Metal chemistry and bioavailability in a biosolids-amended forest soil following conversion of the land for agricultural usage

R G McLaren and L M Clucas

Centre for Soil and Environmental Quality
Lincoln University, Canterbury
New Zealand

Introduction

- Application to forest soils is often considered a relatively safe option with regard to the reuse of biosolids.
- Since the biosolids are surface-applied there is considerable potential for the accumulation of high concentrations of metals within the forest litter layer.

- As long as the land remains under forest, these metals may not be of major concern, **BUT** if the forests are cleared and the land converted to some other form of land use, this may cease to be the case.

- In the Canterbury Plains area of New Zealand, substantial areas of *Pinus radiata* forests are being converted back to agricultural pasture.

- **The completion of a biosolids field trial in a *Pinus radiata* forest enabled us to simulate the conversion of the forest back to agricultural use and examine the fate of metals following conversion.**

Materials and Methods

- The original forest trial consisted of a control plot (no biosolids), a plot receiving unspiked biosolids, and 12 plots that received surface applications of biosolids spiked with increasing amounts of Cu (Cu-1, Cu-2, Cu-3, Cu-4), Ni (Ni-1, Ni-2, Ni-3, Ni-4) and Zn (Zn-1, Zn-2, Zn-3, Zn-4)

Soil at experimental site

- Lismore stony silt loam:
  - Litter layer 2-3 cm in depth
  - Silt loam mineral soil 10-30 cm in depth (many stones)
  - coarse gravels

Property	Litter layer	Mineral soil (0-10 cm)
pH (water)	5.1	4.7
Carbon (%)	38.5	2.8
Total Cu (mg/kg)	5.6	6.4
Total Ni (mg/kg)	8.6	10.1
Total Zn (mg/kg)	43.9	62.8

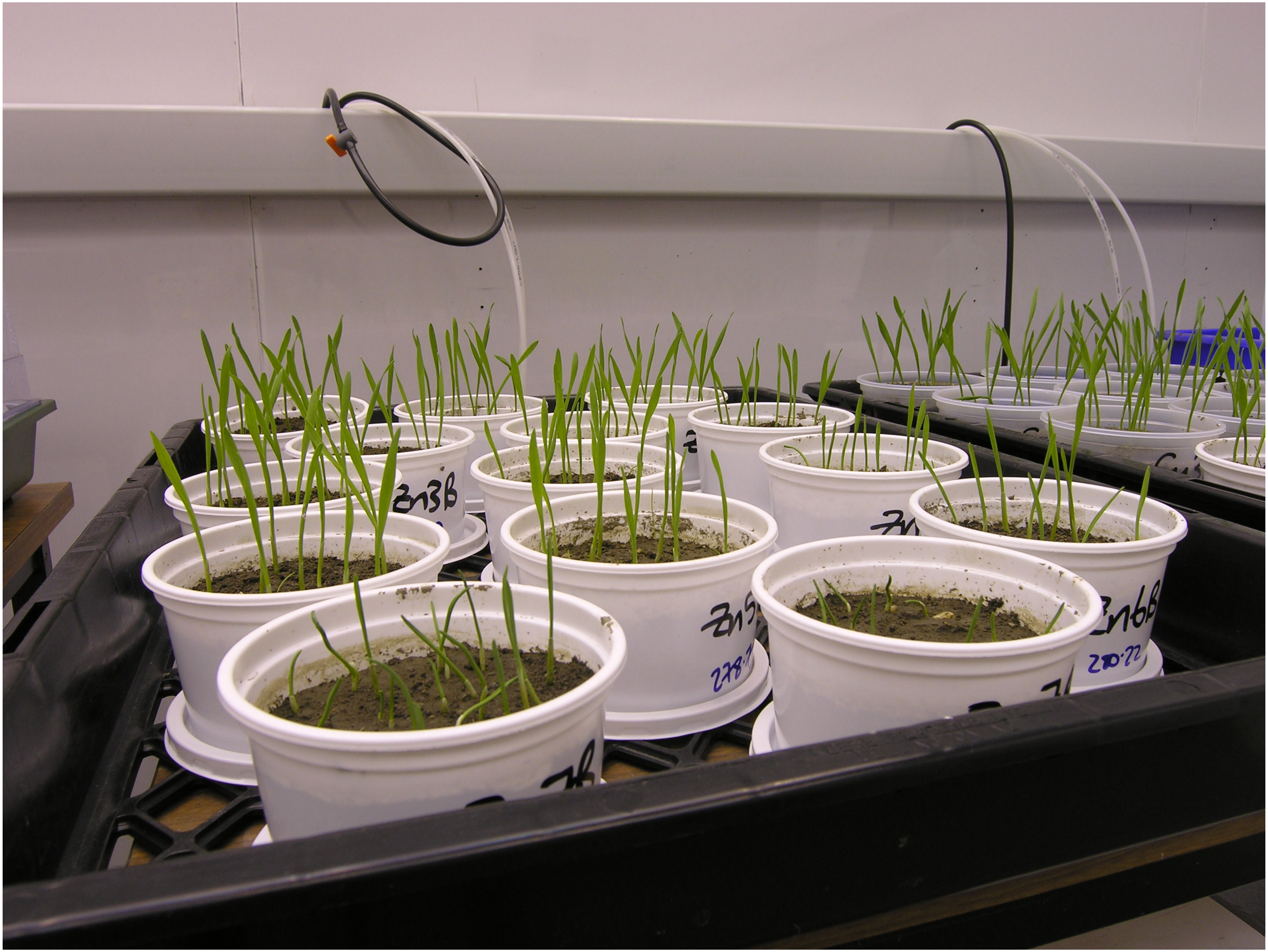
- 6 years after application of the biosolids, material was sampled from each plot from the surface (including litter) down to a depth of 10 cm into the mineral soil.

- The combined litter and mineral soil in these samples was thoroughly mixed in a mechanical mixer to simulate the mixing that occurs during the conversion of the land back to pasture.

- **Experiment 1**
  - Sub-samples of the soils (x 3) were incubated at 25ºC and 80% FC moisture for 2 years.
  - At intervals, soil metal concentrations (total, EDTA-extractable, $Ca(NO_3)_2$-extractable) were determined and soil solution extracted using rhizon soil moisture samples.
  - Metal concentrations determined by FAAS or GFAAS.
  - Ca, Mg, K, Na in soil solutions determined by FAAS, NO_3^-, SO_4^{2-}, Cl^- determined by ion exchange chromatography, DOC determined using a Shimadzu TOC 500A analyser.

