment, their fate and behaviour in soil and groundwater, and techniques for assessing and remediating contaminated sites. These areas are grouped, in this thesis, into five overlapping areas of research:

- Measurement;
- Fate and dynamics;
- Bioavailability;
- Food Chain and
- Remediation.

The key elements of these five themes, and their contribution to knowledge, form Chapters 2-6 of the thesis. Professor Naidu's awards and honours are summarised in his curriculum vitae.

PREFACE

Contamination by the chemical products and by-products of human activity is one of the most pervasive and far-reaching impacts that we have upon the Earth and upon our own health and well-being. Traces of anthropogenic contamination are now found from the stratosphere to the deep oceans, from pole to pole, in many forms of wildlife, in all modern societies, in the food chain, and in most individuals, including newborns. It is estimated that there are over 5 million contaminated sites worldwide, chiefly in urban areas, of which the vast majority are un-remediated. Many such sites are contaminated with hydrocarbons that release toxic volatiles that pose significant risk to people in residential and commercial areas. In addition, modern homes and offices may themselves emit toxic vapours which harm their inhabitants every day. The most recent WHO (2012) report attributes seven million deaths to ambient air pollution with 70% of these in developing countries and 20 to 30% in developed countries.

Although, the adverse impacts from exposure to contamination have long been known, the pace with which contamination and contaminated sites are eradicated has been rather slow and thus far <10% of contaminated sites have been remediated. The slow pace of remediation has been attributed to the complex nature of contaminants, the complex and heterogeneous nature of soils and the subsurface environment that take up toxic substances with ease when in contact, which makes remediation an exceptionally challenging task. Contaminated sites assessment and remediation thus require a multidisciplinary approach best conducted by teams. The research environment and structures at CSIRO and the more recently established Centre for Environmental Risk Assessment and Remediation (CERAR) at the University of South Australia have reflected this team-based approach.

CERAR is made up of researchers in major disciplines including biostatisticians, chemists, engineers (civil, chemical and industrial), hydrogeologists, microbiologists, clay mineralogists, molecular microbiologists, mathematical modellers and transport physicists. The Centre commenced with one person (Naidu) in 2002 and now boasts 100 researchers, all funded via industry and Australian Government competitive grants. The candidate was the driving force in securing the funds to establish a National Centre of

Excellence through the Commonwealth Government's Co-operative Research Centre Program which he won in 2004 with a subsequent extension to 2020.

The work presented in this thesis has been conducted by teams of varying sizes. However, the candidate led the planning and the initiation of the research, the conduct of the experiments, the analysis of the results, the theory development, and the writing of the papers. He has been either the Principal Investigator, or at least an equal collaborator in all the projects that have been cited in Chapters 2 - 6, as well as in the majority of the papers in his appended *curriculum vitae*.

Projects contributing towards the candidate's research include:

1. Australian Research Council Linkage Grant – Bioavailability of toxic metal(oids) - project initiated by the candidate and extended to include his team members Drs Juhasz and Smith.
2. Australian Research Council Linkage Grant - Heavy metal phytotoxicity in long-term contaminated soils: implications for the development of Australian regulatory guidelines and realistic environmental risk assessment. Project initiated by the candidate and extended to include his team members- Prof Megharaj Mallavarapu, Dr Hui Ming and Dane Lamb (PhD student)
3. ACIAR project grant- Pathways of arsenic transfer in soils irrigated with arsenic contaminated groundwater. Project initiated by the candidate but extended to Dr Euan Smith (then a PhD student and who was later appointed as a postdoc)
4. Ausaid project grant- Bangladesh-Australia Centre for Arsenic Mitigation Program (BACAMP). Project initiated by candidate but extended to Drs Euan Smith, Mohammad Rahman (postdoc) and Ray Correll
5. Australia-Korea International Grant (2003-2005): Development of highly efficient immobilization and soil washing technology for the treatment of soils contaminated with heavy metals. Project initiated by the candidate, later involving Drs Euan Smith and Gary Owens.
6. CRC for Soil and Land Management Grant (1993 to 1997)- Soil contamination, environmental impacts and food quality- focus toxic inorganic and organic substances- project initiated by the candidate and extended to Drs Rai Kookana

(research fellow), S Baskaran (postdoc), Prof Megharaj Mallavarapu (research fellow), Dr R Hamon (postdoc), Dr GSR Krishnamurti (visiting fellow).

7. CRC CARE- project initiated and led by the candidate- raising \$500 million over 15 years (2005 to 2020) and projects supported for most of the co-authors.

