Chapter 1 Introduction

1.1 Mixed Waste Organic Outputs (MWOO) production and management

Mechanical and biological processing technologies have been used for many years to produce compost from source separated green waste streams. Since the 1980s, treatment of municipal solid waste and other wastes has also become popular, especially in Northern Europe and the United States (US), as a way of reducing the waste volume going to landfill, soil improvement and fertiliser benefits (Hangen 1991; He *et al.* 1992; Jakobsen 1995; Otten 2001; Hansen *et al.* 2006a). However, in the early 1990s there was a decline in the use of outputs as a soil fertiliser (Hangen 1991; Krauss and Grammel 1992; Kassel 1993; Zhang *et al.* 2006) due to growing concerns about the presence of contaminants (Harms and Sauerbeck 1982, 1983). More recently, international efforts have focused on improving source separation and reforming the regulation of land application (EA 2009a) due to renewed interest in using mixed waste organic output (MWOO) for soil amendment (Hyder 2006).

In Australia around 44 million tonnes of waste (approximately 2,080 kilograms of waste per person) was produced in 2006-7, of which 29 % originated from municipal sources (DEWHA 2009a; ABS 2010; DEWHA 2010). As the population increases, it is predicted that around 81 million tonnes of waste per year will be generated by 2020 (DEWHA 2010). New South Wales (NSW) generates approximately 35 % of the total national figure (Hyder 2009a; ABS 2010). A national policy framework for waste management and resource recovery was agreed in 1992 by the Council of Australian Governments (COAG) through its endorsement of the National Strategy for Ecologically Sustainable Development. This included an agreement on the national approach to waste minimisation and management.

To meet the objectives of the National Strategy for Ecologically Sustainable Development and address policy requirements, an improvement in waste recovery and re-use technologies occurred not just in NSW but throughout Australia, and this included recovery of resources from waste streams which would otherwise be sent to landfill. One such technology is the processing of mixed solid waste (mostly municipal solid waste [MSW]) to produce an organic output for application to land as a fertiliser or soil amendment. Throughout this thesis, and with reference to NSW, this organic output is referred to as MWOO. The technology to produce MWOO has been expanding rapidly in recent years, with the development of many new commercial facilities, mostly in Western Australia and NSW, and with at least 10 more under consideration (WMAA 2010).

1.2 Process of MWOO production

In order to produce an organic output that can be used as a soil fertiliser, a series of treatments that are more complicated than traditional compost processes are applied to a mixed sourced waste stream. These remove physical contaminants and recyclables to produce degradable organics that are suitable for application to the soil. Green and green/food waste is often processed separately and does not usually form part of the MWOO.

1.3 Mechanical preprocessing

Before material can be sorted or biologically treated, the input mixed waste must undergo initial preparation, including the removal of bulky and easily separated material and items that could hinder the process. In NSW facilities, a variety of preparation methods are used to split bags or to shred, homogenise and reduce raw material size for sorting and biological treatment. These include: bag openers, shredders, rotating drums, ball mills, bag splitters and hammer mills. Mechanical separation is then used to sort mixed waste into different fractions, with biodegradable fractions separated from non-biodegradable and dry recyclable materials (glass, metal [including batteries], plastic). A range of different techniques are available in NSW facilities to separate the different materials according to their type, size, shape, density, weight and magnetism. These include manual separation, vibrating screens, magnetic or ballistic separators, trommels and cyclones, in addition to optical, electrical and wet technologies (DEFRA 2007). A large proportion of the materials separated at this stage are plastic, glass, steel, cardboard and aluminium.

1.4 Biological treatment

The biological treatment stage involves the decomposition of output from mechanical preprocessing to simple compounds by aerobic or anaerobic treatment, or a combination of both; aerobic treatment is utilised by NSW facilities. Waste is placed in windrows or large beds enclosed in semi-permanent covers or static tunnel facilities, which undergo either periodic turning or continuous agitation. In this way oxygen is used as the terminal electron acceptor to produce heat, water and carbon dioxide (DEFRA 2005).

The composting process can be divided into four major stages dependent on temperature and microbial consortia. In the first stage of composting, temperatures increase from ambient to approximately 40 ºC. This is classed as the mesophilic stage (characterised by temperatures in the 30–45 ºC range), during which the greatest microbial diversity is usually observed (Nakasaki *et al.* 1985). With continued degradation, the exothermic process generates more heat and raises temperatures to the thermophilic range of 45–75 ºC. This is followed by cooling and maturation (Potter *et al.* 1999). The compost pile volume is decreased during this stage and pathogens are also reduced by the heat generated. In the final stages of cooling and maturation, microbial activity slows because of decreasing availability of nutrients with reduced heat generation. The compost mass dries and is then considered ‘stabilised’ or ‘matured’.

Depending on the composition of the waste material and the method of composting, the product is matured for 3 to 18 months. It is then screened prior to use as a soil amendment, with outputs from the process being MWOO.

1.5 Factors affecting the quality of the MWOO product

Many factors affect MWOO quality and contamination content, but the physical, chemical and biological nature of the source waste material have the most significant influence on the final product. Mechanical preprocessing is important for inert contaminant separation and for preparing the organic material for more effective degradation. The rate and duration of biological treatment determine the activity and proliferation of the microorganisms and therefore the degree of degradation of substrate material, including degradable contaminants. In turn, nutrient concentrations, carbon to nitrogen ratio, aeration, moisture, temperature, pH and particle size of the feedstock are major factors controlling the rate and degree of decomposition. Any change in one factor often leads to change in the others.

Despite all the beneficial aspects of MWOO, it can contain high concentrations of metals and metalloids, originating from items such as batteries, plastics, paints, inks, body care products, medicines and household pesticides that may be present in the source waste streams (NHHWF 2000; Bardos 2004). According to the NSW General Exemption, the metals and metalloids of greatest concern with application of MWOO to soil include As, Cd, Cr, Cu, Ni, Pb, Se and Zn because of their toxicity and effects on humans and the environment (Wilson *et al.* 2014). Risks include long-term accumulation due to persistence in soil and negative impacts with ecosystem exposure through food chains, soil organisms, plants, animals and humans (Smith 1996, 2009).

1.6 Australian regulation of MWOO application: NSW General Exemption

In Australia, regulation of waste management is primarily the responsibility of State, territory and local governments. Since 1992, all Australian governments have introduced a range of legislative and policy instruments for waste management and resource recovery. In NSW, the definition for mixed waste that can be used for MWOO production and a range of criteria for MWOO and conditions for its soil application in NSW, are included in the NSW General Exemption approved by the Environmental Protection Authority (EPA) in 2014. This exempts a most recent person from certain regulatory requirements that would normally apply to the land application of a waste material. The processor responsibilities, consumer responsibilities, application rates, buffer zones, land use limitations and maximum allowable concentration of certain metals in soil and MWOO are also provided in the General Exemption.

1.7 Thesis aims and structure

The NSW General Exemption guidelines described above is in many parts based on the NSW biosolids guidelines, and refers to information from the only study on MWOO for NSW carried out by Dorahy *et al*. (2006). Many knowledge gaps remain with regard to MWOO application on NSW soils, and it is critical to address these to underpin reliable and realistic guidelines and truly understand the risks for humans and the environment. The overall objective of this project was to understand the risk created by MWOO application to soils by considering: (a) the total concentration and distribution of metal and metalloid pollutants in soils; (b) the proportion of metal and metalloid pollutants that may be available and leachable. This thesis aims to respond to the following questions:

- How does MWOO application change the total concentration of targeted pollutants in a range of NSW soils considering different application rates, methods of application, depths and time?

- How does MWOO application change the proportion of the metals and metalloids in different soil fractions, as an indicator of availability and mobility?

- How does MWOO application impact metal and metalloid concentration in different leaching agents and what are the consequences for soil water contamination and potentially plant available fractions?

To address these questions the following experimental investigations occurred:

Chapter 3 An examination of hot plate and microwave extraction methodology with ICP-OES analysis for multi-elemental determination of metals and metalloids in MWOO and soils

We first carried out a method development to ascertain the optimum method for total metal extraction and analysis by ICP-OES, from soils and MWOO amended soil samples with special consideration of targeted elements of concern including As, Cd, Cr, Cu, Ni, Pb and Zn based on the NSW General Exemption.

Chapter 4 Effects of MWOO application on metal and metalloid accumulation and distribution in ten different NSW soils after 6, 12 and 18 months

The method developed was then used in a large scale glasshouse trial (Chapter 4), whereby columns containing soil collected from ten locations across NSW were treated with a single application of MWOO either surface applied or incorporated at rates of MWOO were 20, 50 and 140 t ha^{-1}. At 6, 12 and 18 months, soil samples were collected from various depths within the columns to allow evaluation of changes in total metal and metalloid concentrations and distribution down the soil profile through time.

Chapter 5 Speciation and availability of metals and metalloids in mixed waste organic output (MWOO) and MWOO amended soils

The influence of MWOO application on metal and metalloid speciation as exchangeable, reducible, oxidisable or residual fractions was assessed using soils from the glasshouse experiment (acidic sand and clay) soils in which risks was considered greater and also at 6, 12 and 18 months. The analysis of the soils involved using different chemical extractants in the BCR sequential extraction procedure to evaluate changes in potential bioavailability of contaminants with MWOO application.

Chapter 6 A study of metal and metalloid leachability in a sandy loam soil amended with MWOO: a kinetic approach and evaluation of element distribution after extraction

Finally, a batch extraction was conducted to study metal and metalloid leaching from MWOO amended soils. Three well-known leaching agents; deionised water, 0.01 M $CaCl_2$, and 0.05 M ethylene-diaminetetraacetic acid (EDTA) were used and leachate was monitored for 48 hours after MWOO application to evaluate potential risk for water resources. The bioavailability of the metals and metalloids remaining in leached samples was assessed and leaching data was applied in kinetic modelling to assess the modeling approach as a predictor of contaminant desorption.

Chapter 2 The impact of MWOO application on total metal and metalloid concentration, speciation, bioavailability and leaching in soil with associated risks: a review

2.1 Introduction

The use of MWOO as a soil amendment has proliferated recently, not just in Australia but globally, despite it being well understood that metals and metalloids are common contaminants of MWOO products. Concerns regarding metal and metalloid include long-term accumulation due to their persistence in soil, their negative impacts on ecosystems, and exposure through the food chain, to soil organisms, plants, animals and humans (Smith 1996, 2009). Although a number of studies have documented contaminant fate in MWOO amended soils (Walter *et al.* 2006; Perez *et al.* 2007; Weber *et al.* 2007; Ayari *et al.* 2010), these are usually carried out on only one or two different soil types and for a limited range of elements. This chapter describes the metals and metalloids of concern and commonly found in MWOO, and reviews the literature available on their concentrations in MWOO and our current understanding on their fate and behavior in soil following MWOO application. The latter part of the review specifically focuses on availability and leachability of metals and metalloids in soil amended with MWOO, as these are important considerations in assessing risks to plants, animals and humans when MWOO is applied to soils.

2.2 Sources of metals and metalloids in MWOO and effect of production process on concentrations

Metal contamination enters MWOO feedstock from a variety of sources such as glass, batteries, plastic, green and food waste. Plastics are a major source of Cd (Lopez *et al.* 2004), leather is a major source of Cr, and Pb and Cu are usually derived from materials made with iron (Lopez *et al.* 2004). Some plastic bags contain high concentrations of Cu, Pb and Zn , and Pb can also be found in glass, batteries and paper (Paradelo *et al.* 2009). Haynes *et al*. (2009b) listed personal care products such as creams, ointments and deodorant as a source of Zn. The type of waste processed therefore, directly effects metal concentrations in MWOO.

Paradelo *et al*. (2009) reported that modern separation technologies and processing improvements, such as magnetic separation, effectively reduce metal concentrations in MWOO. For example, metal concentrations can be considerably decreased in source separated waste because a large amount of non-biodegradable and dry recyclable material (such as cardboard, plastic, glass, steel, aluminium and batteries) is removed from waste following mechanical treatment (Lopez *et al.* 2004a; Albaladejo *et al.* 2009). However, metal concentrations in source separated waste are still likely to be higher than in green waste (Whittle and Dyson 2002; Brinton 2005; Smith 2009). Smith (2009) reviewed a variety of waste stream sources from different countries and concluded that the organic output derived from source separated green waste contained significantly lower metal concentrations than other sources. An example of this is the work of He *et al*. (1995) in the US, whereby they report significantly higher concentrations of Ni, Se, Pb and Zn in MWOO amended soils compared to soils treated with a mixture of MSW compost and biosolids.

Metal concentrations can fluctuate during MWOO production and processing, with final concentrations dependent on composting techniques, parameters such as aeration, moisture, temperature, pH and particle size of the feedstock, and the nature of the metal. One process that can result in decreased concentrations of metals is leaching (Gautam *et al.* 2010). For example, Cu and Zn concentrations increased for 3 years in MWOO which was biologically treated, whereas, Ni, Cr, Cd, and Pb stabilised or reduced due to leaching (Chica *et al.* 2004). Ciavatta *et al*. (1993) also observed an increase in metal concentrations as a result of biological treatment, and they attributed this to the decrease in waste volume during decomposition plus the incorporation of crushed plastic, metal and glass into the organic mass during the stabilisation period. Gautam *et al*. (2010) demonestrated that metal reduction mostly occurs during the thermophilic phase (refer to Section 1.4) and they suggest this is due to metals being released from organic matter, plus the increased water content and changes in the anionic and oxidic properties of the compost improving metal solubility.

2.3 Total metal and metalloid concentrations in MWOO and maximum limit values

Representative median concentrations of metals and metalloids and the range of concentrations detected in MWOO are summarised in Table 2.1 (extracted from Wilson, Bayat and Wilson (2014)), along with the maximum allowable values specified in the NSW General Exemption (DECCW 2014) and the critical phytotoxic concentration (where available) as reported by Kabata-Pendias and Pendias (2001) for priority pollutants. The Australian data used in the development of Table 2.1 is mainly from NSW MWOO facilities that accept mixed waste streams but that did not source-separate during 2006 to 2010. All other data are for organic outputs sourced from municipal solid waste (MSW) and mixed waste streams that contained both source separated and non-source MSW output from mostly European and Northern America countries with high socio-economic profiles and usage of MWOO amendment.

Table 2.1 Summary of metals and metalloid concentrations reviewed in MWOO (Wilson *et al.* 2014) (data in mg kg^{-1} dry weight). Australian data presented in brackets []. Number of detections presented in parentheses ().

Metal/metalloid	**Representative median of values reported**	**Range reported**	**Number of Samples**	**NSW Exemption limit value (DECCW 2014)**	**Critical phytotoxic concentration (Kabata-Pendias and Pendias 2001)**
Antimony (Sb)	- [5.15]	- [5.1 – 5.2]	- [10(2)]	-	
Arsenic (As)	5.14 [5.74]	1.1 – 13 [3.0 – 9.8]	27 [12(10)]	20	1-20
Barium	- [120.63]	- [85 – 150]	- [8(8)]	-	
Beryllium	- [0.22]	- [0.17 – 0.31]	- [10(6)]	-	
Cadmium	3.00 [1.24]	0.02 – 20.48 [0.76 -14.0]	~2528 [365(363)]	3	10-20

Chromium	77.33 [32.3]	0.1 – 365 [8 - 340]	~2466 [365(365)]	100	1-10
Cobalt	67.59 [4.2]	3.0 – 609.65 [3.0 – 7.6]	17 [10(10)]	-	
Copper	212.97 [175.8]	3.0 – 829 [24 – 690]	~2483 [365(365)]	375	10-30
Lead	273.57 [245.66]	7.9 – 1570 [17 – 580]	~2529 [365(365)]	420, 300, 250 †	30-300
Lithium	- [3.8]	- [3.5 – 5.2]	- [8(4)]	-	
Manganese	538.94 [280]	150 – 1500 [150 – 460]	26 [10(10)]	-	
Mercury	6.50 [0.40]	0.02 – 14.7 [0.02 – 6.60]	~2421 [365(364)]	4	
Molybdenum	17.36 [2]	2.0 – 76 [2.0 – 2.0]	17(9) [10(2)]	-	
Nickel	74.18 [24.8]	5.1 – 649 [18 – 65]	~2408 [365(365)]	60	10-30
Selenium	0.87 [ND]	0.2 – 1.7 [ND]	7 [10(0)]	5	
Silver	- [1.41]	- [1.0 – 2.1]	- [8(7)]	-	
Strontium	- [113.9]	- [69 – 180]	- [8(8)]	-	
Thallium	- [ND]	- [ND]	- [8(0)]	-	
Tin	- [18.8]	- [7.5 – 60]	- [10(10)]	-	
Titanium	- [114.8]	- [40 – 530]	- [8(8)]	-	
Vanadium	- [8.82]	- [4.4 – 14]	- [10(10)]	-	
Zinc	600.36 [495.4]	13.1 – 3083 [100 – 1500]	~2489 [365(365)]	700	100-500

† for land uses mines sites: plantation forestry/non contact agricultural and broad acre agricultural until 31 Dec 2011: plantation forestry/non contact agricultural and broad acre agricultural from 1 Jan 2012

Non detect values have not been included in calculations.

As the list in Table 2.1 illustrates, there is a wide range of metals and metal concentrations in final MWOO products. In Australia, the order of metal concentrations is:

$$Zn > Mn > Pb > Cu > Cr > Ni > As > Co > Mo > Cd > Hg > Se$$

And the order in concentrations from samples elsewhere is (Wilson *et al.* 2014):

Zn > Mn > Pb > Cu > Cr > Ni > Co > Mo > Hg > As > Cd > Se

Arsenic concentrations are higher in Australia compared to other countries, and Hg is lower (possibly because of lower recent use). Maximum concentrations of all priority targeted metals in the Australian MWOO samples, with the exception of As and Se, exceeded threshold values as outlined in the NSW General Exemption. This is a concern for application of MWOO to NSW soils. The metals Zn, Pb and Cu are present at the highest concentrations and occurred in Australian MWOO at high frequency, but Se was consistently the element with the lowest concentration. Concentrations of As (median 5.74 mg kg^{-1}) found to be higher in Australian MWOO compared to concentrations reported in the international literature (median 5.14 mg kg^{-1}), hence, determination of the concentration of As and Cd in Australian MWOO and MWOO amended soil must be considered for inclusion in Australian studies. Certain metals such as Ba, V, Be, Co, Mn, Ag, St, Sn, Ti, for which limits are not stated in the NSW General Exemption, have also been reported at high concentrations in MWOO. Further research should therefore include these elements due to their possible toxic impacts on the environment (Wilson *et al.* 2014).

2.4 Available fractions of metals and metalloids in MWOO

It is well accepted that total metal and metalloid concentrations in MWOO and soil provide only some of the information needed to accurately assess risk. It is suggested that assessment of mobility and bioavailability may be a better approach to determine risk (Illera *et al.* 2000; Kabala and Singh 2001; He *et al.* 2005; Barral and Paradelo 2011).

Bioavailability of metal contaminants is defined as the degree to which the element in the MWOO may be absorbed or metabolised by ecological receptors such as plants and humans (ISO11074 2005). This is influenced by many factors, but one of the main factors is the strength of sorption i.e., the association with MWOO solid phase constituents. The stronger sorbed the heavy metal, the lower the potential for leaching and bioavailability, hence the lower risk of potential contamination of ground water and plant uptake. Sorption in soil is strongly influenced by a range of factors, including organic matter and mineral composition, cation exchange capacity (CEC), pH and redox (Jones and Jarvis 1981). Soil clay content, organic matter and Fe, Mn and Al oxides and hydroxides are the main sorption sites for heavy metals (McBride 2000).

Metals and metalloids in soil are typically distributed among a number of different associations with different strengths of adsorption. As a result, a wide selection of solvents and different extraction techniques have been used to determine heavy metal distribution in contaminated soils and for assessment of their potential bioavailability. The following is a list of the most commonly extracted heavy metal fractions, their relative availability, and extractants used (Pare *et al.* 1999; Korolewicz *et al.* 2001; Brunori *et al.* 2005):

- Water soluble fractions-these are immediately available and are extracted with water.

- The most weakly adsorbed fraction is termed the "exchangeable" fraction and can include certain carbonate associations. This fraction is highly available and mobile and is often extracted using mild extractants such as acetic acid (CH3COOH), potassium nitrate (KNO_3) or calcium nitrate ($Ca(NO_3)_2$).

- The water soluble and exchangeable fractions show the greatest leachability and bioavailability and present the greatest risk for metal transfer in the environment.

- Metals associated with reducible Fe or Mn oxides are referred to as the reducible fraction. This fraction is considered potentially available as it becomes available with changing conditions, such as redox and pH, that result in dissolution of the Fe and Mn phases. Hydroxylammonium chloride is a common extractant for these associations.

- The oxidisable fraction is associated with organic matter and sulfides and is considered less available than the fractions described above. The fraction associated with organic matter only becomes available as organic matter is broken down or with its dissolution. This fraction may be extracted using oxidising agents such as sodium hydroxide or hydrogen peroxide.

- Metals remaining in the final component of a sequential extraction are termed the residual fraction. This is considered largely unavailable to plants and soil microorganisms and can only be extracted using aggressive acid digestion, commonly with concentrated nitric acid or aqua regia. Residual metal is associated with the residual solids and is occluded in crystalline structures (Ciavatta *et al.* 1993; Castaldi *et al.* 2006; Jalali and Arfania 2011).

The metal complexing extractants such as ethylenediaminetetraacetic acid (EDTA) or diethylentriaminepentaacetic acid (DTPA) are also commonly used to predict metal and metalloid phytoavailability (McLaughlin *et al.* 2000), and are often used as single extractions or incorporated in sequential extraction schemes (Ciavatta *et al.* 1993).

Understanding metal and metalloid associations with different soil fractions is key for evaluation of their bioavailability and ultimately a better estimation of actual risk. The three step BCR (Community Bureau of Reference of the European Commission, now the Standards, Measuring and Testing Programme) sequential extraction is one of the more common standardised extraction methods used to evaluate potential bioavailability of metals and metalloids in soils (Quevauviller *et al.* 1993; Bakircioglu *et al.* 2011). The four fractions determined by this method include, i) the exchangeable or acid soluble fraction using acetic acid; ii) the reducible or Fe and Mn oxide bound fraction using hydroxylamine hydrochloride; iii) the oxidisable or organic matter bound fraction using hydrogen peroxide and ammonium acetate; and iv) the residual fraction using aqua regia extractant.

Most of the studies using sequential extraction for estimation of metals and metalloids in MWOO report that the soluble and exchangeable fractions account for less than 10% of total metals in mature, stable MWOO (Pare *et al.* 1999; Soumare *et al.* 2002; Castaldi *et al.* 2006). He *et al*. (1995) reported that a high proportion of Zn in MWOO was detected in the labile, reactive fraction, whereas Cu was relatively immobile and bound to organic matter. Farrel and Jones (2009) stated that after composting of MWOO, less than 5% of the total Ni, Cu and Pb was in the exchangeable fraction, rather, the Cu was mostly bound to MSW organic matter, Pb was associated with the reducible and oxidisable fractions, and Ni was mostly bound to the residual fraction. Of all the elements they measured, Zn was recorded at the highest proportion in the exchangeable fraction. In a study of MWOO effects on soil conducted by Tisdell and Breslin (1995), they found that Zn in MWOO was bound to inorganic fractions, whereas Cu and Cr were mainly associated with the organic and residual fractions respectively, and a high proportion of Pb was found in the oxidisable and reducible fractions. Soumare *et al*. (2002) examined the metal fraction in Belgian MWOO and the main proportion of Cu, Pb and Zn was present in the residual fraction, with Cu showing a strong association with organic matter. Furthermore, Paraelo *et al*. (2011) reported that a high proportion of Cu found in MWOO was in the oxidisable fraction, Zn was mainly associated with the reducible fraction, and Ni and Cr was mostly found in the residual fraction.

This evidence suggests that, in general, a low proportion of metals in MWOO are associated with the soluble and exchangeable fractions (< 10 %). However, Zn and Cd are generally more available with higher solubility and exchangeability, and therefore, they are considered to constitute a higher risk to plants and soil organisms. Copper is mainly bound to the organic fraction, and although Ni, Cr, and Pb can be associated with many different fractions, they are mostly present in residual forms and less potentially bioavailable.

2.5 Factors influencing risk for MWOO amended soils

Several studies have investigated risks associated with MWOO derived metal accumulation in soils, which include leaching, plant uptake and plant toxicity (phytotoxicity), impacts on organisms, and transfer to the wider ecosystem, including through grazing animals and human exposure (Dorahy *et al.* 2006; Ghaly and Alkoaik 2010).

Some authors have also acknowledged the potential for using MWOO derived organic matter as a strong sorbent to ameliorate leaching and plant uptake of metals and metalloids already present in contaminated soils (Cao and Ma 2004; Clemente and Bernal 2004; Brunori *et al.* 2005; Cunha-Queda *et al.* 2010; Farrel *et al.* 2010). Most of these studies report that metal and metalloid accumulation in plants significantly decreased following MWOO application, but they highlight the need to better understand the stability of MWOO derived metal accumulation in soil in the long term (Farrel *et al.* 2010).

The actual risk depends on the element itself but also the soil to which the MWOO is applied. The following part of this section the factors that influence the risk are reviewed.

2.5.1 MWOO effects on metal and metalloid retention in soils

The risks in MWOO amended soils depend critically on metal and metalloid retention and accumulation in the soil. This is influenced by several factors, including organic matter, mineral composition, CEC, soil redox and pH (Jones and Jarvis 1981). More specifically, the clay particles, organic matter, and Fe, Mn and Al oxides and hydroxides are the main sites for metal sorption, and therefore availability and mobility of metals and metalloids is usually lower in soil containing these in high proportions. A range of mechanisms control metal sorption in soil, including non-specific electrostatic attraction, specific adsorption (often on Fe, Al and Mn oxides and hydroxides), formation of organic matter complexes, and chemi-sorption (important in calcareous soils) (McBride 2000). An important parameter which can influence the strength of these mechanisms is the pH of soil. In acidic soils, the negative charge on Fe, Mn and Al oxides and hydroxides and organic matter surfaces is reduced, and this can lead to less sorption of cationic metals such as Cu, Zn, Ni, and therefore increased metal mobility and availability (Smith 2009). However, elements such as As, which forms anions in acidic conditions, can become less available in acidic soils.

Application of MWOO to soil, can directly influence the capacity of soils to retain metals and metalloids, although this will also introduce MWOO derived contaminants. For example, organic matter in MWOO can provide additional sorption sites through mechanisms such as chelation and ligand exchange. Metals such as Cu can be strongly bound to organic matter, and in addition, soluble organic carbon Cu complexes can be formed which may influence mobility of the Cu cation (Mkhabela and Warman 2005). Application of MWOO to soil can also increase the pH and buffering capacity of the soil, although this is likely to be most evident in sandy soils compared to those with a high clay content (Garcia-Gil *et al.* 2004; Smith 2009). Adding MWOO to soil is also an additional source of Fe and Mn hydroxides which provide negative surfaces for sorption of cations (Illera *et al.* 2000). Metal and metalloid concentrations in the MWOO are also important because MWOO with low heavy metal content will tend to have a higher sorption capacity (Shelton 1997; Baldwin and Shelton 1999; Jordao *et al.* 2006; Jordao *et al.* 2007; Smith 2009).

2.5.2 Impact of MWOO application on total metal and metalloid accumulation and distribution in MWOO amended soil

Several studies have reported with MWOO application resulted an increase in total concentrations of metals and metalloids in the soil (Richard and Woodbury 1992; He *et al.* 1995; Tisdell and Breslin 1995; Amlinger and Ludwig-Boltzmann 1996; Petruzzelli 1996; Vogtman *et al.* 1996; Illera *et al.* 2000). An example of this is a study conducted by Weber *et al*. (2007) in a sandy soil with slightly acidic pH (6.05–6.44). A year after MWOO application at rates of 30, 60 and 120 t ha^{-1}, significant increases in the concentration of soil Zn, Pb and Cu (up to 60, 33.2 and 13.1 mg kg^{-1}, respectively) were recorded for all application rates, and increases were recorded for Ni, Cr and Cd (14.4, 13.2 and 1.3 mg kg^{-1}, respectively) at the 120 t ha^{-1} application rate. The MWOO used in this study was collected from a highly industrialised area, and high concentrations of Zn, Pb, Cu, Ni, Cr, Cd (1825, 972, 366, 168, 100, 11.7 mg kg^{-1}, respectively) were found in the MWOO.

A range of other studies have been reported for sandy soils. Breslin (1999) examined the impact of non-source separated MWOO (with Zn, Pb, Cu, As, Cd concentrations of 340, 310, 120, 5.2 and 2.6 mg kg^{-1}, respectively) incorporated to the 0–5 cm of an acidic sandy loam soil from agricultural land. They reported increases in total concentrations of Zn, Pb, Cu and Cd in the 0–5 cm depth 16 months after application of the MWOO at rates of 21, 41 and 62 t ha^{-1}. The concentration of Zn did not change for the other soil depths measured (5–10, 10–15, 15–20, 20–25, 25–30 cm). However, concentrations of As, Cu and Pb increased in the 25–30 cm layer. In samples collected between 16 and 52 months, no further metal movement was observed except for Cd, which was observed in the 5–10 cm layer after 52 months.

Dorahy *et al*. (2006) report that application of MWOO at 100 and 200 t ha^{-1} to an Australian soil (acidic dermosol) and sown with radish, resulted in significant increases in Zn, Cu and Pb in the soil; up to 222, 90 and 78 mg kg^{-1}, respectively. The total concentration of Zn at the 200 t ha^{-1} MWOO application rate also passed the allowable concentration of 200 mg kg^{-1}. The study also showed that regardless of MWOO source, concentrations of Zn, Pb and Cu (normally found at high concentrations in MWOO) consistently increased in soil even with lower application rate (100 t ha^{-1}). For other elements, such as Ni, Cr and Cd, the increase was usually only observed after application of MWOO at the high application rate (200 t ha^{-1}), unless the MWOO was highly contaminated. Cadmium also showed some downward movement to the depth immediately below MWOO application.

In sandy soils with slightly alkaline pH, Walter, Martinez and Cuevas (2006) tested metal and metalloid concentrations in soil after application of MWOO (concentration of Zn, Cu, Pb, Cr, Ni, Cd: 334, 203, 193, 32.9, 2.6 and 1.48 mg kg^{-1}, respectively) at three different rates; 40, 80, 120 t h^{-1}. Significant increases in Zn, Pb and Cu concentrations in the top 15 cm of soil were observed one year after application for all three rates. This pattern was again observed in the second, third, fourth and fifth years after application. For Ni, the concentration in soil was observed to increase for only the 120 t ha^{-1} application rate in years 2, 3, 4, however, by year 5, the Ni concentration in soil was observed to increase in response to all application rates. Cadmium and Cr were the only metal concentrations that did not change during the 5 years (Walter *et al.* 2006).

Madrid *et al.* (2007a) examined concentrations of Zn, Cu, Pb and Ni in a slightly alkaline (pH 7.5) sandy soil during and after three consecutive applications of a non-source separated MWOO (concentration of Zn, Cu, Pb and Ni: 512, 244, 203 and 39 mg kg^{-1} respectively). The MWOO was applied at days 0 (21 t ha^{-1}), 317 (21 t ha^{-1}), and 445 (18 t ha^{-1}) and measurements were taken from the 0–25 cm depth and 25–50 cm depths on days 216, 441, 676 and 948. A significant increase in total Zn and Pb concentrations was observed in the 0–25 cm depth at the first two sampling times, and also for Zn at the third sampling time, and furthermore, a significant increase in both Zn and Pb was observed in the 25–50 cm depth at day 441. Increases were also observed for Cu and Ni in the 0–25 cm depth, but only after the second sampling period for both, and then again for Cu at the third sampling. However, no movement of either Cu or Ni to the 25–50 cm depth was observed at any time. The Zn and Pb movement to the deeper 25–50 cm layer was explained by high amounts of water addition and the sandy texture of the soil, which allowed leaching of these elements.

Pinomanti *et al.* (1997) applied non-source separated MWOO with relatively high concentrations of Zn, Pb, Cu, Ni, Cr and Cd (1206, 650, 447, 132, 61 and 3.2 mg kg^{-1}, respectively) to the 0–30 cm depth of soil (medium sandy, calcareous soil with alkaline pH) collected from an orchard. They reported significant increases in Zn, Cu, Ni, Pb and Cr in the soil in response to higher (80 and 160 t ha^{-1}) application rates, but Cd was below detection limits. The authors attributed the increase in Zn, Cu and Pb concentrations in soil (including for the lower application rate e.g. 21 t ha^{-1}) to the initial high concentration in the MWOO. For other metals, the increase was attributed to either high application rates (> 80 t ha^{-1}) or as a result of repeated application. Vertical movement of Zn and Pb down the soil profile was also observed and was related to their higher concentration in the MWOO, the sandy texture of the soil and the associated leaching effect.

Effects of MWOO application have also been studied in soils with higher loam and clay contents. Perez *et al*. (2007) examined acidic clay soil samples one year after surface application of MWOO at 12.5, 25, 50 and 100 t ha^{-1} and a rotation of four vegetable crops. In the 0–5 cm surface layer, increased total concentrations were observed for Cu, Cr and Pb in the 50 and 100 t ha^{-1} treatments, and Cr and Cu again at the lower rates (12.5 and 25 t ha^{-1}). No change was observed in the 0-5 cm for Cd and Ni. In the 5–10 cm layer, Cu and Pb concentrations increased in response to all four application rates, but in the 10–20 cm layer, these increased only in response to the two highest rates (50 and 100 t ha^{-1}). Chromium increased at the 20–40 cm depth of the 50 and 100 t ha^{-1} treatments, and an increase in Ni concentrations was recorded for all rates at this depth. It also showed how the distribution of Cr, Cu, Pb and Ni can change in the depths below MWOO application, especially at high application rates and MWOO effect evident at depth with greater down profile movement observed for Ni.

In another study on a clay soil, Ayari *et al*. (2010) examined the long term impact of MWOO application at two rates (40 and 80 t ha^{-1}) on a Tunisian clay loam with a slightly alkaline pH (7.88). The MWOO contained concentrations of Zn, Pb, Cu, Ni, Cr, Cd at 1174.5, 411.5, 337, 90.8, 78.87 and 5.17 mg kg^{-1}, respectively. They reported no significant increases in total concentrations of Cd, Ni, Pb, Cu and Zn in the 0–20 cm soil layer in the first year following MWOO application, however, by the end of the second year, Pb and Zn concentrations had increased significantly in response to both application rates. After the third year, Cd and Cr increased significantly in the 80 t ha^{-1} treatment and Ni, Pb, Cu, Zn in both the 40 and 80 t ha^{-1} treatments. By the end of the fourth year, concentrations of all metals in the soil had increased significantly in response to both the 40 and 80 t ha^{-1} application rates. Similarly, Giusquani *et al*. (1994) reported significant increases in total metal and metalloid concentrations in an alkaline clay soil three years after MWOO application at 30, 90 and 270 t ha^{-1}: Zn and Pb for all three rates, Cu at 90 t ha^{-1} and Cd at 270 t ha^{-1}.

The impact of MWOO application to the alkaline Tunisian clay-loamy soil (pH 8.40) was also examined by Achiba *et al*. (2009) using rates of 40, 80 and 120 t ha^{-1} in a field plot experiment. After 5 years, the total concentration Cu, Pb, Ni and Zn, but not Cr, increased significantly in the surface soil (0–20 cm), and this was positively correlated to increasing rates of MWOO application. Significant increases were also reported for Pb and Cd concentrations in the 20–40 cm layer in response to all application rates.

Overall, and similar to studies on sandy soils, significant increases in concentrations of especially Zn, Pb and Cu in the top 0–20 cm of high clay content soils have been observed following MWOO application. These observed increases can mainly be attributed to the initially high concentration of the metals in the MWOO. Increases in soil concentration of elements that occur in lower concentrations in the MWOO, such as Cr, Ni and Cd, are also observed, but mostly at higher MWOO application rates. A change in distribution of element analysed at depths below the point of MWOO application have also been observed in clay soils (eg Pb, Cd and Ni) illustrating down profile movement can also occur but seems to be less often observed than in sandy soils.

In summary, studies indicate that MWOO application to soil can increase the total soil concentration of metals and metalloids, and this is particularly so for those metals found in higher concentrations in MWOO (e.g. Zn, Pb and Cu), and occurs when MWOO is surface applied rather than incorporated. The increase in metal and metalloid concentrations is usually greater with higher MWOO application rates and also with repeated application. A change in the distribution of metals throughout the soil profile has also been reported, and this seems to be related to application of MWOO containing higher metal concentrations, high application rates, soil texture (usually high sand content), and soil with acidic pH. Despite this, the influence of a range of different soil factors, such as soil texture, soil pH and soil organic matter content, and different methods of application on metal accumulation and distribution in soil has been little studied, and when it is reported, it is usually examined in only one or two soil types. Furthermore, the study of metal and metalloid accumulation and distribution following MWOO application in Australian soils is scarce, with only one study documented to date (Dorahy *et al.* 2006).

2.5.3 Impact of MWOO application on available fractions of metals and metalloids associations in MWOO amended soils

As described previously (Section 2.4), total metal and metalloid concentration in soil is considered a poor measure of actual risk. Understand the soil associations provides a much better estimation of this and potential bioavailability and mobility. Application of MWOO to soil can change the speciation an associations of metals and metalloids in soil, in both the short or long term. However, this is dependent on the soil characteristics. Initially, the labile and extractable fraction of metals can be increased following MWOO addition leashing to concern with regards to plant uptake and mobility (Pichtel and Anderson 1997; Pinomanti *et al.* 1997). However, in certain soils, strong associations between soil components and some elements, leads to greater adsorption through time.

Studies have reported that application of MWOO to soils increases the relative amount of Cu in the oxidisable fraction (Zheljazkov and Warman 2004; Perez *et al.* 2007; Achiba *et al.* 2009). This can be explained by a strong affinity of Cu with organic matter (He *et al.* 1995; Illera *et al.* 2000; Korolewicz *et al.* 2001) which is enhanced by the increased pH often seen with MWOO addition. A significant increase in the proportion of Zn bound to the reducible fraction has also been observed following MWOO application (Zheljazkov and Warman 2004; Achiba *et al.* 2009). This can be related to the high affinity of Zn for Fe and Mn oxides in soil, which is, again, affected by increases in soil pH usually observed following MWOO addition to soil (Shuman 1991; Luo and Christic 1998; Zheljazkov and Warman 2004). The relative amount of Pb in reducible and residual fractions has also been observed to increase (Pinomanti *et al.* 1997; Achiba *et al.* 2009), and Perez *et al.* (2007) and Planquart (1999) also reported increases in Pb in the oxidisable fraction.

It is generally accepted that Pb shows high affinity for Mn oxides, clay minerals and organic matter and has low availability (Kabata-Pendias and Pendias 1992; Brown *et al.* 2003; Brown *et al.* 2004).

A significant increase in the exchangeable fraction of Ni has been observed following MWOO application and may be explained by the high proportion of Ni associated with the exchangeable fraction in MWOO (Illera *et al.* 2000; Achiba *et al.* 2009). For Cr, the addition of MWOO was shown to significantly increase concentrations in the residual and oxidisable fractions of a calcareous Tunisian soil (clay–loam soil) (Achiba *et al.* 2009), and it has been shown that Cr speciation and mobility largely depend on organic matter and clay content (Banks *et al.* 2006).

Therefore, it seems that the extent of labile fraction of greater potential concern depends on the element and the soil but that some certain elements e.g Ni show a significant labile fraction.

2.5.4 Metal and metalloid leachability and mobility in MWOO amended soils

Another potential negative aspect of MWOO application to soil is an increase in metal and metalloid concentrations in runoff and leachate and possible contamination of water resources. Metal mobility is influenced by the initial concentration of metals in MWOO, MWOO maturity, application rates, the soil characteristics, the type of metal and the capacity for formation of soluble organic carbon complexes (Senesi 1992; Kaschl *et al.* 2002; Mkhabela and Warman 2005). For example, leaching of cationic metals is expected to be higher in sandy and acidic soils because the number of negatively charged absorption sites on the soil surface is lower than in soils with higher clay content and a neutral to alkaline pH (Gregori *et al.* 2004).

Several leaching tests, including column or batch experiments, have been used for evaluation of the potential impacts of MWOO on the soil solution (Kaschl *et al.* 2002; Hage and Mulder 2004; Song and Greenway 2004; Brunori *et al.* 2005), and a range of different chemical reagents has been used in these tests (Beckett 1988). For instance, deionized water is normally used to indicate the proportion of metal and metalloids which easily move to soil solution (Paradelo *et al.* 2011), and calcium chloride ($CaCl_2$, 0.01 M), is reported in some studies as an effective agent for estimation of metal and metalloid availability to plants and simulates the leaching of metals in a neutral salt solution (Menzies *et al.* 2007). Other studies also report the use of EDTA (Brunori *et al.* 2005).

The number of MWOO leaching studies is limited. However, those undertaken report that application of MWOO to soil columns significantly increases metal content in the leachate. Kaschl *et al*. (2002) examined Zn, Cu, Hg, Pb, Ni, Cr and Cu leaching in a long term study where MWOO was surface applied to a calcareous sandy soil and a sandy loam in Germany. Copper, Ni and Zn were found in leachate from both soils, although they were highest in the sandy soil (0.087, 0.064 and 0.258 mg kg^{-1}, respectively). The majority of the water-soluble fraction of heavy metals accumulated in the topsoil (except for Ni which accumulated at 25 cm depth in sandy soil) and the concentrations exceeded the maximum limit values for drinking water (which in Germany is 50 µg L^{-1} for Ni). The metals in leachate were found to be in association with dissolved organic matter, in particular for Ni, Zn and Cu, which bound to smaller organic molecules with greater mobility.

Farrell *et al*. (2010) investigated the impact of MWOO application on a highly acidic soil heavily contaminated with As, Cu, Pb and Zn, by collecting soil solution from 45 cm soil columns across 112 days following MWOO application. They reported that the concentration of Cu, Pb and Zn increased in soil solution and increased with increasing depths immediately following application of MWOO to the contaminated soils. However, the metal concentrations reduced throughout the 112 days but this decline was different for each element. This initial flush of mobile contaminants is commonly observed (Wilson *et al.* 2014).

Giusquani *et al*. (1992) reported that application of MWOO to 50 cm soil columns significantly increased the concentration of Cr, Cu, Ni and Zn in leachate compared to controls, although the fractions in leachate were still low compared to the total concentration in the soil. Breslin *et al*. (1999) reported that Zn, Pb and Cu remained confined to the 0–5 cm depth of a sandy loam soil in the United States following application of 21–62 t ha^{-1} of MWOO, however, Cd leached to the 5–10 cm depth below the point of MWOO application after 52 months, demonstrating mobility of Cd and the potential for this element to leach to lower horizons.

Another approach to investigating metal and metalloids in leachate, is the use of EDTA which is also used to estimate the potential for plant uptake (Bermond and Gestem 2001). For example, in a single leaching experiment, Pichtel and Anderson (1997) reported an increase in the mobile fraction of Pb and Zn in a neutral loamy soil amended by MWOO and leached by EDTA. Pinomanti *et al*. (1997) also observed a significant increase in EDTA extractable Cd, Cu, Cr, Ni, Pb and Zn after application of MWOO, and this was proportional to application rate (80 and 160 t ha^{-1}). The EDTA is mostly an aggressive leaching agent which can extract the exchangeable, reducible and that part of the metal fraction which binds to organic matter (Ure 1995).

Overall, application of MWOO to soils has been shown increase the concentration of metals and metalloids in leachate, and for some cations, such as Zn, Ni, Cu and Pb, greater vertical movement to depth has been reported following MWOO application. However, the fraction of leached metals in MWOO amended soil would seem to be small compared with total soil metal concentrations. Of concern, is that research on leaching from MWOO amended soils is limited, both in Australia and internationally, yet it is critical to understanding the potential extent to which metal and metalloid move when MWOO is applied soils. Attempting to address this using a range of NSW soils will therefore help define limits for MWOO application in the NSW environment, and contribute to the protection of water resources and crops.

2.5.5 Simulation of metal availability and mobility

Some authors suggest that a kinetic approach is a better simulation of metal distribution in the natural environment (Yu and Klarup 1994; Li and Shuman 1996; Bermond and Gestem 2001). For MWOO, this follows the subdivision of metal extracted (by EDTA) into labile (quickly extracted) and non-labile (less quickly extracted) fractions and examination using a non-linear regression model for the first-order reaction (Bermond and Gestem 2001; Greenway and Song 2002; Brunori *et al.* 2005). The following equation is used:

$$y = a\,(1- e^{-k_1}) + b\,(1- e^{-k_2})$$

where y represents the amount of metal extracted at time t which can be considered by mg kg^{-1} or the percentage leached over time: a and b represent the labile and non-labile fractions, respectively, and k_1 and k_2 are the kinetic constants related to a and b, respectively, for a given metal.

In a kinetic study by Song and Greenway (2004) using this approach, Zn and As extracted by EDTA from MWOO samples was shown to be present in significantly greater proportions in the labile fraction compared to non-labile fraction, whereas the proportion of Ni, extracted by citrate from the same MWOO, was similar in both the non-labile and labile fractions. In contaminated soils, Bermond *et al.* (1998) reported a high concentration of labile Cd and Zn, followed by Pb and Cu, compared to the non-labile fraction extracted by EDTA, demonstrating generally higher leachability of Cd and Zn compared to other metals. Brunori *et al.* (2005) reported that the labile and non-labile fraction of Zn and Ni was similar using the same model.

The results from kinetic studies have indicated higher mobility and potential bioavailability of Zn, Cd and As following MWOO amendment. The kinetic approach seems to be a useful way of evaluating metal contaminant desorption process and potential leachability. However, only a few studies have applied the kinetic approach for evaluating the impact of MWOO application on metal and metalloid leachability, and none have been undertaken in Australian soils.

2.6 Plant uptake, animal and human exposure

Data on plant uptake of metals and metalloids in MWOO amended soils are available for a limited number of the elements detected in MWOO. The literature on plant systems is however, extensive and includes predictive soil chemical extraction studies and plant accumulation investigations. Many of these investigations are summarised in Hargreaves *et al*. (2008), who reviewed the available literature on metal behaviour and plant uptake in MSW compost amended soils, and in Smith (2009), who reviewed bioavailability of metals in MWOO and biosolid amended soils.

Numerous authors reported plant accumulation with MWOO amendment. For example, Ayari *et al*. (2010) examined the long term impact of MWOO (with high Zn concentration of 1174 mg kg^{-1}) application at two rates (40 and 80 t ha^{-1}) on a Tunisian clay-loamy soil with slightly alkaline pH (7.88). Four years after application, total concentration of Cd, Cr, Ni, Pb, Cu and Zn in soil increased significantly for both the 40 and 80 t ha^{-1} application rates. They reported that Zn was observed in wheat grains at mean concentrations of 66.8–118.7 mg kg^{-1} and in other plant parts was 176 mg kg^{-1}. These concentrations of Zn would be considered toxic, as the critical toxic concentration range for Zn in plants is 100-500 mg kg^{-1} (Kabata-Pendias and Pendias 2001).