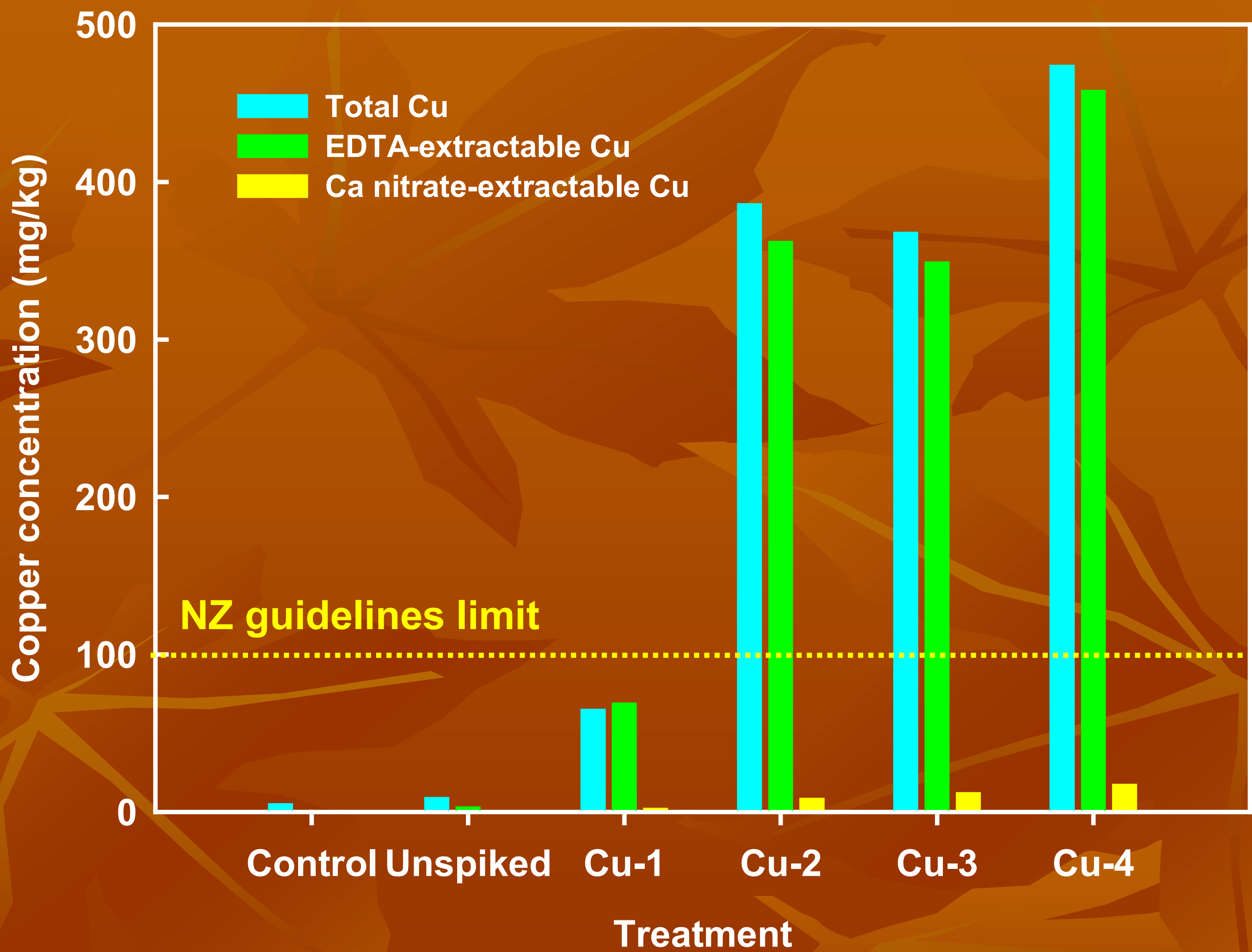
- **Experiment 2**
  - **Samples of soil were incubated with or without hydrated lime until soil pH stabilised.**
  - **The soils were then used for a simple germination and seedling growth bioassay**
    - **Samples of soil placed in containers, moistened to 50% MWHC and planted with 20 viable wheat seeds per pot.**
    - **Containers placed in constant environment room and germination recorded after 5 days.**
    - **Seedlings thinned to 10 per pot and grown for further 15 days before harvesting:**
      - **Dry matter yield recorded**
      - **Cu, Ni or Zn content determined**

- Following harvest of the seedlings, the soils were used to determine:
  - effective soil solution metal concentrations using DGT, and
  - soil solution was extracted using rhizon soil moisture samplers.
- Other soil and soil solution analyses were also carried out as per Experiment 1.

