

# **Copper Availability in Biosolids**

**Ian William Oliver**

In fulfilment of the requirements for the degree of

**Doctor of Philosophy**

A thesis submitted to

**Soil and Land Systems**

**School of Earth and Environmental Sciences**

**The University of Adelaide**

**Australia**

**June, 2004**

## Table of Contents

Abstract .....	iv
Declaration .....	vi
Acknowledgements .....	vii
List of Tables .....	viii
List of Figures .....	x
<i>1. General Introduction and Literature Review</i> .....	1
1.1 Generation and Disposal of Sewage Sludge (Biosolids) .....	1
1.2 Benefits of Biosolid Land Application .....	2
1.3 Land Application of Biosolids: Potential Detrimental Effects .....	3
1.3.1. Pathogens, Nutrients and Organic Contaminants .....	3
1.3.2. Heavy Metals .....	4
1.4 Biosolid Copper .....	6
1.4.1 Sources of Biosolid Copper .....	6
1.4.1.1 Copper Plumbing Systems .....	6
1.4.1.2 Other Sources .....	8
1.4.2 Copper Concentrations in Biosolids .....	9
1.5 Background Levels and Regulations .....	9
1.6 Copper Associations in Biosolids and Soils .....	10
1.6.1 Inorganic Forms .....	10
1.6.1.1 Solution Inorganic Copper .....	10
1.6.1.2 Solid Phase Inorganic Forms .....	12
1.6.2 Organic Forms .....	13
1.6.2.1 Solid and Solution Phase Organic Forms .....	15
1.7 Copper in Plants & Ecosystems .....	16
1.7.1 Copper Essentiality in Plants .....	16
1.7.2 Plant Uptake .....	18
1.7.3 Copper Toxicity .....	22
1.7.4 Food Chain Effects .....	25
1.7.5 Mobility in the Environment .....	26
1.8 Copper Bioavailability & Controlling Factors .....	28
1.8.1 pH .....	29
1.8.2 Organic Matter .....	31
1.8.3 Biological Activity .....	34
1.8.4 Time .....	34
1.8.5 Other metals .....	38
1.9 Copper Bioavailability Measurement .....	38
1.9.1 Plant Uptake Studies .....	39
1.9.2 Chemical/Solution Extraction of Metals .....	41
1.9.2.1 Single Extractants .....	41
1.9.2.2 Sequential Extraction Schemes .....	44
1.9.3 Solution Ion Concentration/Activity .....	46
1.9.4 Isotopic Tracer Techniques .....	49
1.10 Aims & Objectives .....	52
<i>2. Biosolids Characterisation and Cu Availability</i> .....	53
2.1 Introduction .....	53
2.2 Methods .....	53
2.2.1 Biosolid Preparation .....	54
2.2.2 General Properties .....	54

2.2.3 CaCl <sub>2</sub> -Extractable Elements .....	55
2.2.4 Isotopically Exchangeable Cu (E-values) .....	55
2.2.5 Effect of pH adjustment on Isotopically Exchangeable Cu.....	56
2.2.6 Copper Ion Activity (pCu <sup>2+</sup> ).....	57
2.2.7 Statistical Analysis .....	58
2.3 Results and Discussion.....	59
2.3.1 General Biosolid Properties.....	59
2.3.2 CaCl <sub>2</sub> -Extractable Elements.....	63
2.3.3 Isotopically Exchangeable Copper (CuE).....	68
2.3.4 Effect of pH adjustment on Isotopically Exchangeable Cu.....	73
2.3.5 Copper Ion Activity (pCu <sup>2+</sup> ).....	77
2.4 Conclusions .....	82
<i>3. Temporal Trends of Total and Potentially Available Element Concentrations in Sewage Biosolids: A Comparison of Biosolid Surveys Conducted 18 Years Apart .....</i>	<i>83</i>
3.1 Introduction .....	83
3.2 Methods and Materials .....	83
3.3 Results and Discussion.....	85
3.3.1 All Biosolids – Total Element Concentrations.....	85
3.3.2 All Biosolids – Calcium Chloride Extractable Element Concentrations.....	87
3.3.3 Individual Treatment Plants – Total Concentrations.....	90
3.3.4 Individual Treatment Plants – Extractable Elements .....	91
3.4 Conclusions .....	92
<i>4. Effect of Incubation Time on Biosolid Properties and Cu Availability.....</i>	<i>93</i>
4.1 Introduction .....	93
4.2 Methods .....	94
4.2.1 Biosolid Preparation and Incubation Treatments .....	94
4.2.2 Measures of pH, Carbon content, and Abiotic determinations of Bioavailability .....	97
4.2.3 Biosolid Fractionation and Cu Distribution .....	98
4.2.4 Plant Uptake Study .....	99
4.3 Results and Discussion.....	102
4.3.1 Carbon .....	102
4.3.2 pH .....	107
4.3.3 Isotopically Exchangeable Cu.....	108
4.3.4 CaCl <sub>2</sub> -Extractable Metals .....	114
4.3.5 EDTA -Extractable Metals.....	118
4.3.6 Cupric Ion Activity (pCu <sup>2+</sup> ).....	122
4.3.7 Biosolid Fractionation and Cu Distribution .....	124
4.3.8 Plant Uptake .....	128
4.4 Conclusions .....	138
<i>5. Distinguishing Between pH and OC Effects by pH Normalisation.....</i>	<i>140</i>
5.1 Introduction .....	140
5.2 Methods .....	140
5.3 Results and Discussion.....	142
5.4 Conclusions .....	153
<i>6. Cu Partitioning Amongst Biosolid Fractions – What Binds the Cu? .....</i>	<i>154</i>
6.1 Introduction .....	154
6.2 Methods .....	155