In contrast, an experiment on a low pH soil that focused on Pb, found that Pb concentrations in crops, including wheat, basil, squash fruit, tomato and Swiss chard were not affected by MWOO application, even at high application rates (e.g. 60 % w/w) (Pichtel and Anderson 1997; Zheljazkov and Warman 2004b; Ayari *et al.* 2010). However, Pinamonti *et al.* (1997) have reported significant Pb accumulation in apple leaves (to 3.46 mg kg^{-1}) and apple fruit (to 0.257 mg kg^{-1}) at a high MWOO application rate (160 t ha^{-1}, MWOO Pb at 650 mg kg^{-1}), and also in vine leaves (to 2.96 mg kg^{-1}) at a 54 t ha^{-1} application rate. In spinach grown in a calcareous silty clay loam amended with MWOO (257 mg kg^{-1} Cu) at a very low 4 % w/w, Cu concentrations in the spinach leaves were reportedly up to 13.32 mg kg^{-1} (Maftoun *et al.* 2004) which would be considered toxic as it falls within the critical toxic concentration range (10–30 mg kg^{-1}) for plants (Kabata-Pendias and Pendias 2001)

Generally, the literature reports that plant Cd, Cr and Ni concentrations following MWOO application are significantly below phytotoxic concentrations, although there is some evidence that suggests they can accumulate in plant parts following MWOO addition to soil (Pinomanti *et al.* 1997; Ayari *et al.* 2010).

The critical toxic concentrations of the seven targeted priority pollutants have been reported by Kabata-pendias (2001) and are presented in Table 2.1. Plant concentrations following MWOO addition, as reported in the literature, are usually lower than the critical plant toxicity concentration range for the elements considered, even at high application rates (> 80 t ha^{-1}). The potential for metal and metalloid accumulation in plants to reach the critical plant toxicity concentrations would, therefore, seem to be low, and in the case of NSW, this would be especially so if NSW MWOO meets the NSW General Exemption absolute maximum concentrations and is applied at the more sensitive land uses application rates (10 and 50 t ha^{-1}). When MWOO is applied at the higher rate allowed for soil improvement or rehabilitation at mine sites (140 t ha^{-1}), or in repeat applications, based on plant concentration respond in the literature. It is possible that metal and metalloid concentrations, notably Zn, Cu and Pb, could increase to critical plant toxicity concentrations and also reach maximum residue limits for food crops, especially in plants more sensitive to these elements.

The metals and metalloids reported in MWOO (Table 2.1) also have a range of toxicities to animals and humans. Some, such as Cu, are essential elements, whereas others, such as As, have no known biological function.

Even though studies have demonstrated that the main intake pathway to grazing animals for these contaminants contained in soil is not actually plant intake but through ingestion of soil (Rafferty *et al.* 2004), and there is evidence that many metals accumulate in the surface layers of MWOO amended soil, studies of animal uptake of contaminants from MWOO amended soil remain limited. Further little work has been undertaken to assess whether maximum allowable concentrations for foodstuffs could be exceeded, especially at higher MWOO metal and metalloid concentrations and applications rates in MWOO amended soils. This may be because desk-top based assessments for MWOO amended soils conclude the risk in these systems is low (Epstein *et al.* 1992), as do studies on human food chain transfer of heavy metals via animals that graze on plants grown in biosolids amended soil (Haynes *et al.* 2009b). However, some studies have expressed concern for potential exposure with long term MWOO application and accumulation of metals and metalloids (Warman *et al.* 2009; Ayari *et al.* 2010) and for NSW, these types of studies would provide useful to confirm indeed whether the risk was low.

2.7 Conclusions and research needs

The application of MWOO to lands can improve some of the chemical, physical and biological properties of soils, and can be beneficial for agricultural and rehabilitation purposes (Smith and Arsenault 1996; Smith 2009). However, there are a number of concerns with regard to metal and metalloid contamination when MWOO is applied to soil, particularly in terms of the risk to the environment and humans.

Several studies have investigated the total concentration of metals and metalloids in MWOO and MWOO amended soils and most report significant increases in soil concentrations with MWOO application, especially at high application rates (> 80 t ha^{-1}), with repeated application and in the longer term. An increase in Zn, Pb and Cu, which are usually found in high concentrations in MWOO, is commonly observed following MWOO application to soil, even at low application rates (< 80 t ha^{-1}). Some vertical movement of the metals and metalloids through the soil profile has also been reported following MWOO application, notably in the longer term. Despite this, many studies have observed that only a small proportion of the metals and metalloids added to the soil by MWOO application are associated with available and exchangeable soil fractions. However, application of MWOO to soil does affect how metals and metalloids are distributed in the different soil fractions, and this is dependent on characteristics such as soil pH, organic matter content, soil texture and redox conditions. Both leaching column and batch experiments have shown increases in metal and metalloid concentrations in leachate following MWOO application to soil.

This literature review has demonstrated that studies on the impact of MWOO application on Australian soils are scarce and that little work has been undertaken in Australia with regard to the quantification of contaminants or the concentrations in MWOO, their distribution and bioavailability when MWOO is applied to soil. There is therefore a real need for accurate quantification of the range of metals and metalloids present in Australian MWOO, and scientific studies that facilitate a better understanding of risks associated with MWOO amended soils. This should include: (i) the effects of different soil properties on the fate and behavior of MWOO derived soil metals and metalloids, (ii) the effects of different application methods, and (iii) the effect of different rates of MWOO application. Moreover, the impacts of MWOO application on the distribution of contaminants in different soil fractions and evaluation of their leachability and mobility is critical to providing accurate predictions of their potential bioavailability to plants and soil organisms and predictions of ground water contamination.

Chapter 3 An examination of hot plate and microwave extraction methodology with ICP-OES analysis for multi-elemental determination of metals and metalloids in MWOO and soils

This chapter has been prepared for publication as: Bayat, S., Wilson, B.R., Kristiansen, P., Lisle, L., and Wilson, S.C. 2016. An examination of hot plate and microwave extraction methodology with ICP-OES analysis for multi-elemental determination of metals and metalloids in MWOO and soils.

Chapter 4 Effects of MWOO application on metal and metalloid accumulation and distribution in ten different NSW soils after 6, 12 and 18 months

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Chapter 5 Speciation and availability of metals and metalloids in mixed waste organic output (MWOO) and MWOO amended soils

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Chapter 6 A study of metal and metalloid leachability in a sandy loam soil amended with MWOO: a kinetic approach and evaluation of element distribution after extraction

This chapter has been prepared for publication as: Bayat, S., Wilson, B.R., Kristiansen, P., and Wilson, S.C. 2016. A study of metal and metalloid leachability in a sandy loam soil amended with MWOO: a kinetic approach and evaluation of element distribution after extraction

Chapter 7 General discussion, conclusions and recommendations

7.1 Summary of findings and key implications

This thesis set out to investigate the impact of MWOO amendment on metal and metalloid concentrations, distribution, mobility and availability in a range of different soils. The thesis describes a sequential series of investigations to this aim that progressed initially from method development, to investigating the impact of MWOO application rate and method on the concentration and distribution of seven elements of concern (As, Cd, Cr, Ni, Cu, Pb and Zn) in ten different soils from across Australia through time. This was followed by specific experiments designed to examine the soil associations, bioavailability, leaching and kinetics of desorption of these elements in the MWOO amended soils to more fully quantify potential risks for contamination of environmental systems with MWOO application.

7.1.1 Method development

Chapter 3 presents the first comparison of a new ultrawave microwave digestion system with hot plate and conventional microwave digestion and a range of different extractants, to best determine concentrations of a wide range of elements in contaminated soils and MWOO, targeting seven priority pollutants; As, Cd, Cr, Cu, Ni, Pb and Zn. Overall, for certified reference materials and the MWOO samples, the determination of the targeted pollutants and many other elements was best achieved using the ultrawave microwave digestion system with aqua regia extractant. In addition, the new ultrawave microwave digestion system was safer, faster, easier to operate, had larger throughput of samples, and used smaller quantities of the acids required for extraction. Consequently, the ultrawave microwave digestion system method was adopted for determination of concentrations of the targeted metals and metalloids in MWOO and MWOO amended soils in all further components of the thesis work and was shown to extend capabilities and efficiency for metal and metalloid analysis from contaminated soil and MWOO amended soil samples,.

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7.1.2 The effects of MWOO application on total metal and metalloid accumulation and distribution in NSW soils across 18 months

In Chapter 4, a large scale glasshouse column experiment was used to comprehensively evaluate the concentrations, accumulation and distribution of metals and metalloids (As, Cd, Cu, Cr, Ni, Pb and Zn) over an 18 month time period following MWOO application to 10 different soils. The soils encompassed a range of different soil types and characteristics and treatments with MWOO included two different application methods (surface or incorporation) and different rates of application rate (0, 20, 50 and 140 t ha^{-1}).

Application of MWOO significantly increased the concentration of metals and metalloids in the MWOO contacts depths (0–5 cm for surface applied treatments and 0–15 cm for incorporated treatments) in all 10 NSW soils for many of the elements examined regardless of soil properties. Increases were most significant for metals with high concentrations in MWOO (Cu, Pb and Zn) and for soils with the lowest background concentrations compared to MWOO. Increases were also greatest at the highest application rates; 50 and 140 t ha^{-1}, and this was observed for all soils and both methods of application. Overall, the greatest increases in metal and metalloid concentrations were observed in the 0–5 cm depth of the surface applied treatments at the highest rates. The MWOO application rate was generally a more important influence on soil metal and metalloid concentrations than method of application.

Evidence suggested that MWOO addition may, to some extent, limit down profile contaminant mobility for some metals in sandy soil (e.g. Ni). However, for Cu, Pb and Zn, which were present in MWOO at the highest concentrations, there was evidence, especially at the higher MWOO application rates (50 t ha^{-1} and higher), that over 18 months of experiment some movement to soil immediately below the MWOO contact zone (within 5 cm) occurred in many soils, and this was more extensive (up to 10 cm below the MWOO contact depth) for more labile metals. This effect was not, however, observed in highly organic soil. Generally, changes in the total metal concentration were less significant in the clay soil compared to the sandy loam at the 50 t ha^{-1} MWOO application rate used. This was probably undoubtedly due to clay's higher buffering capacity and stronger sorption process. Hence, the risk for contaminant mobility and bioavailability would appear to be lower in clay soils.

7.1.3 Implications for environmental risk and MWOO management

Table 7.1 shows the mean concentrations of the seven elements of concern in the MWOO amended soils at 0–5 cm depth with surface application are compared with maximum allowable concentrations for soils on which MWOO can be applied from the current NSW General Exemption (2014) and also the critical toxic concentration range for plants (Kabata-Pendias and Pendias 2001). It should be noted that for some soils metal and metalloid background concentrations where greater than maximum allowable concentrations, as defined in the NSW General Exemption.

After one application of MWOO to the ten soils, for soils that showed acceptable background values for MWOO application the maximum metal and metalloid concentrations detected in the soil contact depths were less than soil maximum concentrations above which MWOO cannot be applied to soil in NSW. This included surface application of MWOO, the treatment which resulted in the highest soil contaminant concentrations, and also included the silty loam used for mine site rehabilitation (SL2) with MWOO applied at 140 t ha^{-1}. This would therefore not preclude a second application of MWOO to these soils, although, the increase in concentration for some soils highlight possible constraints to this.

Metal and metalloid accumulation was evident in all soils, especially for Pb, Cu and Zn, in the MWOO contact depths over the 18 months of the experiment, and this has important implications for additional application of MWOO to these NSW soils. On the basis of this experiment and under current guidelines, Pb accumulation with surface application of MWOO would be one of the main constraints to repeat applications. In the silty loam used for mine site rehabilitation (SL2), Pb in the background soil increased to 66.4 mg kg^{-1} after only one application (140 t ha^{-1} surface application), and because the maximum soil concentration to which MWOO can be applied for this land use is 150 mg kg^{-1}, a second application may possibly reach this limit.

Accumulation of other metals (e.g. Cu, Zn and Cd) to threshold concentrations acceptable for specific site uses, could also occur with only one to two additional surface applications of the MWOO used in this experiment for many of these NSW soils. However, the incorporation of MWOO would extend this capacity due to the dilution effect on metal accumulation with increased contact depth.

It should also be noted that for some elements (e.g. As, Cr, Cu and Ni), with only the one MWOO application, concentrations increased to values that were within or close to the range considered potentially phytotoxic for some plants, (Kabata-Pendias and Pendias 2001).

The column experiment highlighted potential limitations for repeat application of MWOO to a number of the NSW soils, and also possible constraints for plant protection. With this in mind, only concurrent assessment of element bioavailability would truly evaluate the actual risks associated with MWOO applications.

Table 7.1 Total metal and metalloid concentration following 50 t ha^{-1} MWOO application in the 10 soils and 140 t ha^{-1} in the minesite soil at 0–5 cm depth after 18 months, their maximum allowable concentration in soils and MWOO and the critical toxic concentrations for plants

Element	Acidic Sand (n=3)	Neutral Sand (n=3)	Alkaline Sand (n=3)	Acidic loam (n=3)	Neutral loam (Mine-site) (n=3) (50 t ha^{-1})	Neutral loam (Mine-site) (n=3) (140 t ha^{-1})	Alkaline loam (n=3)	High organic Soil (n=3)	Acidic Clay (n=3)	Neutral Clay (n=3)	Alkaline Clay (n=3)	MAV in soil	MAV in minesite	CTC
Total As (mg kg^{-1})	54.0*± 6.2	3.2 ± 0.8	4.3± 0.08	9.9 ± 0.7	6.0 ± 0.84	5.8 ± 0.5	5.5 ± 0.4	2.8 ± 0.3	0.8 ± 0.3	0.8 ± 0.04	2.0 ± 0.03	20	20	1-20
Total Cd (mg kg^{-1})	0.8 ± 0.06	0.3 ± 0.05	0.9 ± 0.1	2.3 ± 0.2	1.50 ± 0.47	1.08 ± 0.1	1.2 ± 0.05	8.3* ± 0.1	5.5* ± 0.2	6.2* ± 0.07	4.1* ± 0.1	1	5	10-20
Total Cr (mg kg^{-1})	34.7 ± 1.7	25.3 ± 2.4	60.0 ± 2.1	65.3 ± 2.1	36.90 ± 3.17	40.6 ± 2.7	32.7 ± 0.2	312.4* ± 3.3	212.8* ± 7.4	258.1* ± 3.0	139.1* ± 1.3	100	250	1-10
Total Cu (mg kg^{-1})	20.9 ± 1.0	17.3 ± 2.1	31.6 ± 1.7	22.9± 0.2	12.70 ± 0.71	35.3 ± 2.9	26.7 ± 0.3	73.5 ± 10.9	52.3 ± 1.2	66.1 ± 0.4	56.2 ± 2.1	100	375	10-30
Total Ni (mg kg^{-1})	8.7 ± 0.5	5.9 ± 0.5	24.0 ± 0.5	13.8 ± 0.3	6.90 ± 0.25	10.1 ± 0.6	8.9 ± 0.08	146.6* ± 0.9	128.9* ± 2.7	160.9* ± 1.1	83.8* ± 1.9	60	125	10-30
Total Pb (mg kg^{-1})	20.2 ± 0.7	24.9 ± 3.7	19.9 ± 3.9	27.1 ± 0.5	17.78 ± 1.19	66.4 ± 6.9	14.8 ± 0.08	34.6 ± 1.7	7.9 ± 0.6	13.7 ± 2.4	18.9 ± 4.1	150	150	30-300
Total Zn (mg kg^{-1})	39.5 ± 1.2	37.8 ± 5.5	79.5 ± 5.7	44.4 ± 0.7	55.28 ± 10.90	104.3 ± 10.1	60.6 ± 0.4	120.2 ± 6.9	114.1 ± 4.6	127.3 ± 1.8	96.9 ± 1.7	200	700	100-500

MAV = Maximum Allowable Values for plantation forestry/non contact agriculture and broad acre agriculture: mine site: the MWOO itself from 1 Jan 2012, CTC = Critical Toxic Concentration to plants (Kabata-pendias et al. 2007), all values are mean ± standard error, results are expressed on dry weight basis, *background concentration > MAV in soil

7.1.4 Applied investigation into metal and metalloid availability and distribution in different fractions and comparison with critical phytotoxic concentrations

Following on from the conclusions of Chapter 4, the work described in Chapter 5 used the three step BCR sequential extraction procedure to assess metal and metalloid associations and availability in NSW MWOO and in two of the MWOO amended acidic soils used in the glasshouse column experiment over the 18 months following MWOO application. The sandy loam and clay soils were chosen as they were representative of higher risk soils to which MWOO could be applied in NSW due to their acidic characteristics.

The most available fraction of the metals and metalloids in MWOO, as the proportion of the pollutant associated with the exchangeable fraction, followed the sequence: Zn > As > Cd > Ni > Cu > Pb > Cr, with 27 % of Zn in exchangeable forms. Despite all the elements having a high proportion in residual form, Cu and Pb were mainly associated with the oxidisable fraction, and significant proportions of Cd and Zn were also associated with the reducible fraction.

The influence of MWOO addition on changes in metal and metalloid concentrations in the clay and sandy loam was strongly dependent on their concentration in the MWOO relative to soil background concentrations, and this was most evident for Zn, Cu and Pb which were present in MWOO at the highest concentrations. Nevertheless, changes in fractionation were less significant in the clay soil compared to the sandy loam at the 50 t ha^{-1} MWOO application rate used. This was probably undoubtedly due to clay's higher buffering capacity and stronger sorption process. Hence, the risk for contaminant mobility and bioavailability would appear to be lower in clay soils.

The greatest proportion of all the elements studied was in the residual and unavailable fraction in both MWOO amended soils, and generally, the smallest proportion was in the exchangeable fraction. Application of MWOO to the soils mostly increased the proportion of the elements in the reducible or oxidisable fractions, which are considered relatively unavailable under consistent soil conditions, and these associations were stable during the 18 months of the experiment.

The proportion of the six targeted pollutants (Cd below detection limits in MWOO amended soils) in the four fractions analysed 18 months after MWOO application, along with total soil concentrations and the critical toxic concentrations of these metals and metalloids to plants are detailed in Table 7.2. The fraction of the elements considered of greatest concern in terms of risk to soil systems is the exchangeable fraction, and the greatest proportion in this fraction for was for Zn in the sandy loam soil (20 % of total soil Zn concentration) (Table 7.2). However, this concentration equivalent (6.6 mg kg^{-1}) was far below the critical risk concentration for plants (100–500 mg kg^{-1}); this was also the case for the other elements assessed.

Table 7.2 Proportion of metals and metalloids studied in four fractions following 50 t ha^{-1} MWOO application after 18 month compared with critical phytotoxic concentration to plants

	EXCH % of total		REDU % of total		OXI % of total		RESI % of total		Total concentration (mg kg^{-1})		CTC (mg kg^{-1})
Soil	S1	C1	S1	C1	S1	C1	S1	C1	S1	C1	
As	2	<dl	2	< dl	10	16	86	84	54.36 ± 1.27	23.00 ± 0.83	1-20
Cr	<dl	<dl	1	<dl	10	12	89	88	26.86 ± 2.43	213.25 ± 12.04	1-10
Cu	3	1	14	3	17	13	66	84	19.13 ± 2.38	54.69 ± 4.28	10-30
Ni	4	3	6	17	5	13	85	67	8.25 ± 1.47	135.45 ± 6.62	10-30
Pb	3	<dl	37	15	13	22	47	63	15.54 ± 3.17	12.09 ± 2.70	30-300
Zn	20	3	6	13	9	12	67	72	33.02 ± 3.98	127.74 ± 8.25	100-500

EXCH = exchangeable fraction; REDU = reducible fraction, OXI = oxidizable fraction; RES = residual fraction, S1 = Sandy loam soil, C1 = Clay soil, <dl = below detection limit, CTC = Critical toxic concentration to plants

In light of the research outcomes in Chapter 5, and also considering the outcomes presented in Chapter 4, soil amendment with NSW MWOO that complies with current NSW guidelines at 50 t ha^{-1} seems to present low risk, when element bioavailability is considered, even on soils that are not compliant with NSW guidelines for MWOO application (e.g As in S1). The risk to soil systems would increase with application of MWOO containing higher metal and metalloid concentrations, applied at high rates (> 50 t ha^{-1}), applied in repeat applications, where applied to more sandy soils. In addition, if soil conditions were to change so that the reducible and/or oxidisable forms become available, such as in flood conditions, risk of exposure may also increase. These limitations should be recognised on a site specific basis for MWOO application and management.

7.1.5 Applied investigations into metal leachability and mobility

In Chapter 6, the impact of MWOO amendment on mobility and leachability was examined for the seven elements of concern in the acidic sandy loam soil used in glasshouse column trial (50 t ha^{-1} incorporated MWOO application) and in the sequential extraction procedure described in Chapter 5. The MWOO amended soil was leached with either deionised water, 0.01 M $CaCl_2$ or 0.05 M EDTA across 48 hours in a batch experiment and the desorption data modelled in a kinetic approach to assess labile and non-labile contaminant. The availability of contaminants remaining in the extracted residue was also examined.

Application of MWOO significantly increased the concentration of metals and metalloids in all extractants in the batch extraction experiment, indicating that MWOO addition to soil can increase contaminant water concentrations. The Cu, Pb and Zn extractant concentrations were greatest, with the batch experiment indicating that the greatest risk to water quality was from Zn, although no more than 4 % of the total element concentration in soil was extracted in the batch experiments with either water or 0.01 M $CaCl_2$. Significantly higher concentrations of the elements were extracted by EDTA, an extractant considered to provide a measure of plant bioavailability, and as for water and 0.01 M $CaCl_2$, extractions indicated a greater risk for Zn and also Pb and Cu plant uptake from MWOO amended soil. Although batch experiments cannot provide a substitute for field monitoring for water quality protection, they do provide direction with regard to risk management considerations. As such, it would seem that consideration of risks presented by the introduction of Zn, Cu and Pb to soil systems with MWOO application should be prioritised, especially for high MWOO application rates and repeat applications.

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A non-linear regression first order, one-component model fitted the EDTA experimental batch extraction data well and demonstrated that the labile contaminant fraction was small and not easily differentiated from the non-labile fraction, as would be expected in these well matured MWOO amended samples. The kinetic approach proved useful for prediction of the pollutants' mobility and availability and further demonstrated that risk of contaminants in water would be greater for Zn, Cd and Pb as a result of weaker sorptive processes in soil for these elements. After extraction, the effects of MWOO application to soil were still evident in the residue, most notably for Zn, Cu, and Pb, with a significant proportion of the elements remaining in the exchangeable, reducible and oxidisable fractions, which has implications for soils where conditions may change.

7.2 Conclusions

This project has evaluated, through a number of different avenues, the impact of MWOO application spatially and temporally on metal and metalloid concentrations, distribution, speciation, availability and mobility in a range of different soils. The results show that MWOO application can significantly increase contaminant concentrations in different soils, with the increase most significant for those contaminants present at high concentrations in MWOO, notably Cu, Pb and Zn. Further, these effects can persist for at least 18 months and some down profile movement can occur, with this being most evident in sandy soils. The effects of MWOO were evident in increased potential bioavailability of contaminants and also increased contaminants in the aqueous phase.

The series of experiments have indicated, however, that the risks for soil systems in NSW are low if MWOO meets the current NSW General Exemption Guidelines and is applied to appropriate soils at rates suitable for plantation forestry, broad acre agriculture and non contact agriculture (< 50 t ha^{-1}) and also at rate < 140 t ha^{-1} for rehabilitation of the minesites. However, if MWOO is applied at higher rates and/or in repeat applications, concerns for exceeding contaminant thresholds increase and should be considered prior to MWOO application.

7.3 Recommendations

The project work described here has enabled the development of a series of recommendations for further research work that would ensure the safe and sustainable use of MWOO as a resource for soil improvement, not just in NSW but elsewhere. These include:

- Better quantification of the metal and metalloid concentrations in MWOO feedstock and during the MWOO processing, for which data can be limited and/or extremely variable, towards improving elimination of some contaminants. Since the MWOO contaminant concentration is a major determinant of environmental impact, elimination of contamination from MWOO products would seem to be the first step towards safe resource reuse. Concurrent assessment of contaminant bioavailability in MWOO would a better estimation of real risk and support optimisation of the processes and technologies that reduce contaminant bioavailability.

- In current study the repacked soil has been used. Repacked soils lack macropores that provide preferential pathways for elemental redistribution in, and possible leaching from, in undisturbed soil. Their absence in repacked soils compromises extrapolation of results to real life situations in the field. However, using intact cores for such a wide soil range was logistically not possible. Additional investigation build on the data presented here is also recommended. This would include plant uptake studies and soil leaching studies and their extension to the field, to further quantify contaminant bioavailability and mobility and fully define the limitations for MWOO additions in real agronomic and environmental systems. Consideration of impacts on soil biology and ecotoxicity should also be included. Additional research to quantify limitations associated with repeat MWOO application to soils would also address the shortage dearth of work published on this topic. This is especially critical for surface application of MWOO to soils with high background metal and metalloid concentrations compared to MWOO concentrations.

- Most of the studies available typically focus on the priority elements also considered in this work. However, numerous other potentially toxic elements i.e. Ba, Be, Co, Mn, Ag, Sr, Sn, Ti and V, can also occur in MWOO, and risks associated with the presence of these elements in MWOO require consideration.

- Additional investigation in regards to other soil contamination might derive from MWOO amendment such as soil physical contamination and also in other types of the soil under other experimental conditions (e.g. tropical regions) which were beyond the scope of this study seem to be required.

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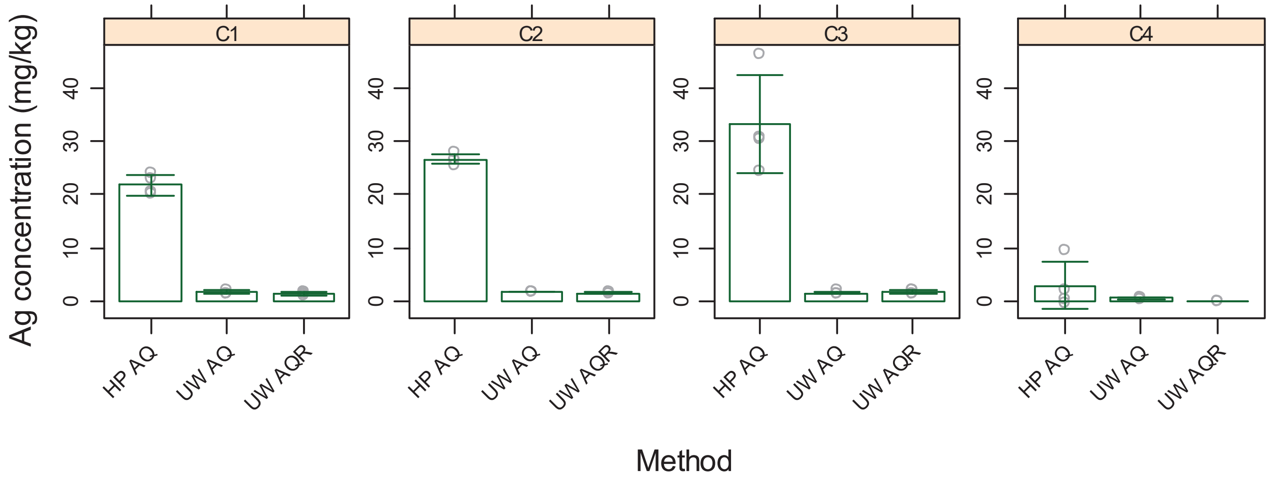
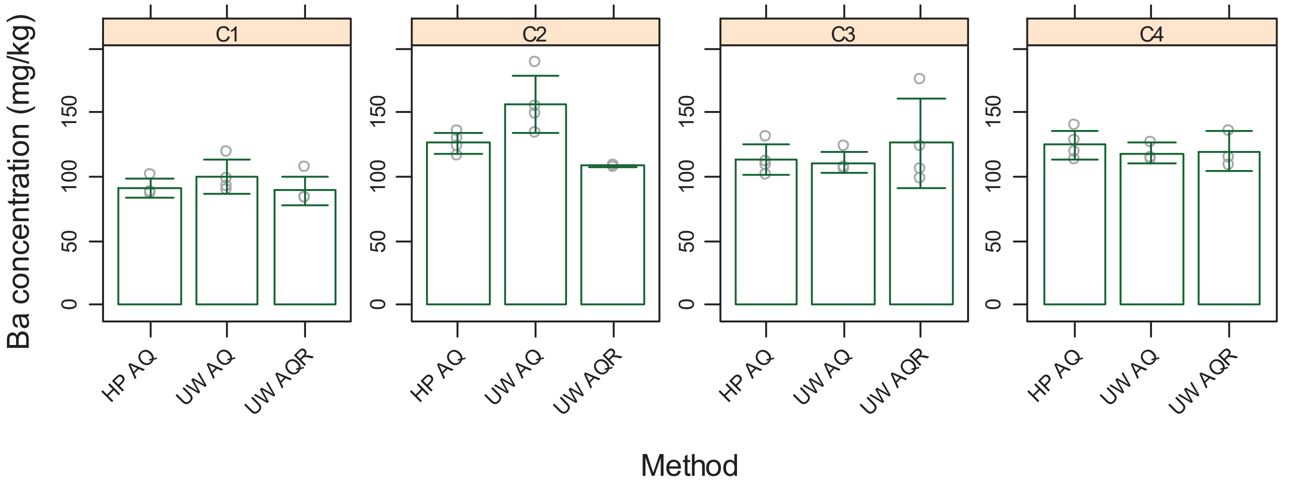
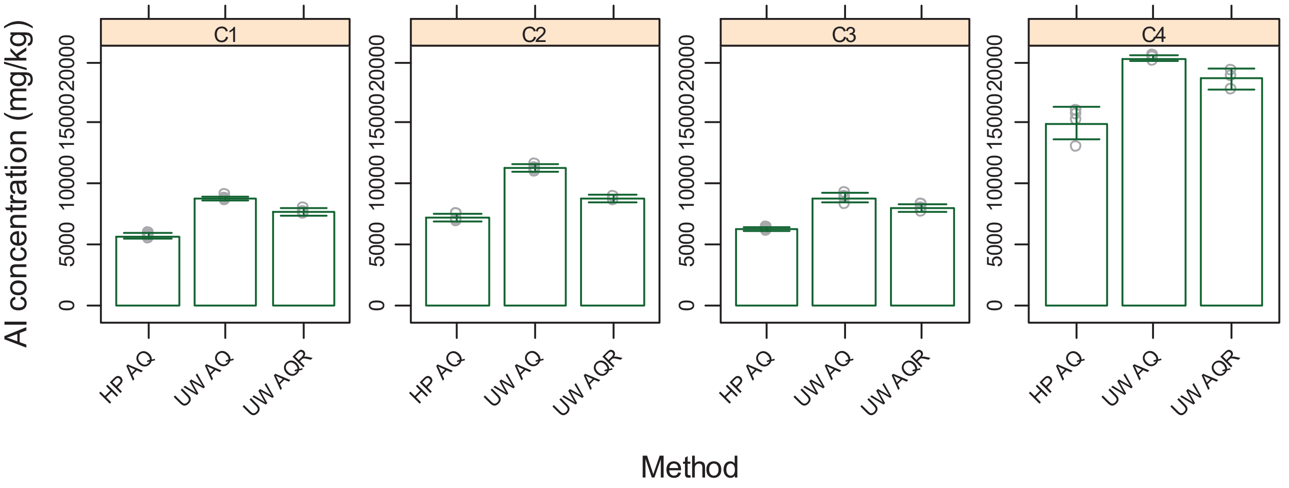
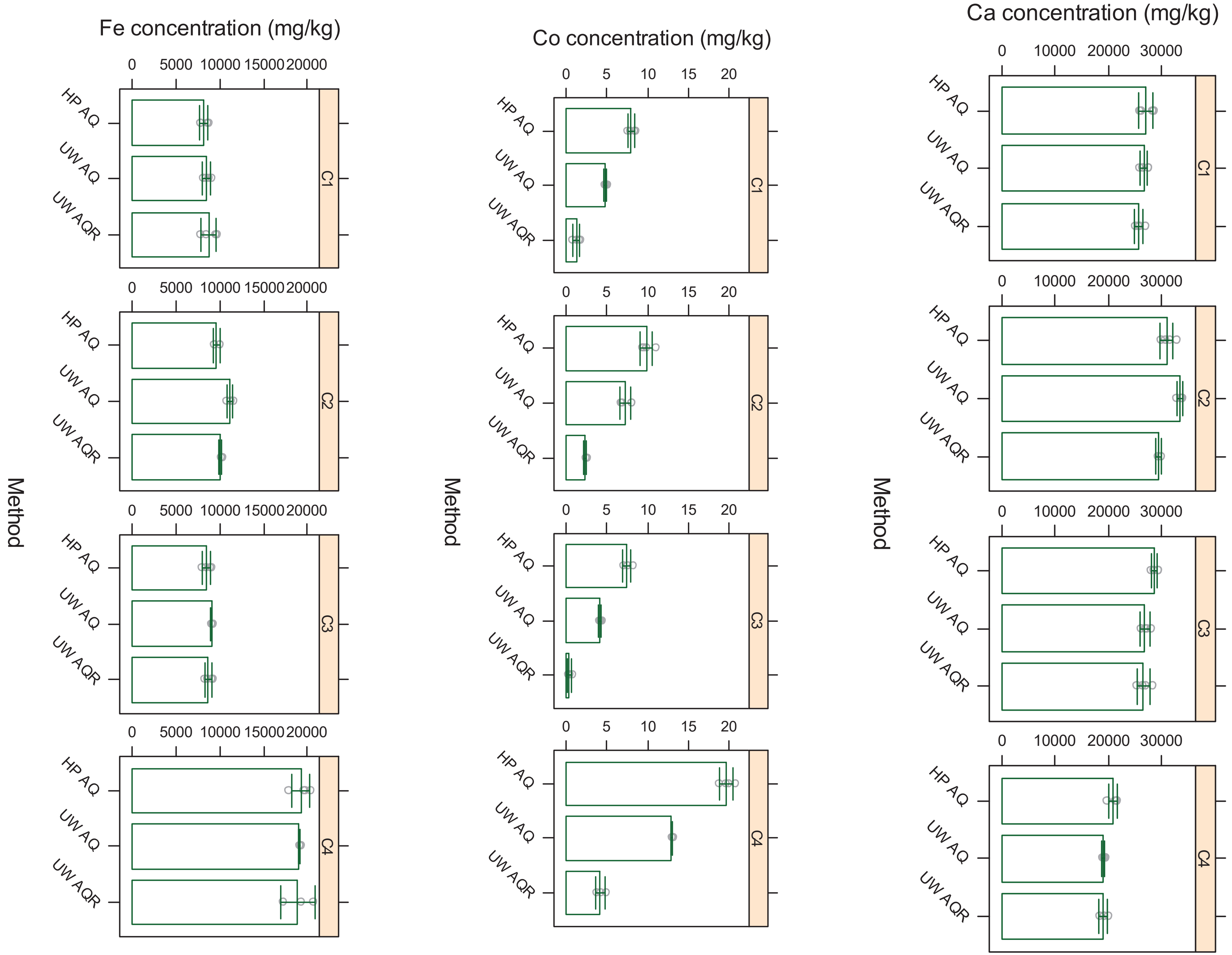
Appendix A

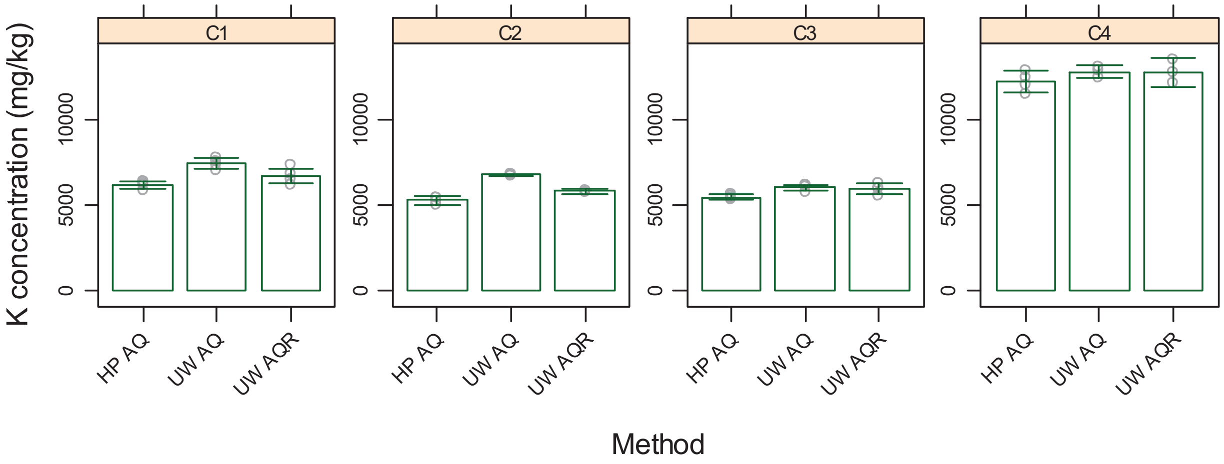
Comparison of first three methods tested including hot-plate aqua regia, ultrawave microwave digestion with aqua regia and aqua regia reverse extractants for determination of 13 elements in four MWOO samples

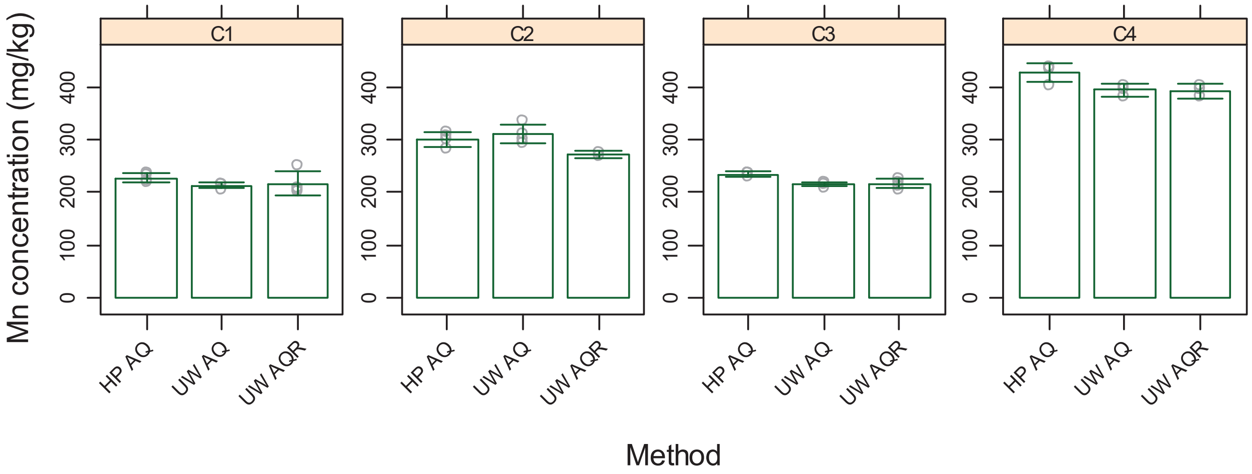

Ag concentration (mg/kg)
C1
C2
C3
C4
0
10
20
30
40
HP AQ
UW AQ
UW AQR
Method

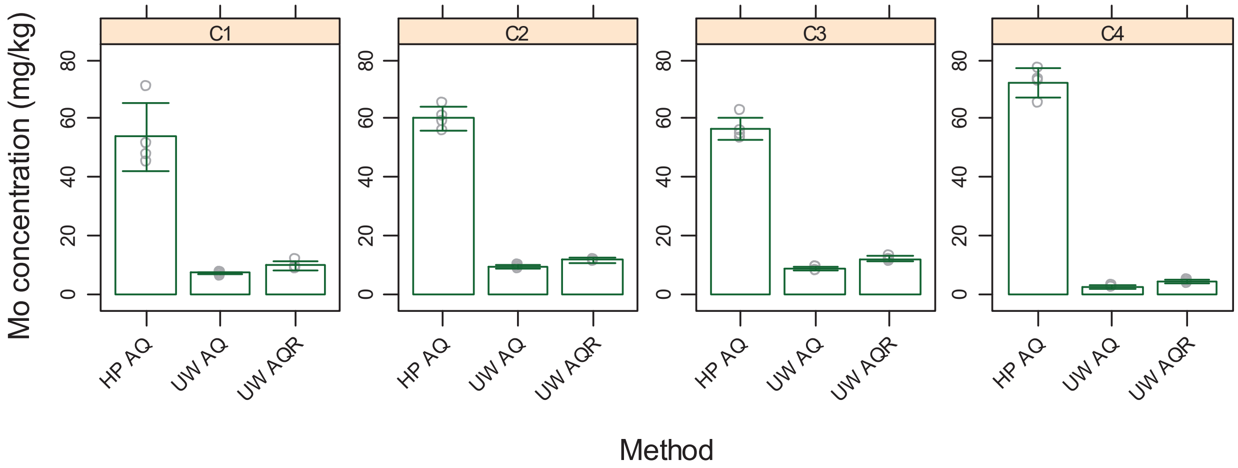

Ba concentration (mg/kg)
C1
C2
C3
C4
0
50
100
150
HP AQ
UW AQ
UW AQR
Method

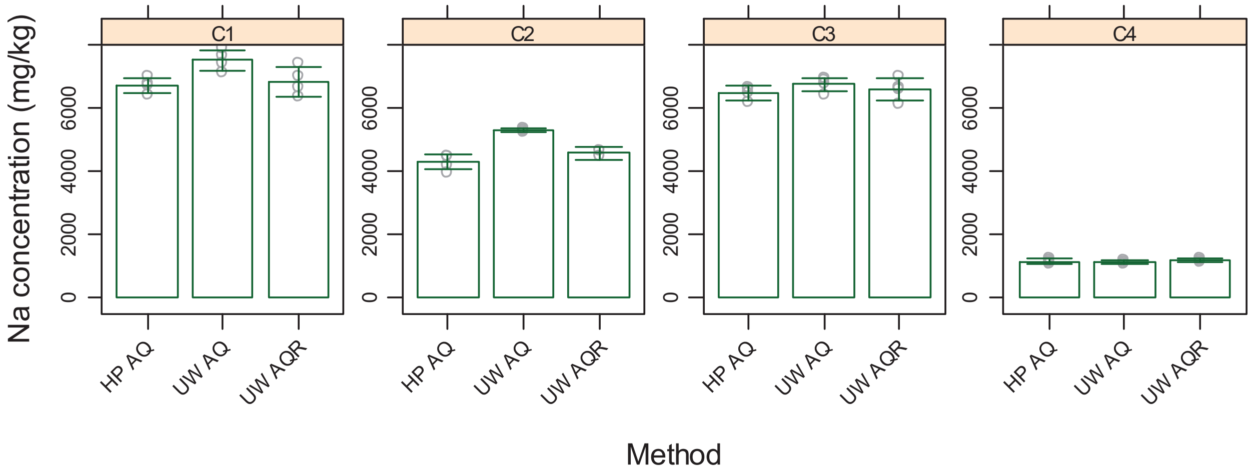

Al concentration (mg/kg)
C1
C2
C3
C4
0
5000
10000
15000
20000
HP AQ
UW AQ
UW AQR
Method

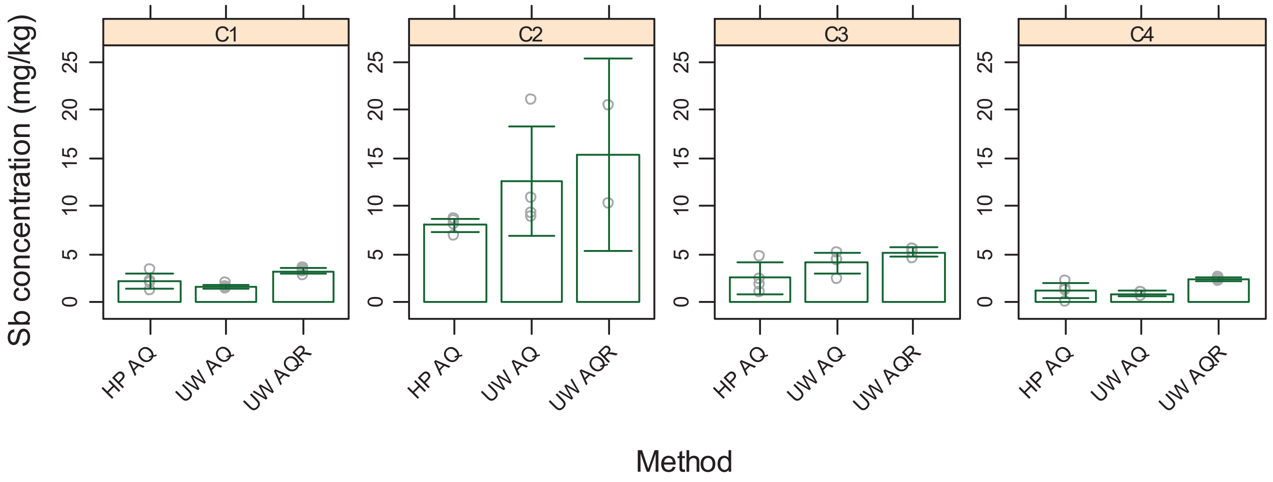

Fe concentration (mg/kg)
0
5000
10000
15000
20000
Co concentration (mg/kg)
0
5
10
15
20
Ca concentration (mg/kg)
0
10000
20000
30000
Method
HP AQ
UW AQ
UW AQR
C1
C2
C3
C4