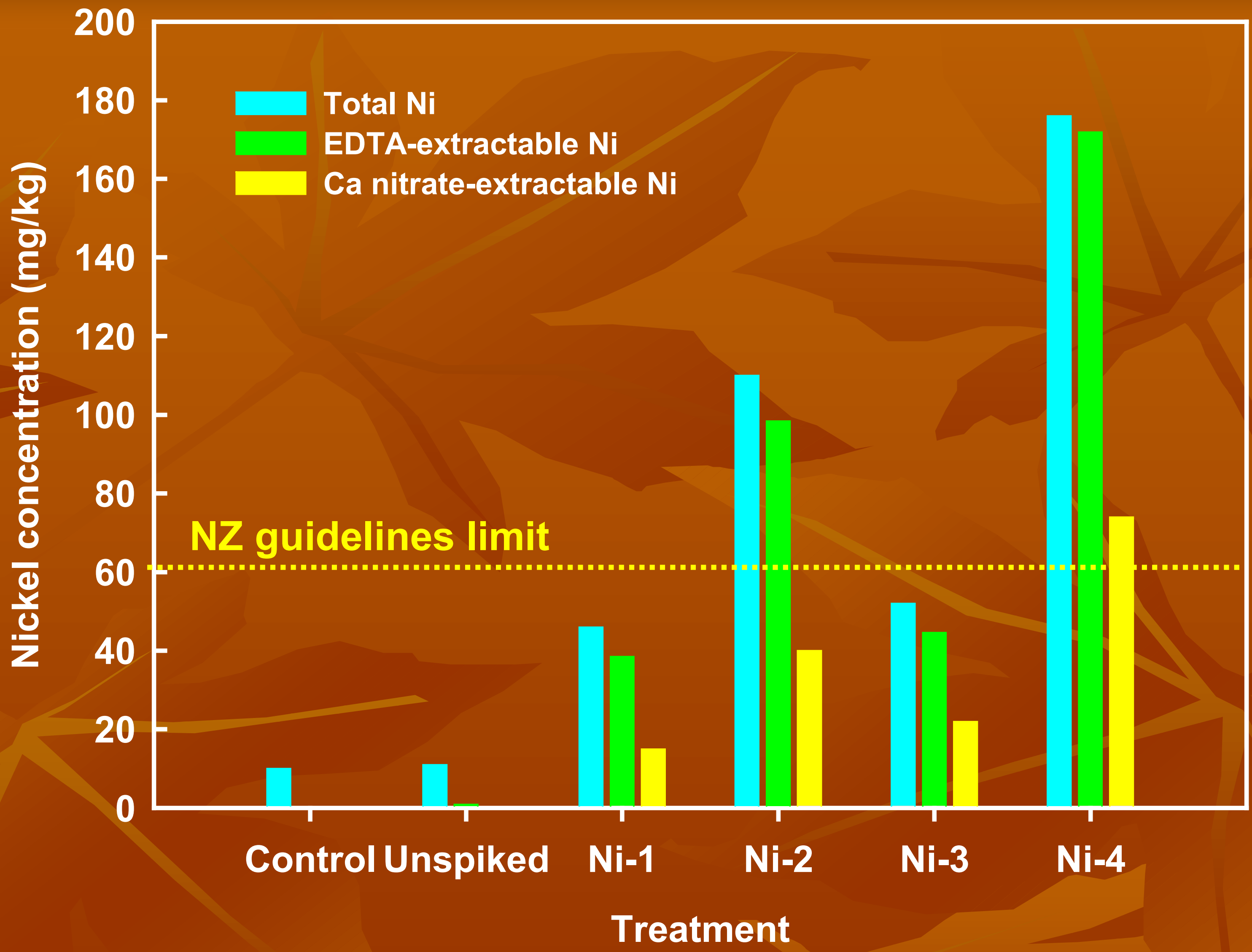

Zn3B
Zn6B


R 125

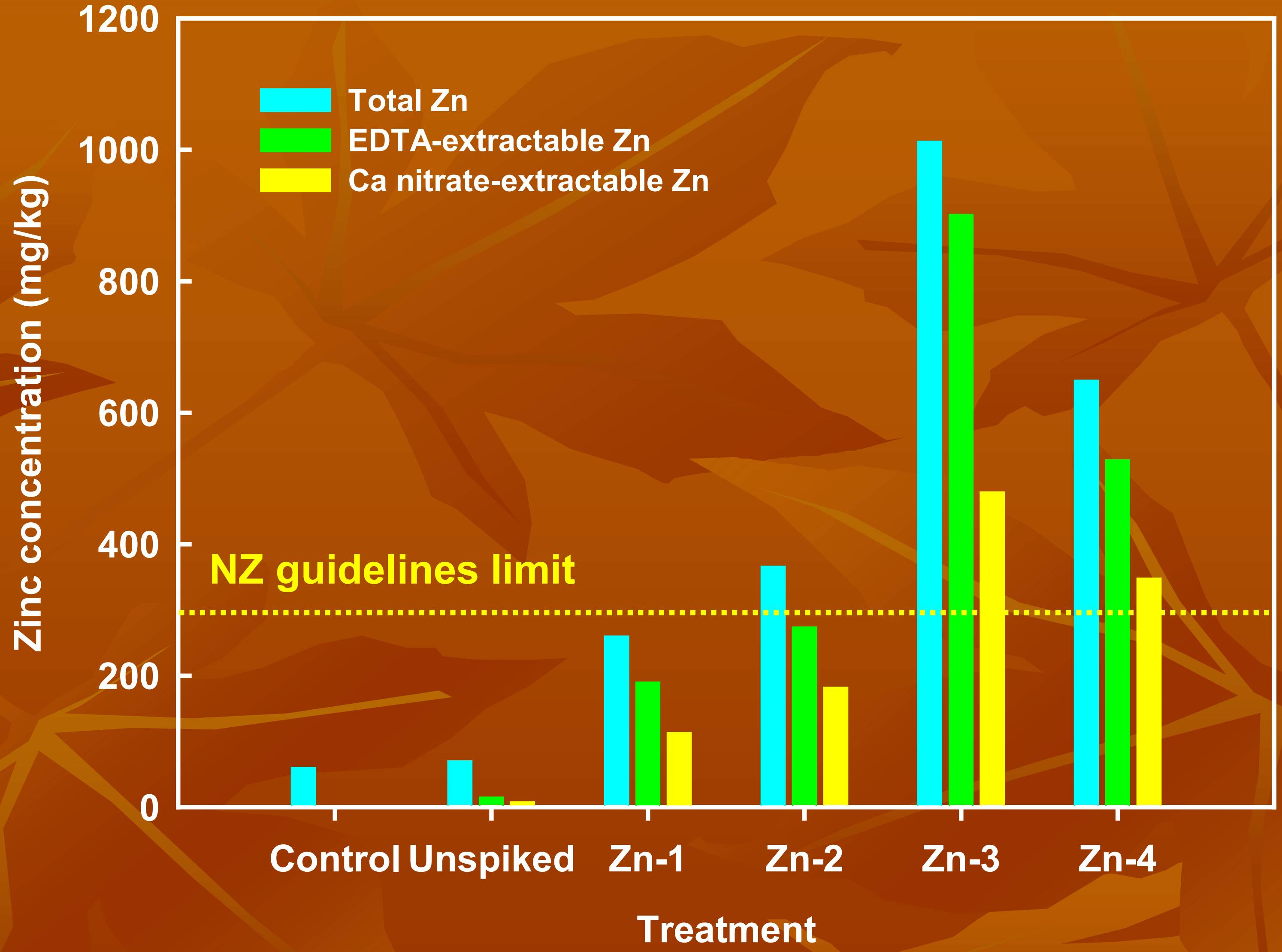
Results



Cu concentrations in mixed litter/mineral soil samples

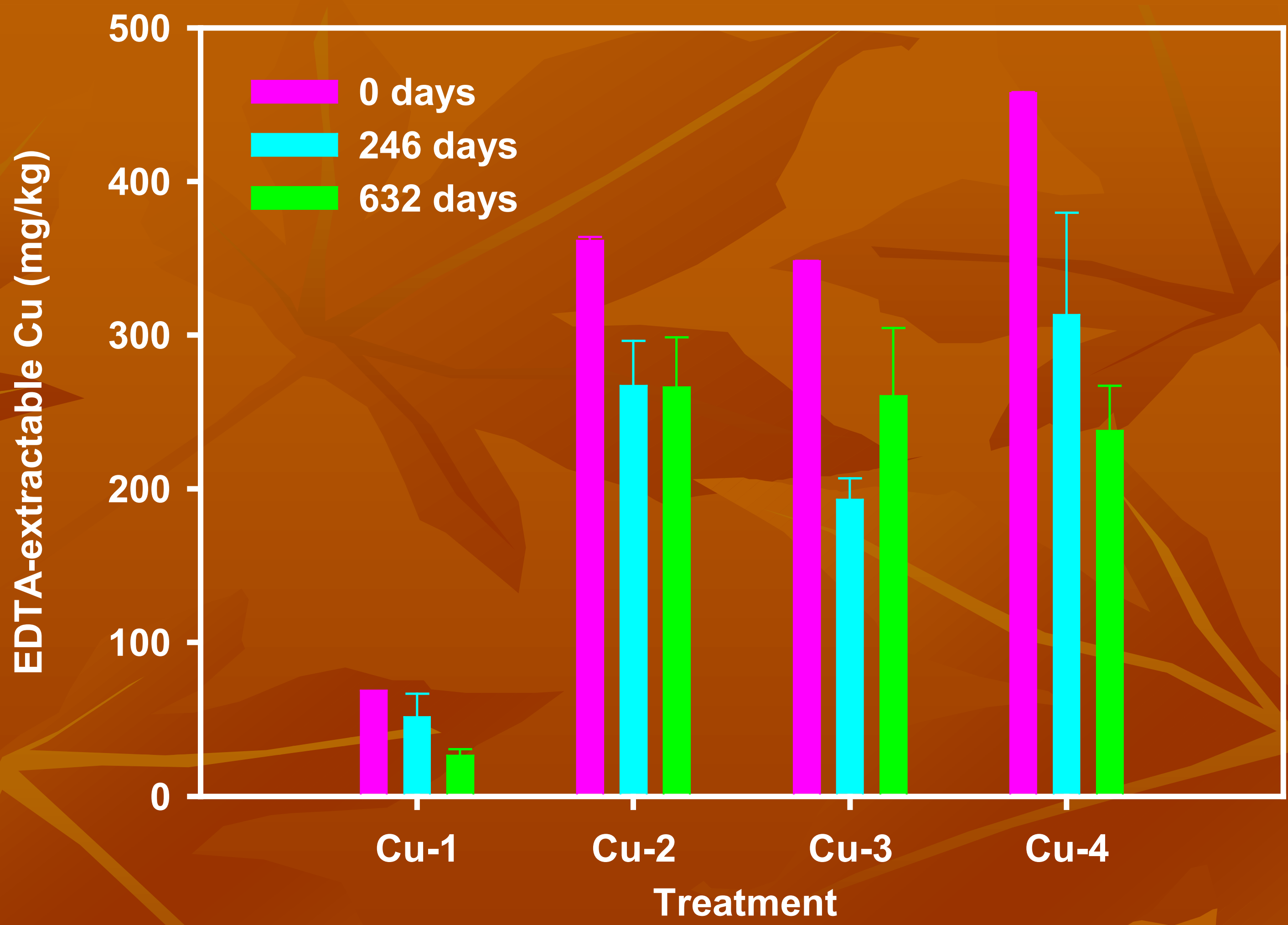


Ni concentrations in mixed litter/mineral soil samples

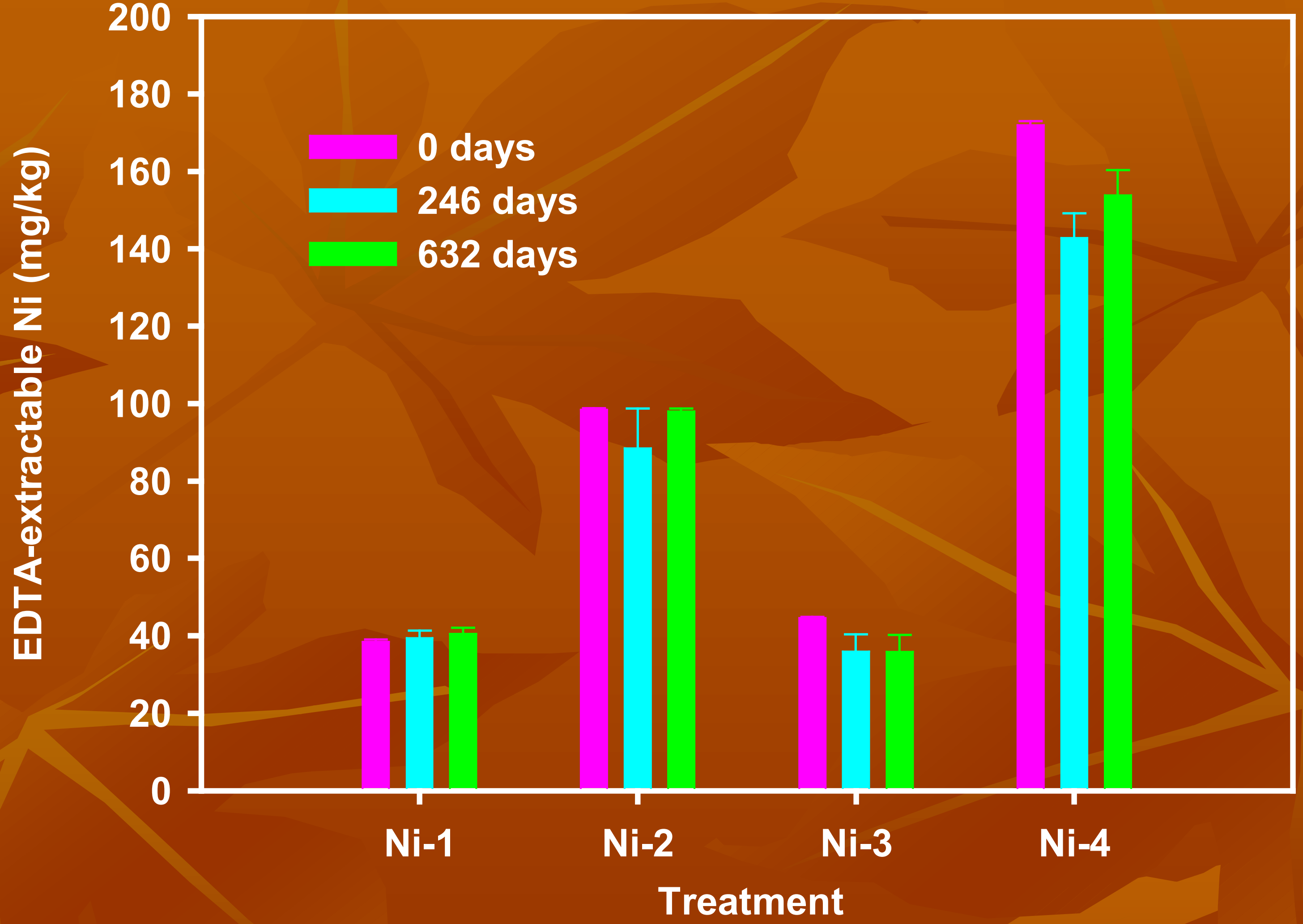


Zn concentrations in mixed litter/mineral soil samples

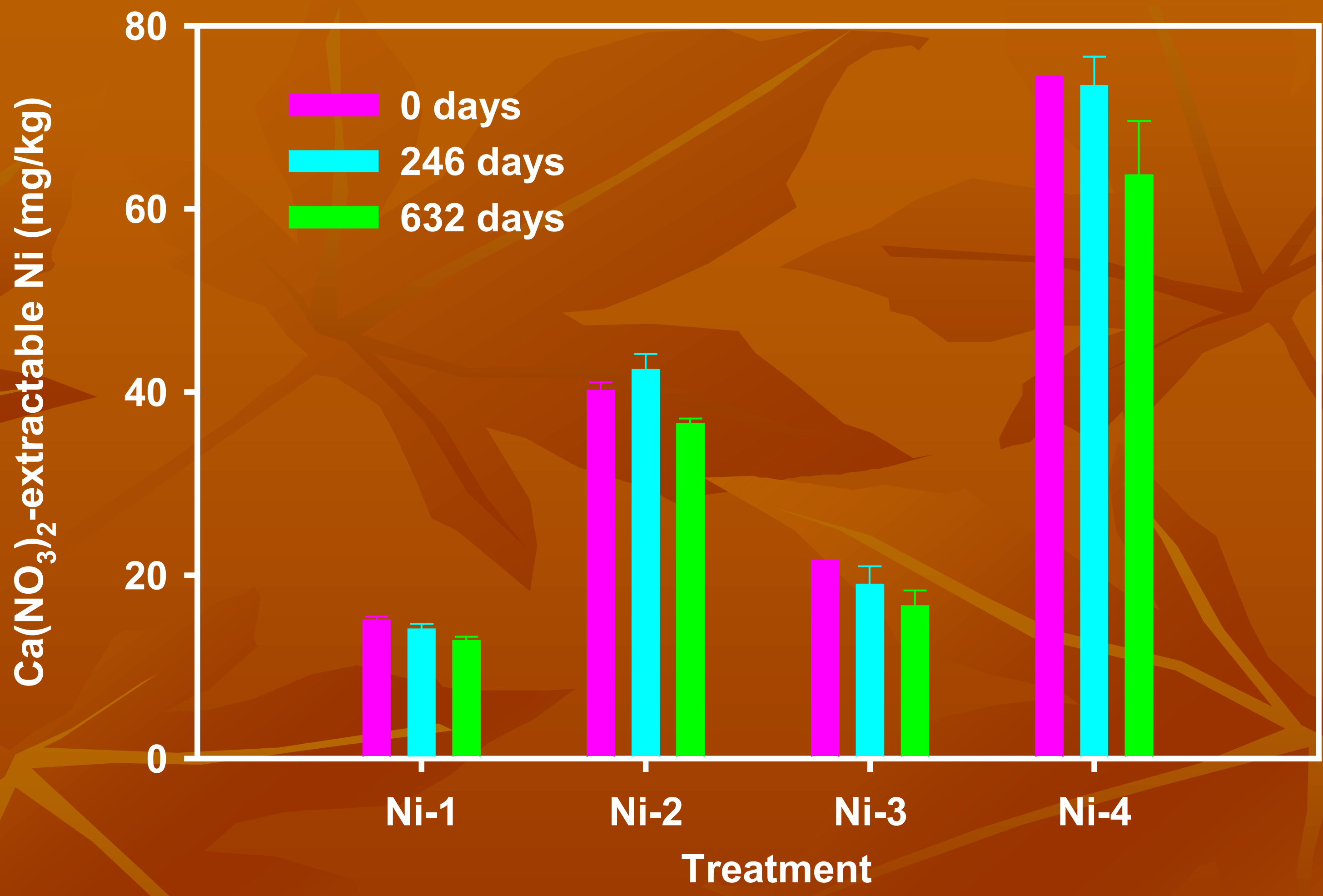
Experiment 1



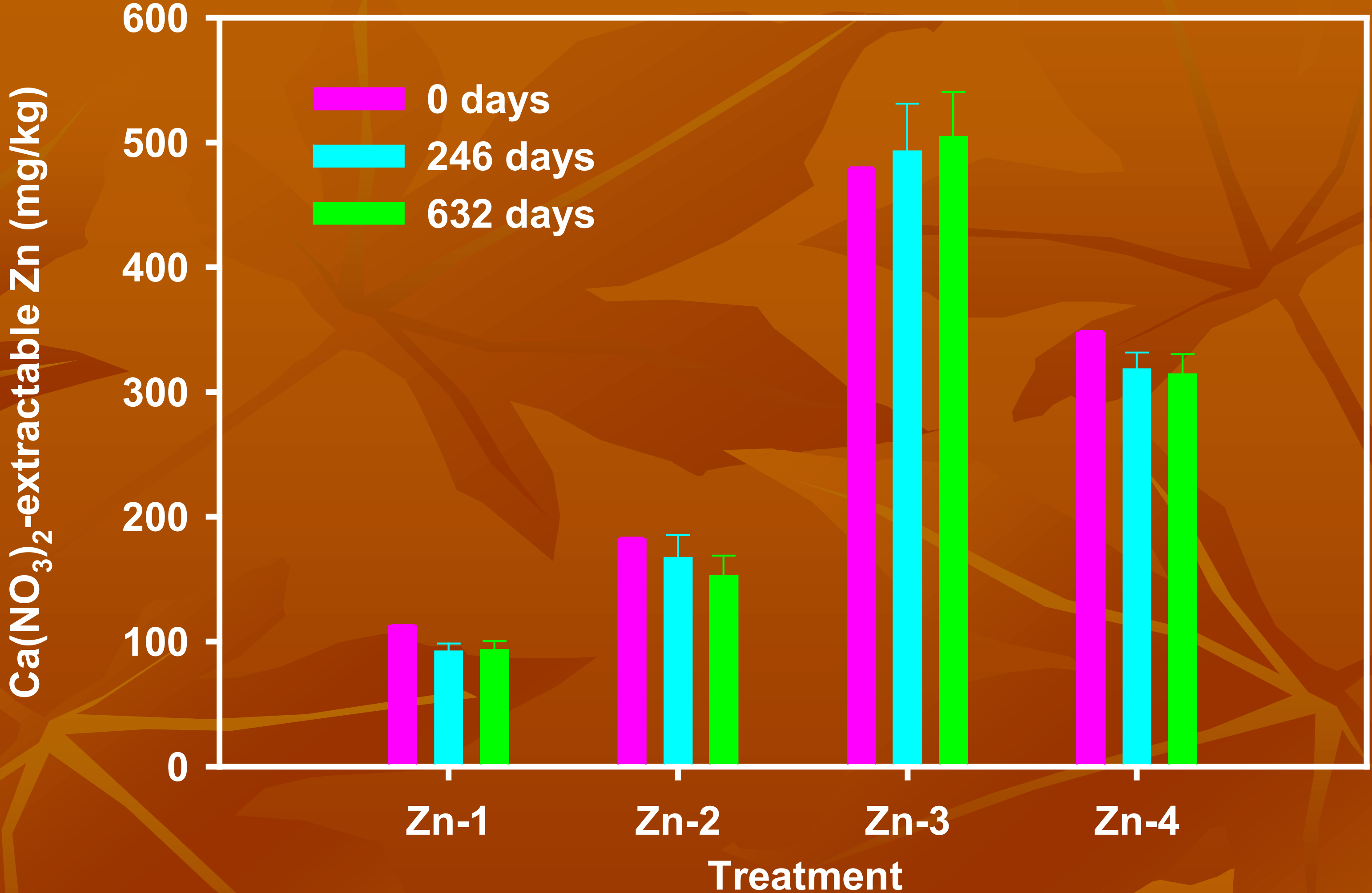
Effect of incubation period on EDTA-extractable Cu concentrations



Effect of incubation period on EDTA-extractable Ni concentrations