I declare that I have carried out, directed, or significantly assisted in all the work submitted here for consideration for the Degree of Doctor of Science. The assistance that I have received is clearly indicated by the joint authorship of the papers, and via the acknowledgements in those papers. I wish to express my sincere gratitude to my various co-authors over the years, including the postgraduate students, postdoctoral fellows and colleagues with whom I have worked since 1994. My thanks go to (in alphabetical order):

Dr Farzana Akter, Dr S Baskaran, Dr Dawit Nega Bekele, Professor Nanthi Bolan, Dr Sreeni Chadalavada, Associate Professor Zuliang Chen, Dr Ray Correll, Dr Luchun Duan, Professor Amir Fotovat, Professor RD Harter, Professor Imamul Huq, Associate Professor Albert Juhasz, Dr Venkat Kambala, Professor Duang Kantachote, Dr Rai Kookana, Dr GS Krishnamurti, Dr Dane Lamb, Dr H Lin, Dr Yanju Liu, Professor S Mahimaraja, Professor Megharaj Mallavarapu, Dr Hui Ming, Professor Ron McLaren, Professor Jack Ng, Dr Mohammad Rahman, Dr Binoy Sarkar, Dr Euan Smith, Professor Malcolm Sumner, the late Dr Kevin Tiller

STATUTORY DECLARATION

No part of the published or unpublished work has been presented, or is being submitted, for any other degree or other academic or professional distinction by the candidate at Massey or any other University. Soil is a complex and heterogeneous system that requires a multidisciplinary approach for sustainable solutions to problem solving and hence the work presented here has been carried out by teams of varying sizes, which has always involved me and my team. I have led research that was supported by an outstanding team of researchers.

Research works reported in this thesis were all externally funded with the funds being generated by the candidate. The general approach within the body of research presented is that the candidate was the originator of the contribution, identifying the research problem and designing the investigations with the detailed analysis, modelling and experimental work being performed with co-investigators. Synthesis and interpretation of the research results and writing of papers was undertaken jointly. Whilst I have been the Principal Investigator in all the work submitted here for consideration for the degree of Doctor of Science, I have in most instances refrained from accepting corresponding authorship of the papers. This was to allow my team members this privilege in recognition of the requirements of our University (November 2002 to present) and CSIRO (1989 to 2002) for the consideration of their own promotion.

I wish to record my special thanks to the late Dr Kevin Tiller who introduced me to contaminants research and the late Professor Keith Syers, whose academic professionalism, generosity of spirit and commitment to environmental health have provided a hugely rewarding stimulus for my career. The majority of papers presented in Chapters 2 to 6 are those in which I took a lead role although I gave senior authorship and corresponding authorship to my junior team members to assist them with their career paths. There are some other papers listed in my *curriculum vitae* in which either Professors Nanthi Bolan or Megharaj Mallavarapu was the significant researcher.

I declare that I have carried out, directed or significantly assisted in all the work submitted here for consideration for the degree of Doctor of Science. The assistance that I have

received is clearly indicated by the joint authorship of the papers and via the acknowledgements in those papers.

Ravi Naidu

DEDICATION

“This thesis is dedicated to my late son Dr Roneal Naidu (1979 – 2009).

Roneal was a gifted and caring surgeon, revered by his colleagues at his NZ hospital , loved by his patients and at the height of his powers when, overnight, he unexpectedly departed this life.

His presence is still felt by myself and his dear mother. He was the love of our lives and we will miss his presence and dear voice each remaining moment of our days. Thought of him provides the living inspiration and the light which drives me more strongly than ever to pursue the science which will bring about a safer, healthier and more sustainable future for humanity, of which this thesis is a part.”

Table of Contents

ABSTRACT	i
PREFACE	iii
STATUTORY DECLARATION	vi
DEDICATION	viii
Chapter 1	1
INTRODUCTION	1
Chapter 2	5
MEASUREMENT	5
Chapter 3	9
FATE AND BEHAVIOUR OF CONTAMINANTS IN SOILS	9
Chapter 4	15
BIOAVAILABILITY OF CONTAMINANTS IN SOILS	15
Chapter 5	24
FOOD CHAIN-EXPOSURE TO GEOGENIC CONTAMINANTS	24
Chapter 6	29
REMEDIATION	29
REFERENCES	49

List of Appendix

- Appendix A: PAPERS REFERENCED IN CHAPTER 1
- Appendix B: PAPERS REFERENCED IN CHAPTER 2
- Appendix C: PAPERS REFERENCED IN CHAPTER 3
- Appendix D: PAPERS REFERENCED IN CHAPTER 4
- Appendix E: PAPERS REFERENCED IN CHAPTER 5
- Appendix F: PAPERS REFERENCED IN CHAPTER 6
- Appendix G: BIBLIOGRAPHY AND CURRICULUM VITAE