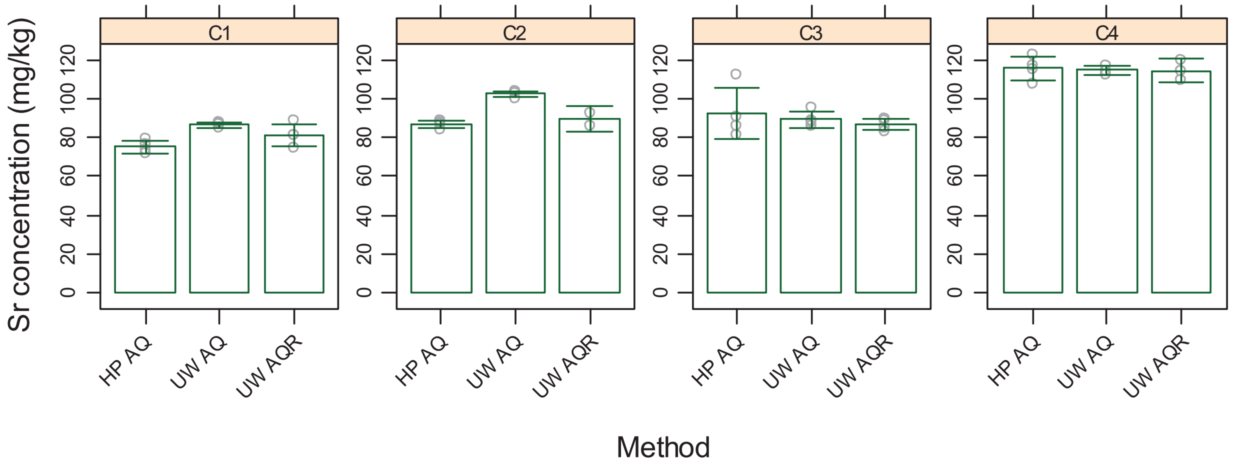

K concentration (mg/kg)
C1
C2
C3
C4
0
5000
10000
HP AQ
UW AQ
UW AQR
Method


Mn concentration (mg/kg)
C1
C2
C3
C4
0
100
200
300
400
HP AQ
UW AQ
UW AQR
Method


Mo concentration (mg/kg)
C1
C2
C3
C4
0
20
40
60
80
HP AQ
UW AQ
UW AQR
Method


Na concentration (mg/kg)
C1
C2
C3
C4
0
2000
4000
6000
HP AQ
UW AQ
UW AQR
Method


Sb concentration (mg/kg)
C1
C2
C3
C4
0
5
10
15
20
25
HP AQ
UW AQ
UW AQR
Method


Sr concentration (mg/kg)
C1
C2
C3
C4
0
20
40
60
80
100
120
HP AQ
UW AQ
UW AQR
Method

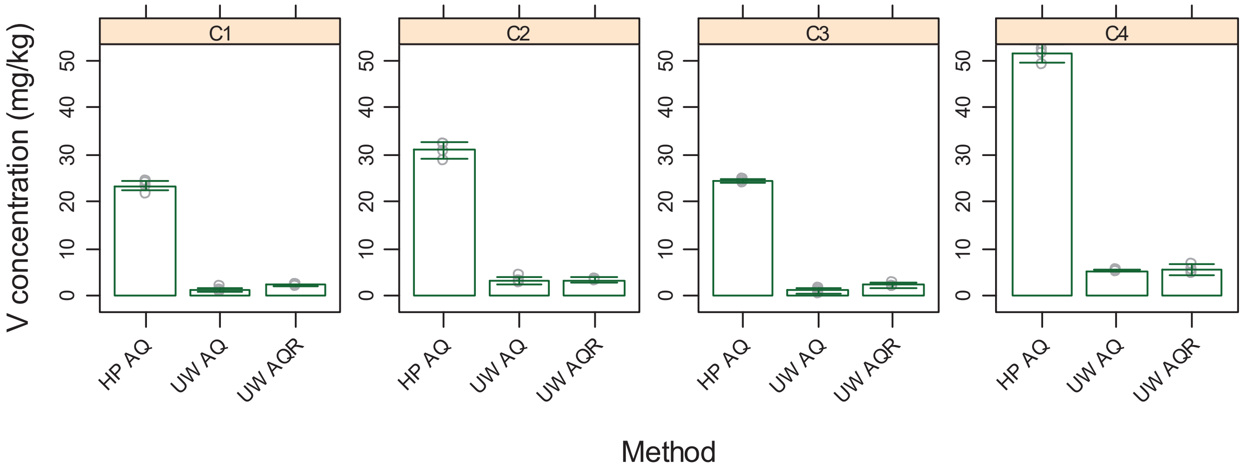
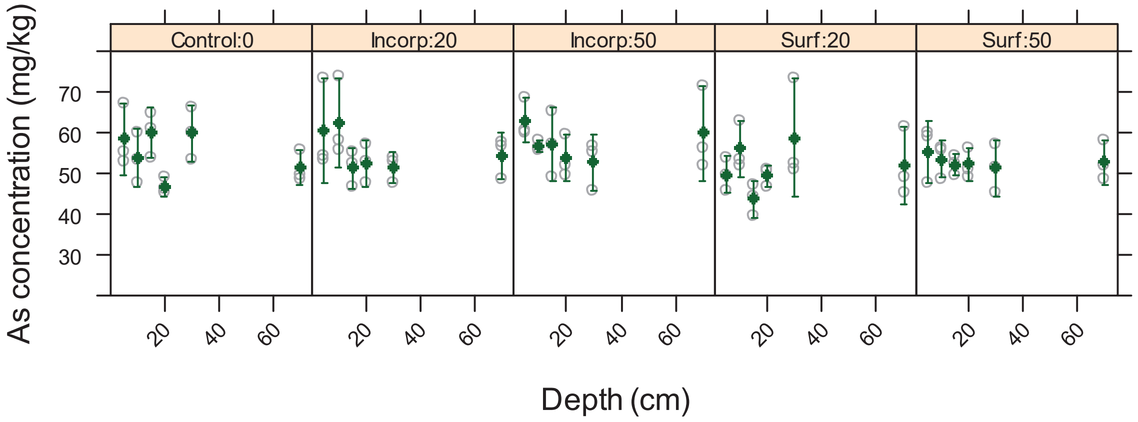


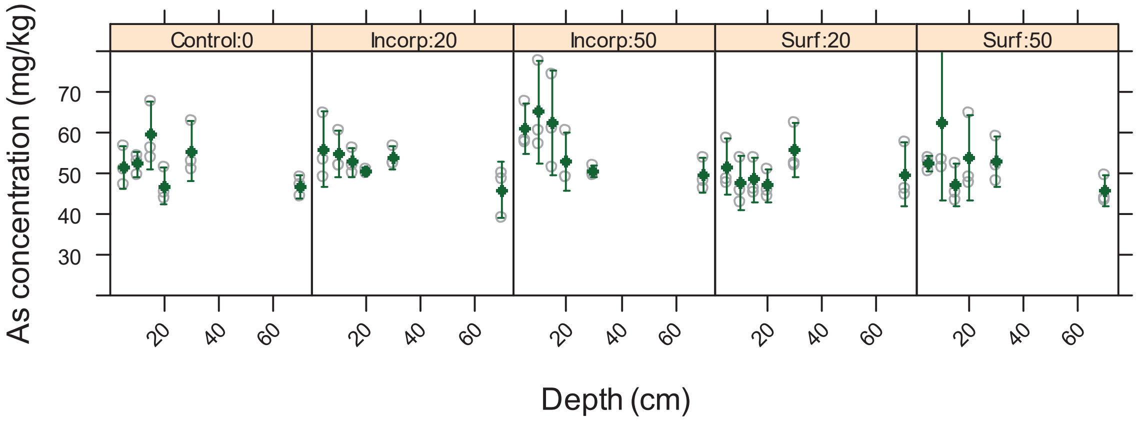
Figure A. Concentrations of 13 elements detected in four different MWOO samples (C1, C2, C3, C4) using three methods including hot-plate aqua regia, ultrawave microwave digestion with aqua regia and aqua regia reverse extractants showed as (H AQ, UW AQ and UW AQR, respectively), Raw data is shown (○) with means and 95% confidence intervals

Appendix B1

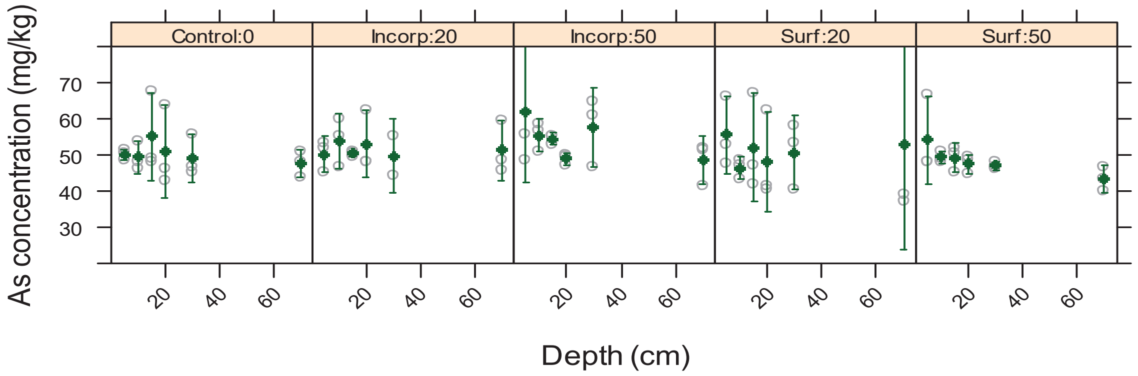
Changes of metal and metalloid concentrations and distribution in three sandy soils (S1, S2, S3)



6 month

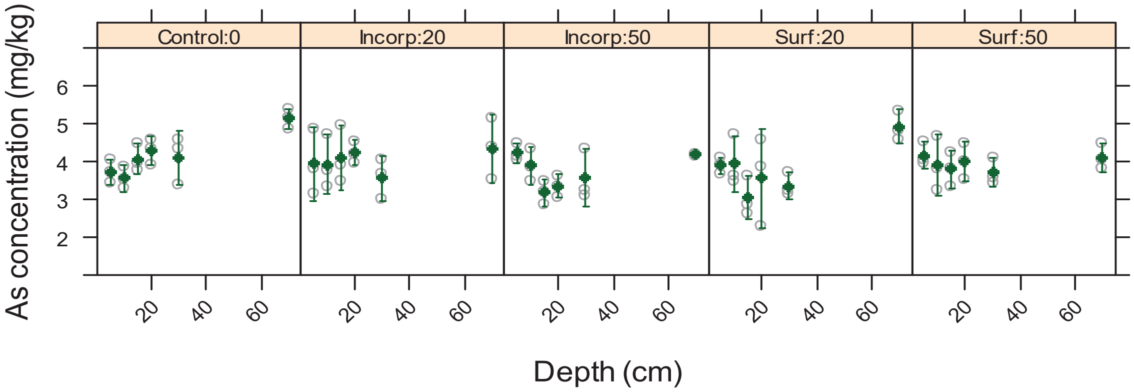


12 month

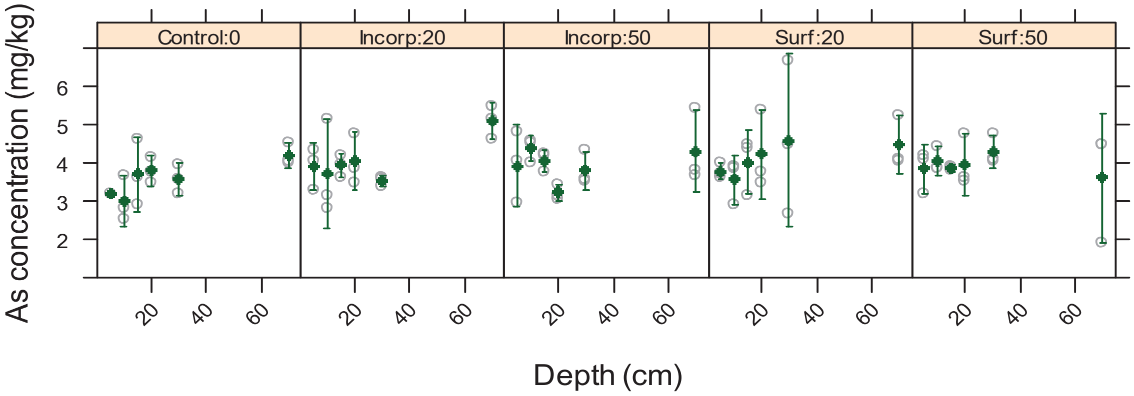


18 month

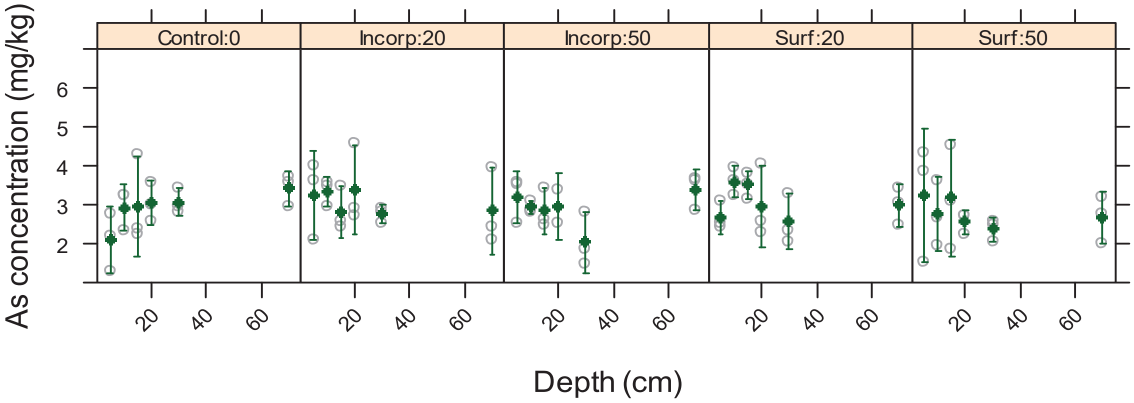
Figure B.1.1. As concentration in S1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



6 month

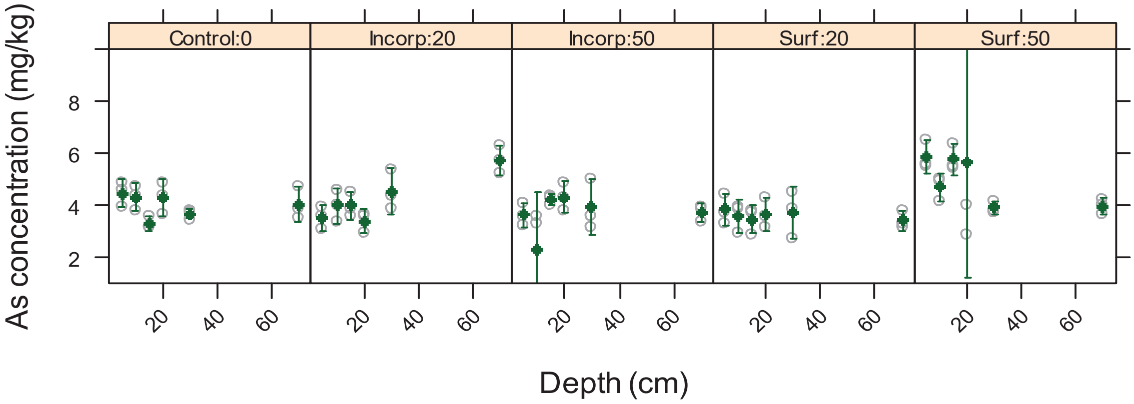


12 month



18 month

Figure B.1.2 As concentration in S2 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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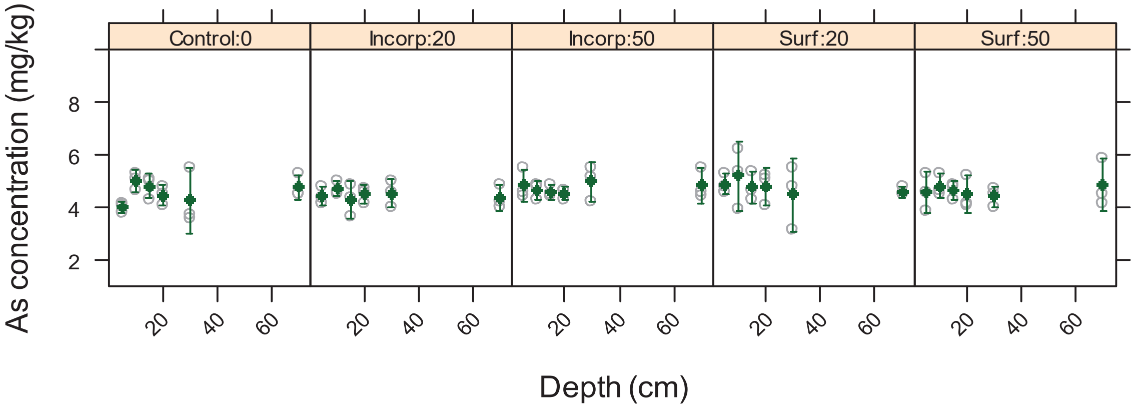

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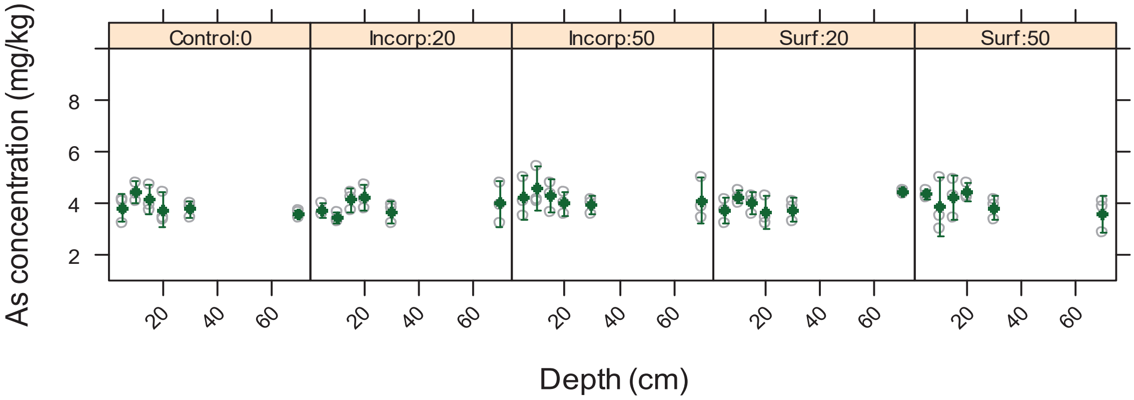
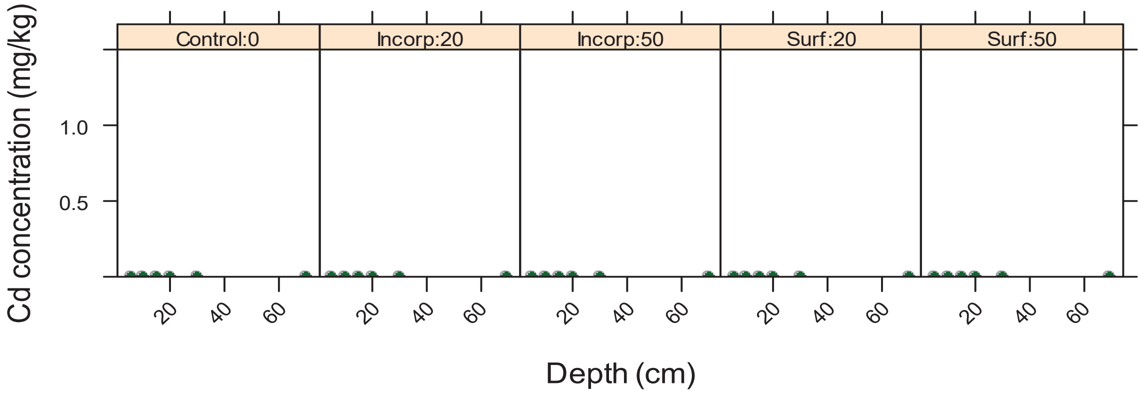
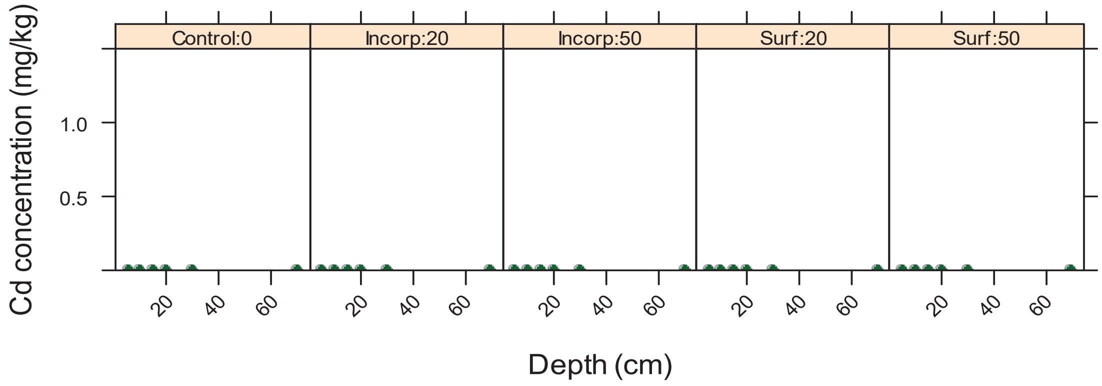


12 month

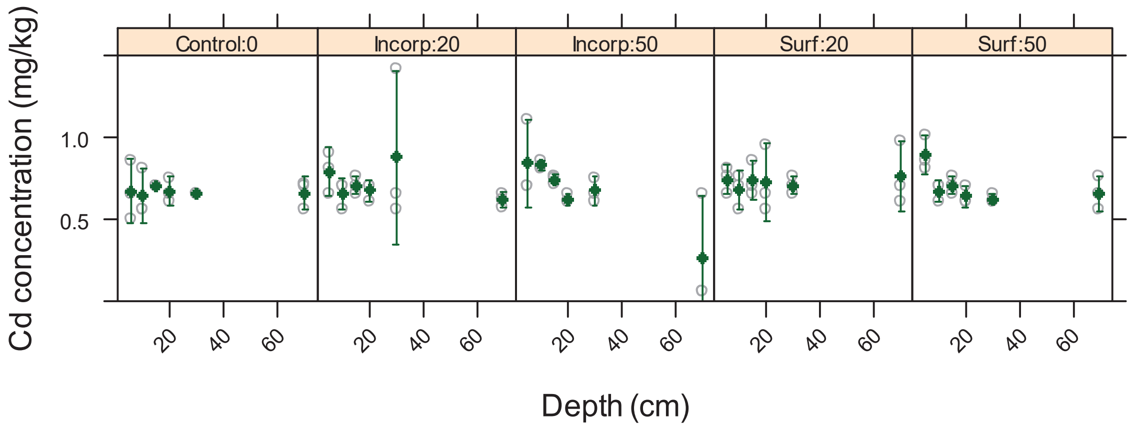
Figure B.1.3. As concentration in S3 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



6 month

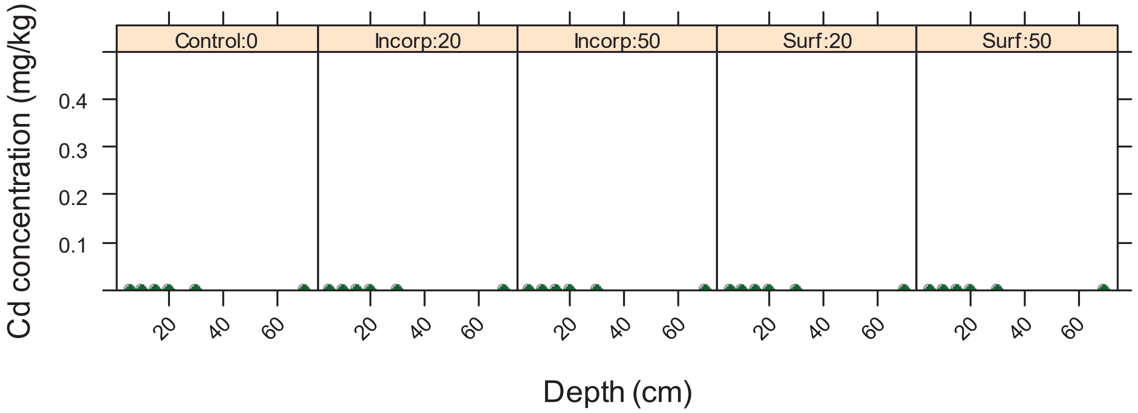


12 month

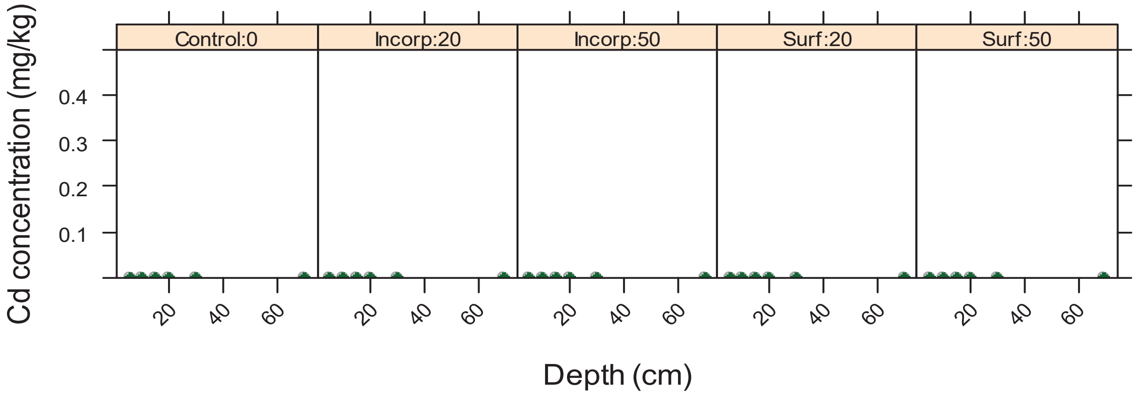


18 month

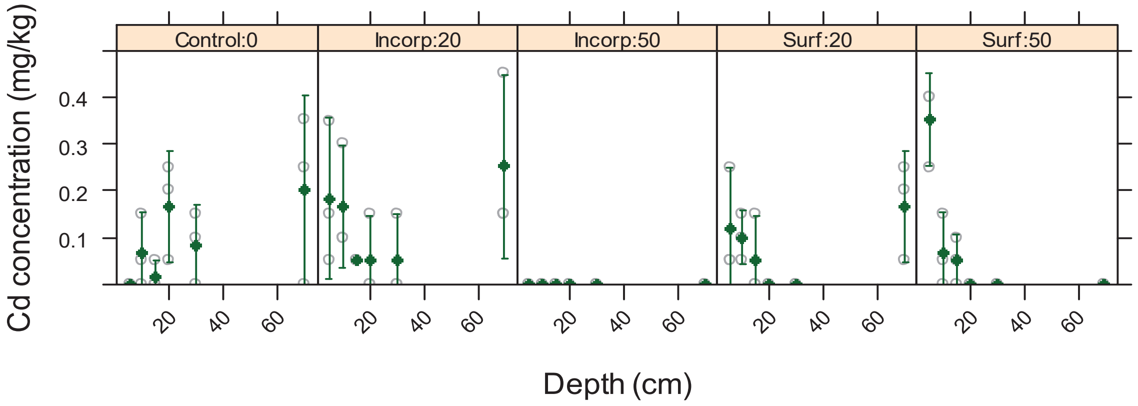
Figure B.1.4. Cd concentration in S1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



6 month

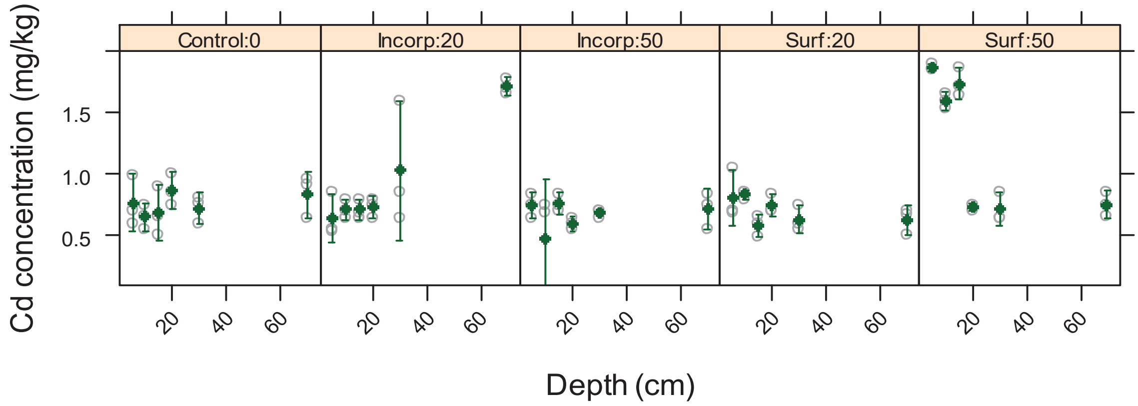


12 month



16 month

Figure B.1.5. Cd concentration in S2 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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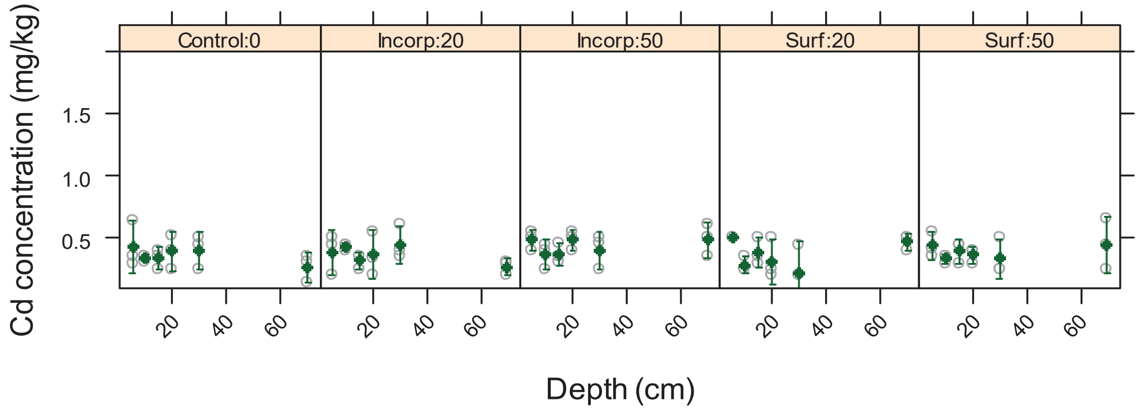

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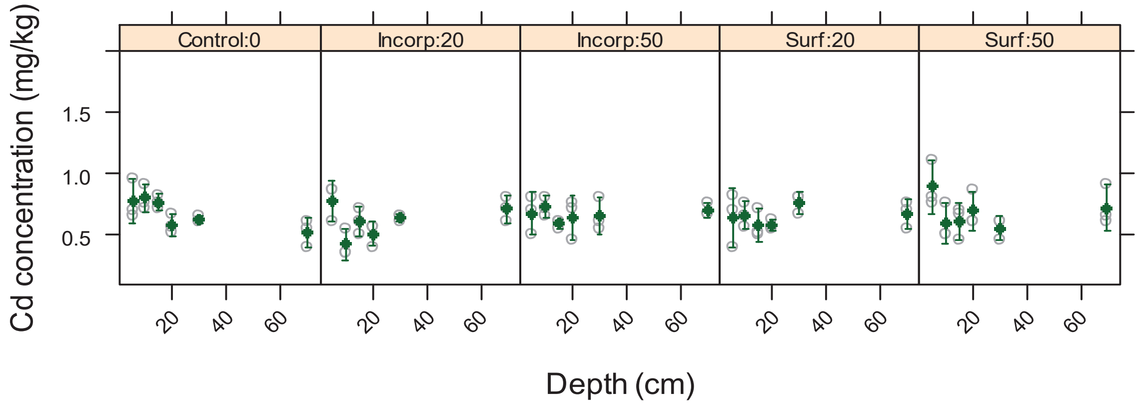
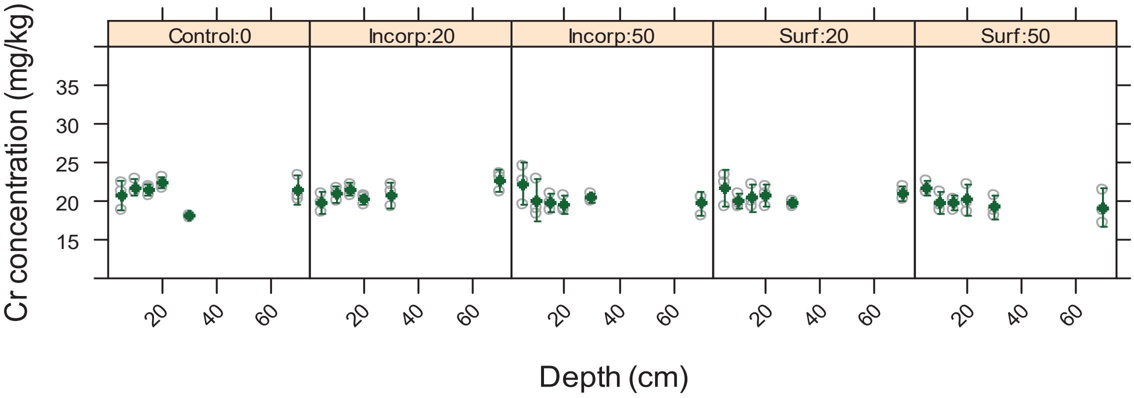


18 month

Figure B.1.6. Cd concentration in S3 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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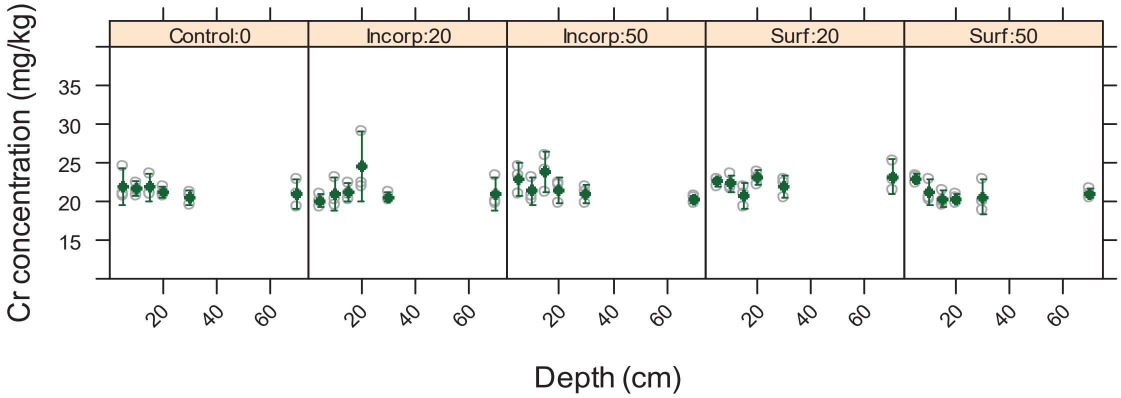

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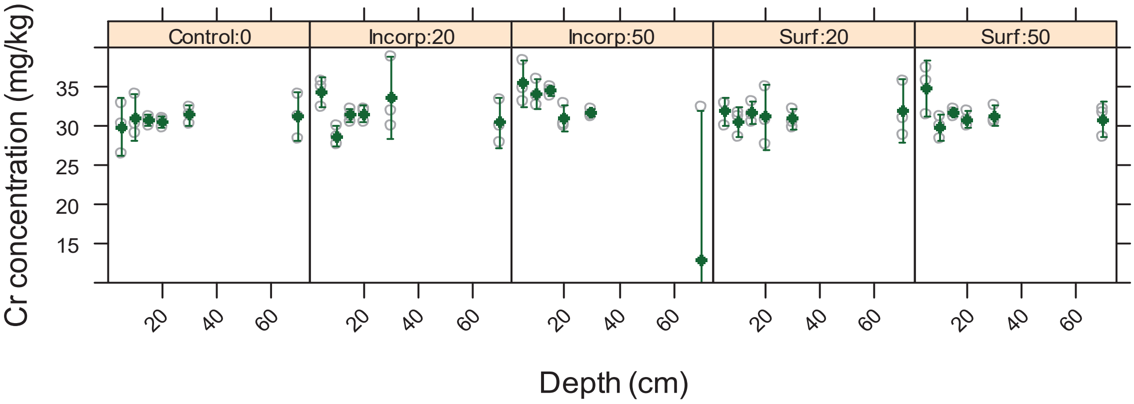
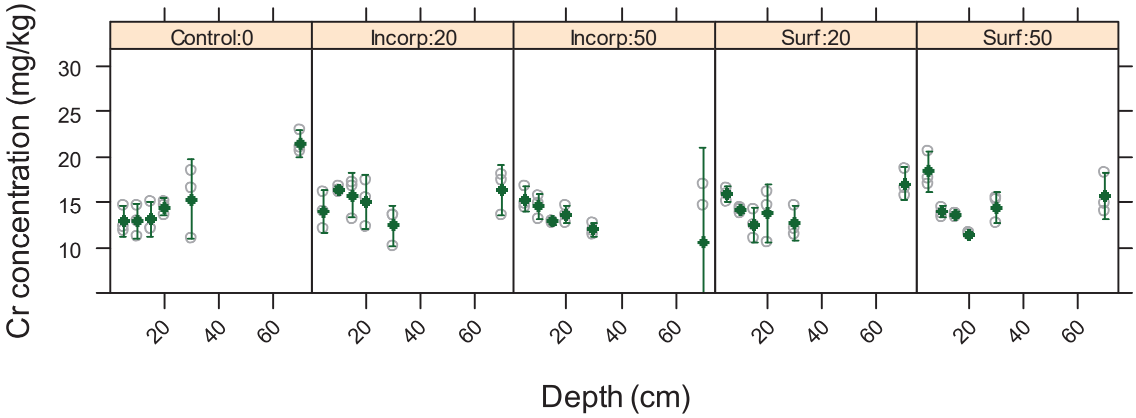
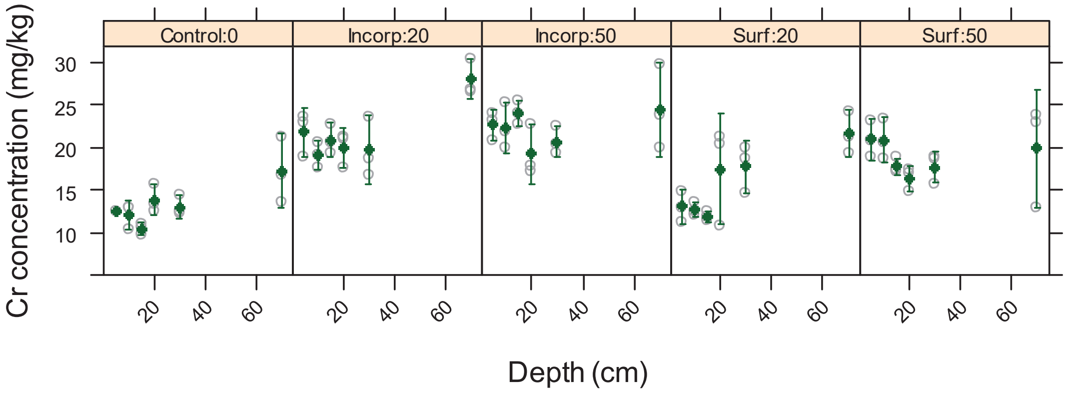


18 month

Figure B.1.7. Cr concentration in S1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



6 month



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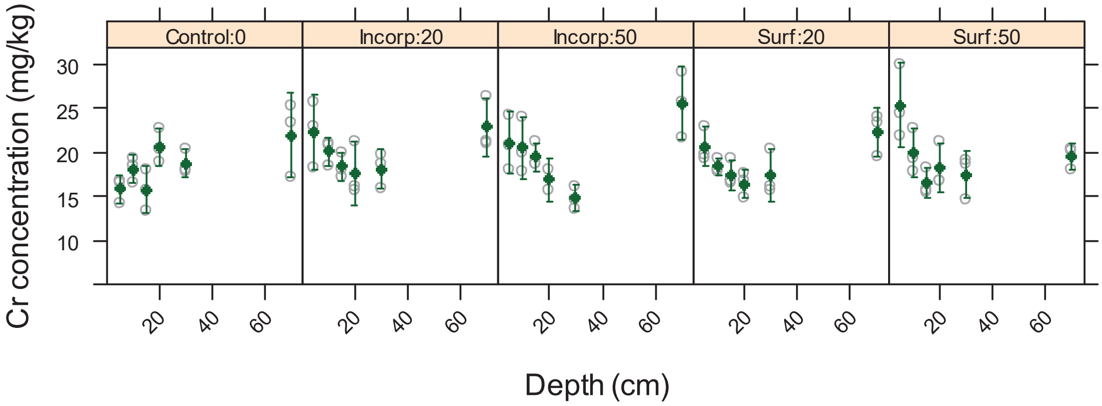
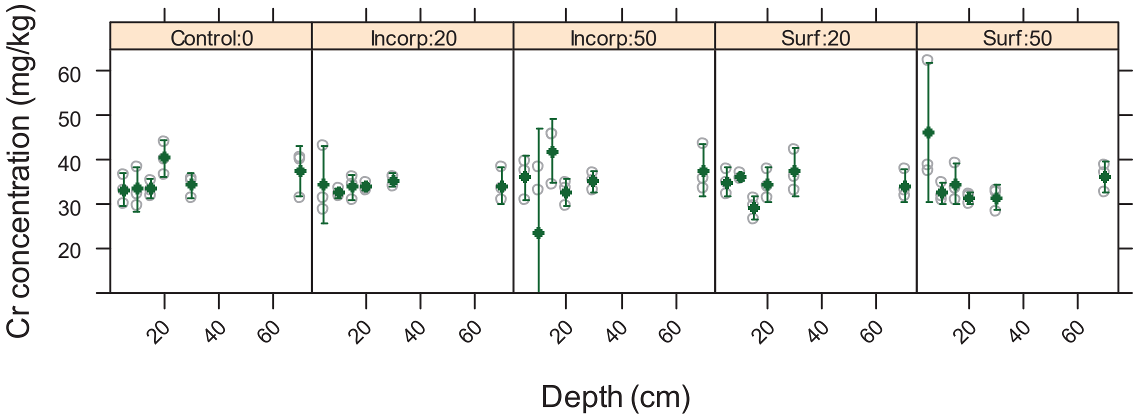
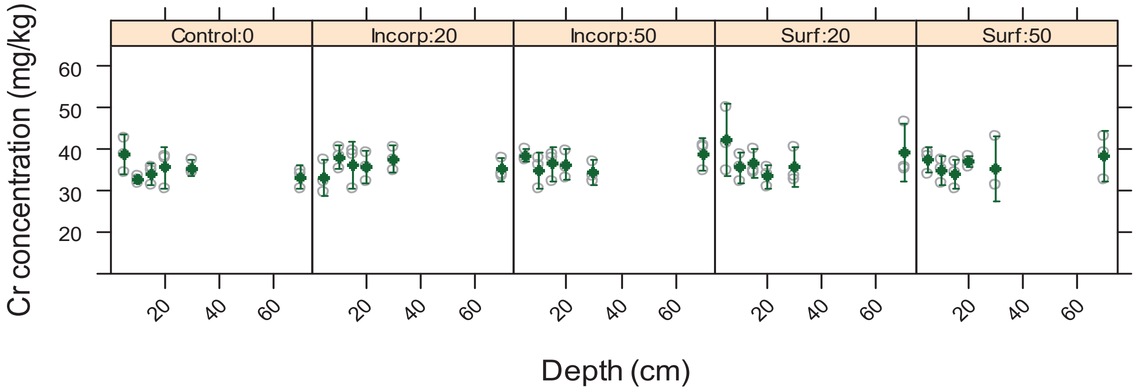


18 month

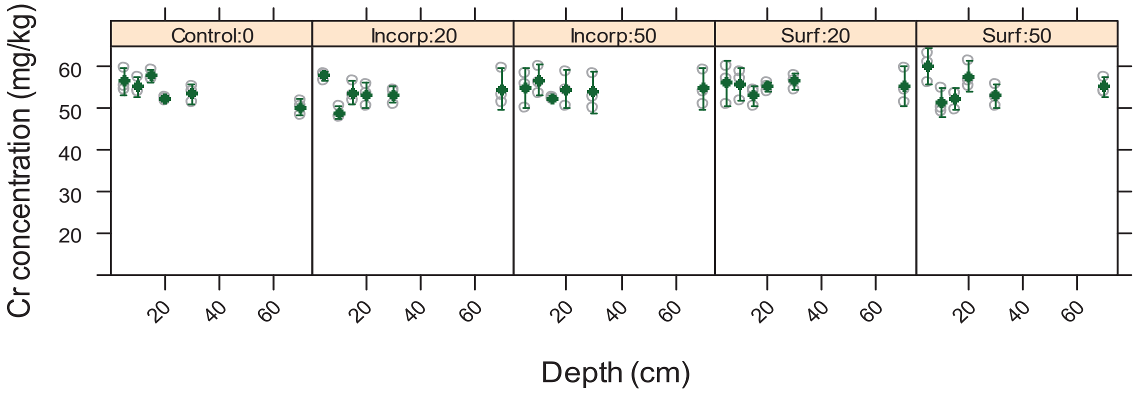
Figure B.1.8. Cr concentration in S2 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



6 month

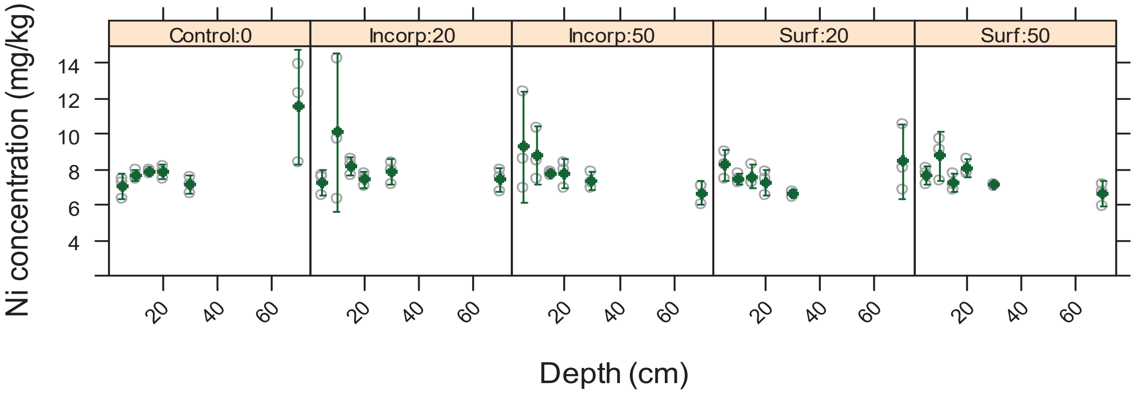


12 month

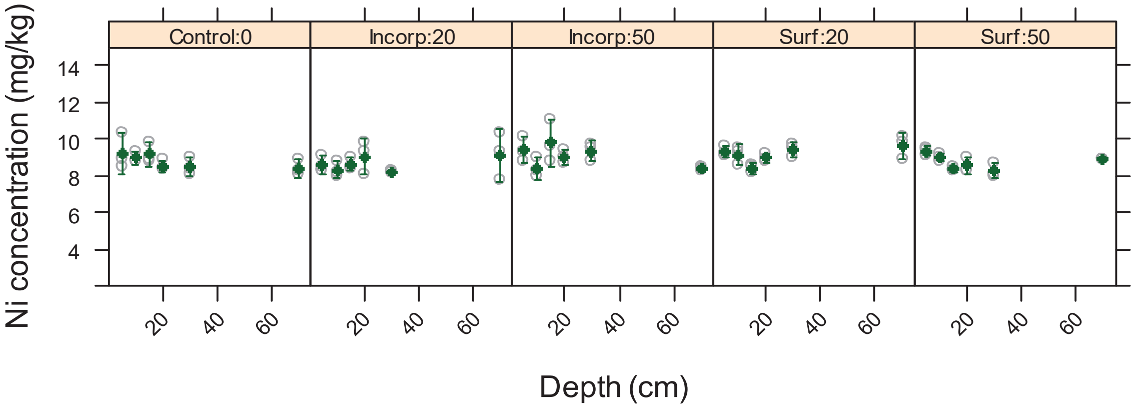


18 month

Figure B.1.9. Cr concentration in S3 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