Effect of incubation period on $Ca(NO_3)_2$-extractable Ni concentrations



Effect of incubation period on $Ca(NO_3)_2$-extractable Zn concentrations

Concentrations and speciation of Cu (WHAM 6) in soil solution

Treatment	Total Cu (mg/L)	Cu speciation (%)			
		Cu^{2+}	$CuSO_4^0$	$CuCl^-$	Cu-org
Control	0.003	0.7	0.0	0.0	99.3
Unspiked	0.07	4.7	0.1	0.0	95.2
Cu-1	0.17	10.6	0.1	0.1	89.2
Cu-2	0.67	19.4	0.5	0.0	80.0
Cu-3	0.77	38.5	0.7	0.1	60.8
Cu-4	1.37	39.4	0.8	0.1	59.7

Concentrations and speciation of Ni (WHAM 6) in soil solution

Treatment	Total Ni (mg/L)	Ni speciation (%)			
		Ni^{2+}	$NiSO_4^0$	$NiCl^-$	Ni-org
Control	0.02	93.1	0.3	0.4	6.1
Unspiked	0.05	94.6	1.3	0.5	3.6
Ni-1	2.31	95.1	1.6	0.3	3.0
Ni-2	8.12	95.2	2.0	0.2	2.6
Ni-3	3.53	94.4	0.9	1.0	3.7
Ni-4	14.21	94.1	2.5	0.3	3.0

Concentrations and speciation of Zn (WHAM 6) in soil solution

Treatment	Total Zn (mg/L)	Zn speciation (%)			
		Zn^{2+}	$ZnSO_4^0$	$ZnCl^-$	Zn-org
Control	0.25	92.5	0.4	0.4	6.7
Unspiked	3.05	93.3	1.4	0.5	4.8
Zn-1	31.00	94.1	2.3	0.4	3.2
Zn-2	47.80	88.8	3.2	1.5	6.5
Zn-3	155.10	93.1	3.5	0.3	3.1
Zn-4	116.90	93.1	3.6	0.7	2.6

Experiment 2

- **Liming increased soil pH by approximately 1 pH unit**

	Unlimed	Limed
Soil pH	4.66 ± 0.031	5.61 ± 0.070

Effect of lime addition on $Ca(NO_3)_2$-extractable soil metals (mg/kg)

Cu plots	No lime	Plus lime	Ni plots	No lime	Plus lime	Zn plots	No lime	Plus lime
Cu-1	0.6	0.3	Ni-1	13.0	4.1	Zn-1	75.5	19.1
Cu-2	4.4	1.0	Ni-2	34.5	10.2	Zn-2	114.0	23.2
Cu-3	7.7	0.8	Ni-3	15.1	2.6	Zn-3	387.0	146.4
Cu-4	11.4	1.4	Ni-4	59.3	23.7	Zn-4	232.8	90.6

Effect of lime addition on soil solution metal concentrations (mg/L)

Cu plots	No lime	Plus lime	Ni plots	No lime	Plus lime	Zn plots	No lime	Plus lime
Cu-1	0.05	0.06	Ni-1	1.05	0.20	Zn-1	4.05	0.71
Cu-2	0.18	0.20	Ni-2	2.87	0.51	Zn-2	11.76	0.69
Cu-3	0.35	0.18	Ni-3	0.43	0.11	Zn-3	58.30	8.34
Cu-4	0.39	0.31	Ni-4	4.13	1.44	Zn-4	45.10	2.05