6.2.1 Isolation of inorganic fraction .....	155
6.2.2 Isolation of organic fraction .....	157
6.2.3 Determination of partition coefficients (K <sub>d</sub> ).....	157
6.3 Results and Discussion.....	158
6.4 Conclusions .....	163
7. <i>Copper Availability in 7 Soils from Israel incubated with and without biosolids</i> .....	164
7.1 Introduction .....	164
7.2 Methods .....	165
7.2.1 Soils and Biosolids .....	165
7.2.2 Incubation procedure .....	167
7.2.3 Changes in Physical Properties and Copper Availability.....	167
7.2.4 Statistical Analysis .....	168
7.3 Results and Discussion.....	169
7.3.1 Changes in Soil Organic C and pH.....	169
7.3.2 Isotopically Exchangeable Cu .....	172
7.3.3 Changes in Cu <sup>2+</sup> Ion Activities.....	174
7.4 Conclusions .....	175
8. <i>Conclusions and Future Directions</i> .....	177
9. <i>References</i> .....	181

## Abstract

Biosolids from sewage treatment plants present both problems and opportunities for society. They are rich in organic matter, nutrients and trace elements and so can be effective soil conditioners, potentially improving both soil structure and fertility. However, they commonly contain high concentrations of heavy metals, which can accumulate to toxic levels in soils receiving frequent or high dose applications. Copper (Cu) is one of the metals of chief concern because it often has high concentrations in biosolids and is capable of exerting a toxic effect on soil microbes. Limits are placed on the amounts of biosolids that can be applied to land to prevent soil accumulation of metals, but these regulatory limits are based on the total metal concentrations in soils and biosolids rather than on the portion that is ecologically active. Therefore, current regulations do not take into account the fact that much of the metal content is bound up in a way that renders it non-active, and thus poses no threat to the environment. A more environmentally relevant regulatory system would set its limits using the available portion of metals. Therefore it is important to quantify this available fraction, and to establish a method by which it can be consistently measured. To do this the nature of biosolids needs to be better understood, and the factors controlling the available fraction need to be identified. Also, it is important to determine how the available fraction may change with time.

This PhD project surveyed 24 biosolids from around Australia and characterised them in terms of chemical and physical properties. Available Cu was measured using radio isotopic techniques ( $^{64}\text{Cu}$ ), a  $\text{Cu}^{2+}$  ion selective electrode, solution extraction, and other methods. A model for predicting available Cu was produced, using the total Cu concentration and the  $\text{Cu}^{2+}$  ion activity in solution extracts:

$$\text{Available Cu (mg/kg)} = 281.5 \text{ Log Total Cu} - 14.9 \text{ pCu}^{2+} - 459 \quad (\text{R}^2 = 0.806)$$

where 'logTotal Cu' is  $\log_{10}$  total biosolid Cu concentration (mg/kg).

A 21-month incubation experiment was conducted to monitor Cu availability over time, with the conclusion that it will remain constant if pH is maintained. Biosolid/soil pH had a strong effect on available Cu, hence a regulatory system based on the available Cu fraction that incorporates a pH protection index is proposed. Mineralisation of organic matter did not lead to increases in available Cu, thus no evidence for the time bomb hypothesis was found. However, organic matter was found to be important for Cu sorption in some biosolids, indicating that over a longer term effects of organic mineralisation on Cu availability may be seen, and therefore longer trials (*i.e.* > 10 years) are needed to determine the long-term fate of biosolid Cu.