6 month



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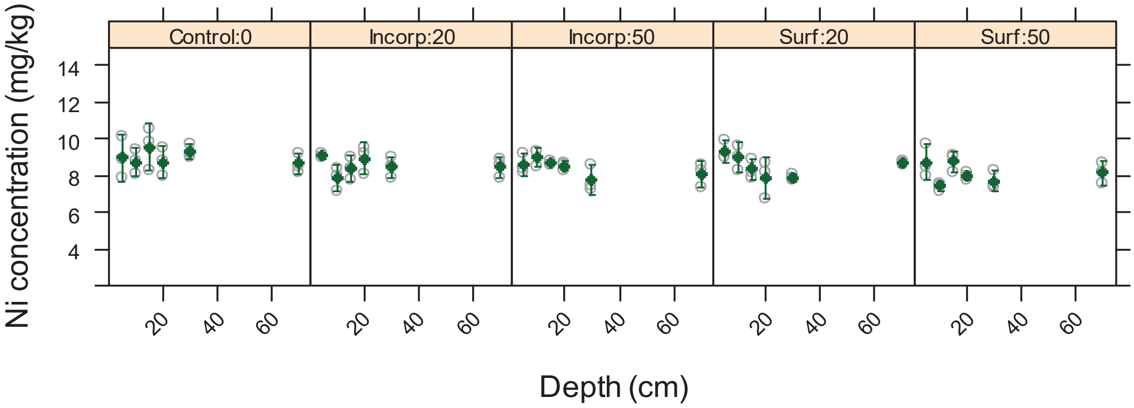
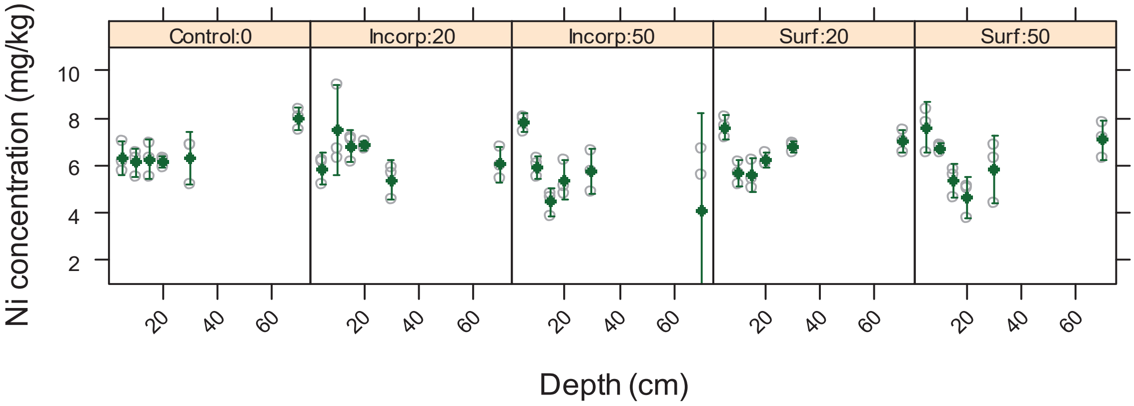


18 month

Figure B.1.10. Ni concentration in S1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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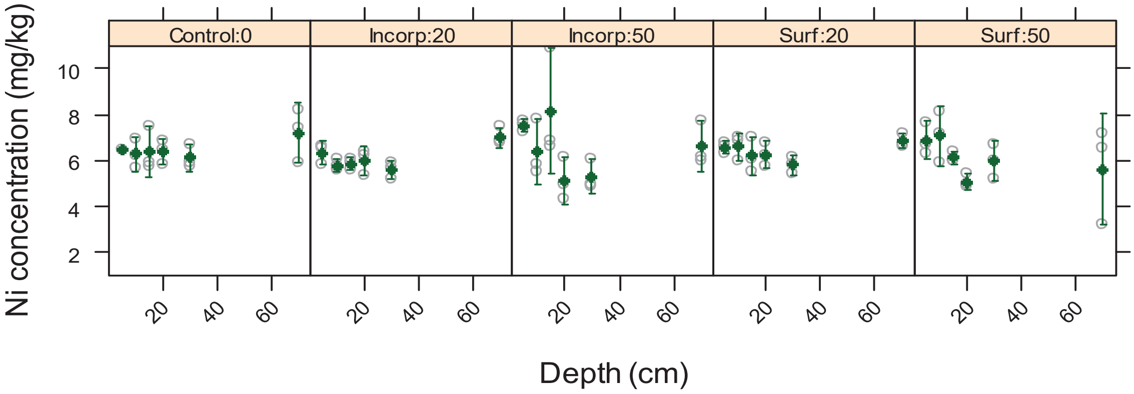

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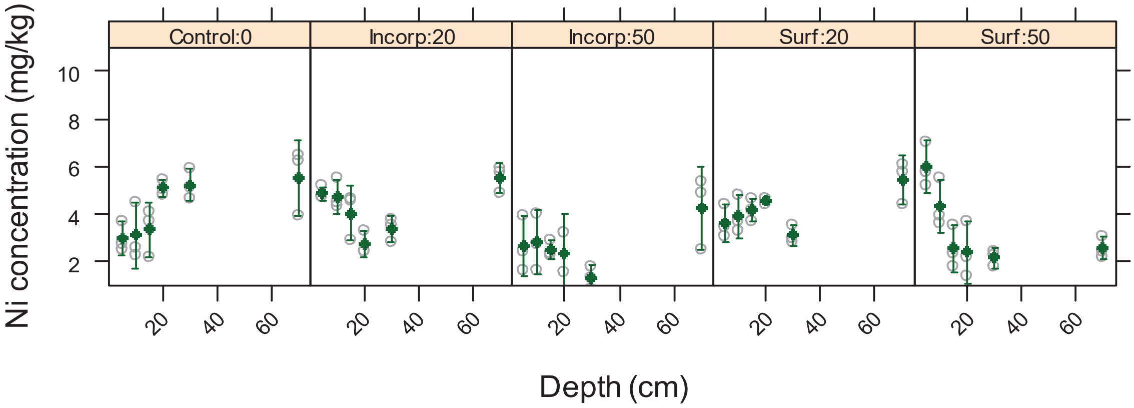
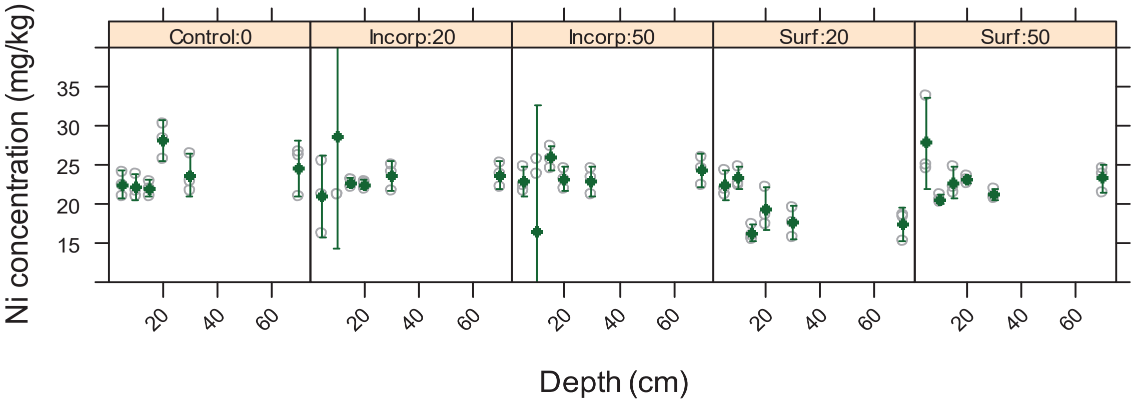


18 month

Figure B.1.10. Ni concentration in S2 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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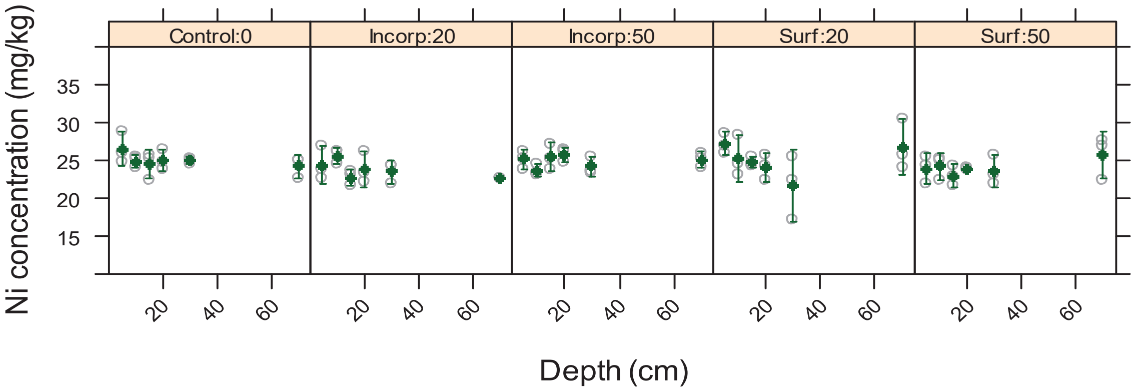

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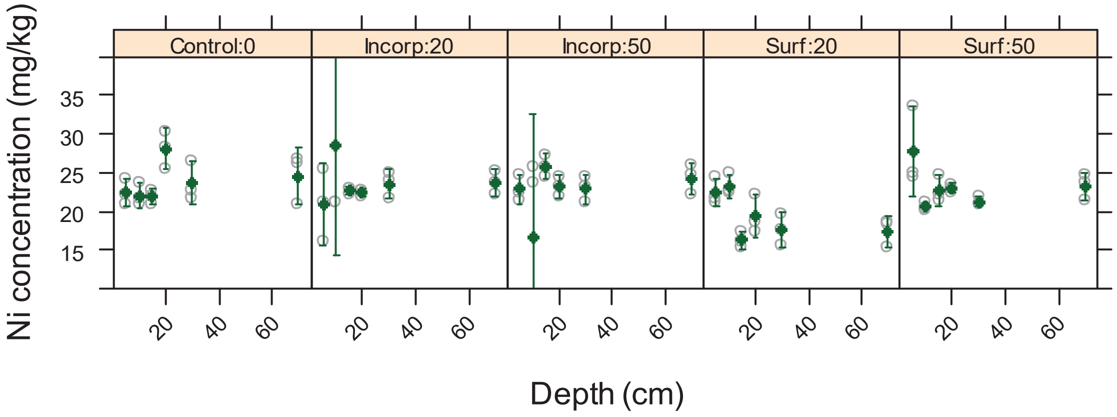
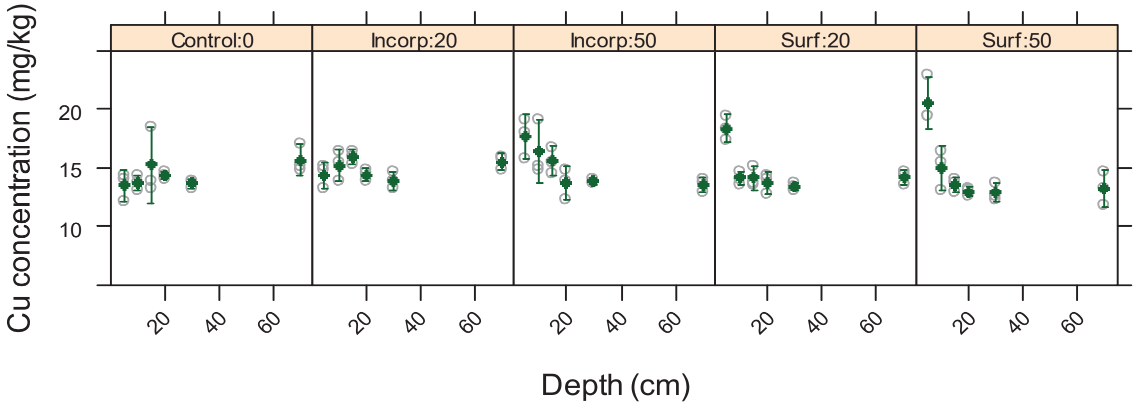
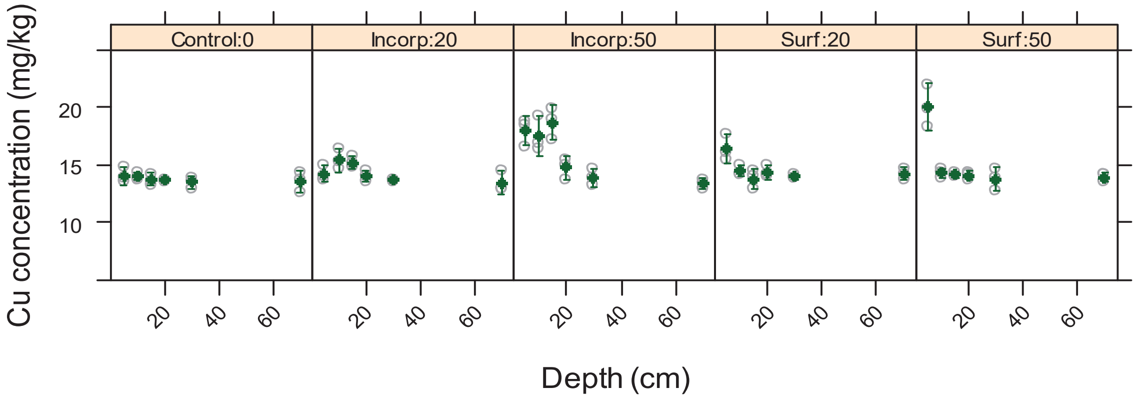


18 month

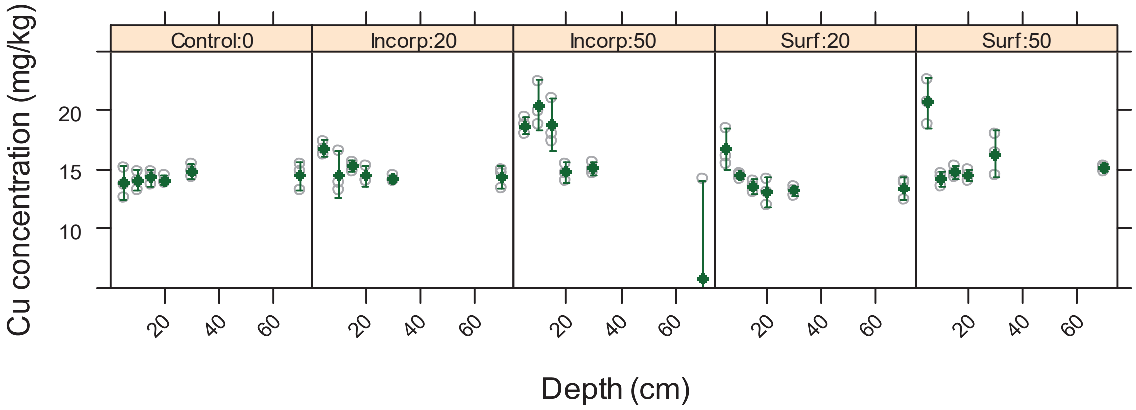
Figure B.1.12. Ni concentration in S3 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



6 month

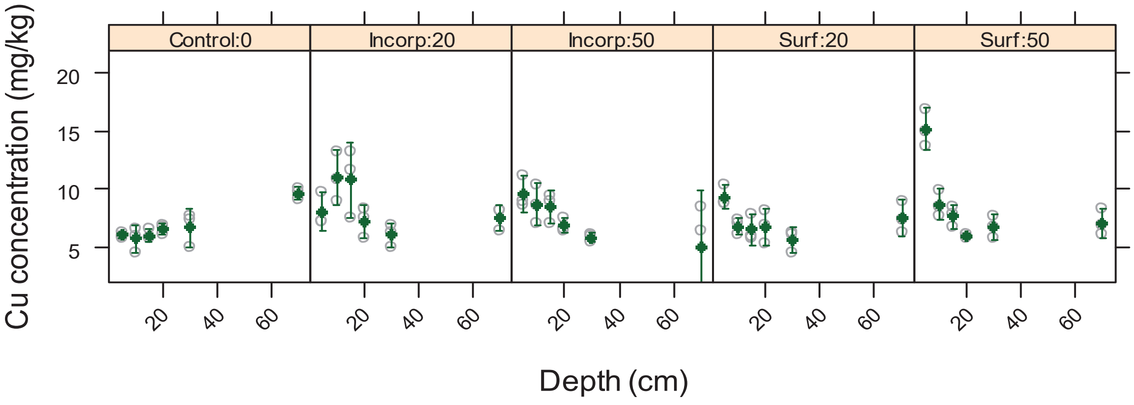


12 month



18 month

Figure B.1.13. Cu concentration in S1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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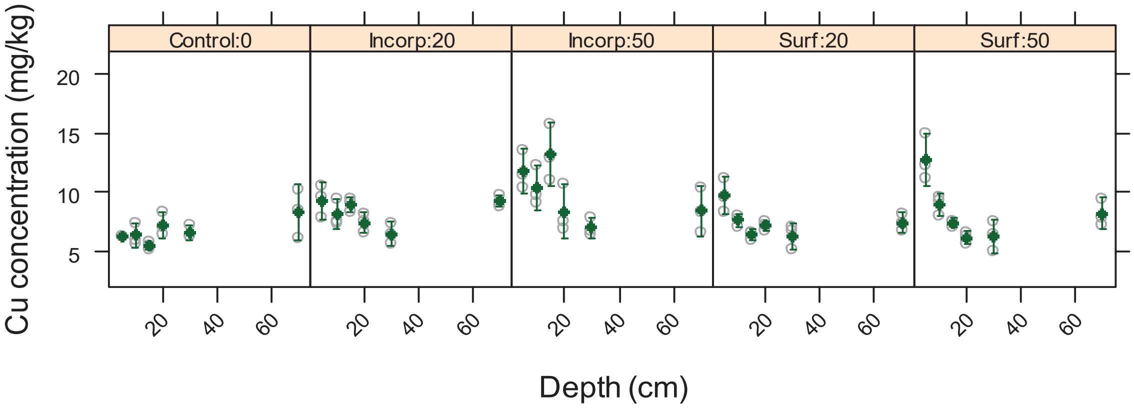

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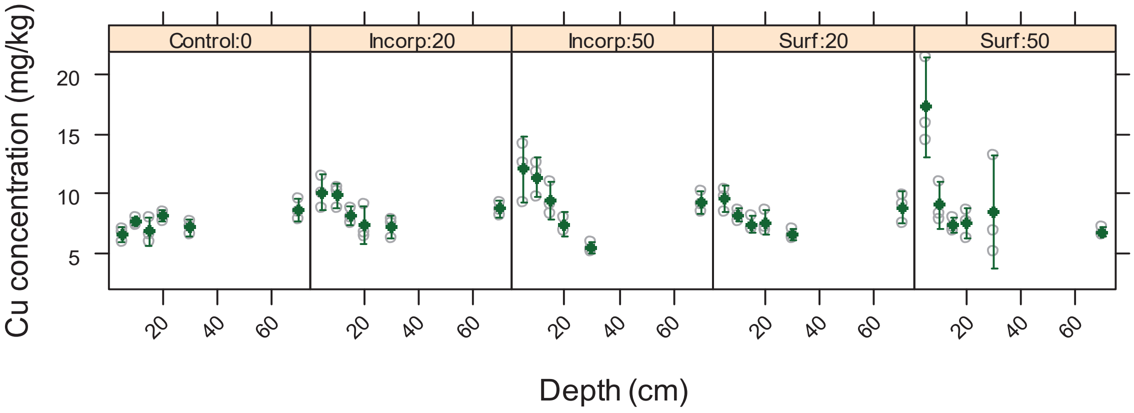
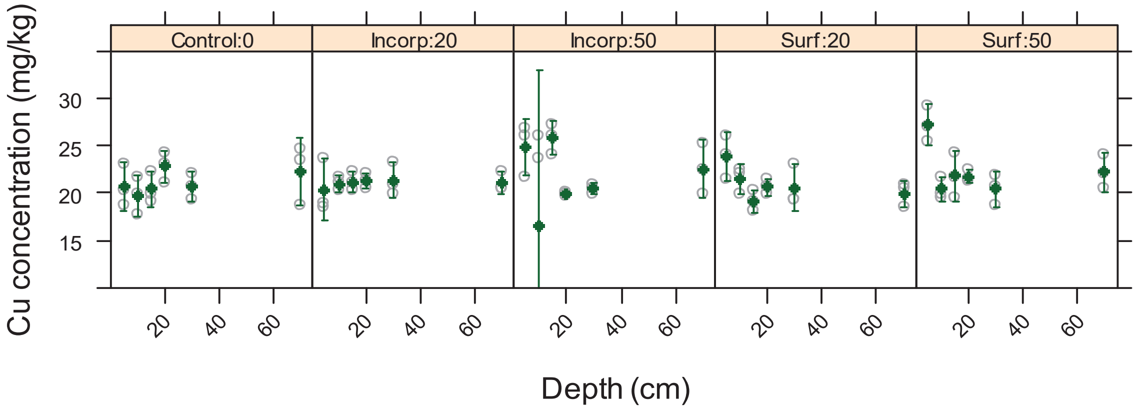


18 month

Figure B.1.14. Cu concentration in S2 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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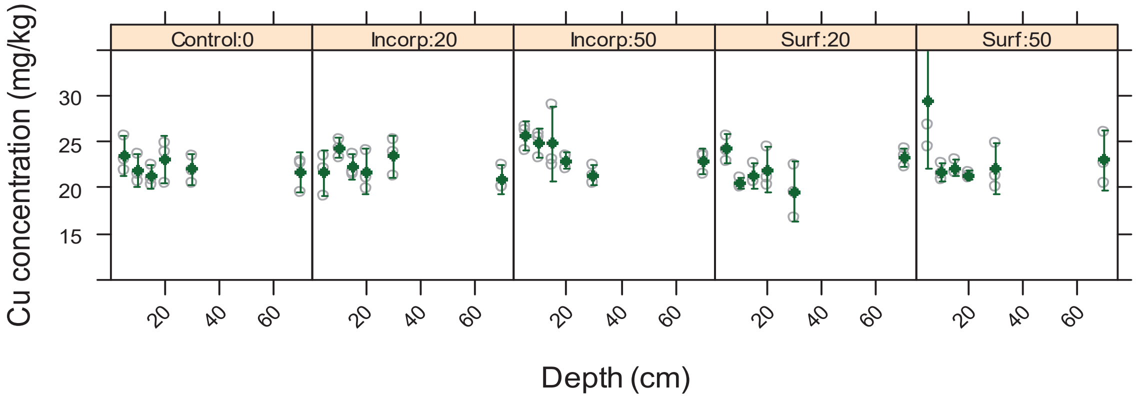

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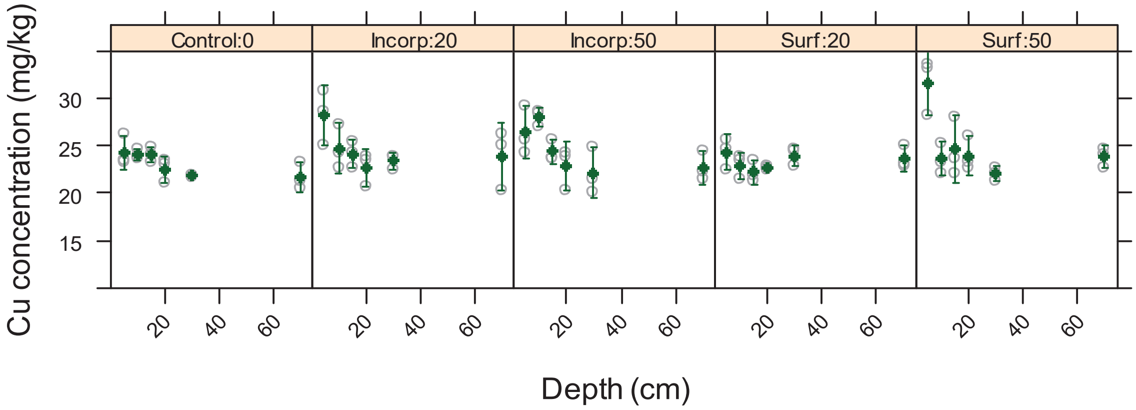
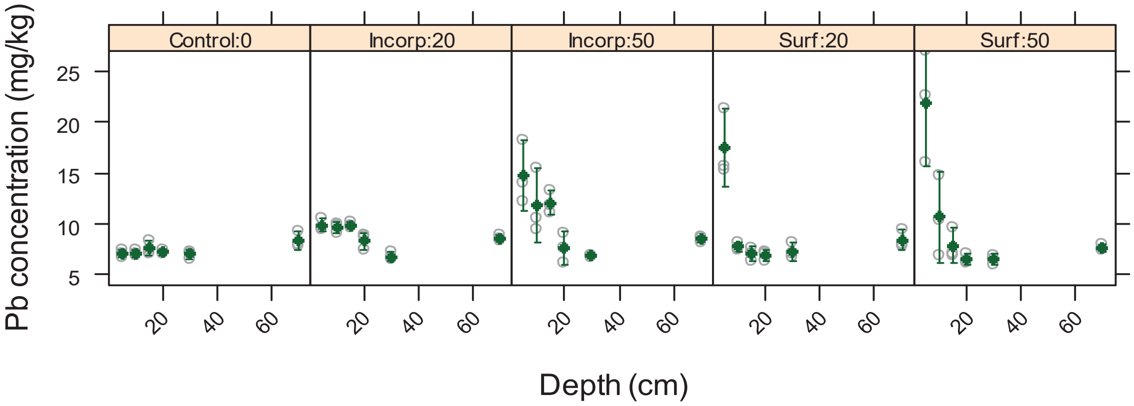


18 month

Figure B.1.15. Cu concentration in S3 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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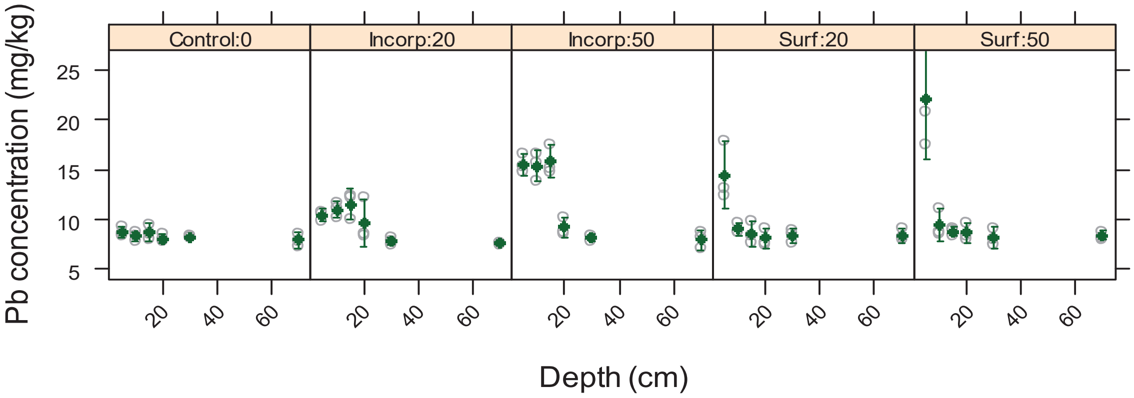

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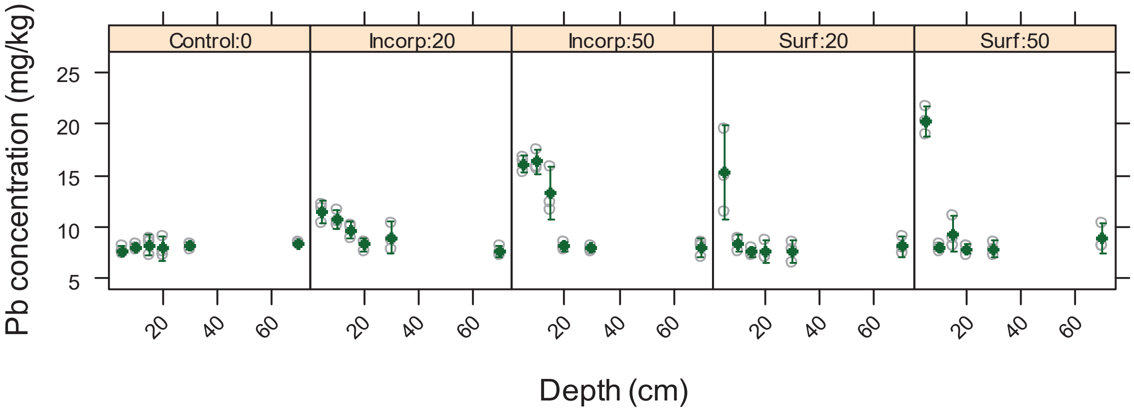
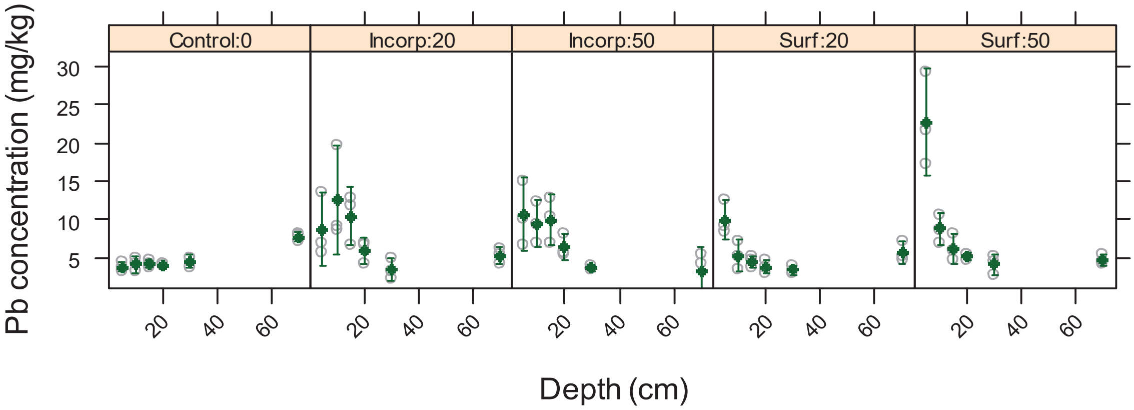
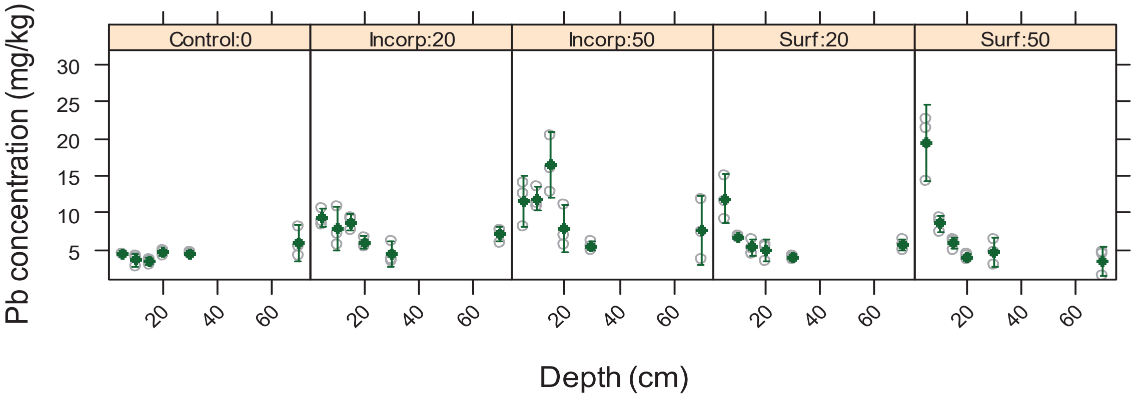


18 month

Figure B.1.16. Pb concentration in S1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



6 month



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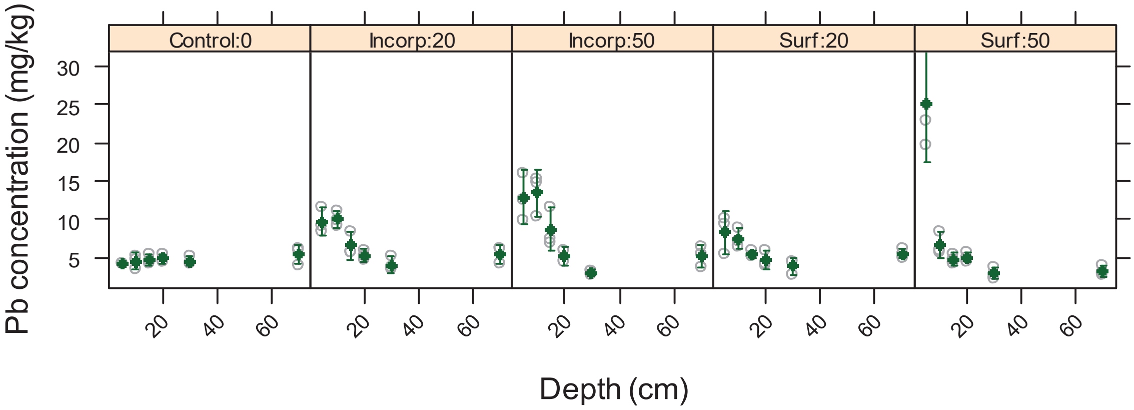
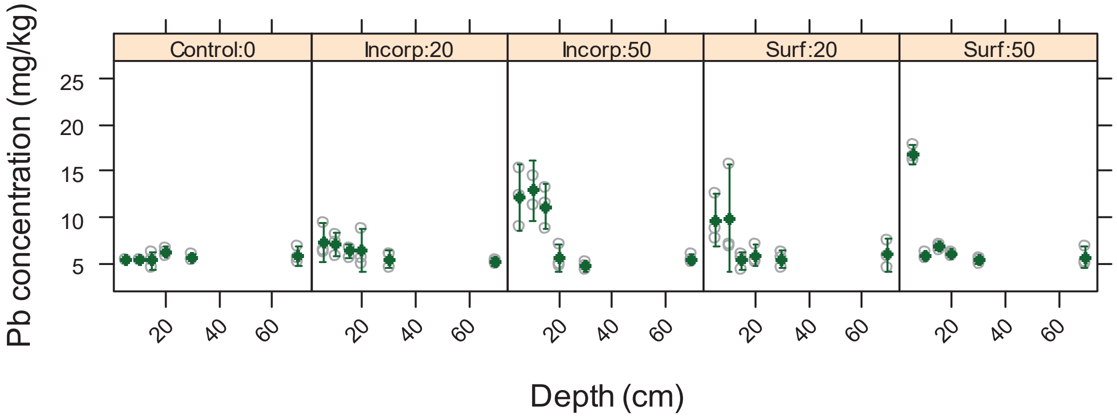


18 month

Figure B.1.17. Pb concentration in S2 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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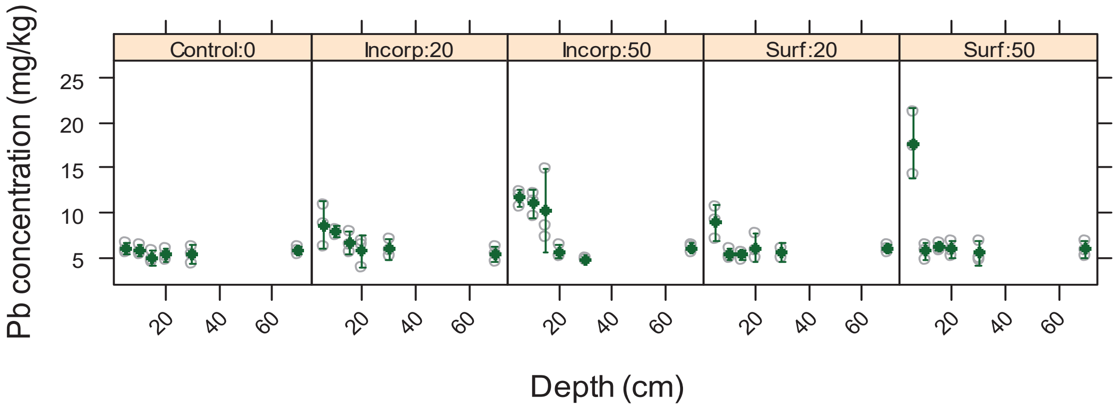

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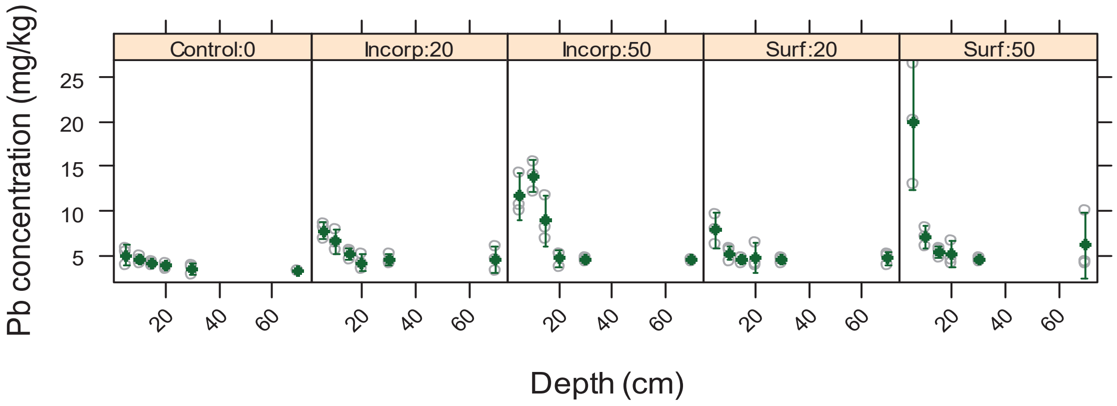
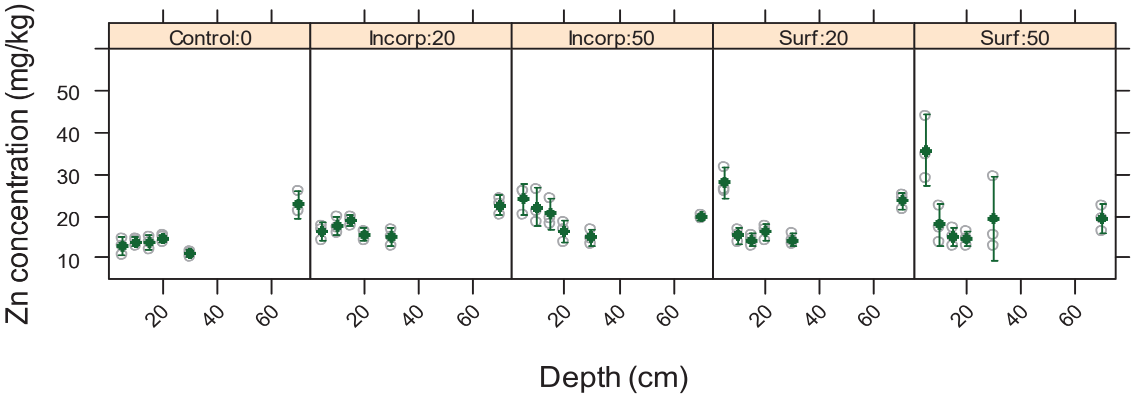


18 month

Figure B.1.18. Pb concentration in S3 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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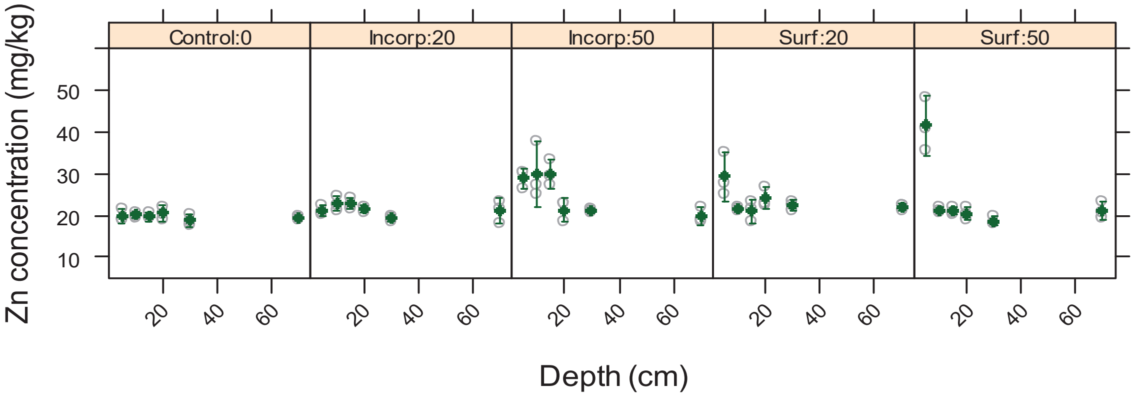

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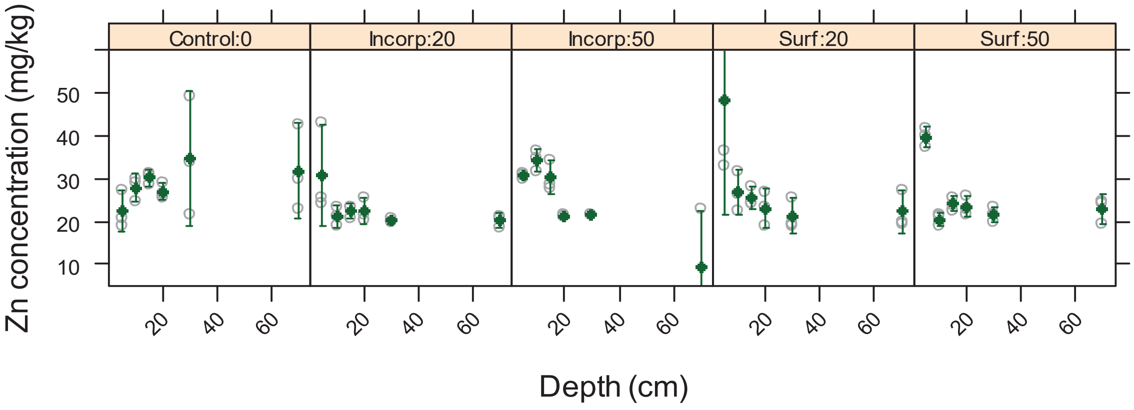
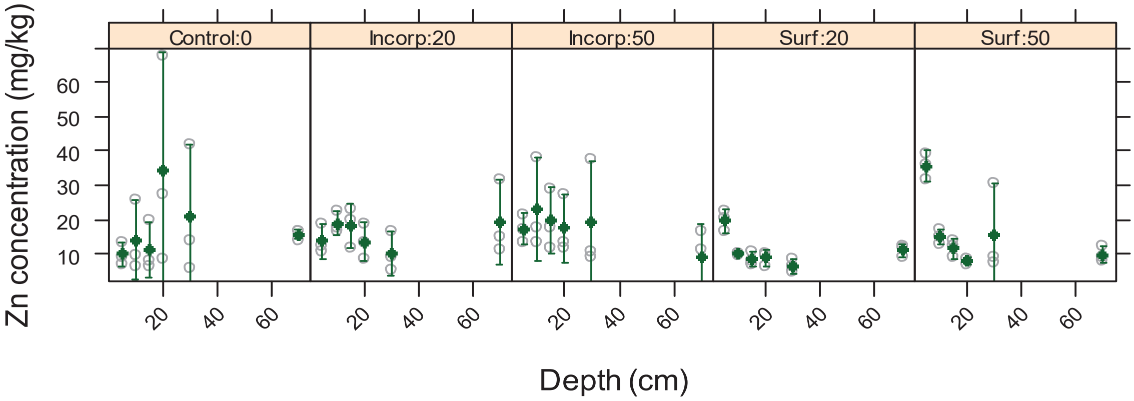


18 month

Figure B.1.19. Zn concentration in S1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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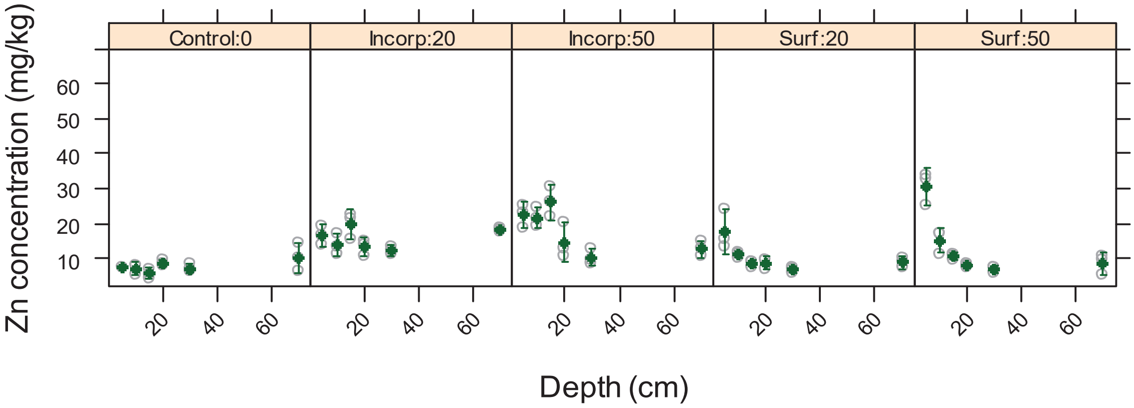