Effect of lime addition on metal speciation in soil solution

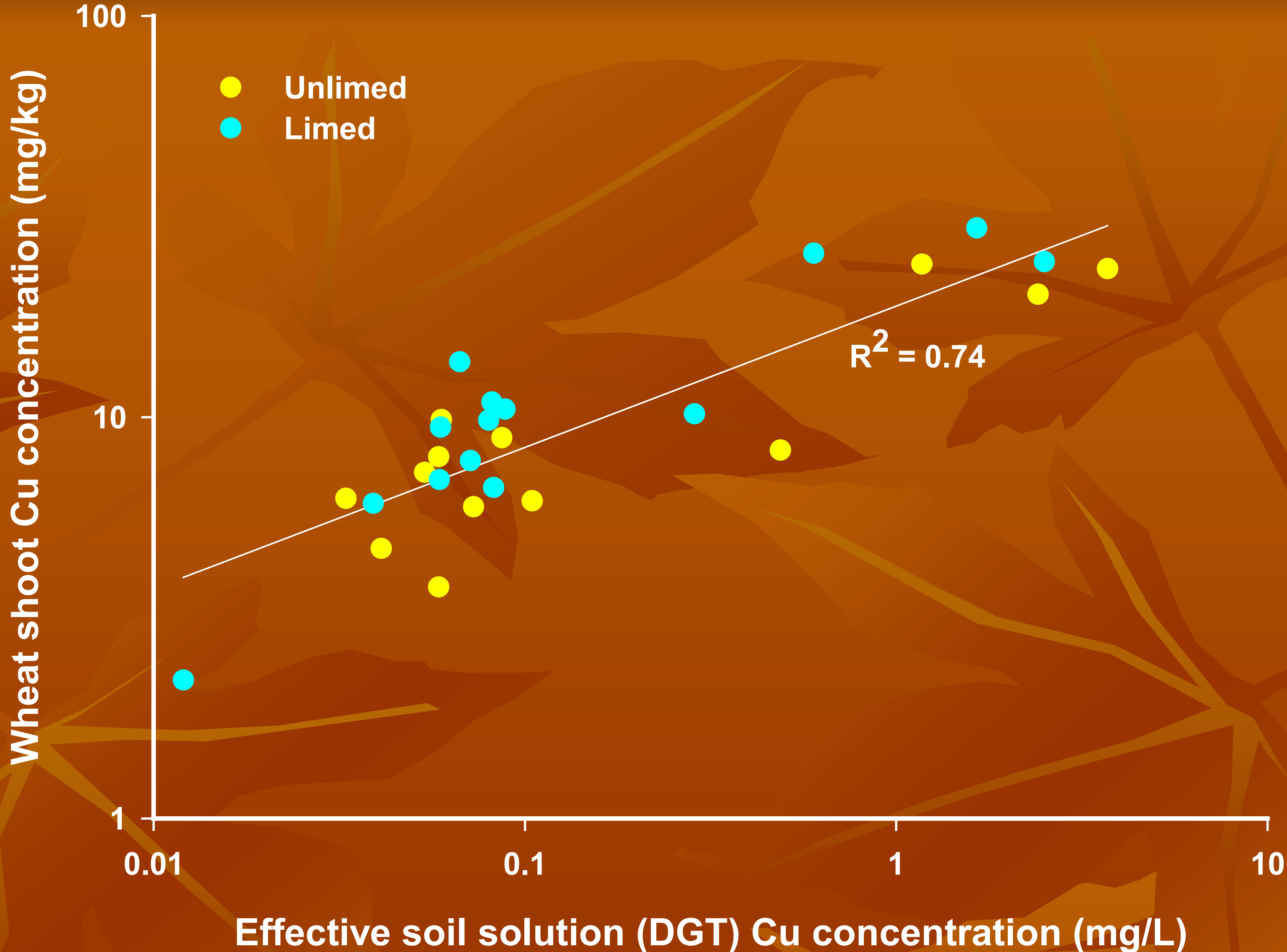
(% metal present as M^{2+})

Cu plots	No lime	Plus lime	Ni plots	No lime	Plus lime	Zn plots	No lime	Plus lime
Cu-1	7.7	0.2	Ni-1	92.8	87.8	Zn-1	83.2	59.1
Cu-2	35.8	-	Ni-2	92.4	79.2	Zn-2	81.3	42.6
Cu-3	67.5	1.5	Ni-3	86.7	51.0	Zn-3	91.5	73.3
Cu-4	75.9	0.9	Ni-4	91.2	89.5	Zn-4	91.1	43.8

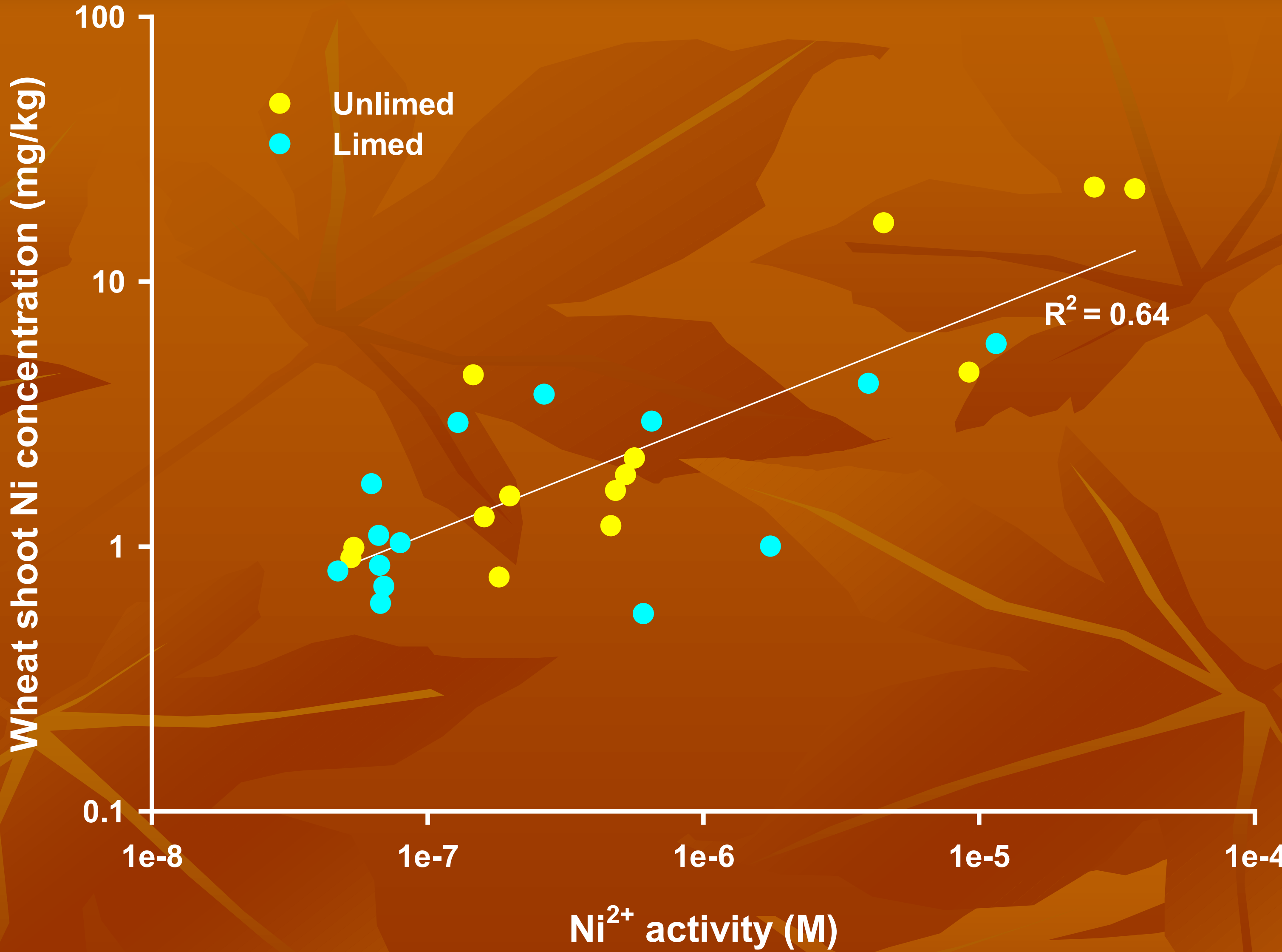
Decreases in % M^{2+} matched by increases in % organic bound M