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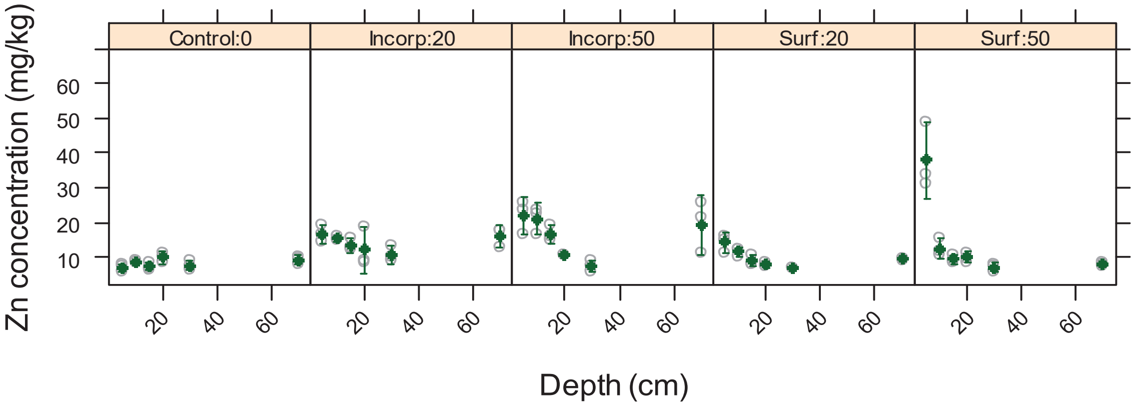
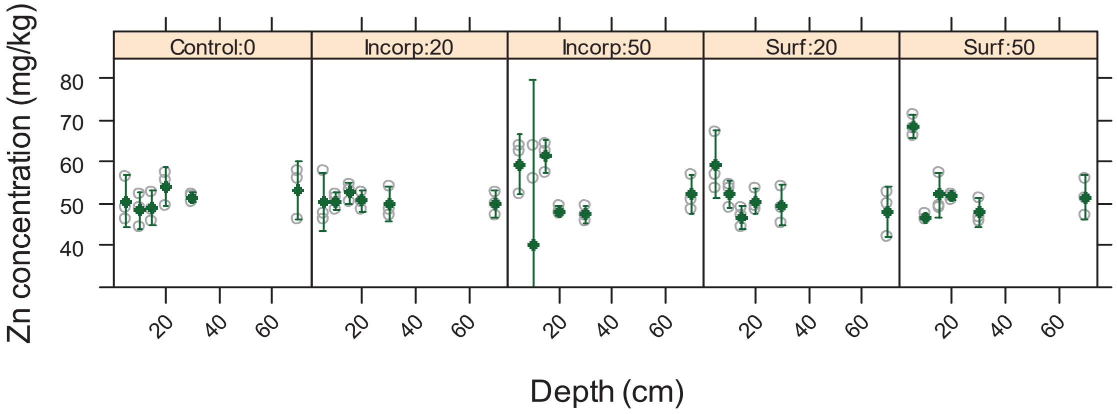
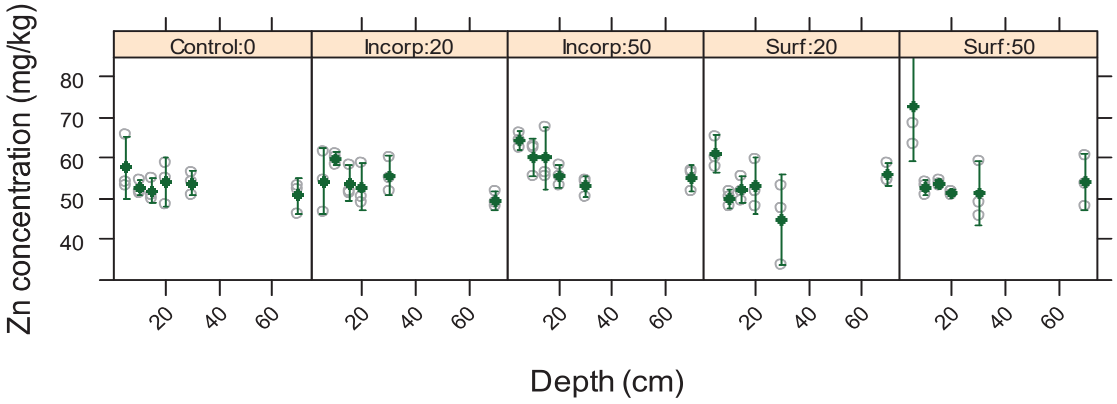


18 month

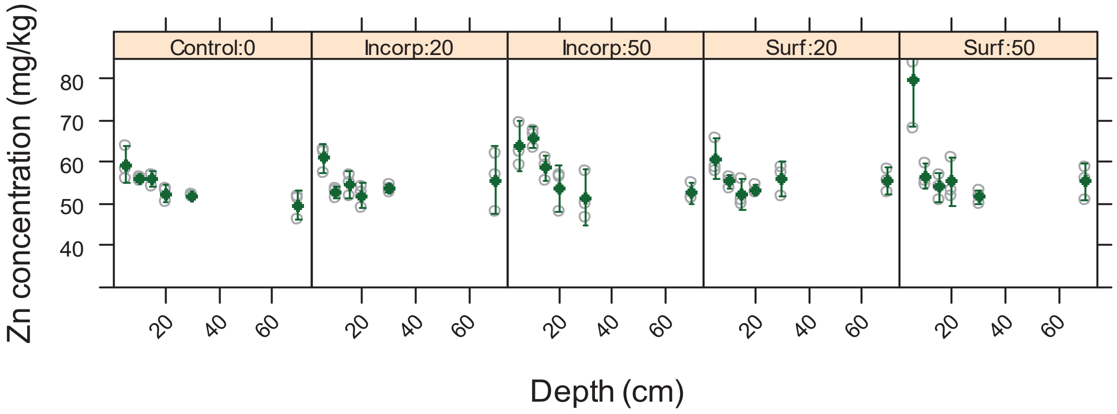
Figure B.1.20. Zn concentration in S2 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



6 month



12 month

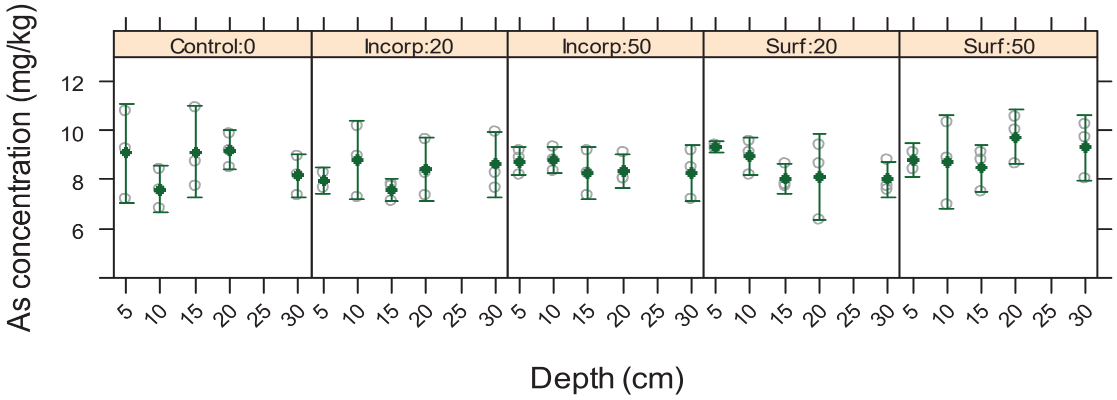


18 month

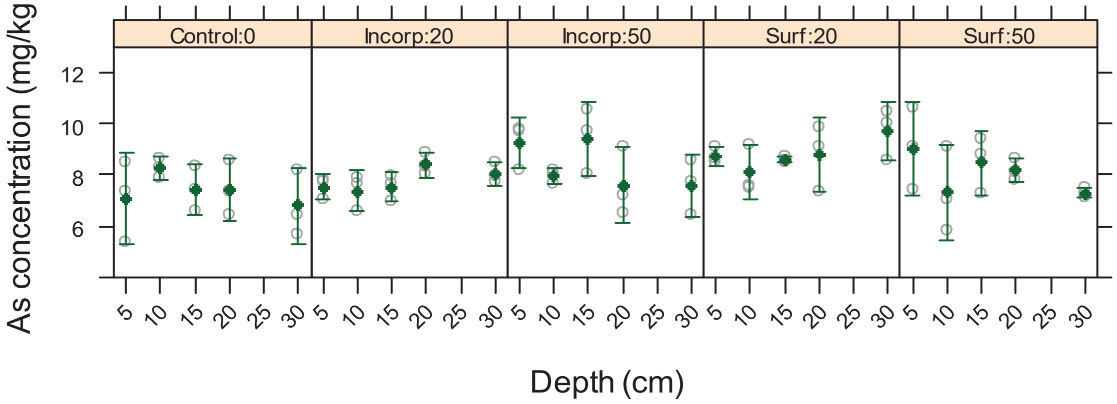
Figure B.1.21. Zn concentration in S3 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals

Appendix B2

Changes of metal and metalloid concentrations and distribution in three silty soils (SL1, SL2, SL3)



6 month



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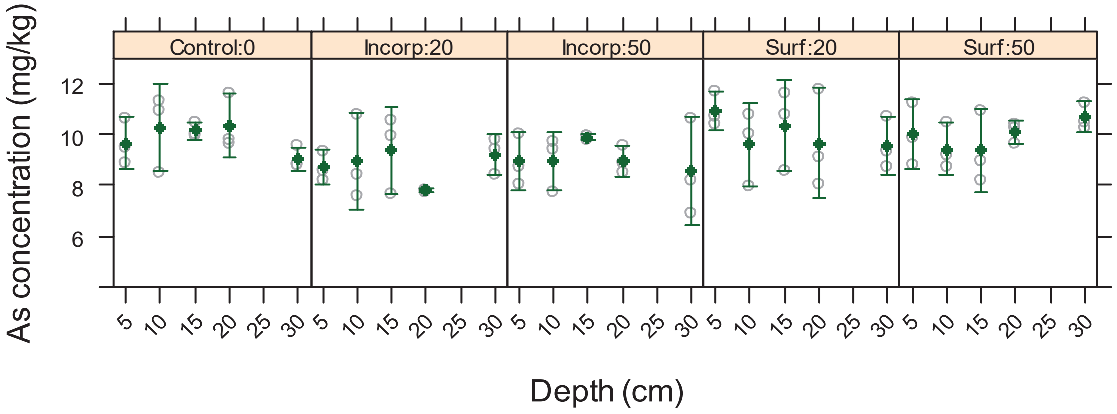
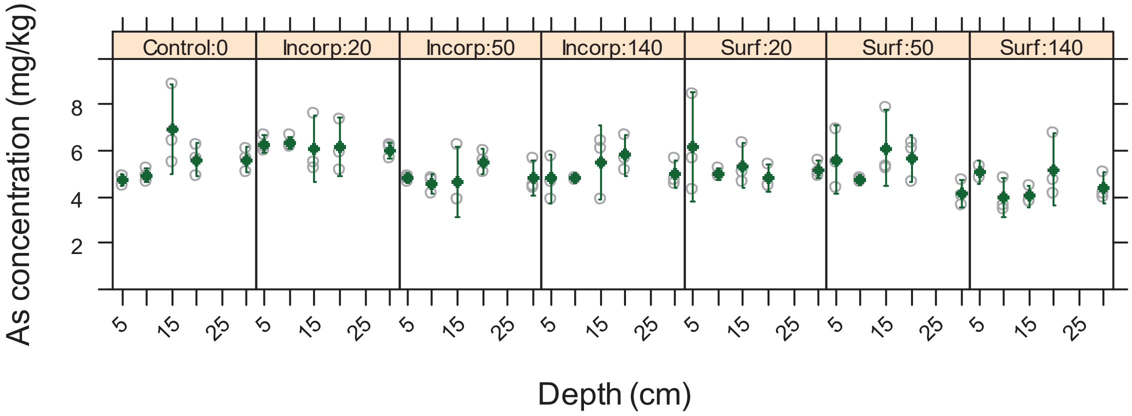


18 month

Figure B.2.1. As concentration in SL1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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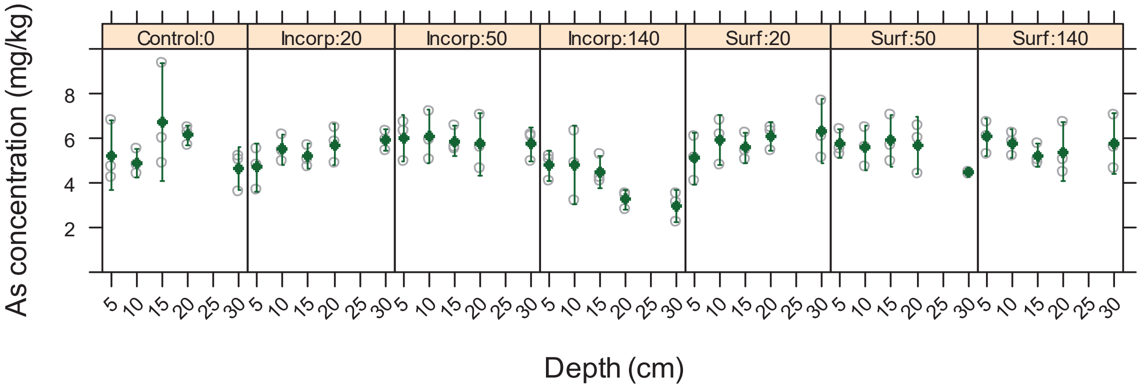

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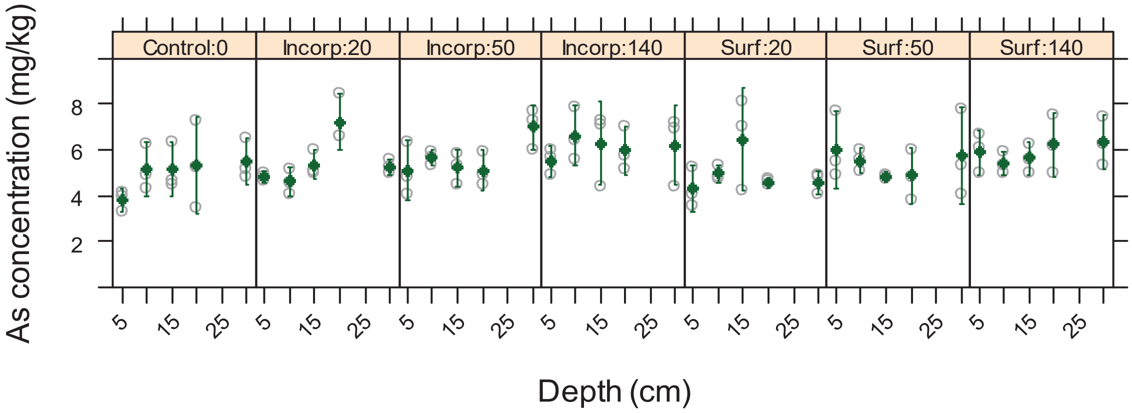
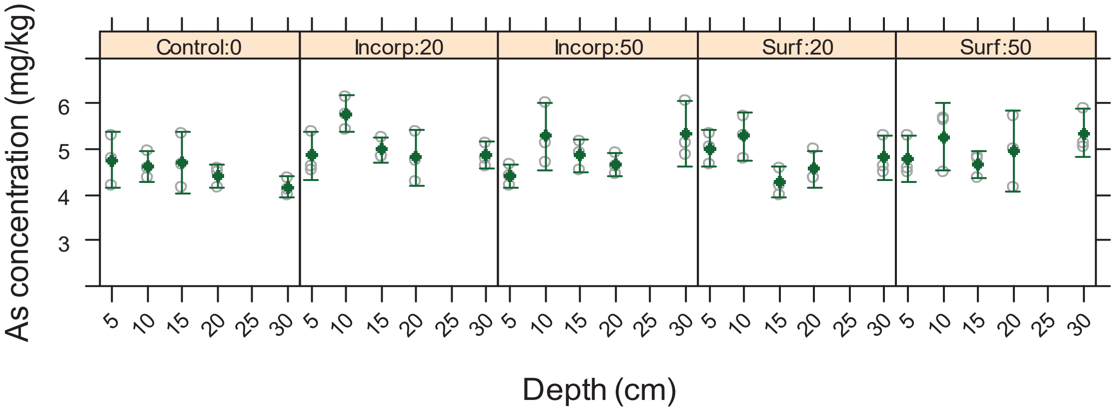


18 month

Figure B.2.2. As concentration in SL2 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20, 50 and 140 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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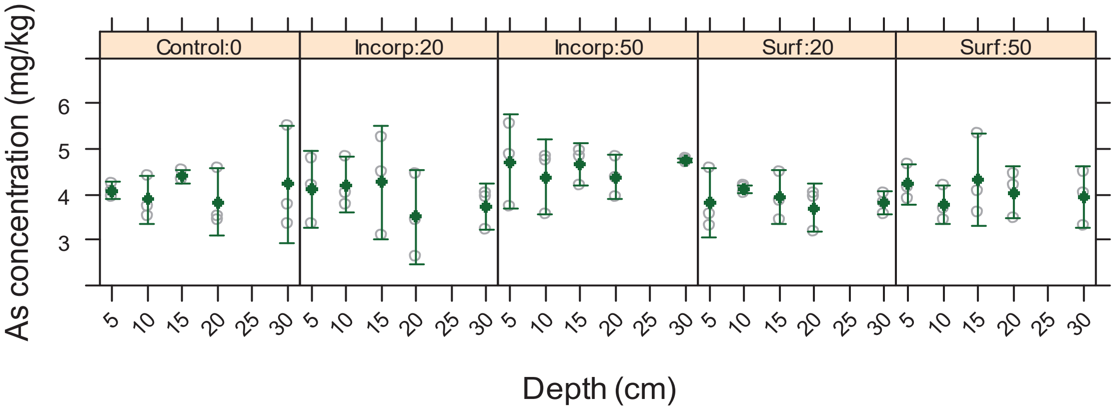

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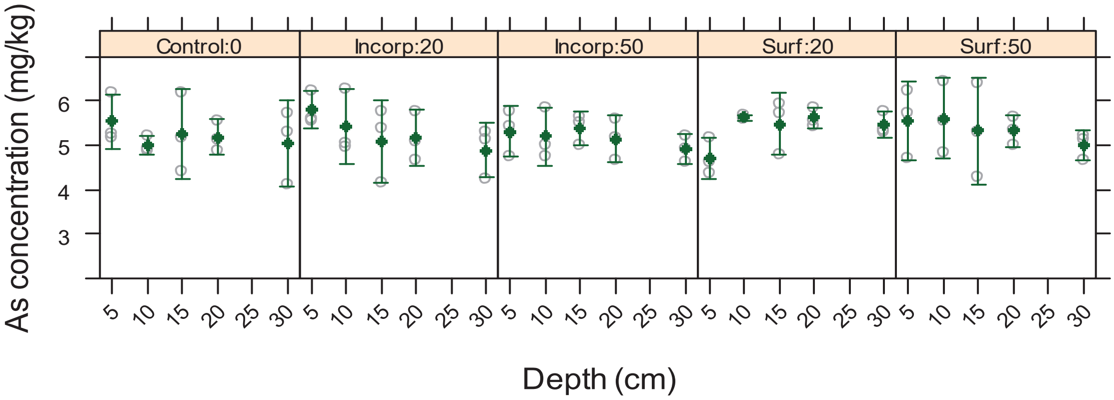
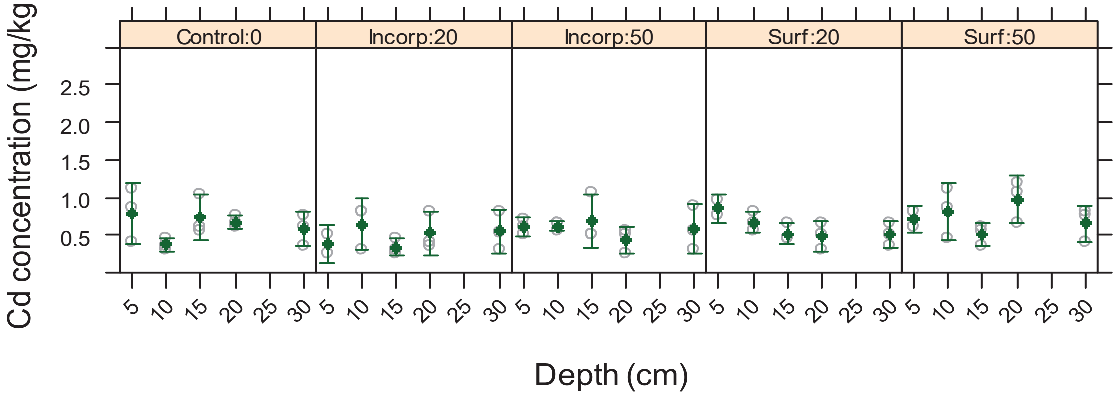


18 month

Figure B.2.3. As concentration in SL3 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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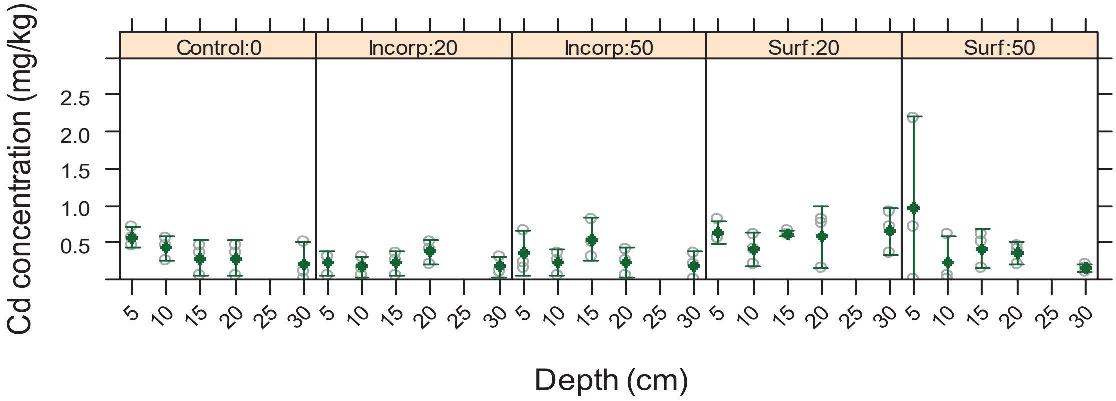

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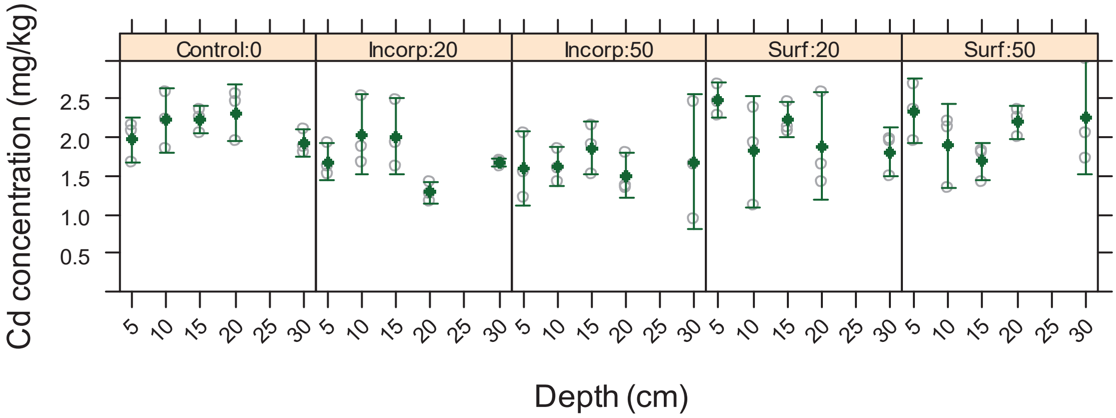
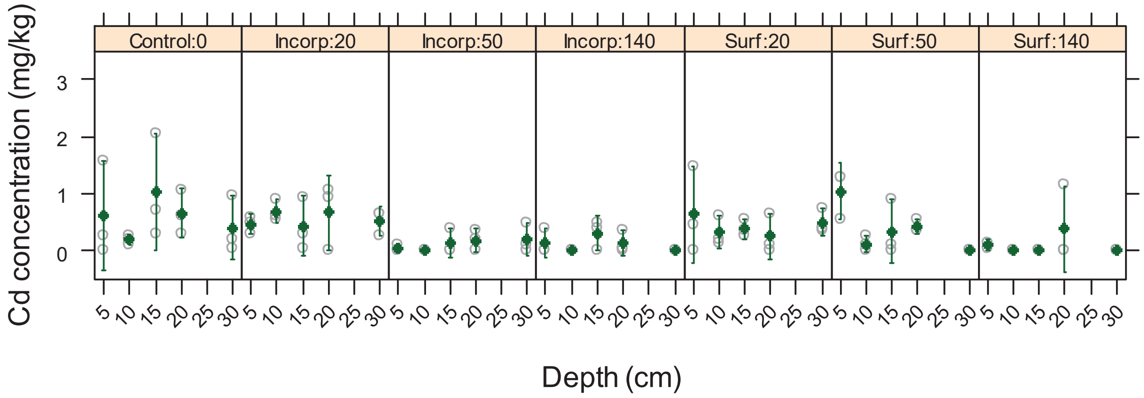


18 month

Figure B.2.4. Cd concentration in SL1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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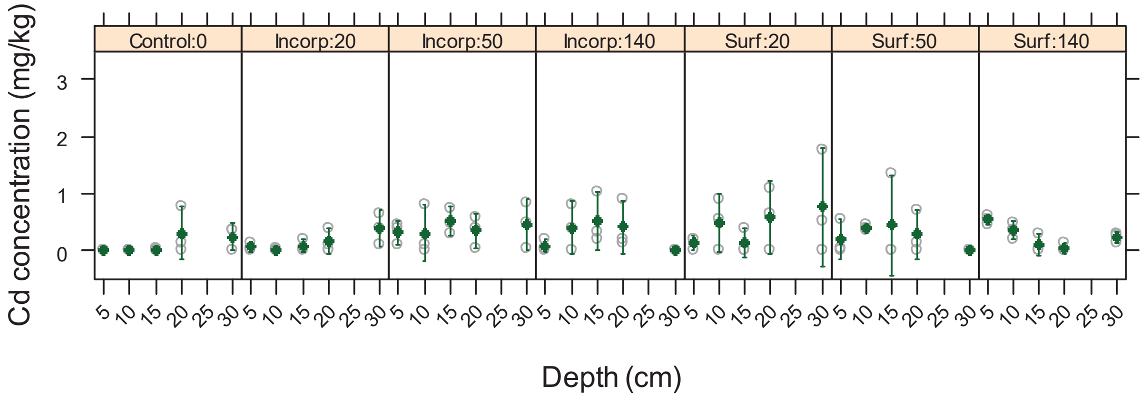

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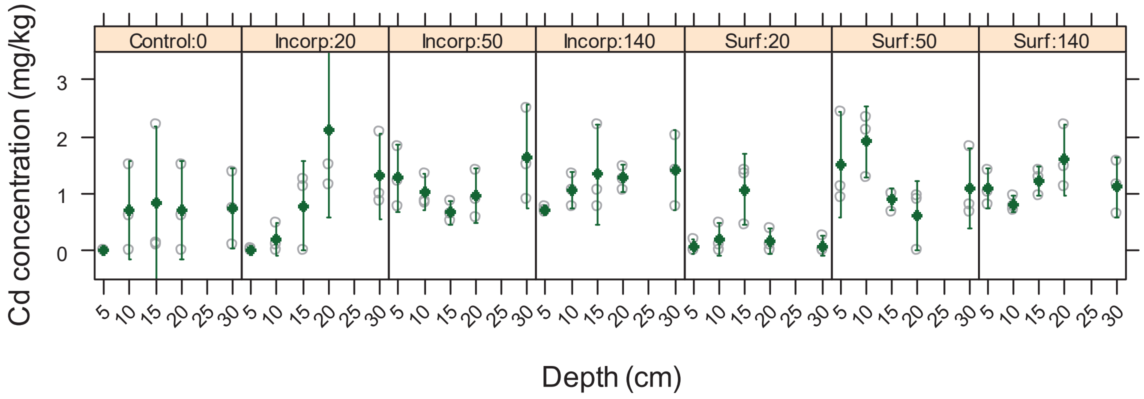
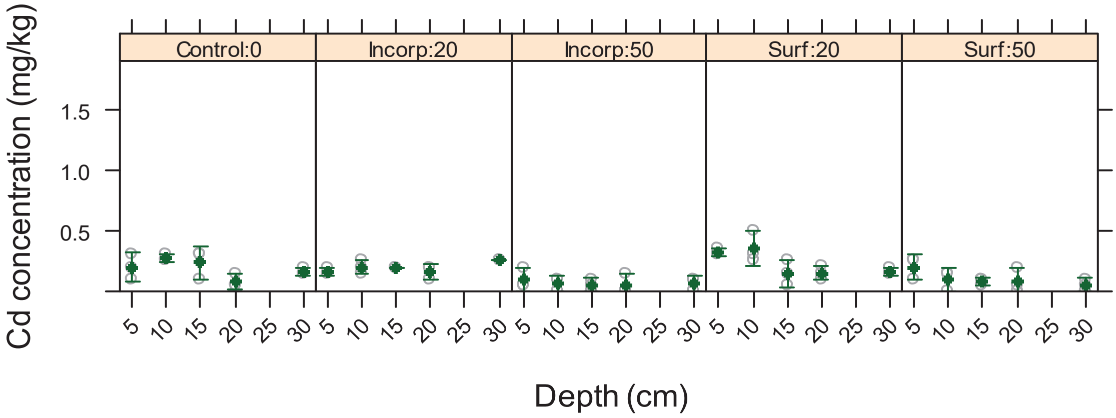


18 month

Figure B.2.5. Cd concentration in SL2 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20, 50 and 140 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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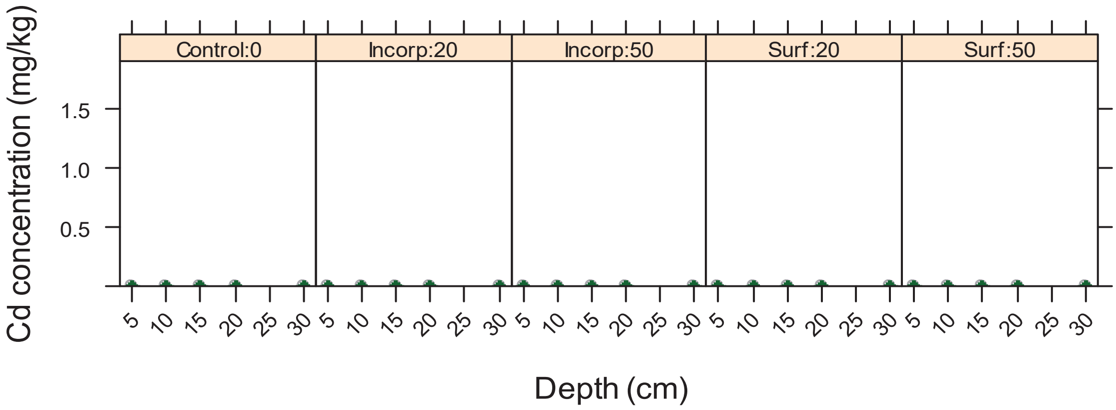

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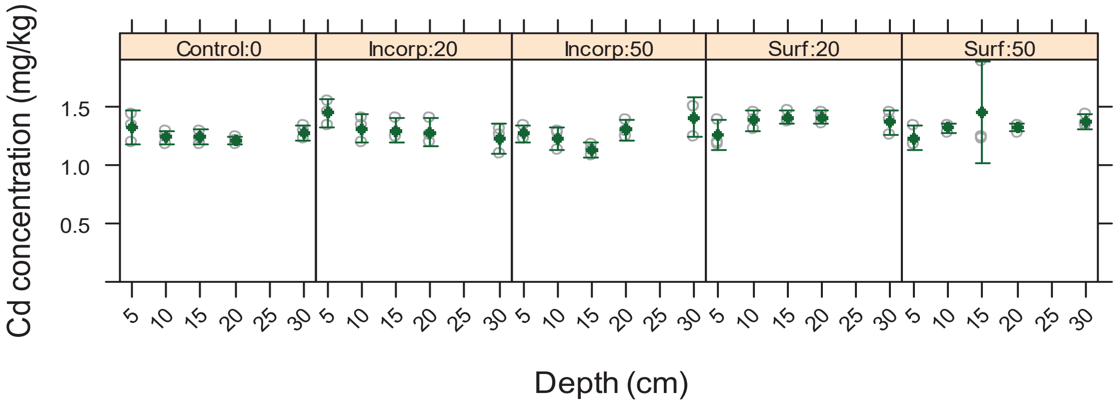
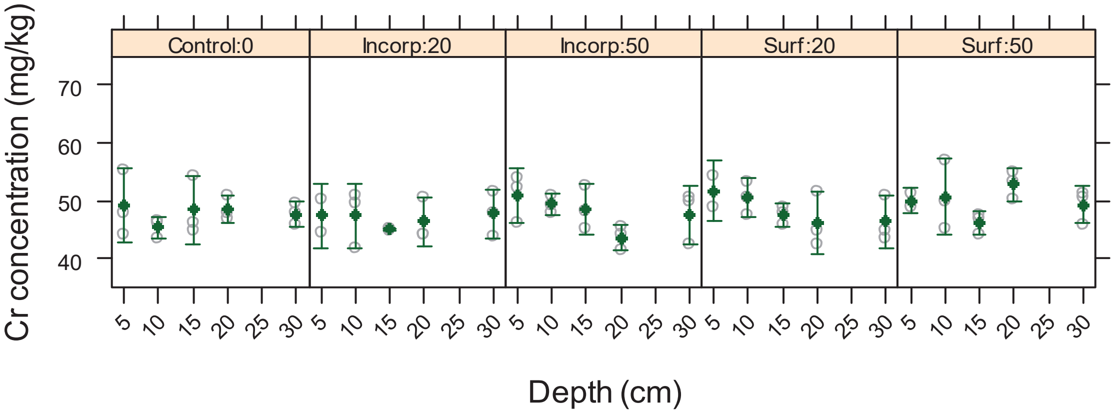


18 month

Figure B.2.6. Cd concentration in SL3 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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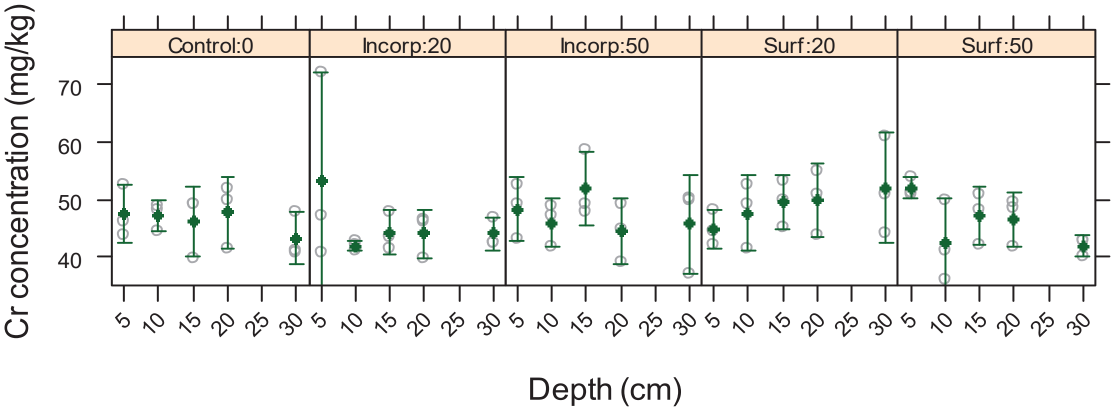

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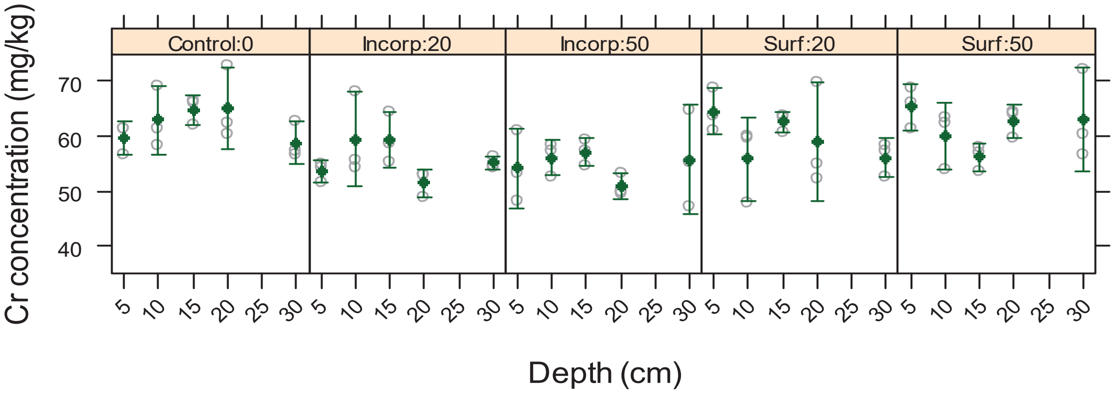
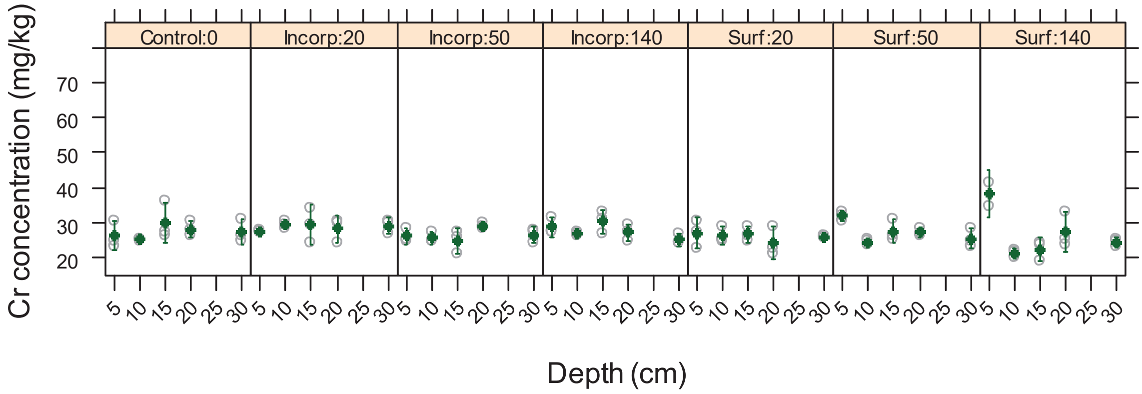


18 month

Figure B.2.7. Cr concentration in SL1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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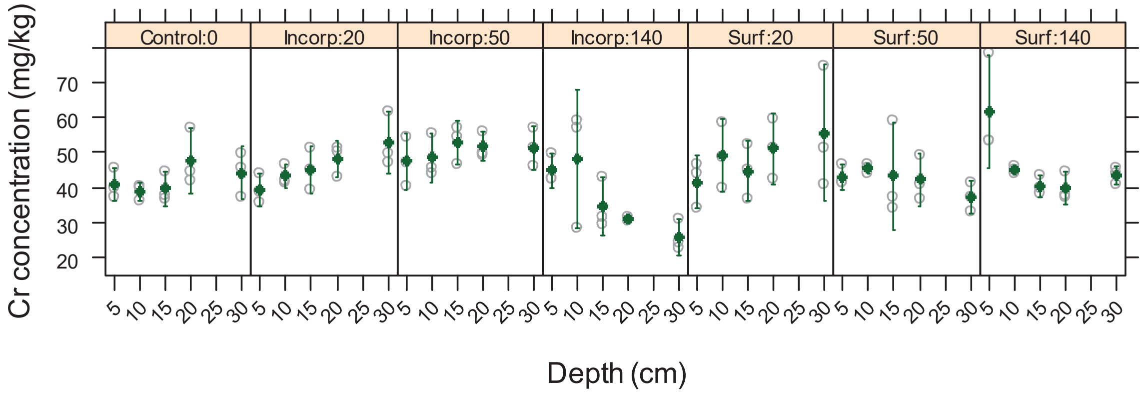

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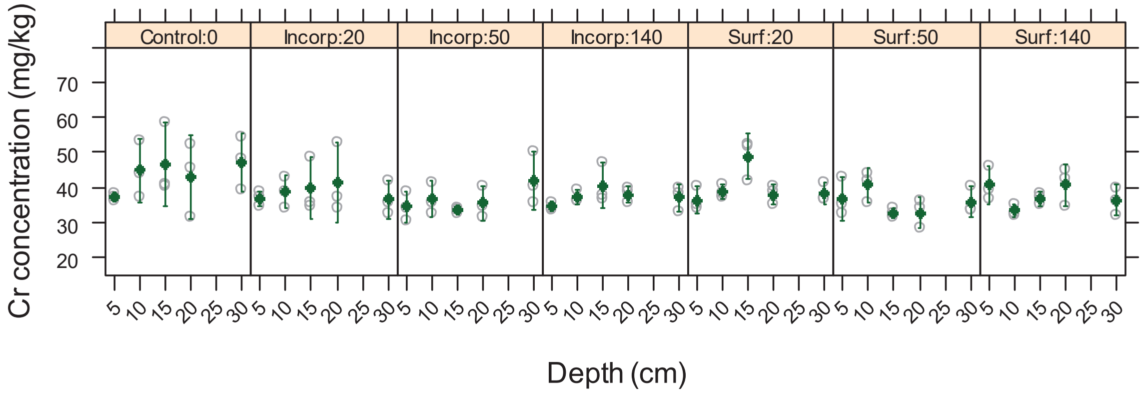
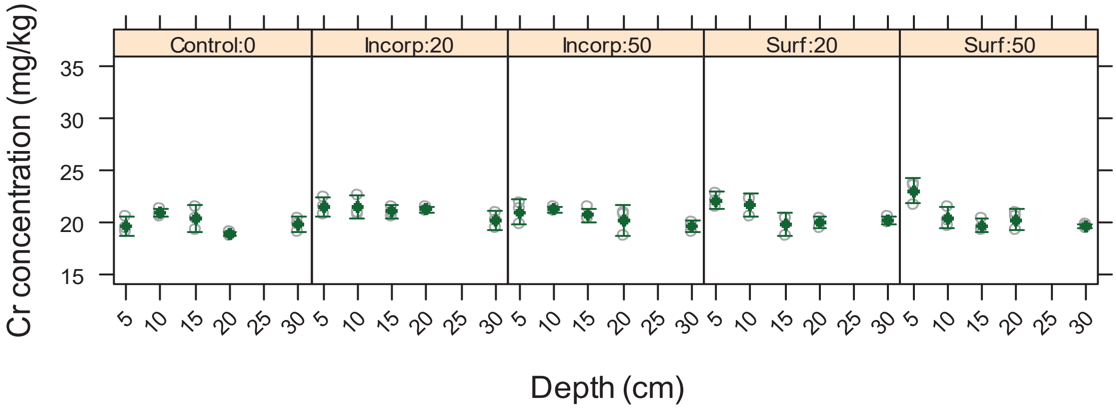


18 month

Figure B.2.8. Cr concentration in SL2 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20, 50 and 140 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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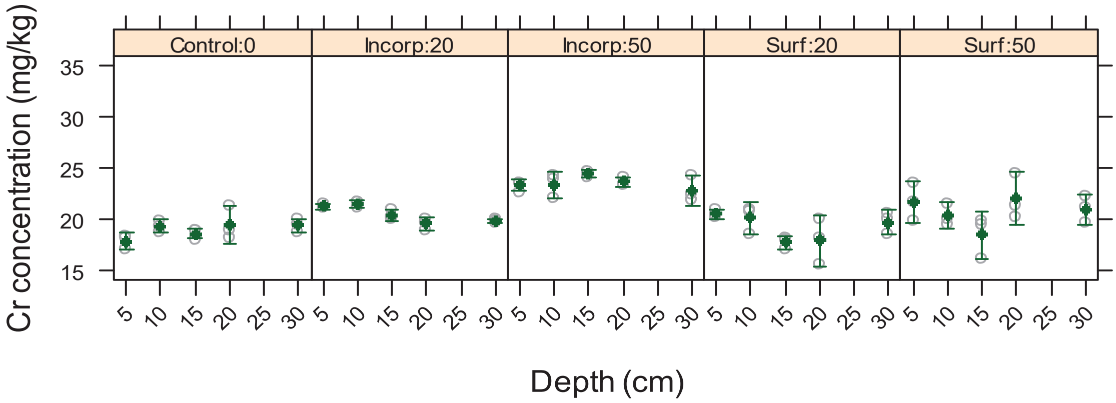

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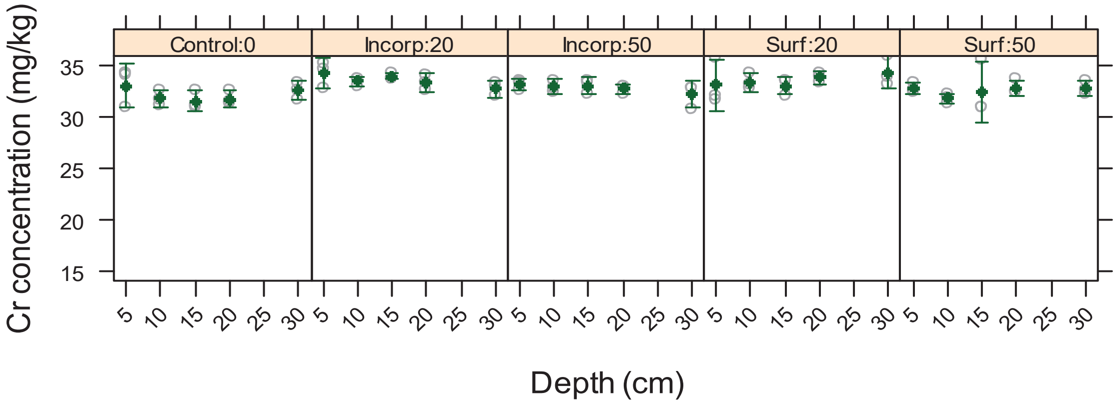
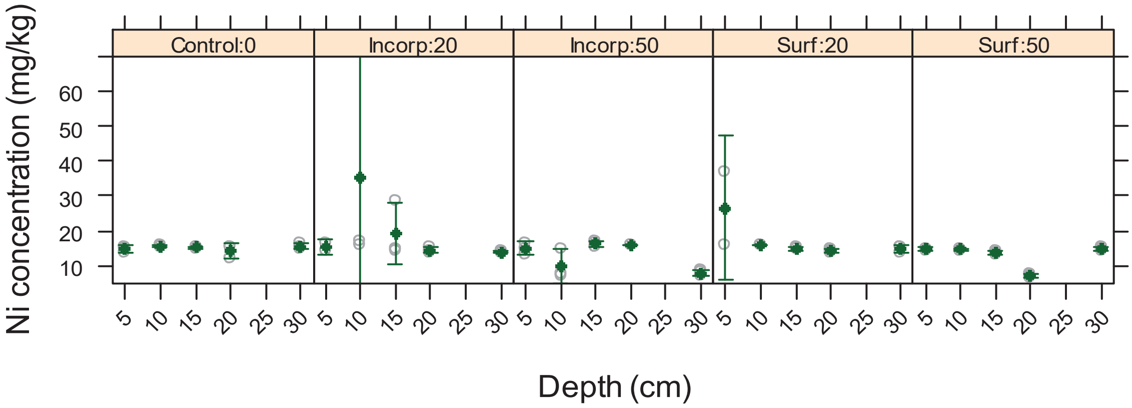


18 month

Figure B.2.9. Cr concentration in SL3 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (o) with means and 95% confidence intervals



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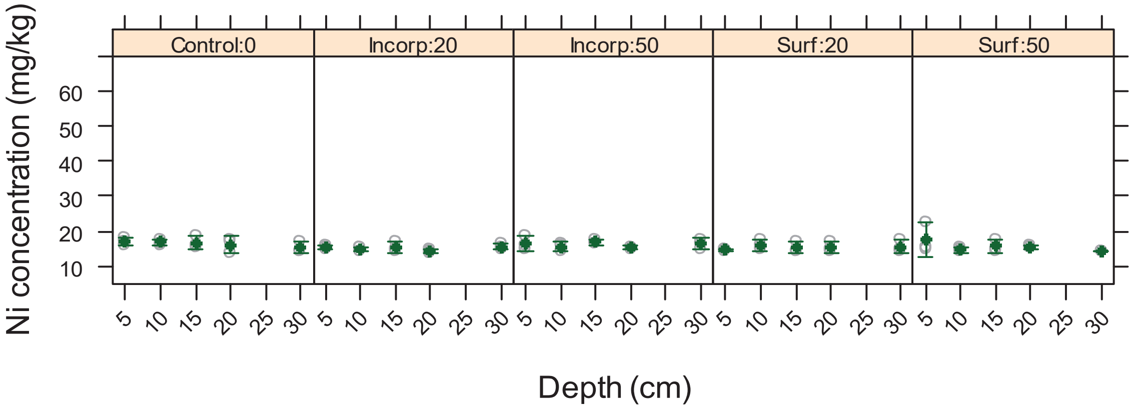

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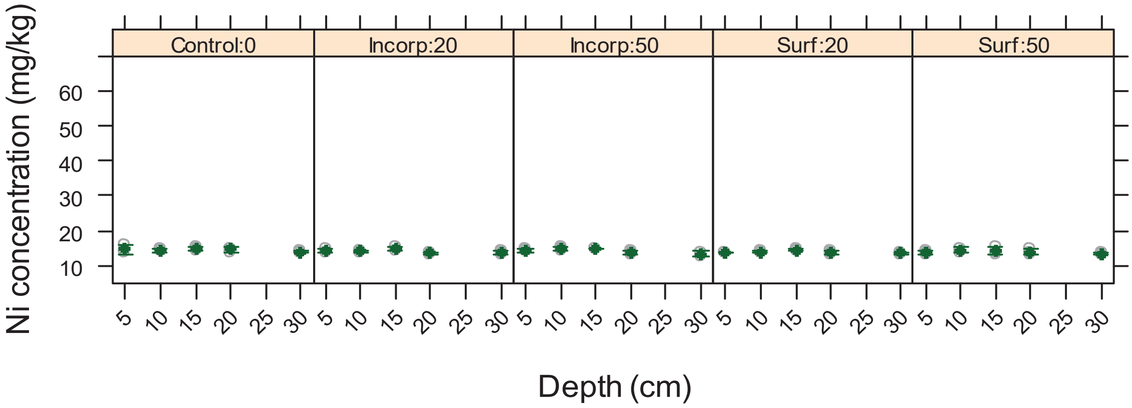
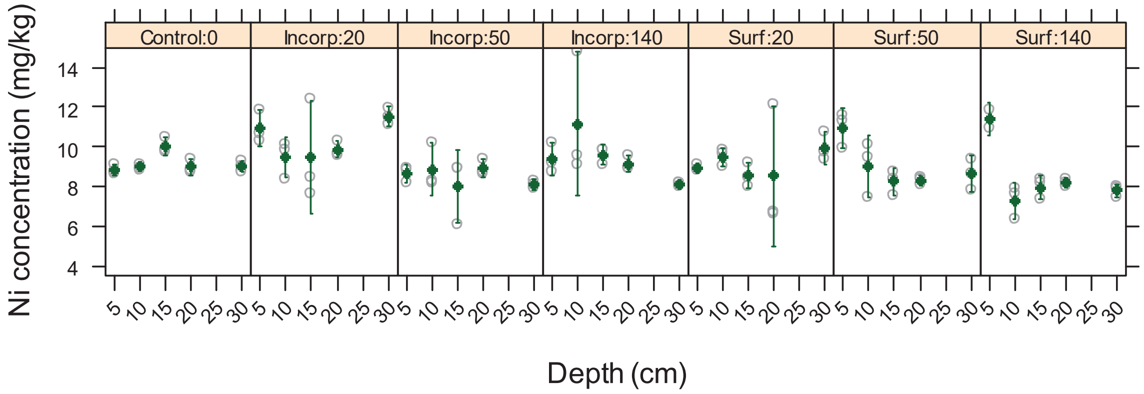


18 month

Figure B.2.10. Ni concentration in SL1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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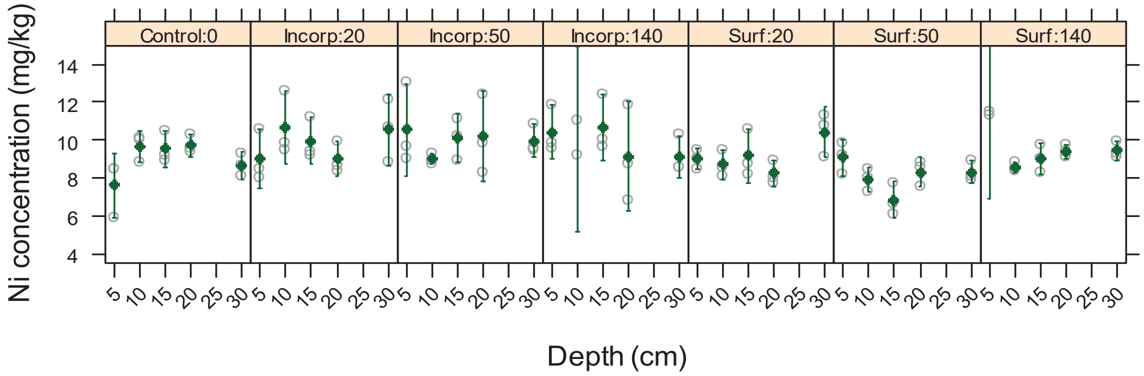

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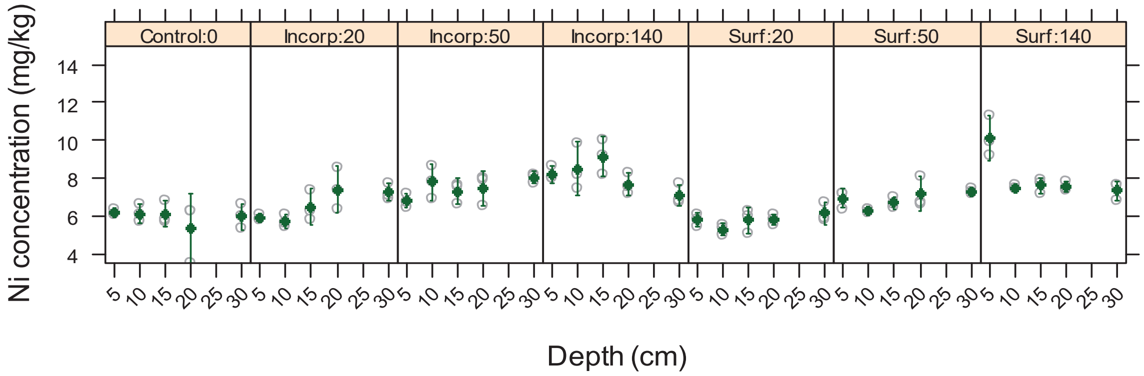
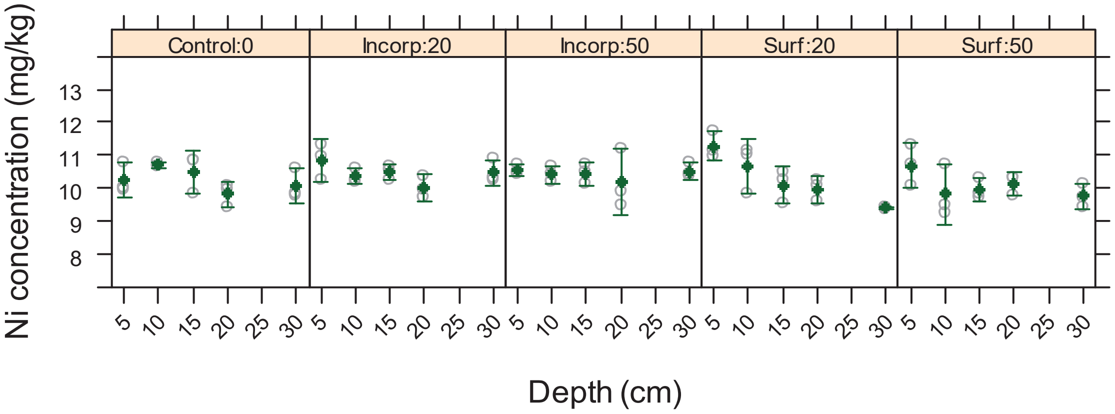


18 month

Figure B.2.11. Ni concentration in SL2 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20, 50 and 140 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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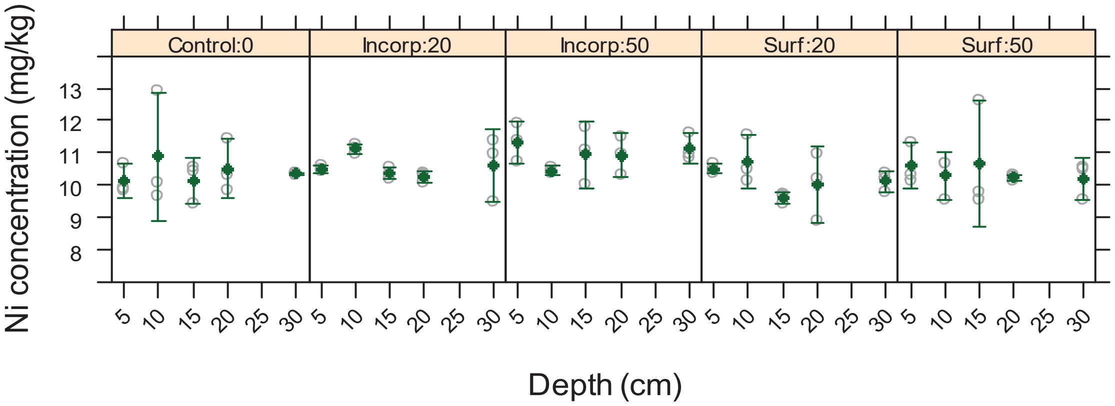

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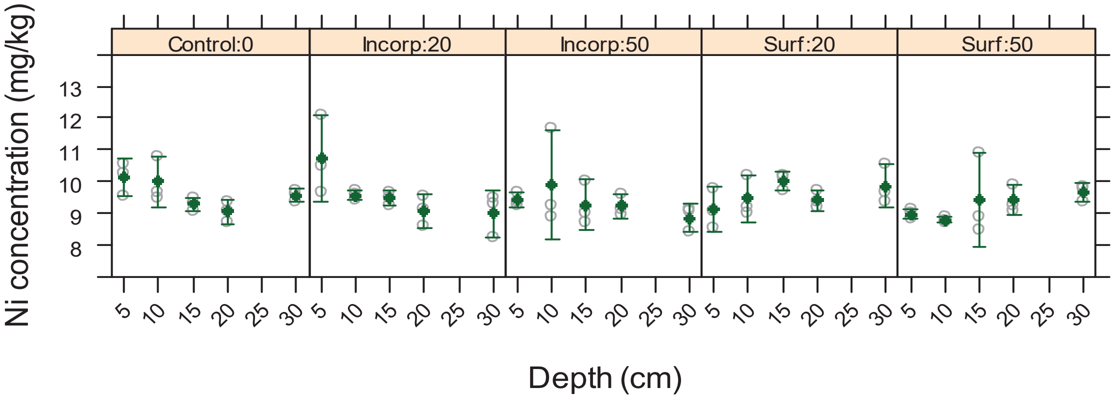
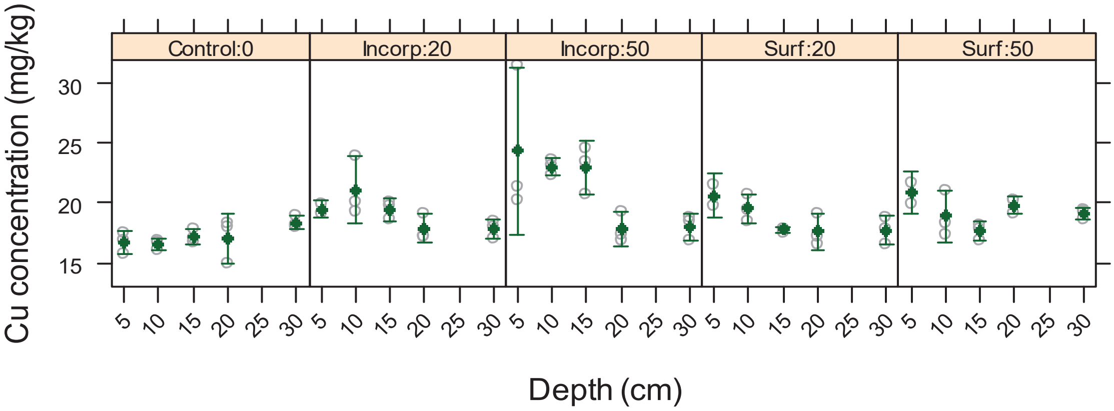


18 month

Figure B.2.12. Ni concentration in SL3 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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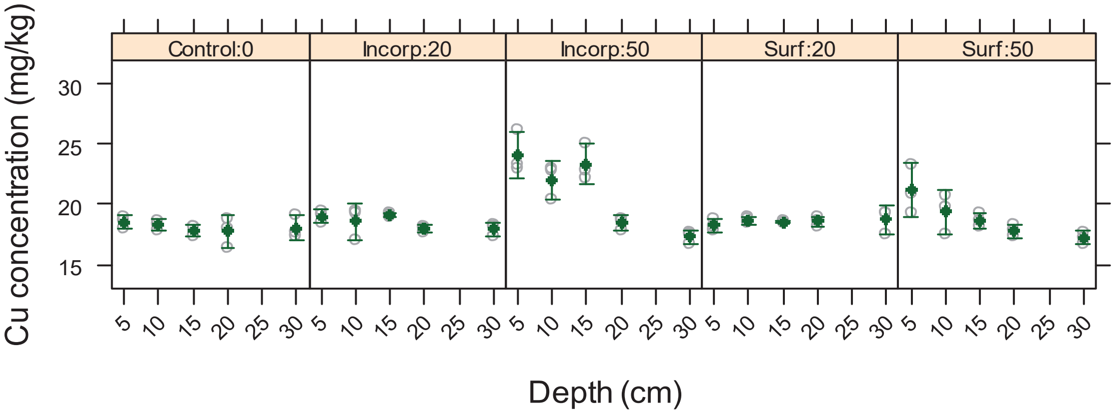

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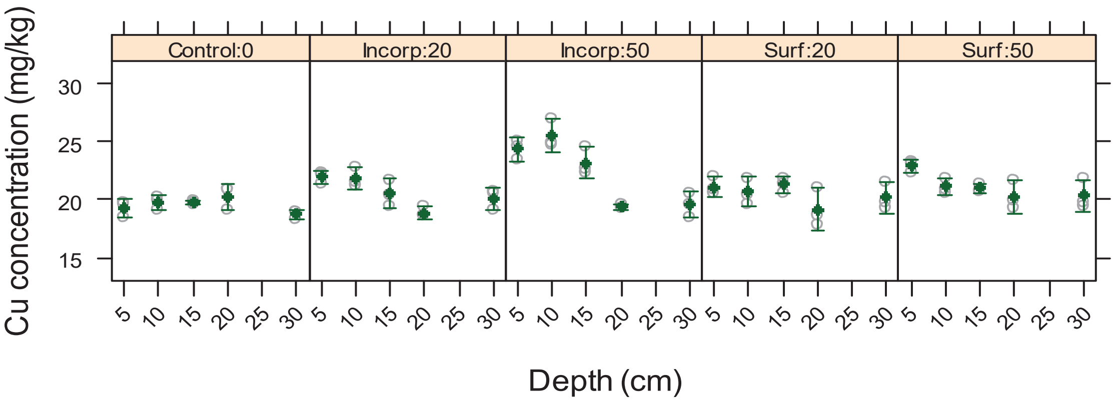
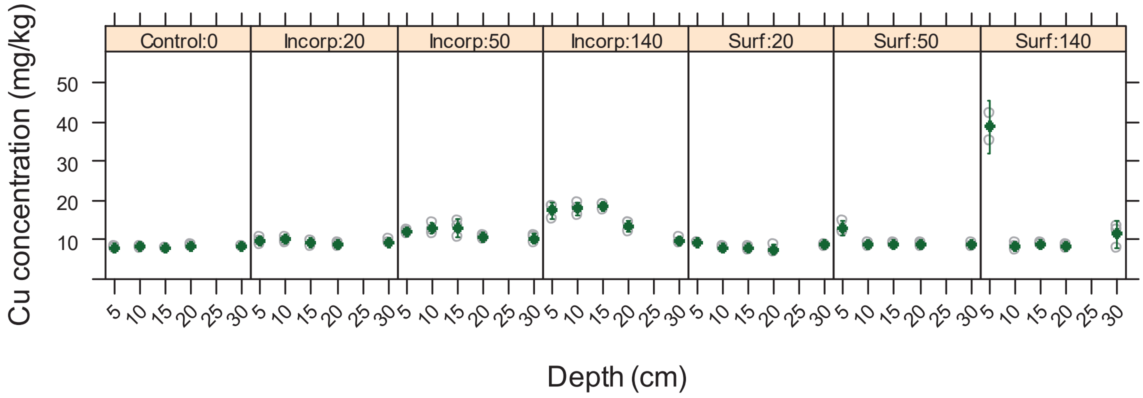


18 month

Figure B.2.13. Cu concentration in SL1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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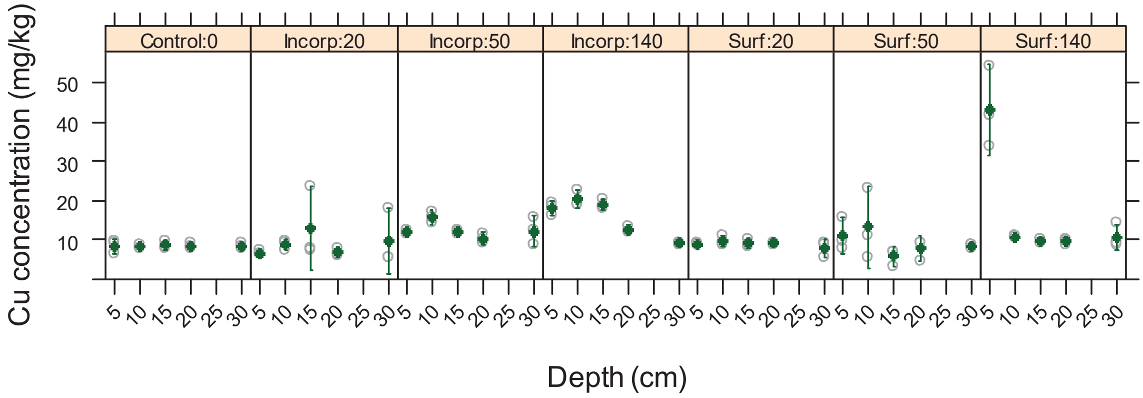

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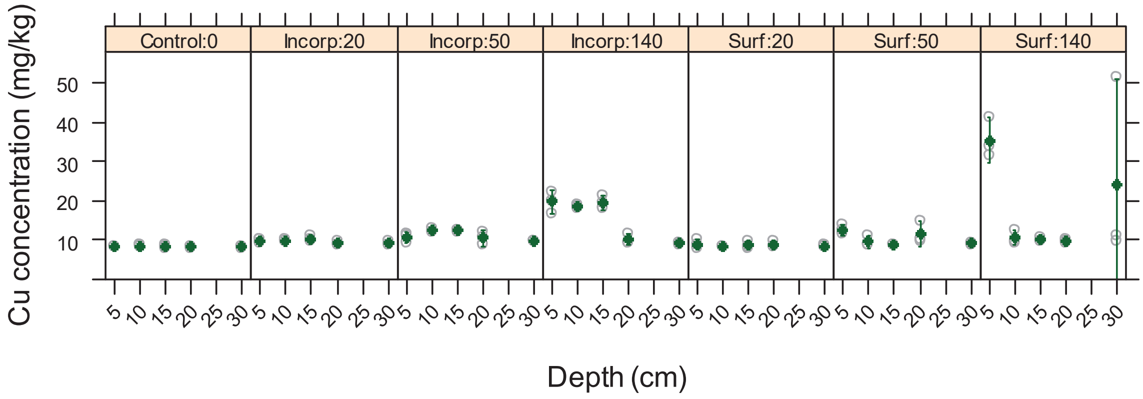
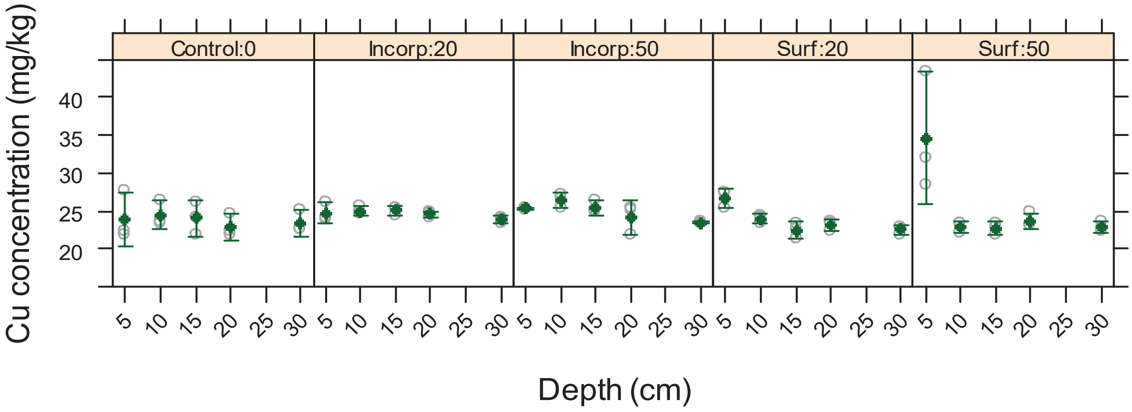


18 month

Figure B.2.14. Cu concentration in SL2 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20, 50 and 140 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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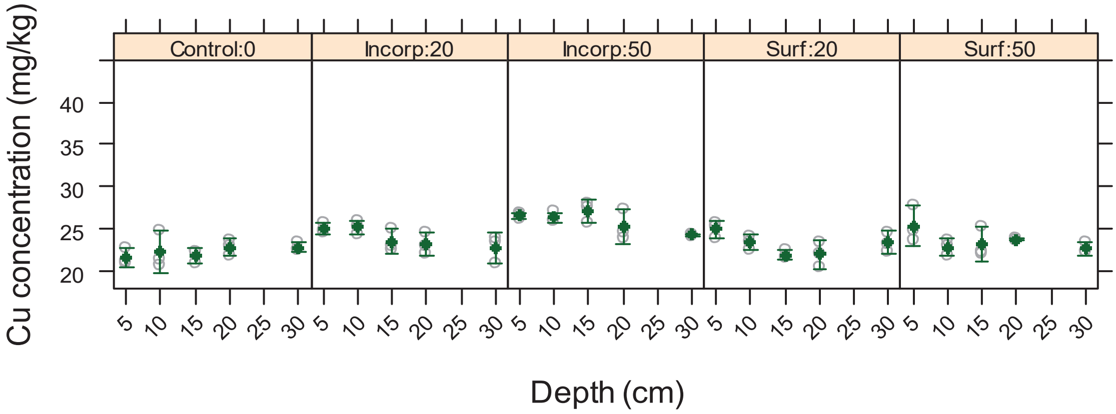

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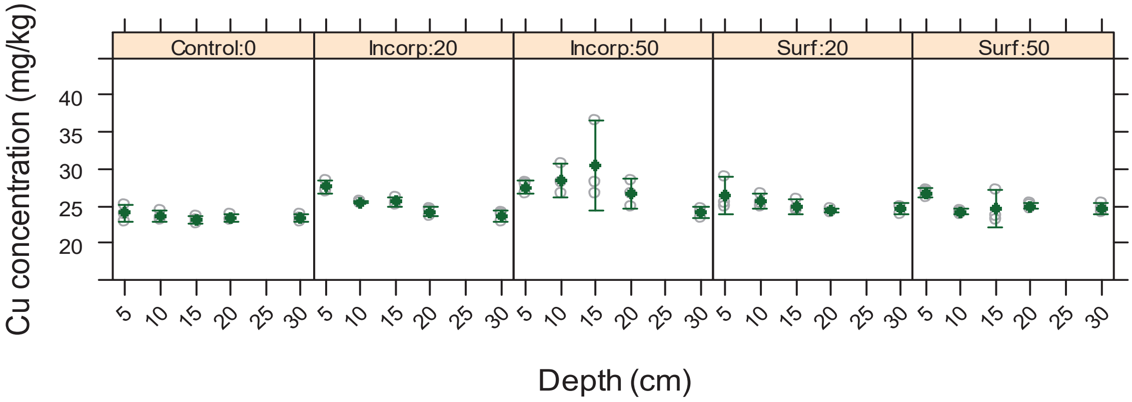
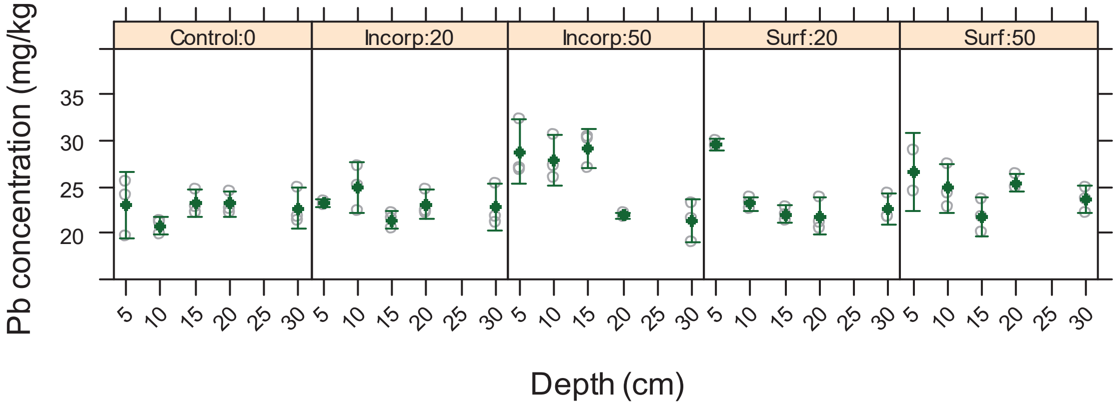


18 month

Figure B.2.15. Cu concentration in SL3 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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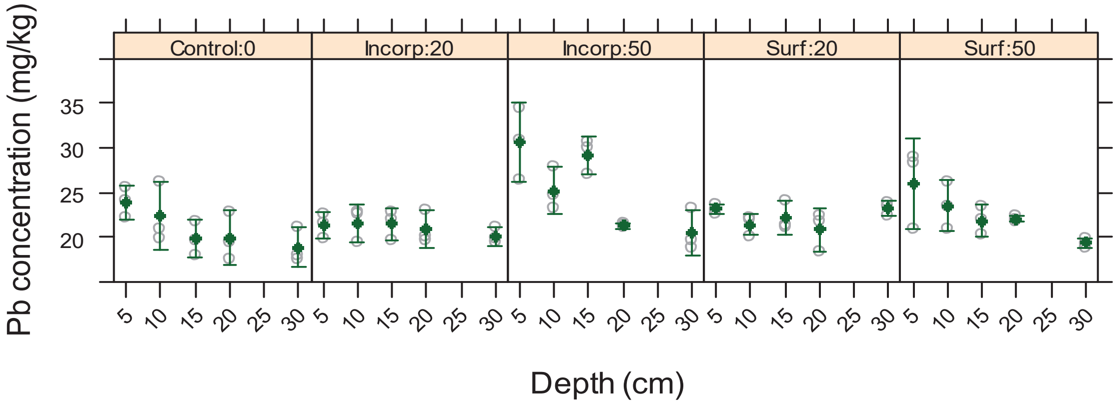

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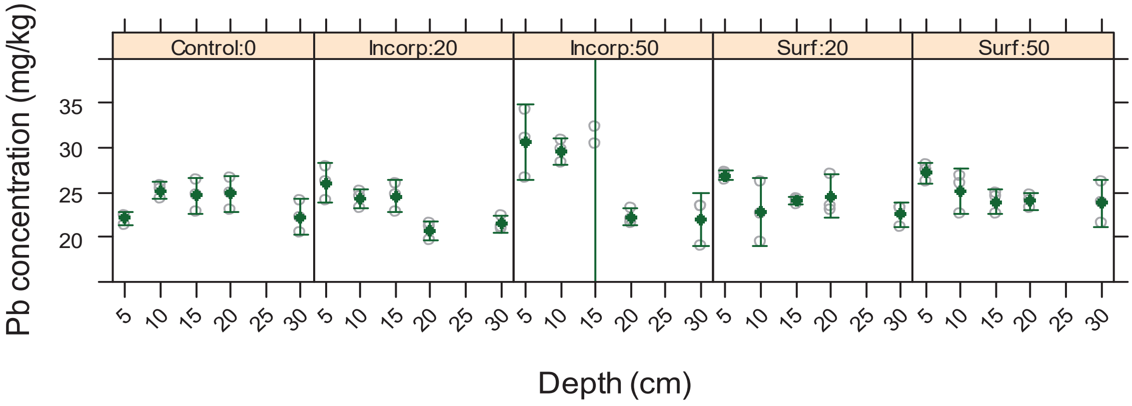
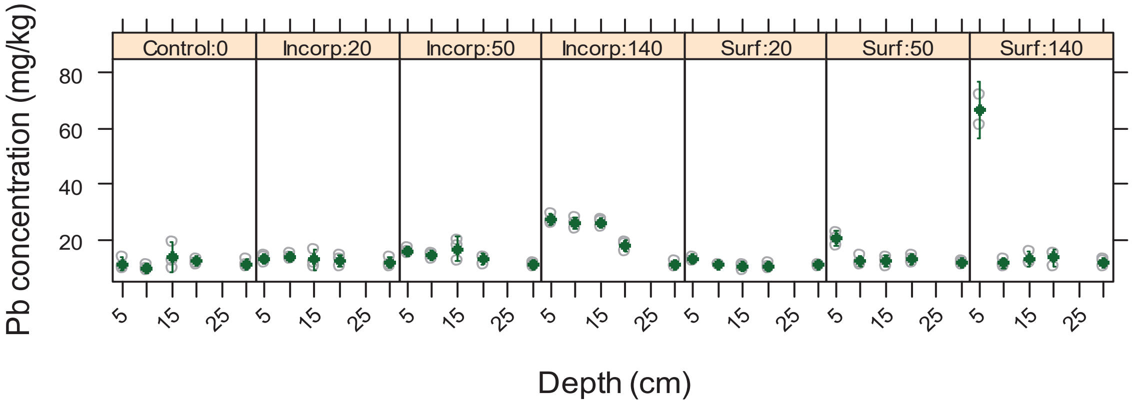


18 month

Figure B.2.16. Pb concentration in SL1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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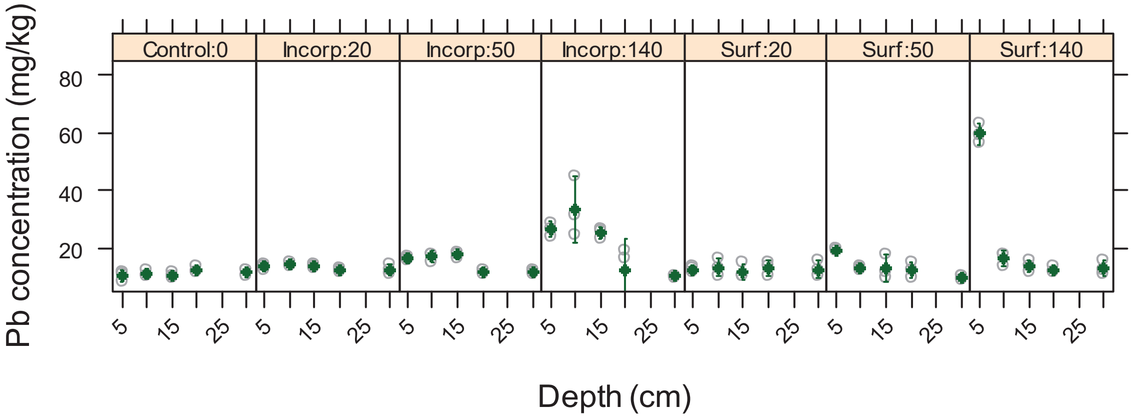

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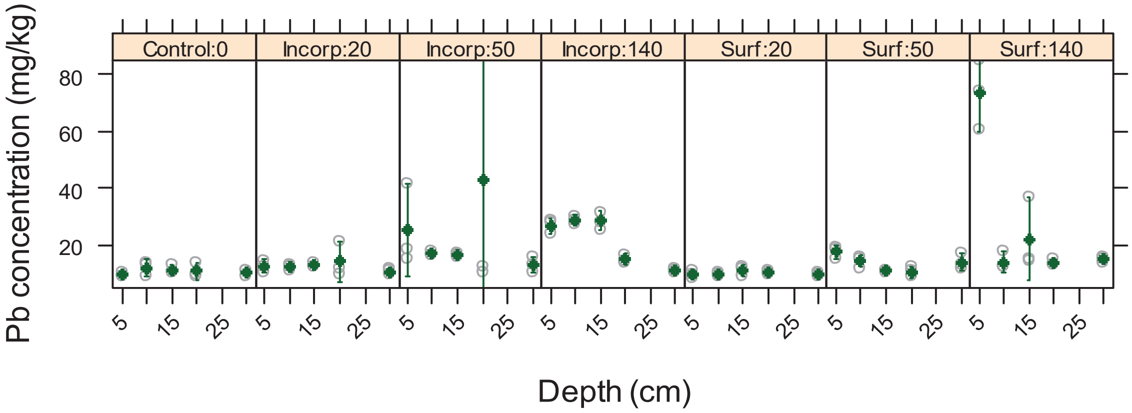
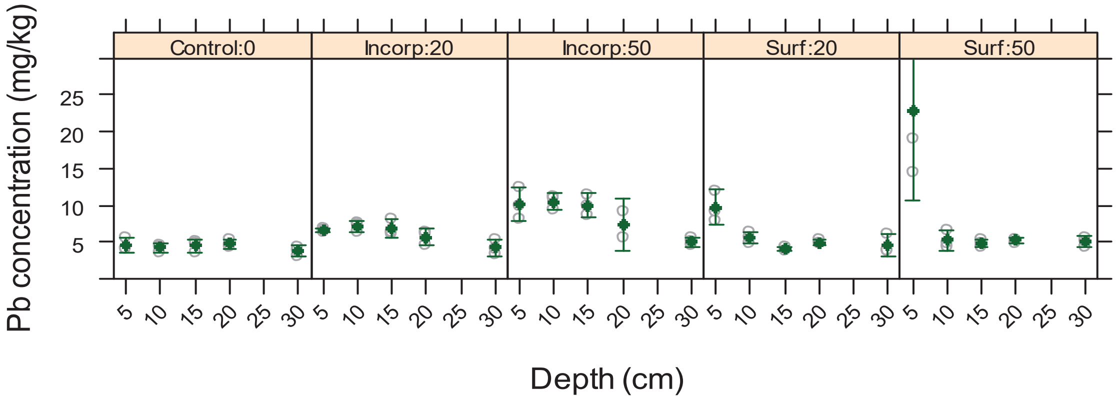


18 month

Figure B.2.17. Pb concentration in SL2 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20, 50 and 140 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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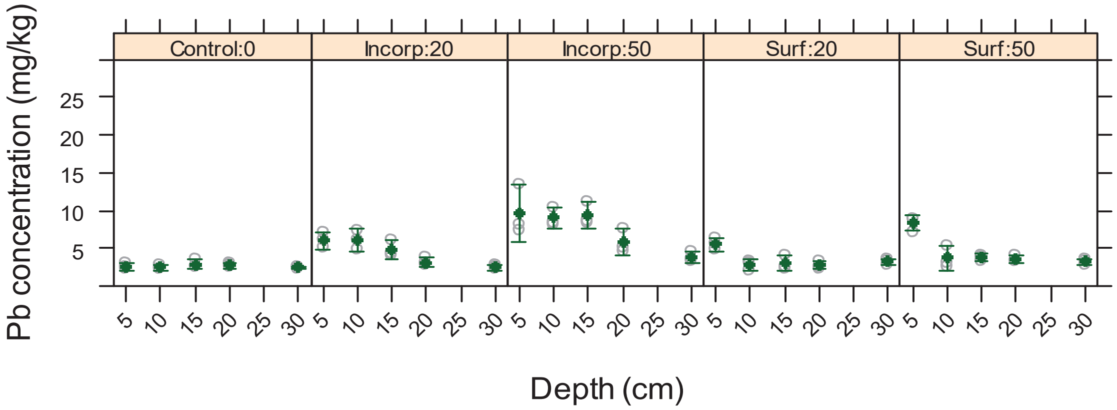

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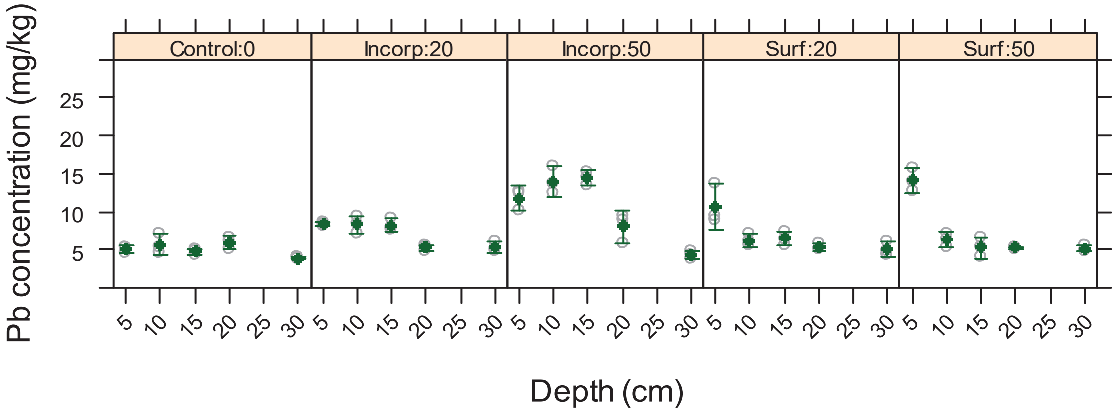
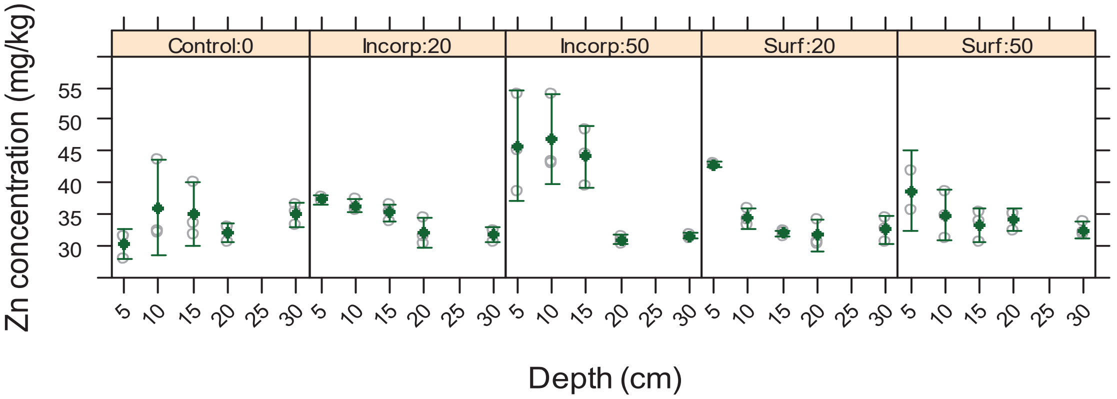


18 month

Figure B.2.18. Pb concentration in SL3 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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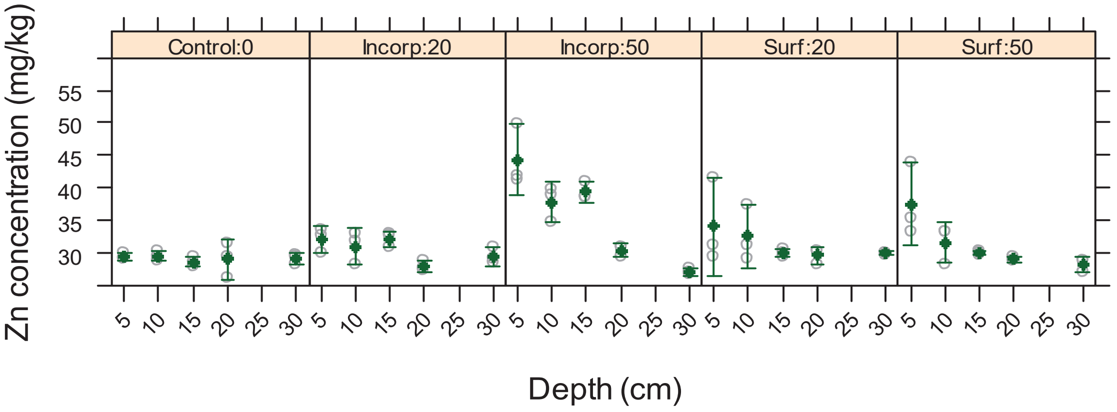

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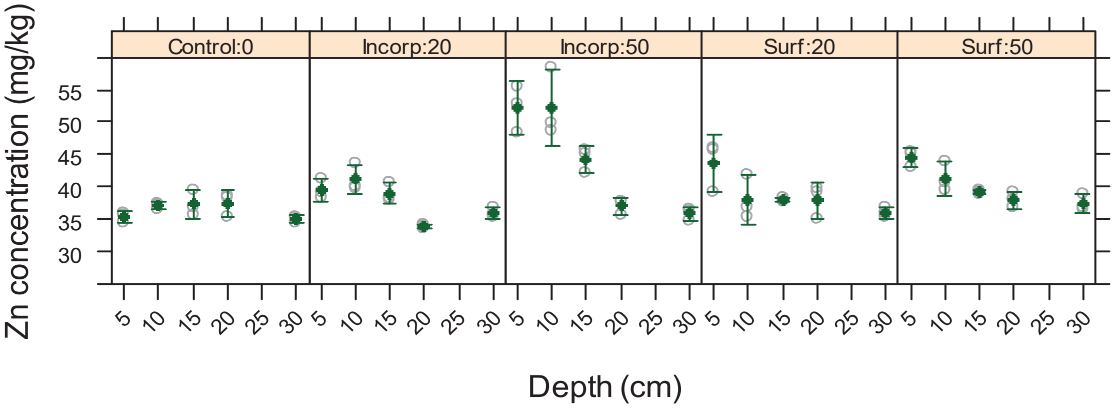
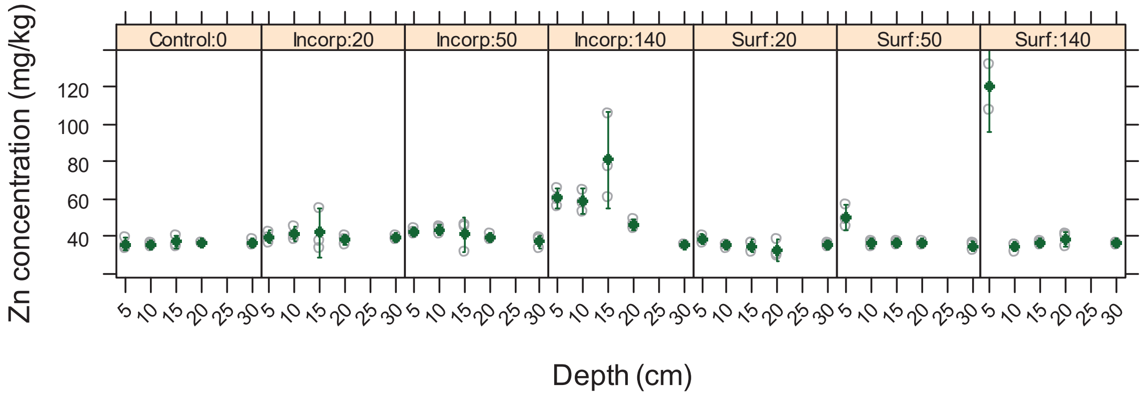
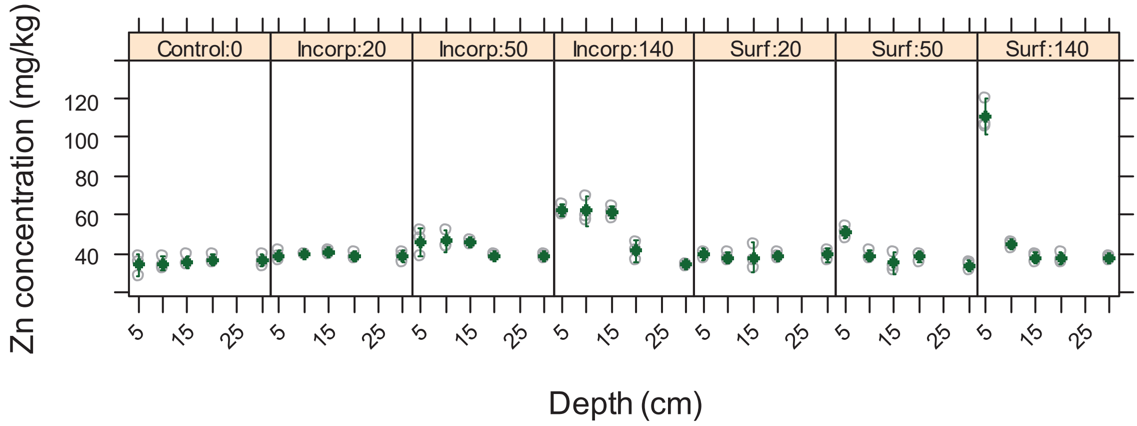