- Neither lime addition or metal concentrations had any significant effects on wheat seedling growth.

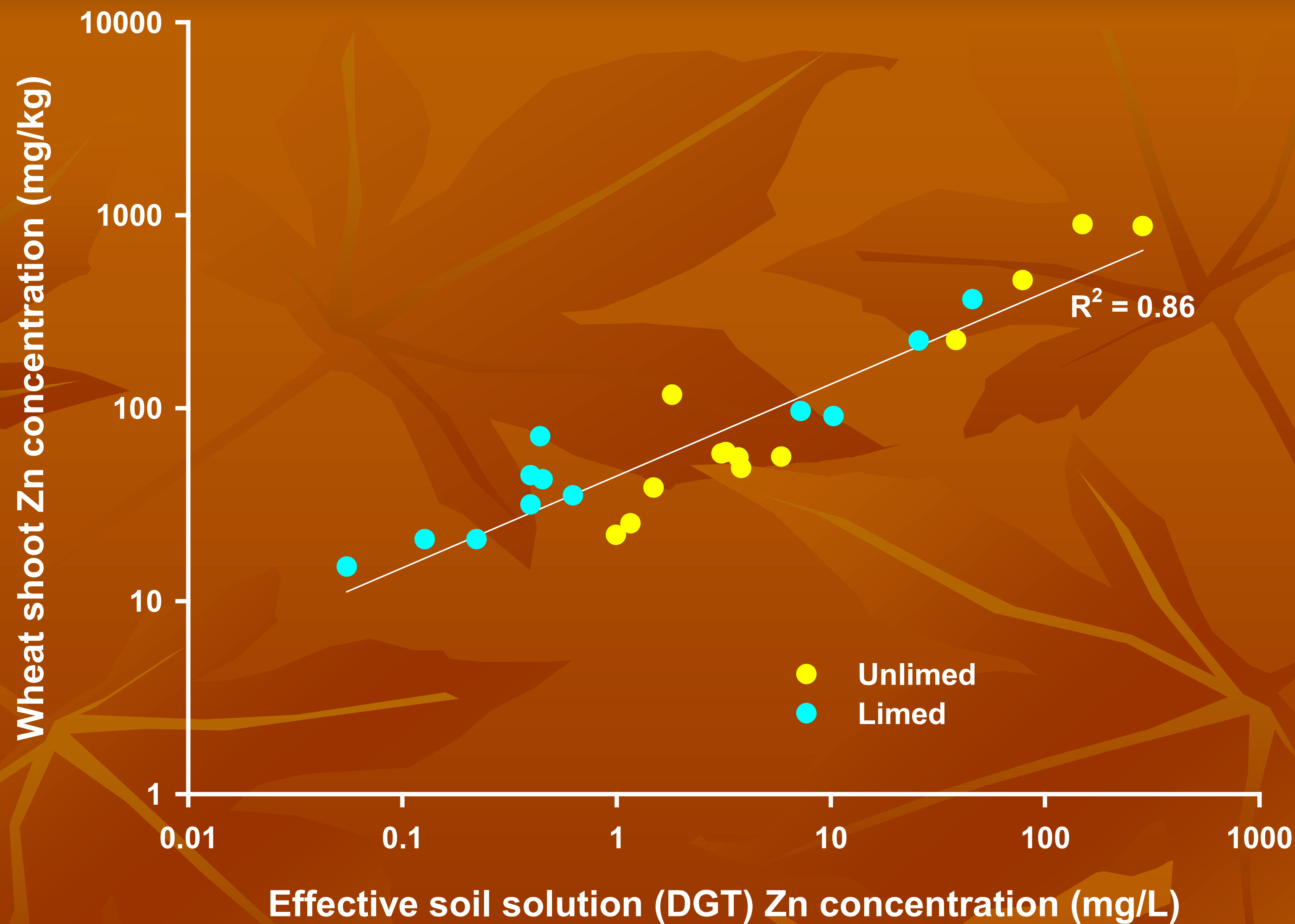
	Unlimed	Limed
Shoot DM (g)	0.30 ± 0.009	0.30 ± 0.013
Root DM (g)	0.28± 0.019	0.28 ± 0.014



Relationship between Cu concentration in wheat shoots and effective soil solution Cu concentration



Relationship between Ni concentration in wheat shoots and Ni^{2+} activity (M)



Relationship between Zn concentration in wheat shoots and effective soil solution Zn concentration

Conclusions

- Incorporation of biosolids-amended forest litter into underlying mineral soil resulted in high total and soluble metal concentrations in the soil.
- Soluble metal concentrations showed little decrease with time.
- Liming decreased both total soluble metal concentrations and the proportions present as free ions.

- Even for the unlimed soils there was no effect of metals on plant growth as determined in the wheat germination/seedling growth bioassay.
- Cu, Ni and Zn concentrations in wheat seedlings were increased by the various metal treatments to the original plots.
- The plant metal concentrations were strongly related to measures of soil metal bioavailability, particularly ‘effective’ soil solution metal concentrations (DGT) and free ion activities.

Acknowledgements

- This work is funded by the New Zealand Foundation for Research, Science and Technology through the Institute of Environmental Science and Research, Ltd (ESR).