18 month

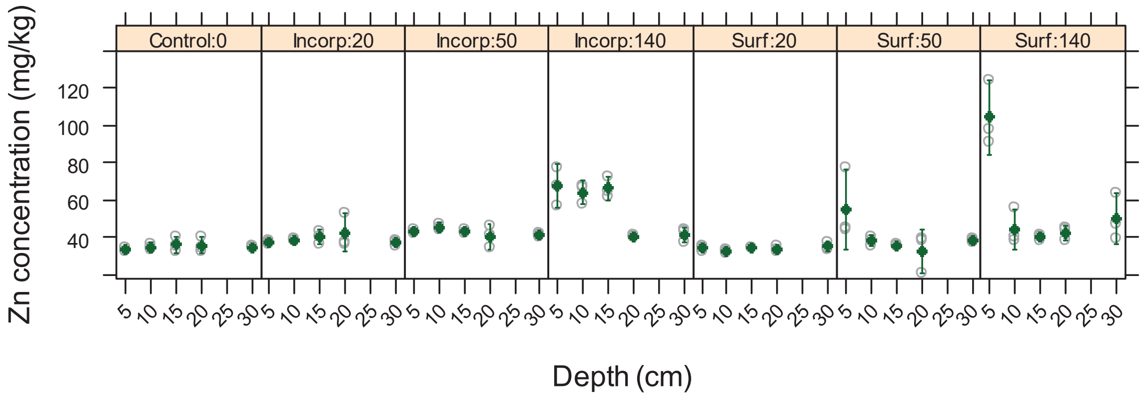
Figure B.2.19. Zn concentration in SL1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



6 month

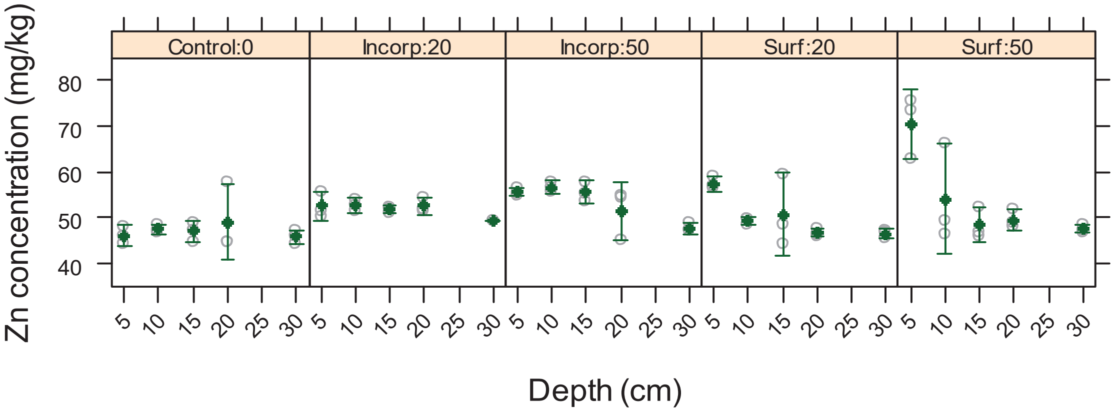


12 month



18 month

Figure B.2.20. Zn concentration in SL2 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20, 50 and 140 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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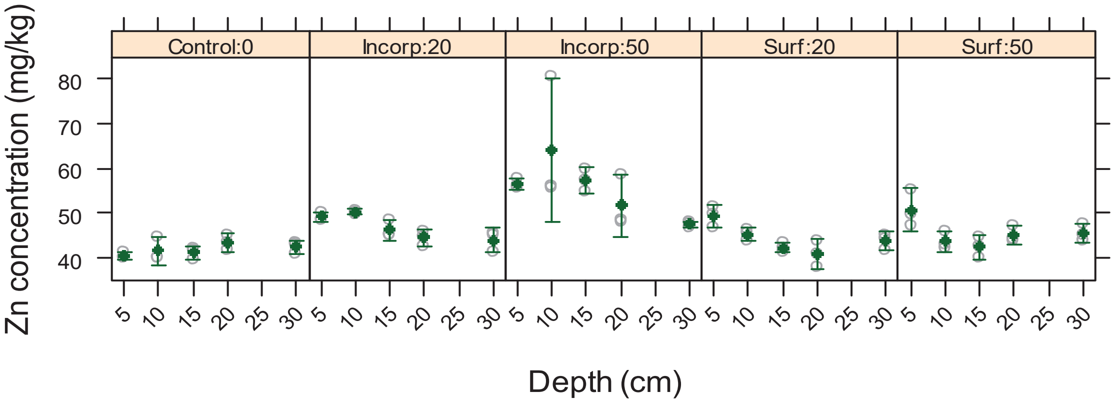

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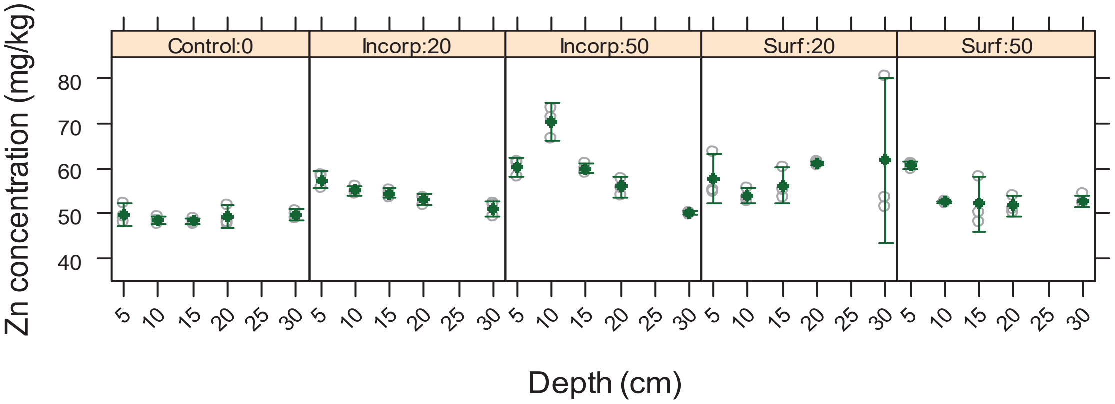
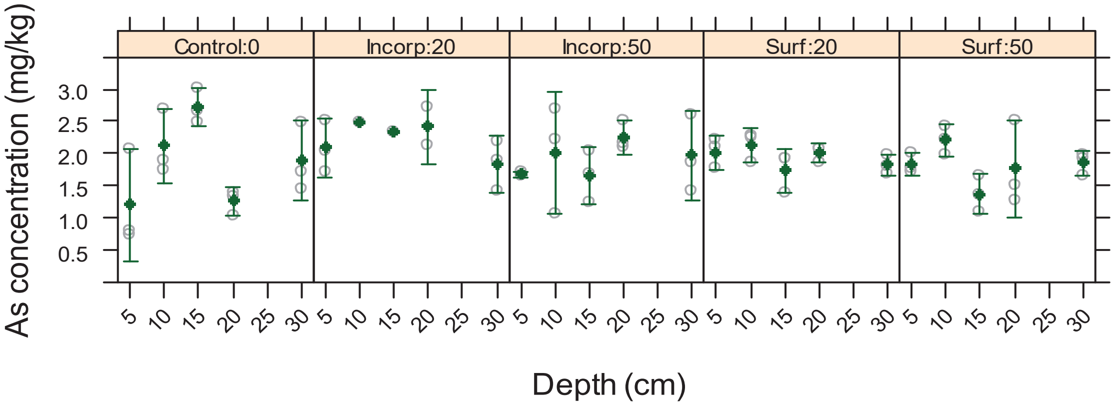


18 month

Figure B.2.21. Zn concentration in SL3 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals

Appendix B3

Changes of metal and metalloid concentrations and distribution in three clay and organic soils (C1, C2, C3)



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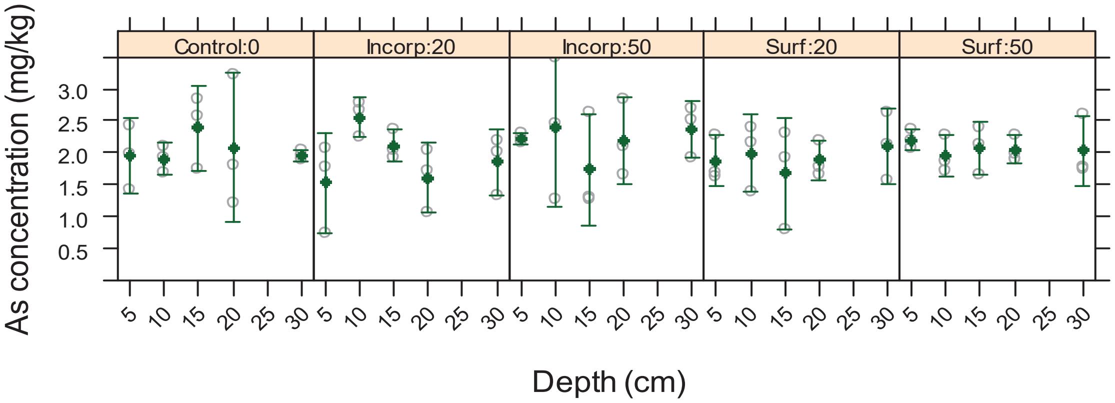

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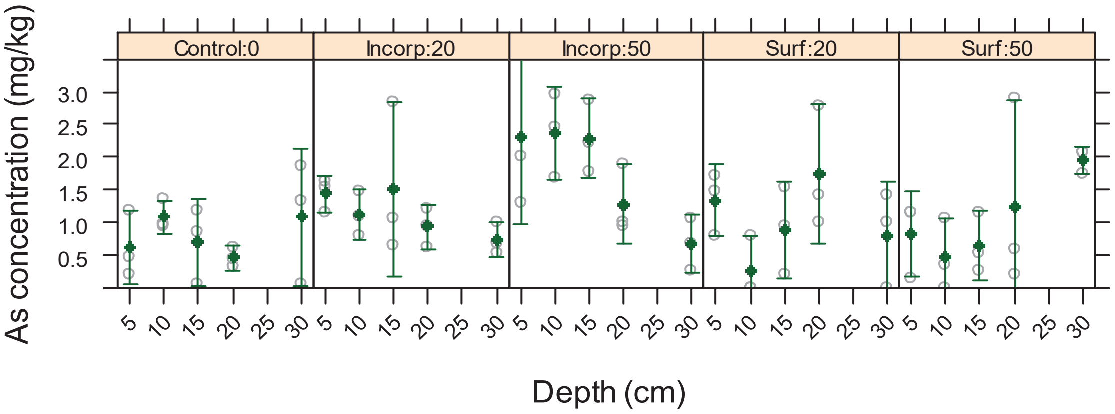
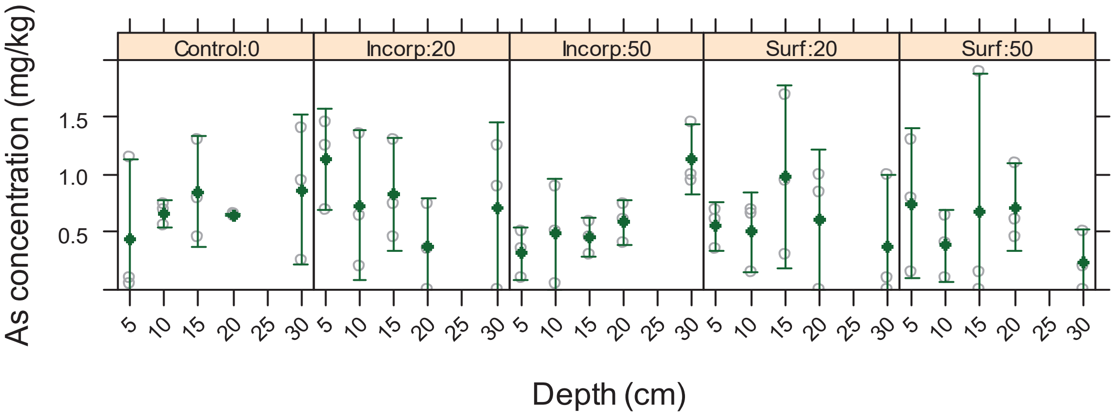
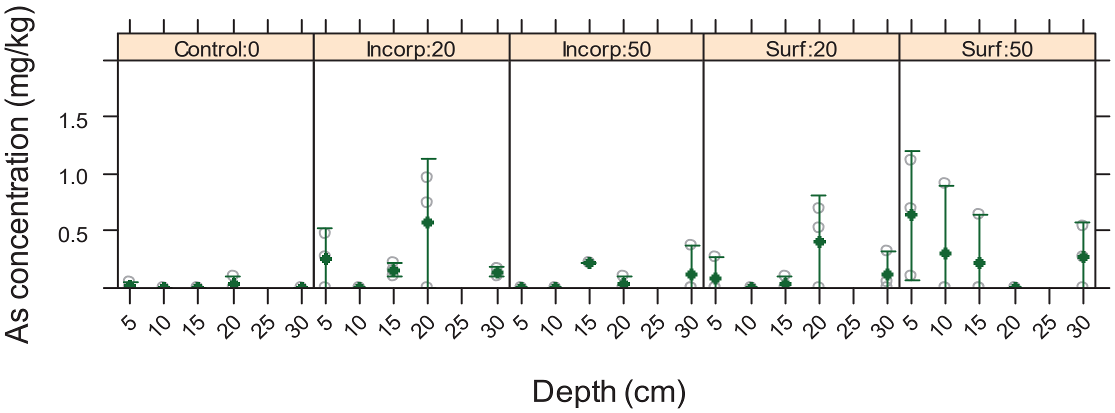


18 month

Figure B.3.1. As concentration in C1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (o) with means and 95% confidence intervals



6 month



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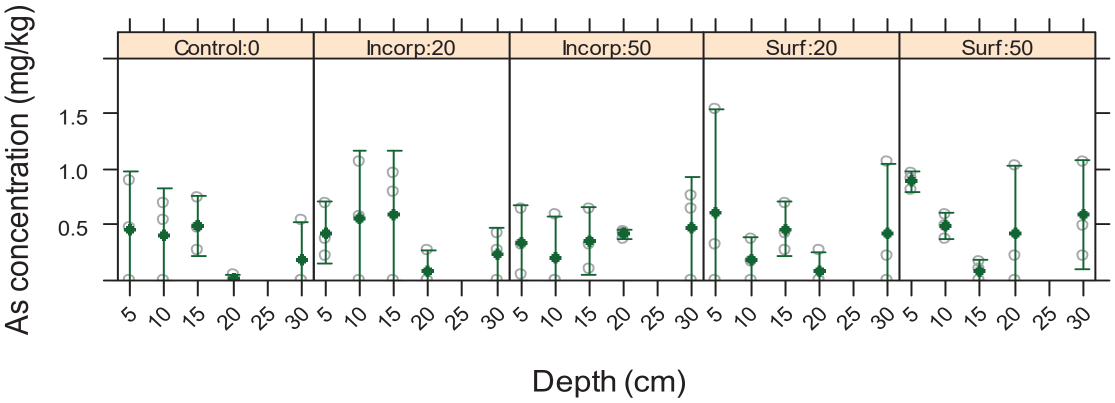
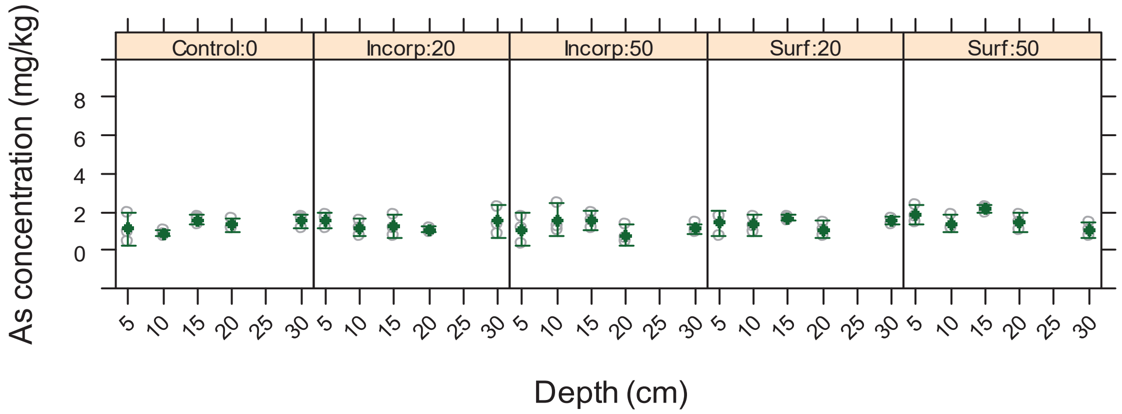


18 month

Figure B.3.2. As concentration in C2 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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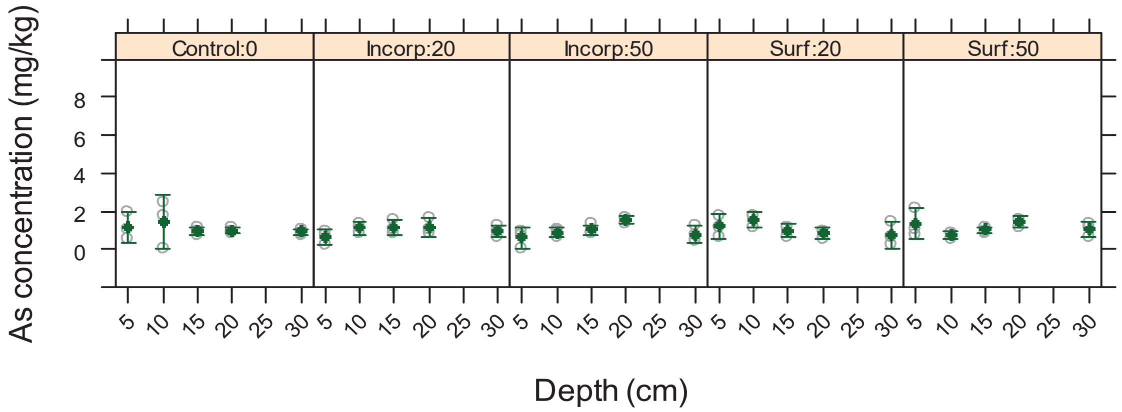

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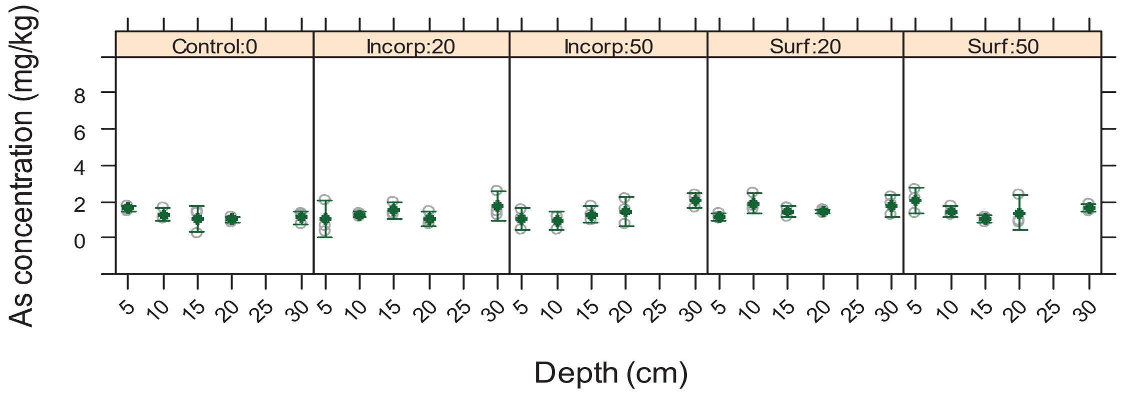
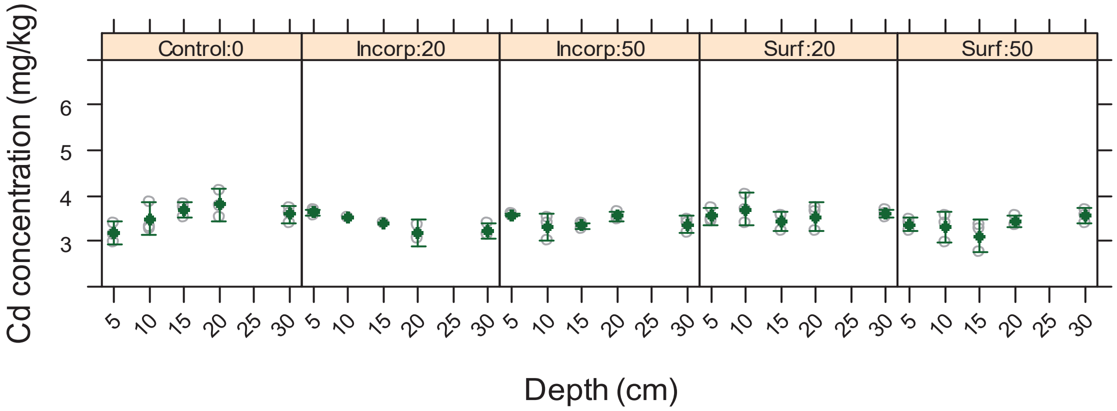


18 month

Figure B.3.3. As concentration in C3 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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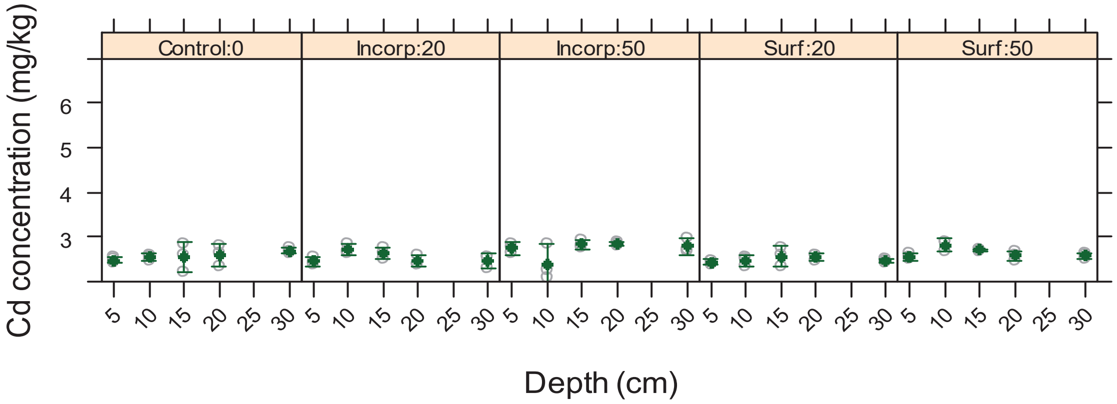

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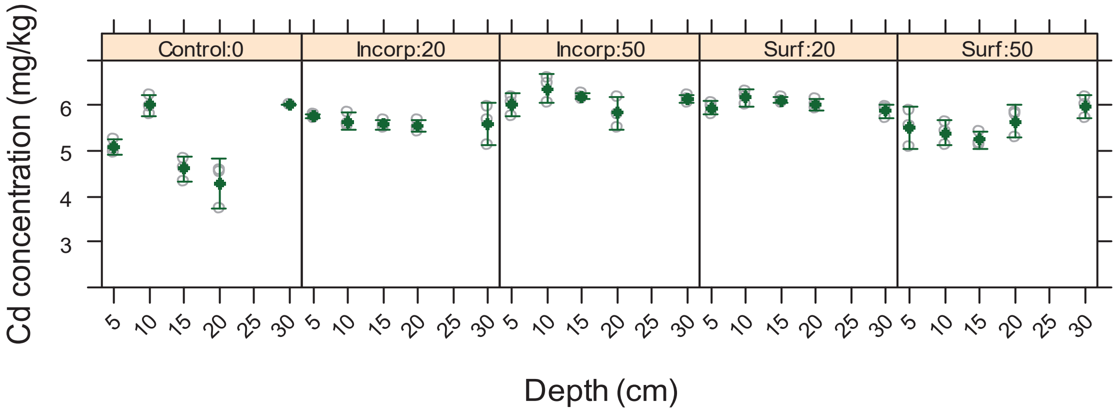
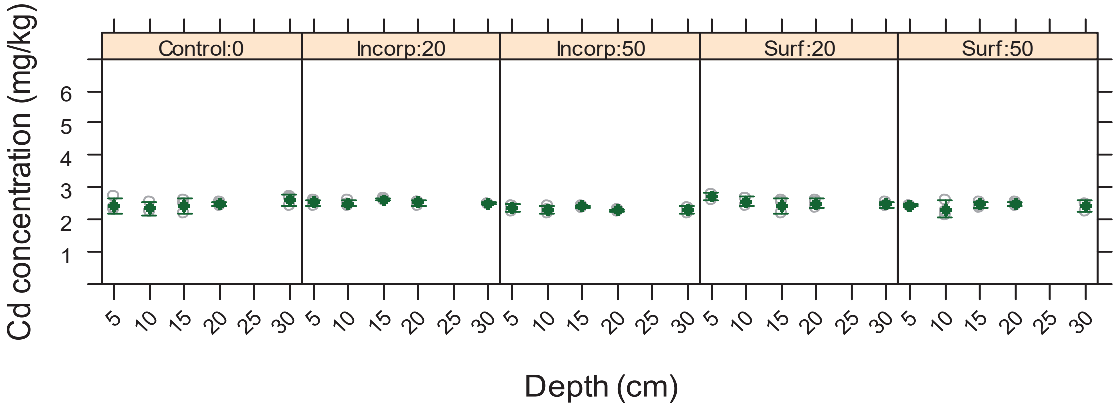


12 month

Figure B.3.4. Cd concentration in C1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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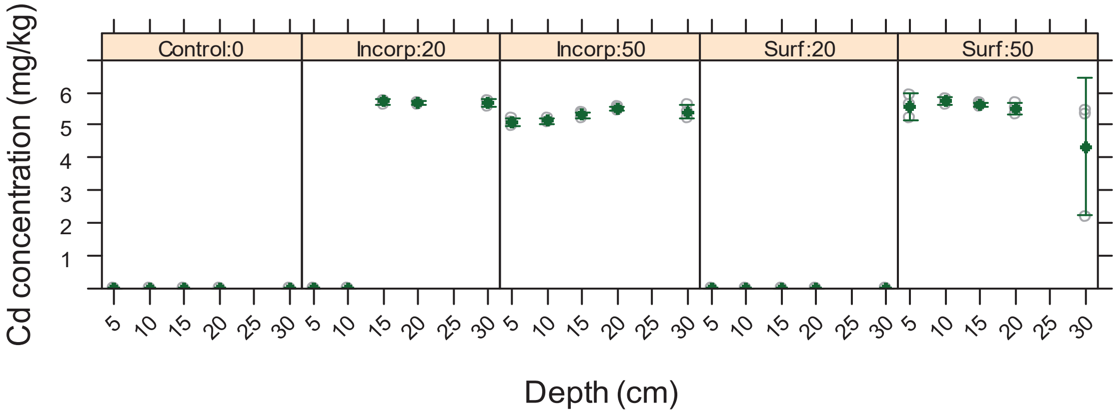

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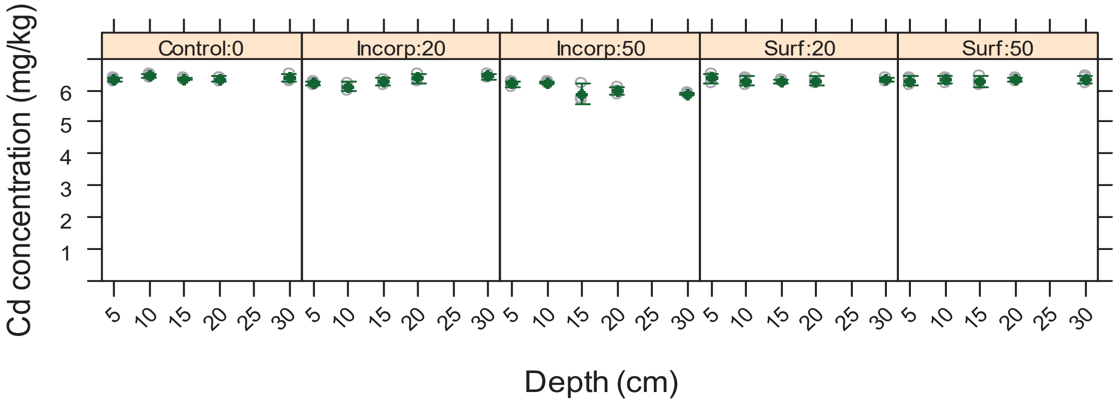
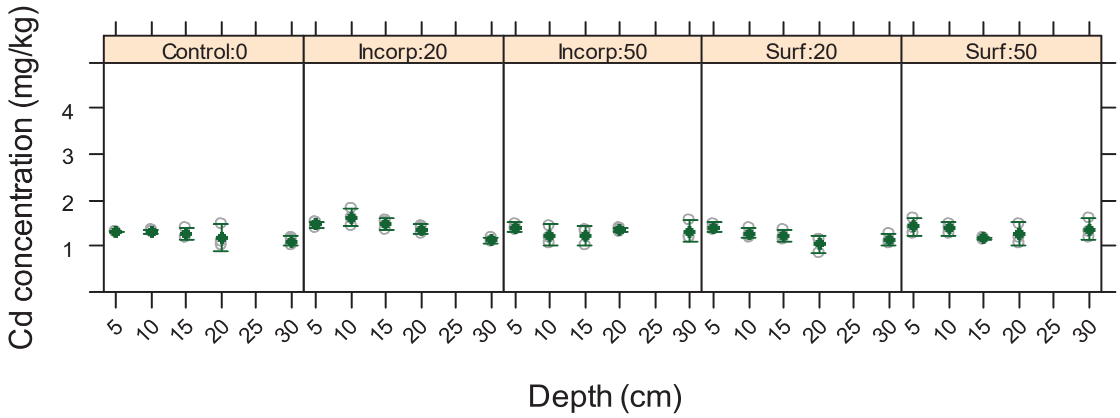


18 month

Figure B.3.5. Cd concentration in C2 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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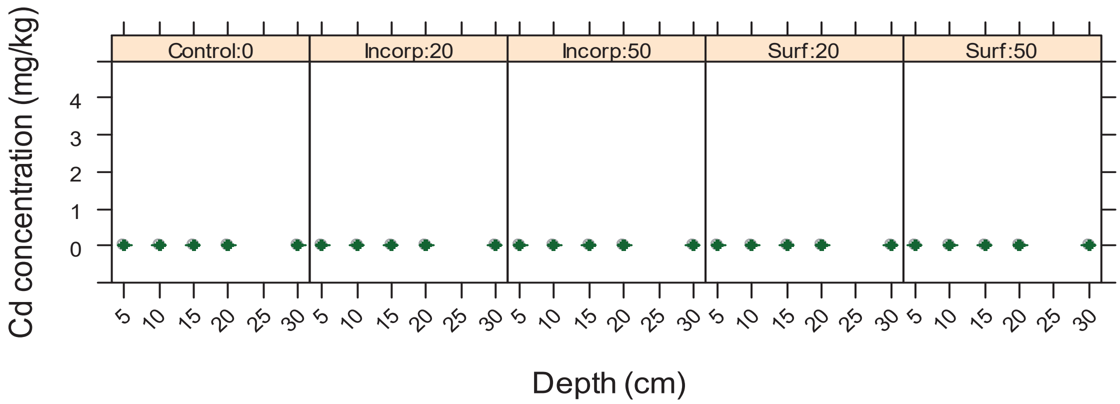

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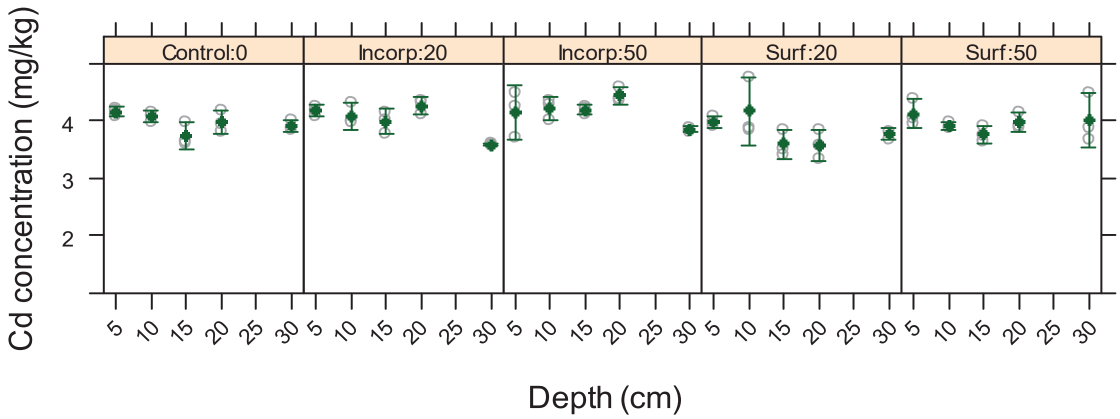
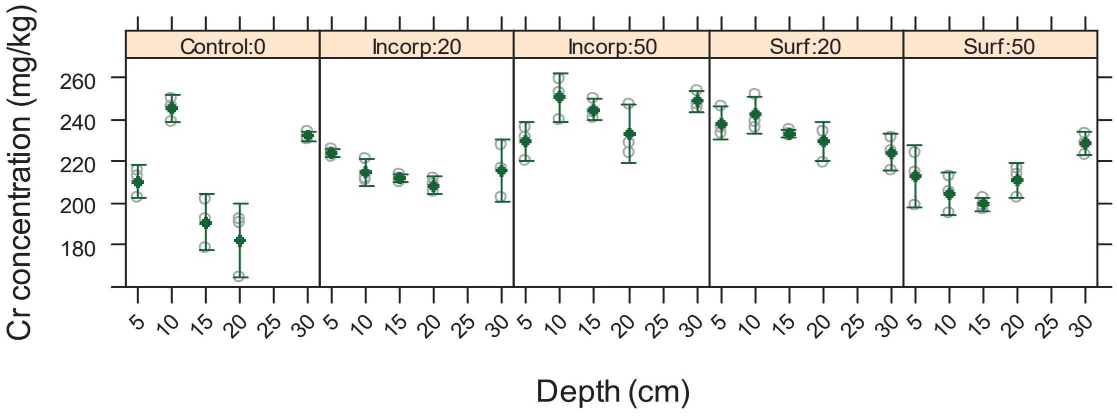


18 month

Figure B.3.6. Cd concentration in C3 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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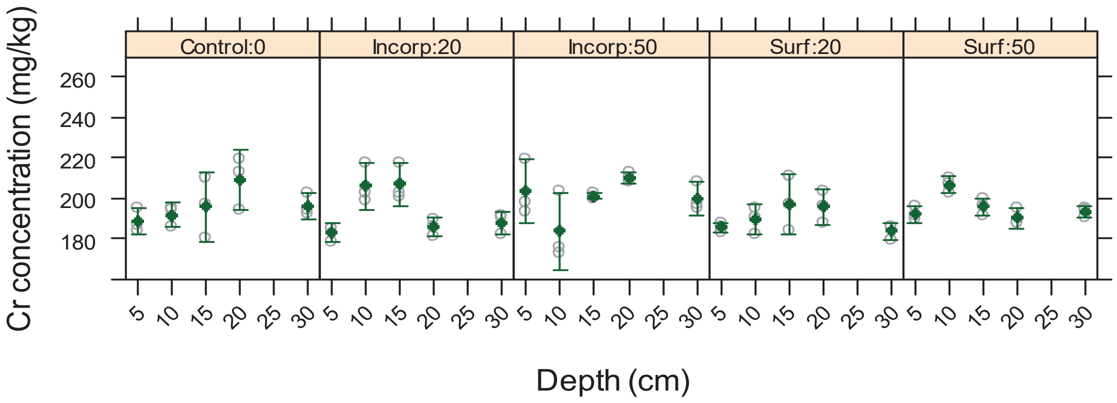

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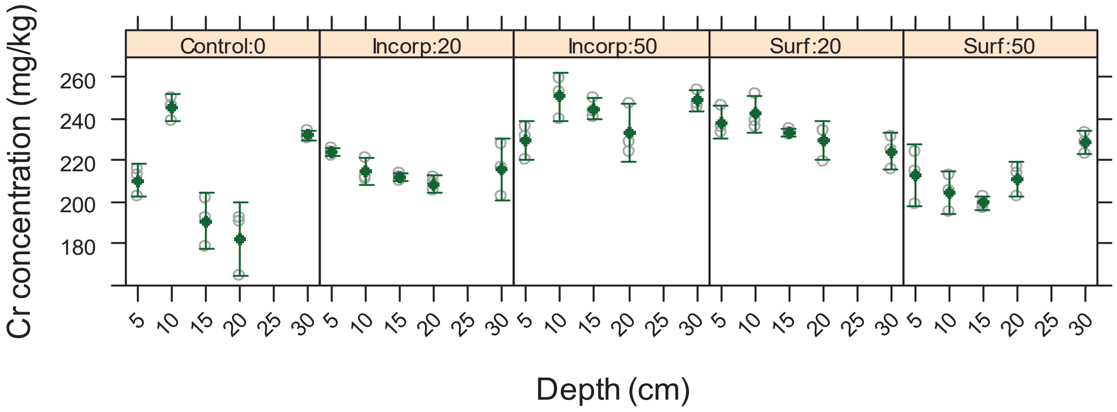
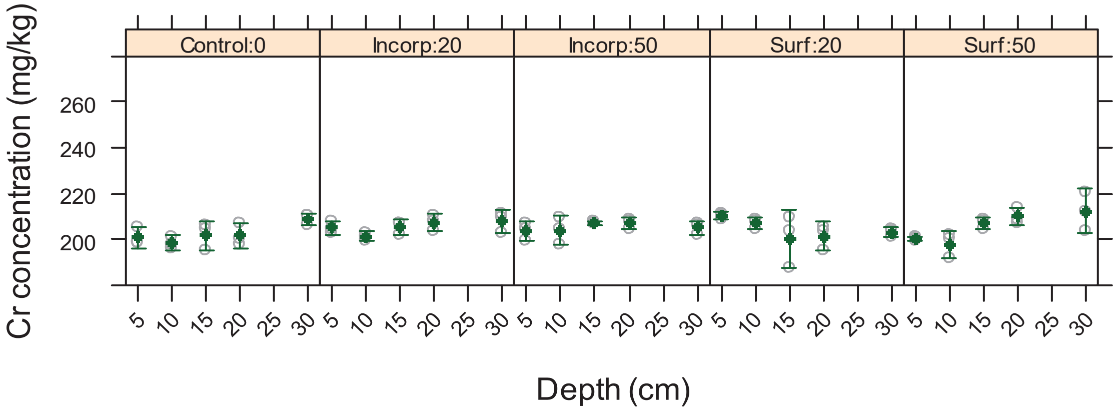


18 month

Figure B.3.7. Cr concentration in C1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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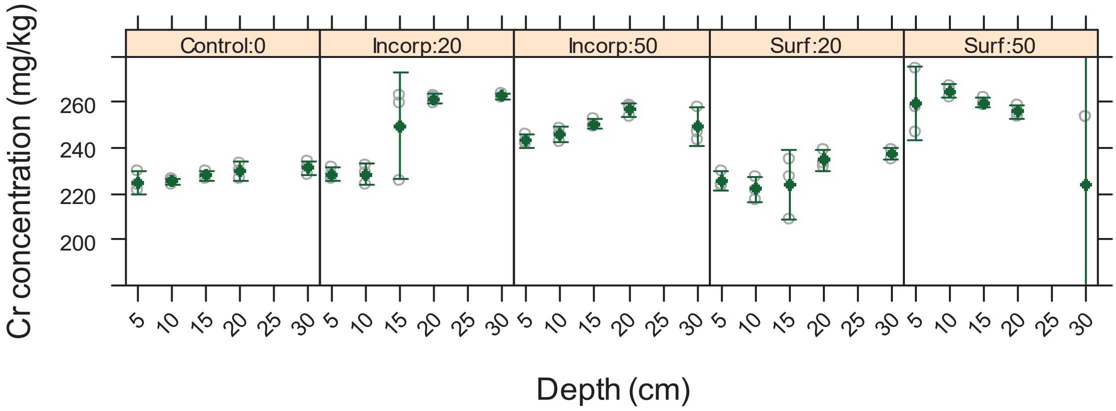

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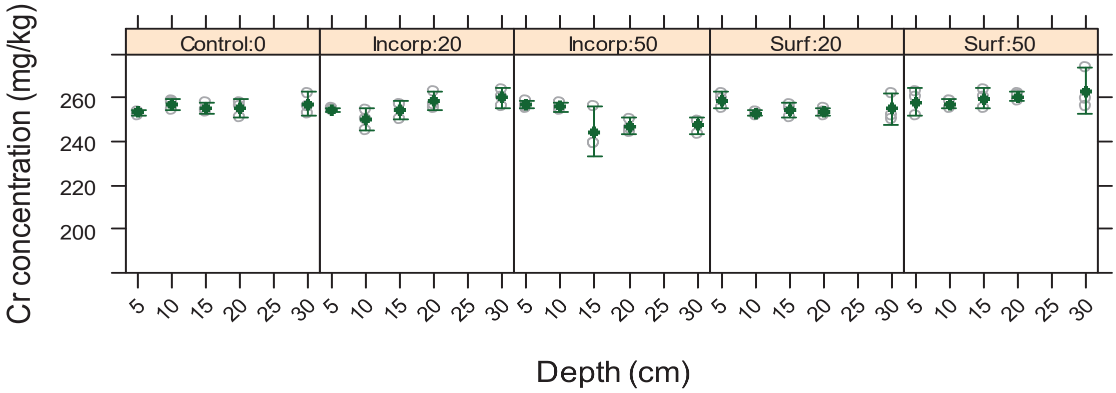
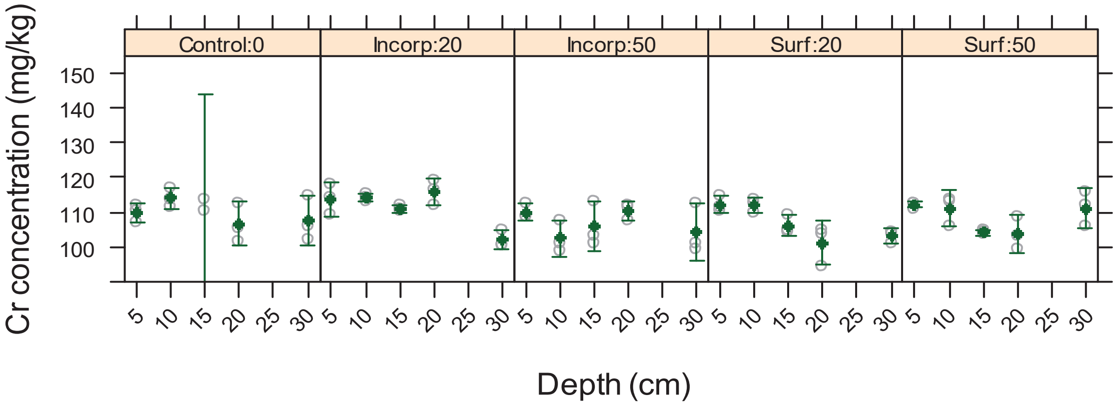


18 month

Figure B.3.8. Cr concentration in C2 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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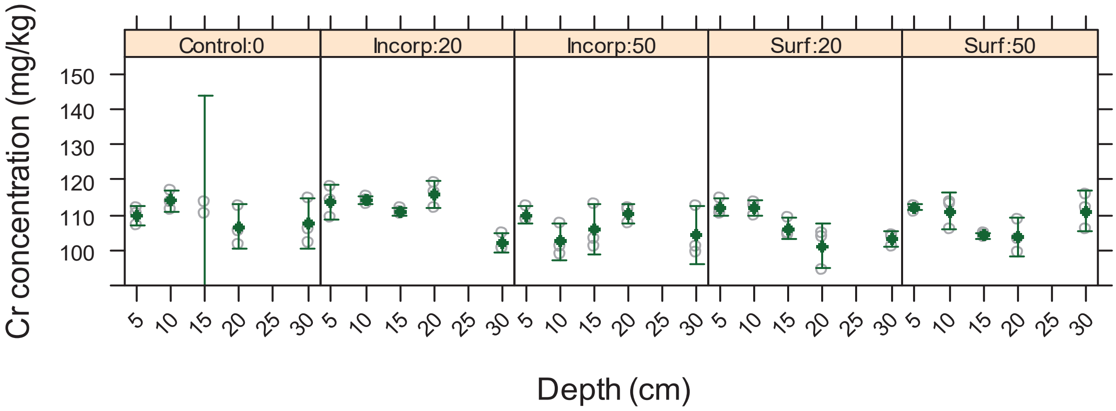

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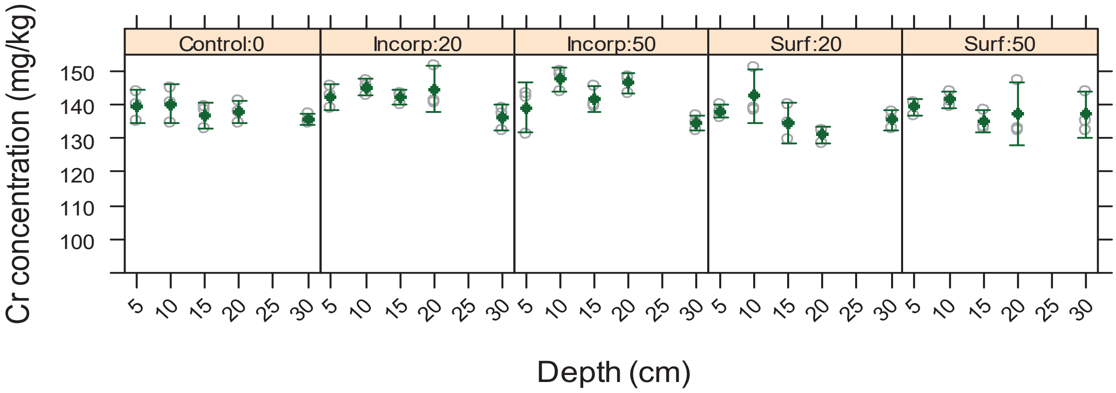
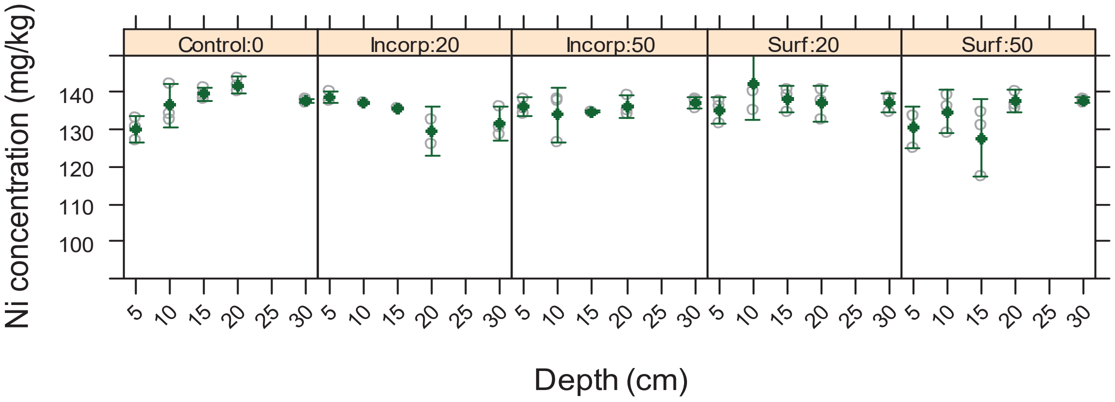


18 month

Figure B.3.9. Cr concentration in C3 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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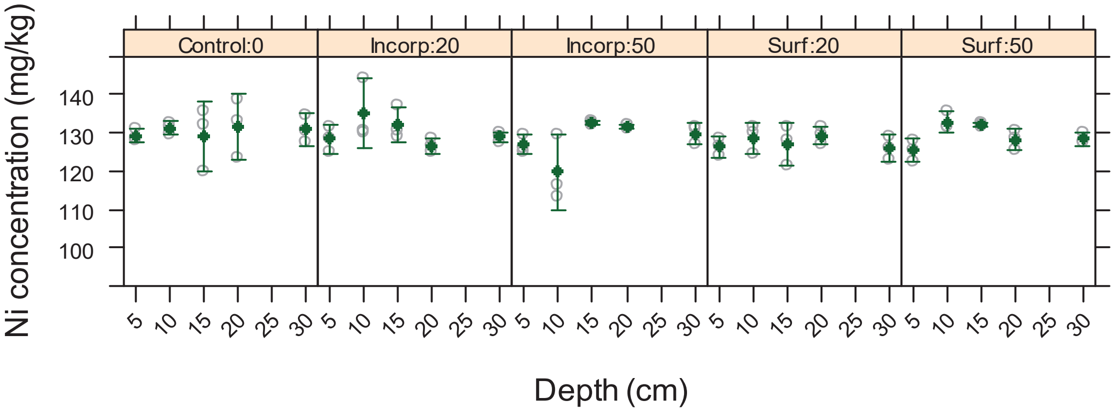

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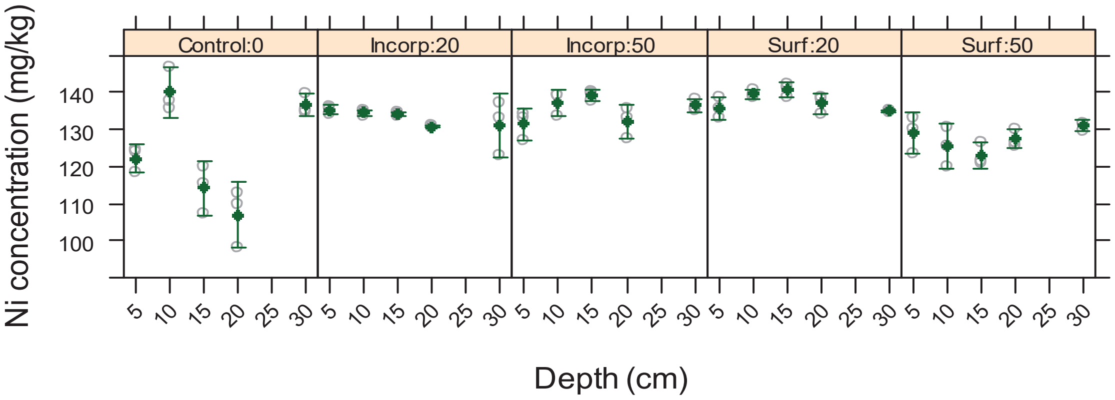
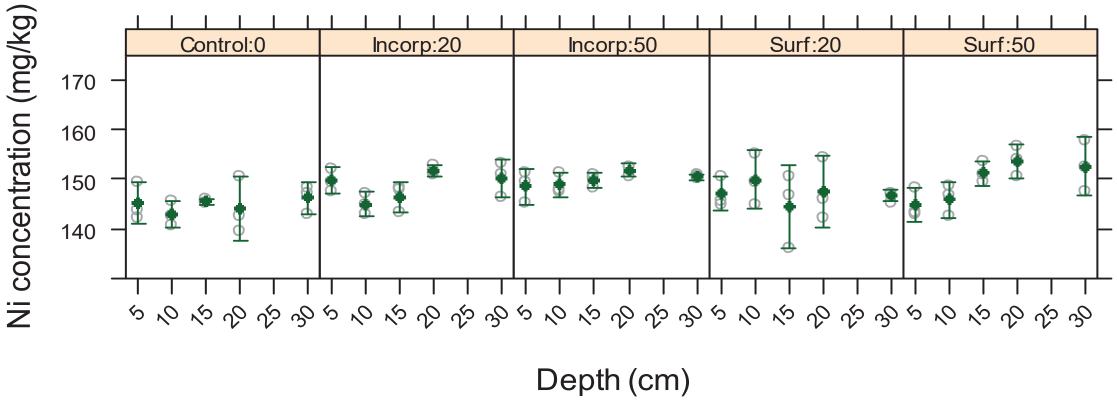


18 month

Figure B.3.10. Ni concentration in C1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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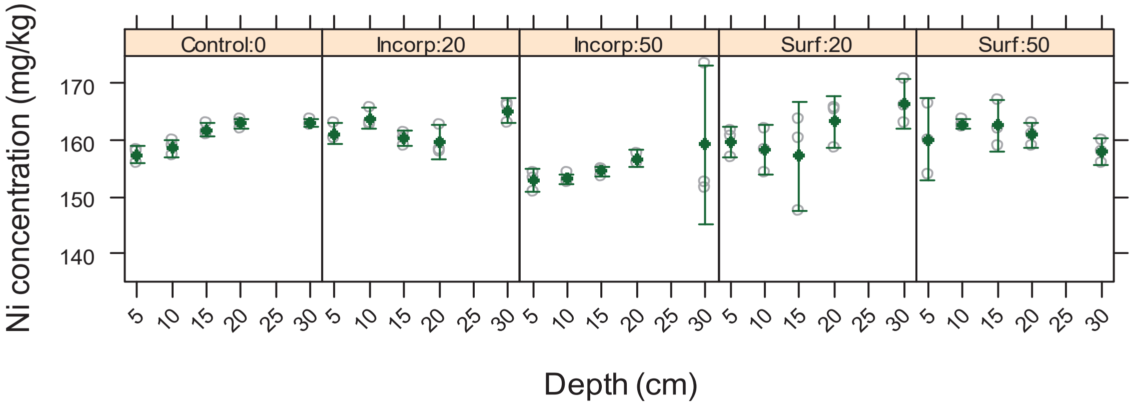

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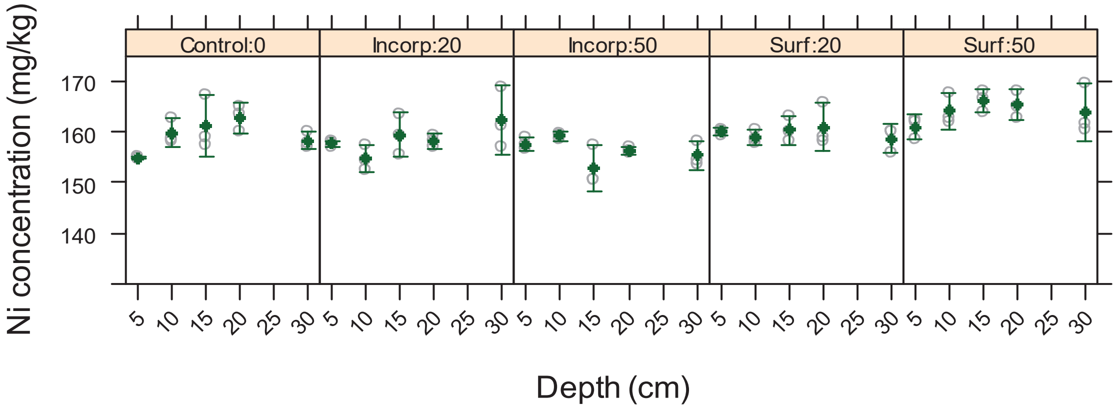
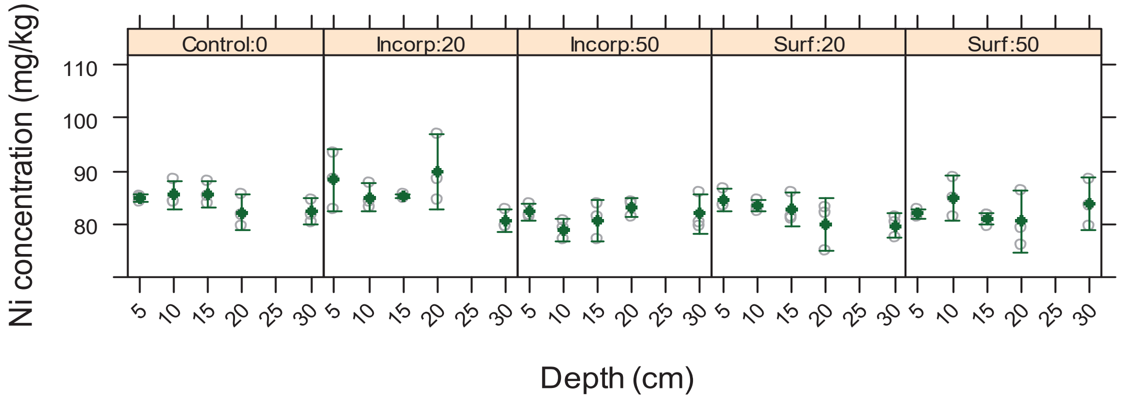


18 month

Figure B.3.11. Ni concentration in C2 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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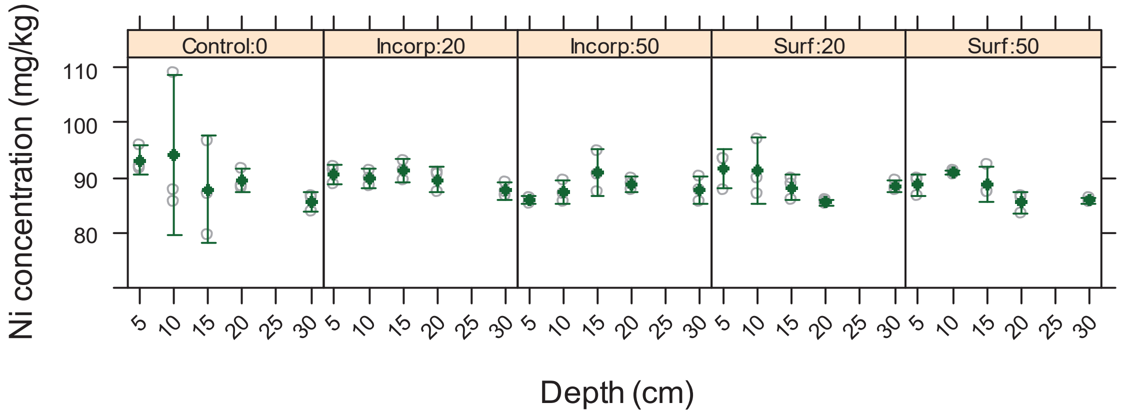

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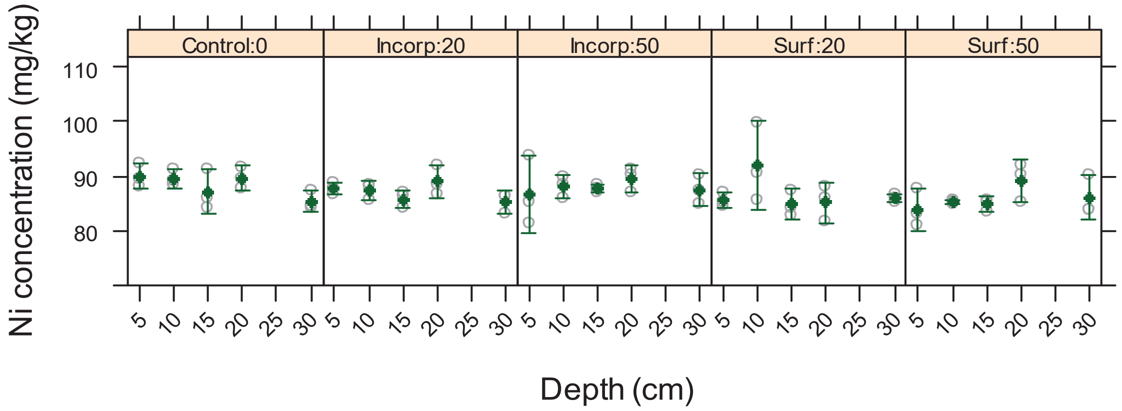
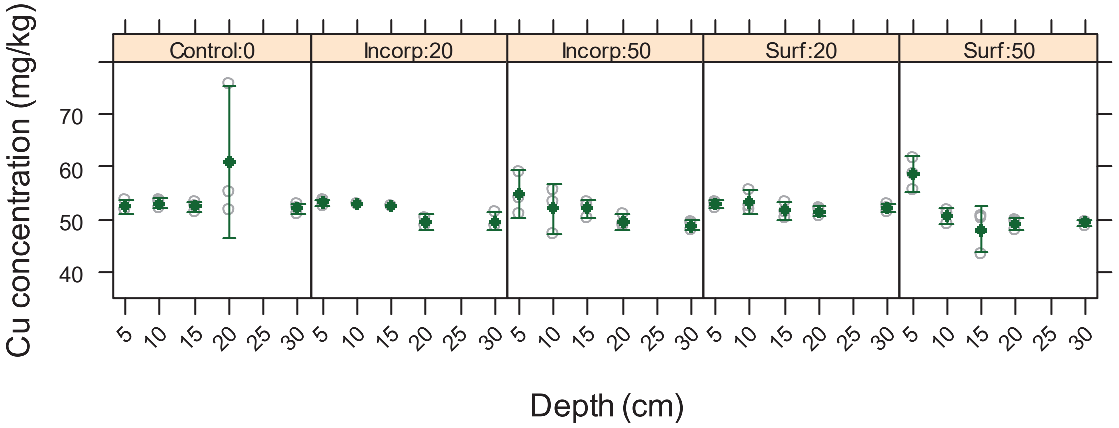
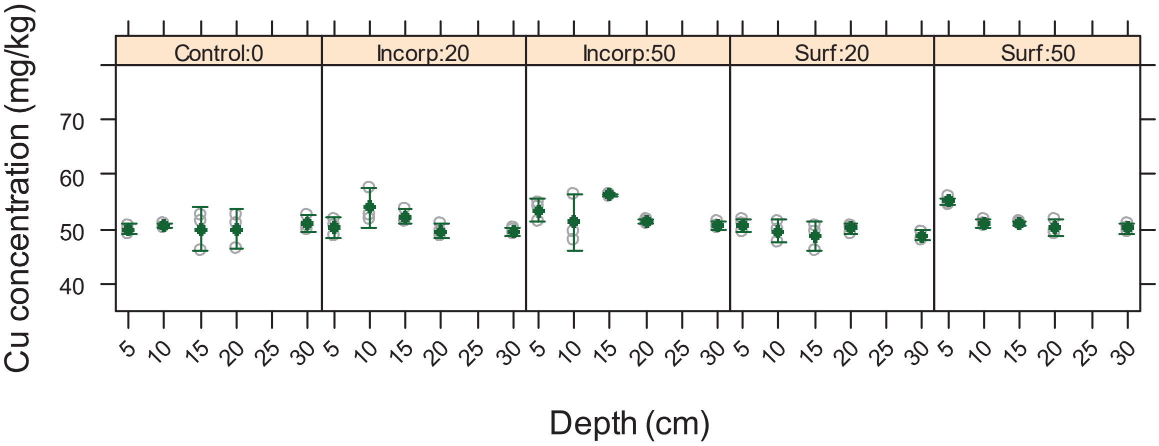


18 month

Figure B.3.12. Ni concentration in C3 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals





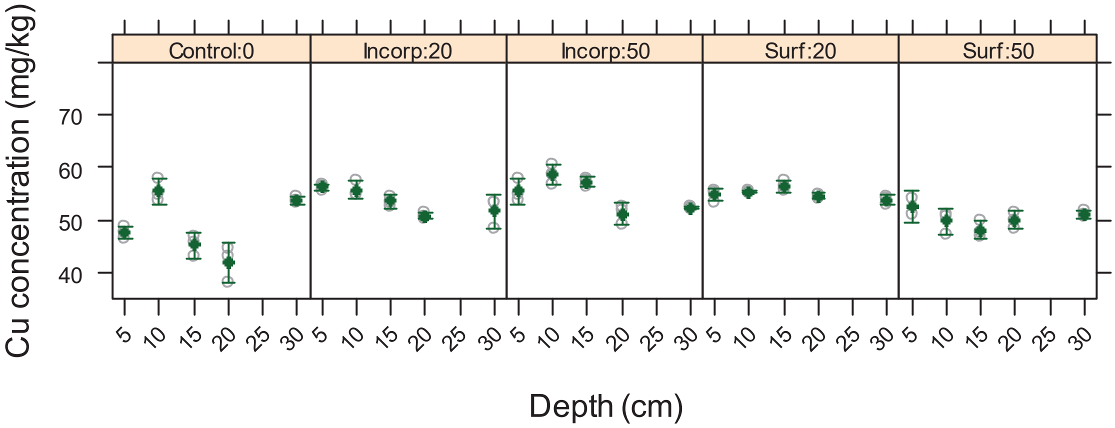
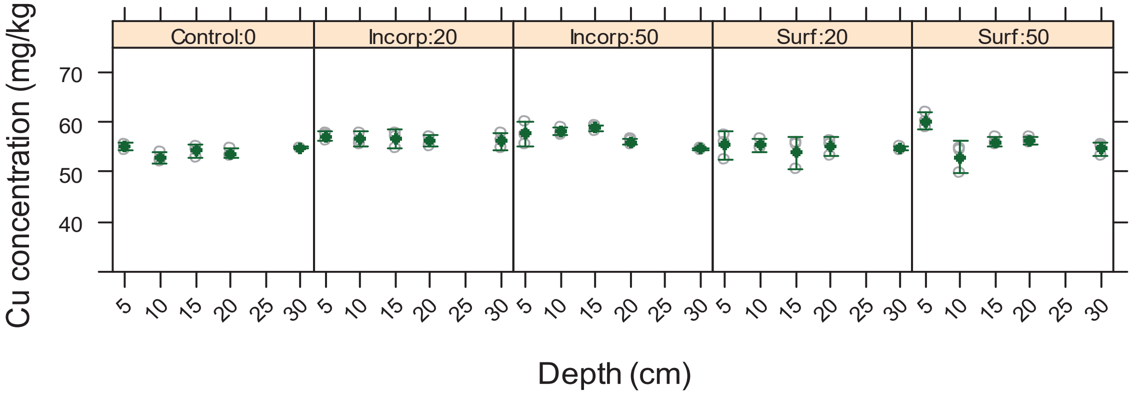


Figure B.3.13. Cu concentration in C1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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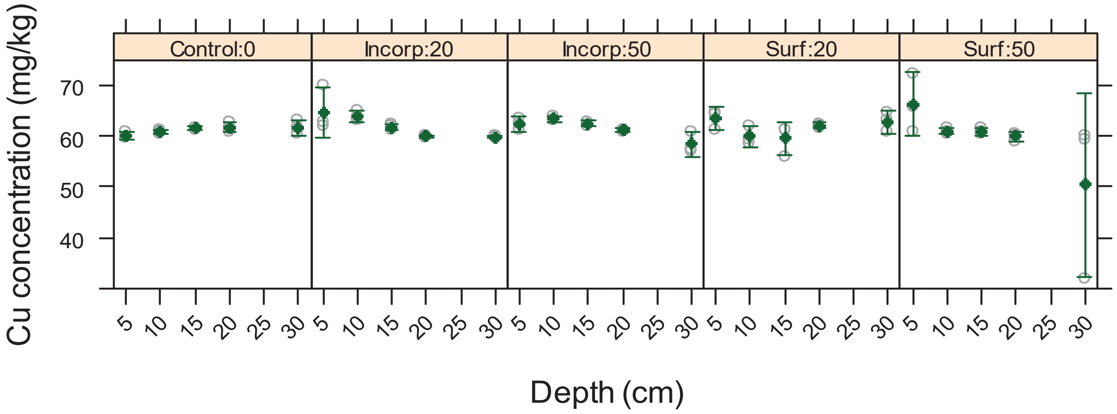

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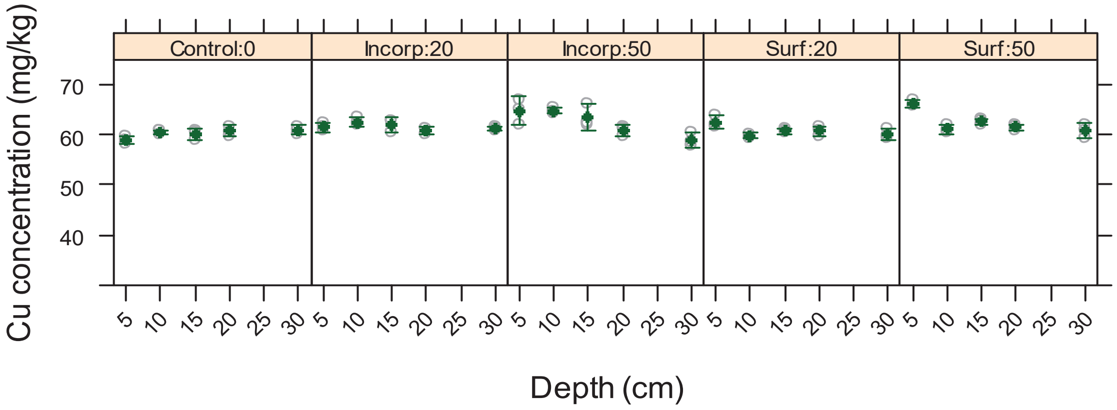
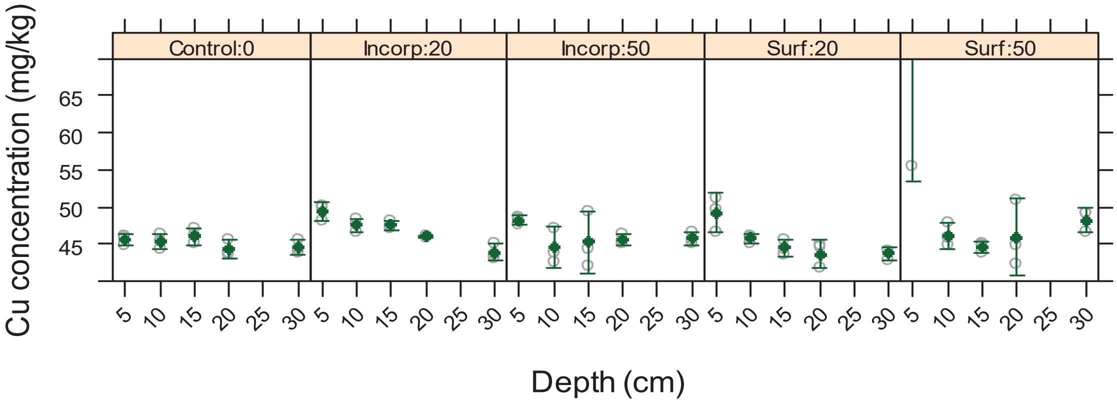
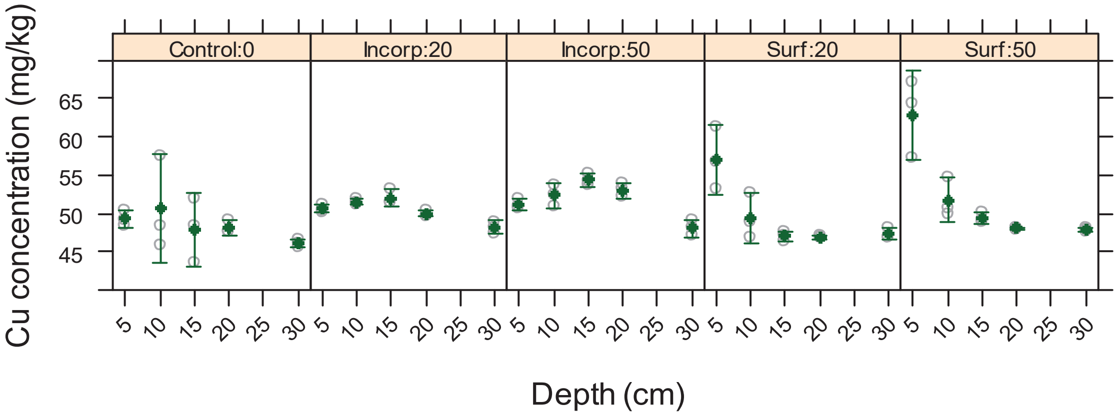


18 month

Figure B.3.14. Cu concentration in C2 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



6 month



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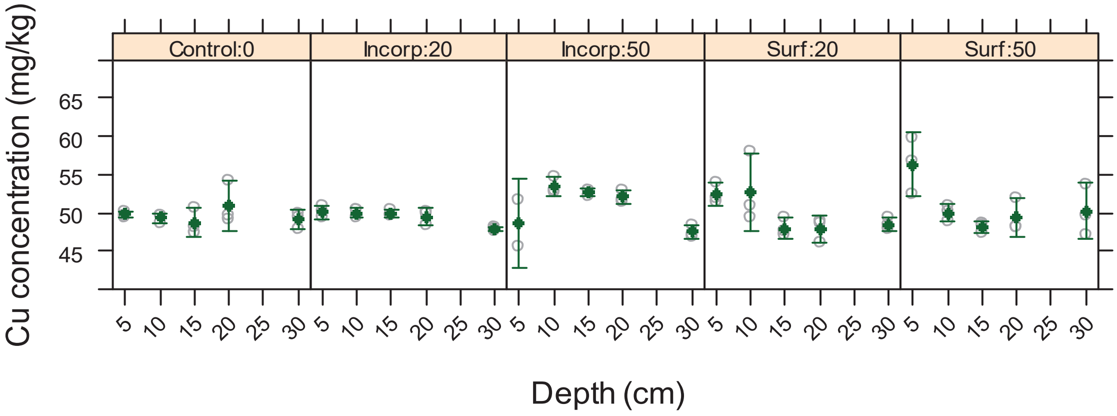
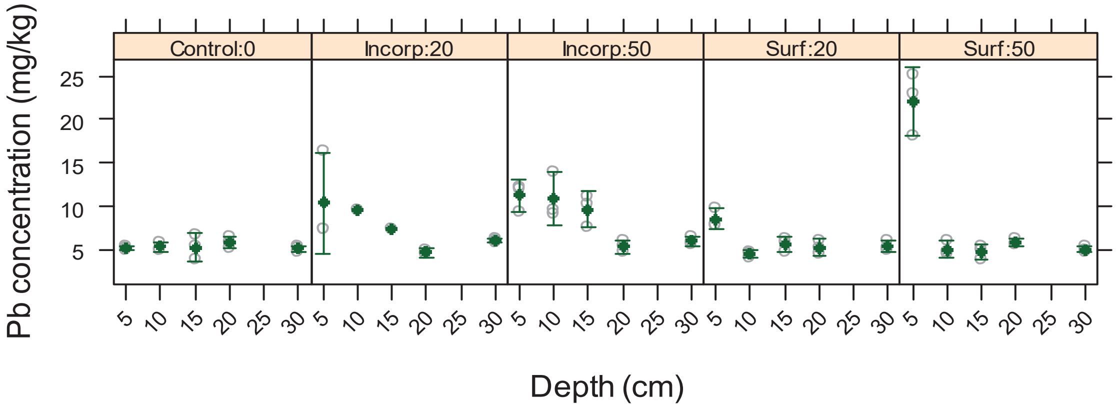
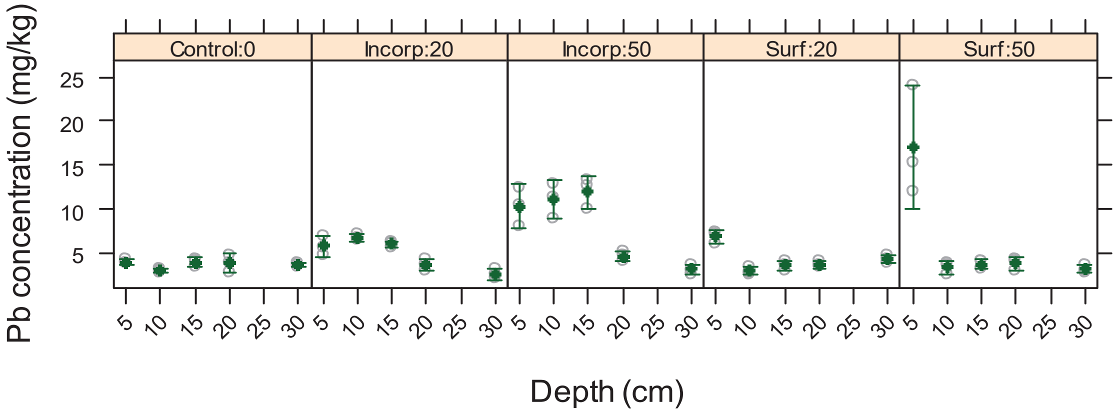


18 month

Figure B.3.15. Cu concentration in C3 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



6 month



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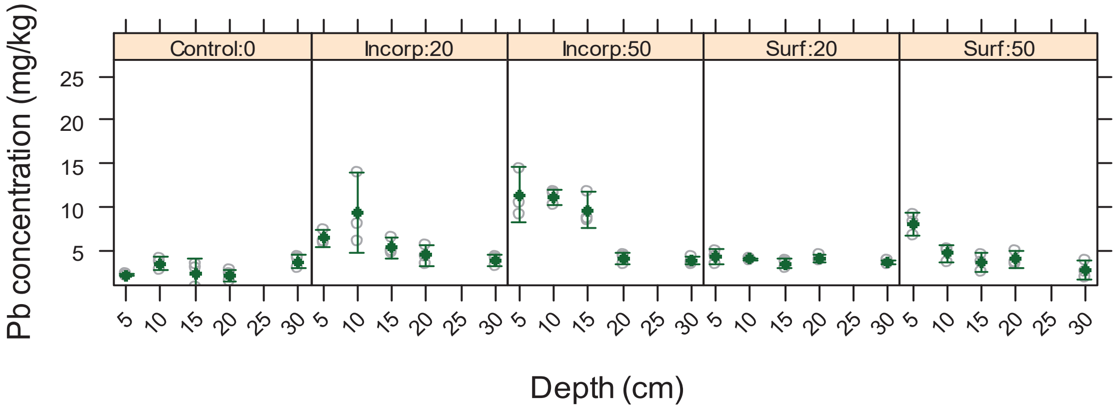
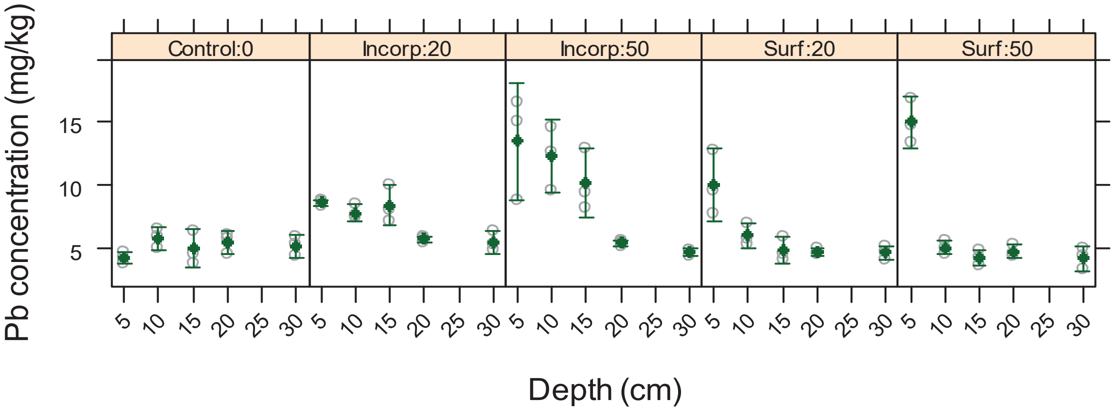


18 month

Figure B.3.16. Pb concentration in C1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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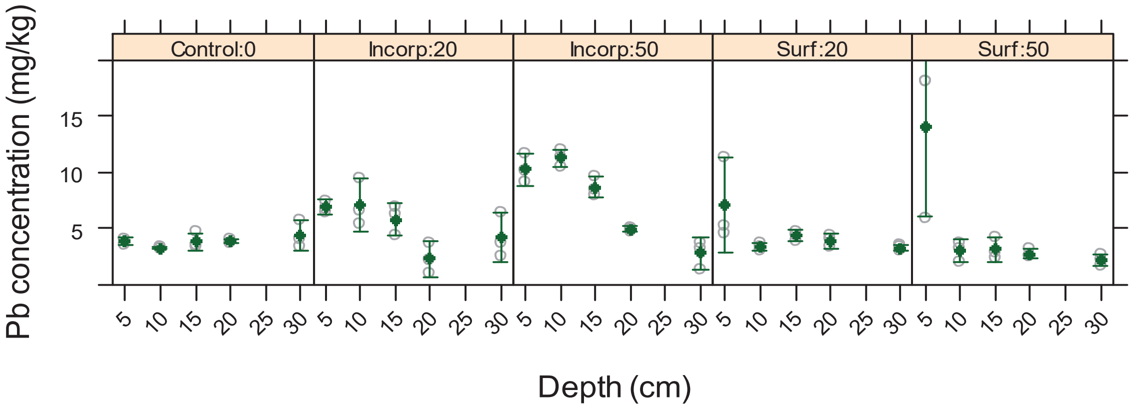

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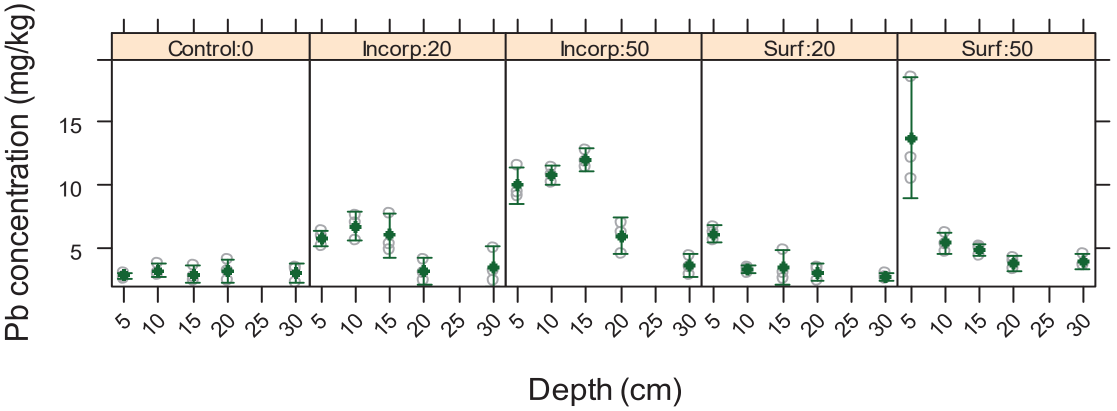
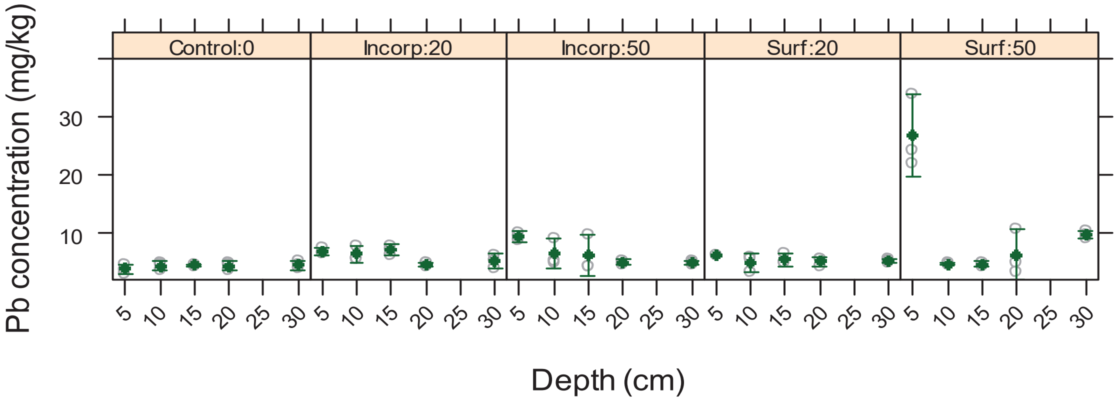


18 month

Figure B.3.17. Pb concentration in C2 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



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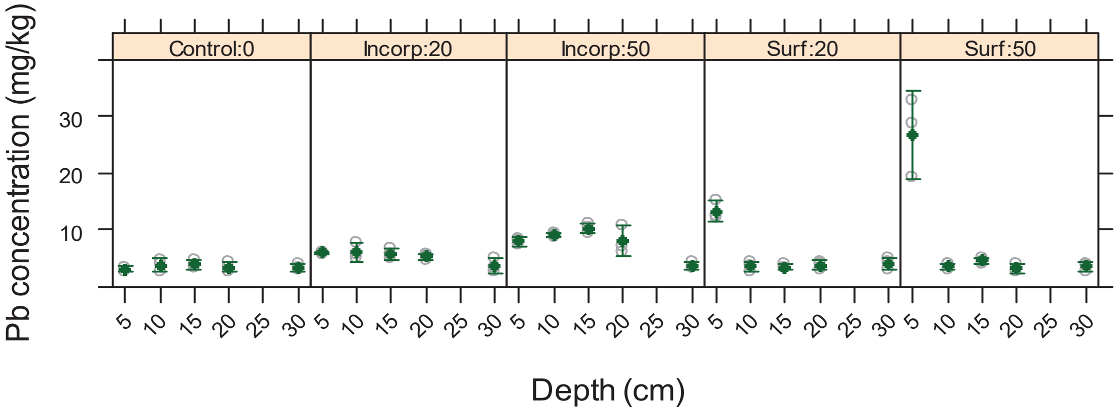
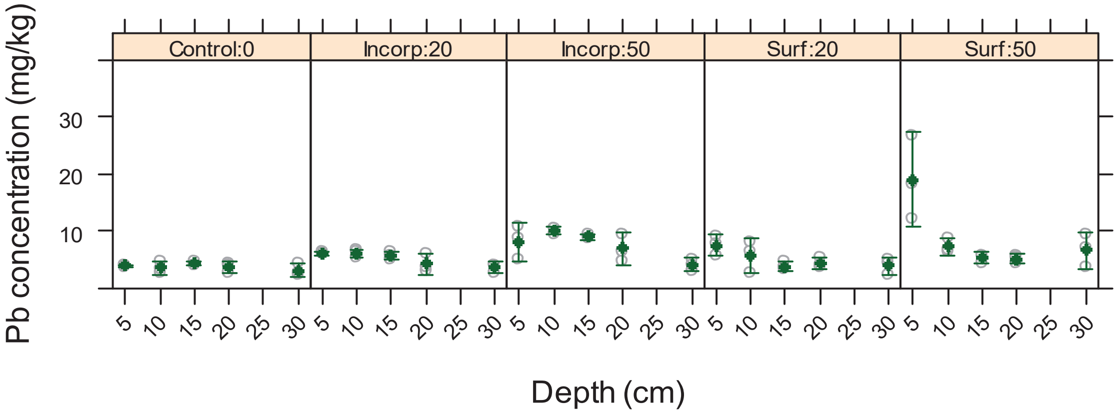
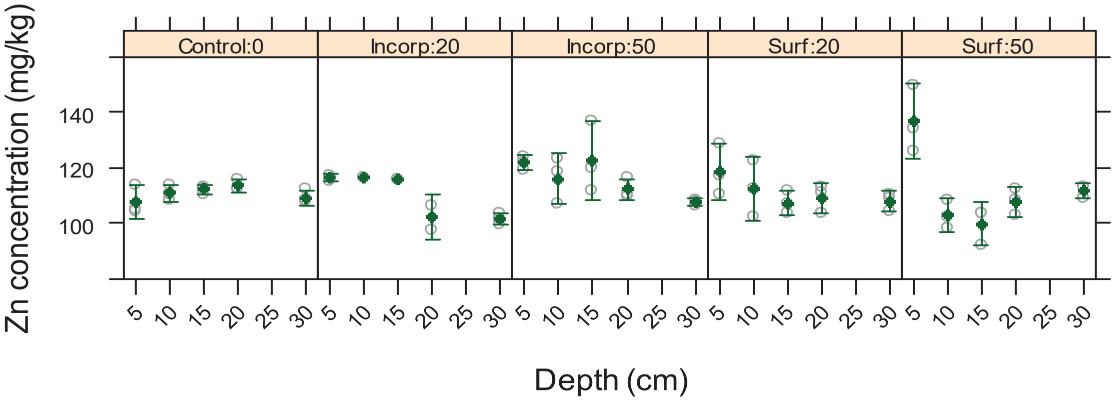


12 month

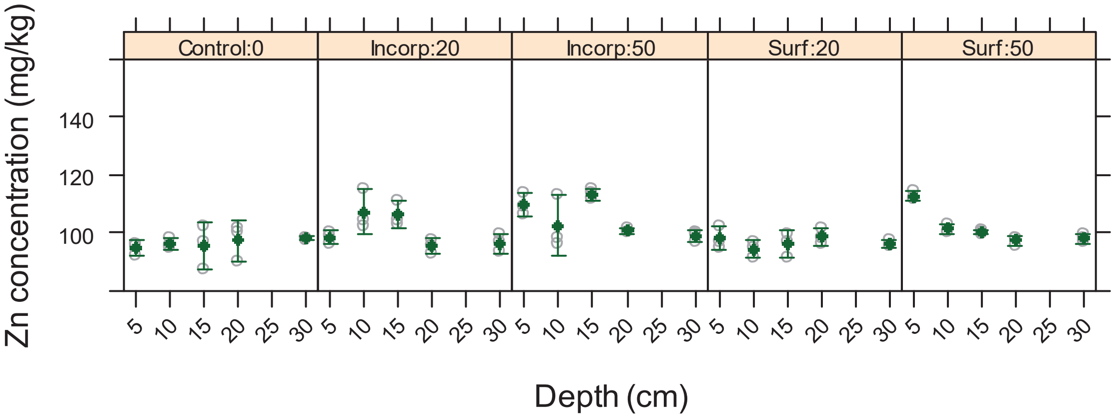


18 month

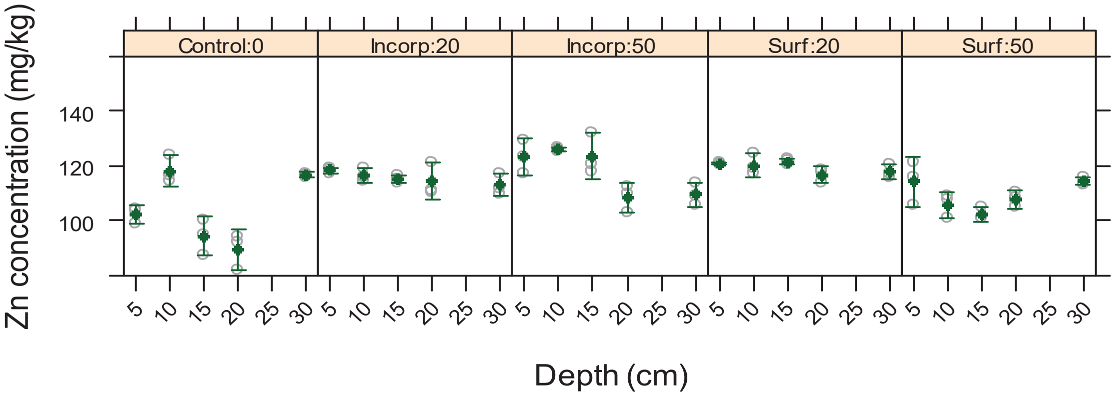
Figure B.3.18. Pb concentration in C3 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



6 month

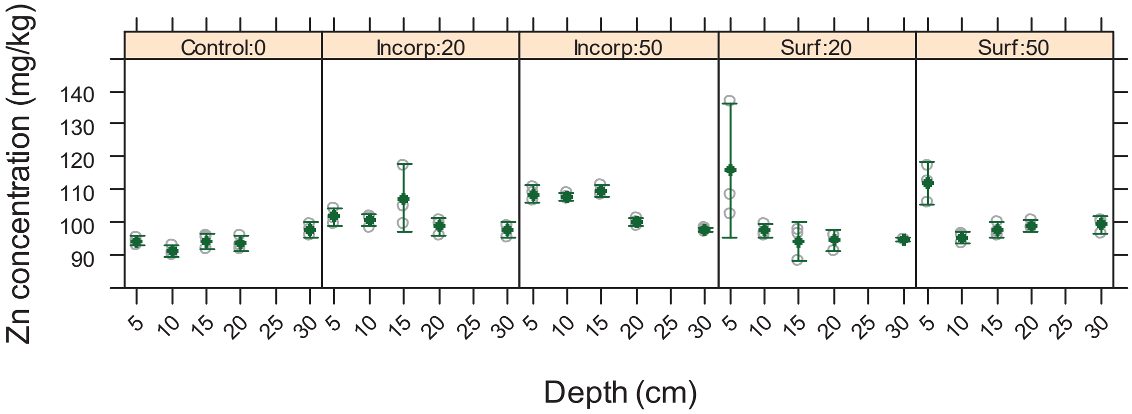


12 month

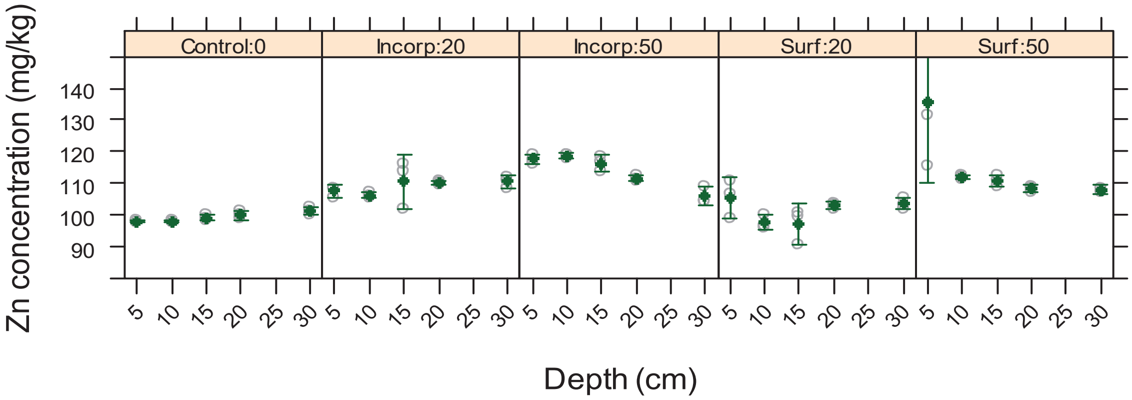


18 month

Figure B.3.19. Zn concentration in C1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



6 month



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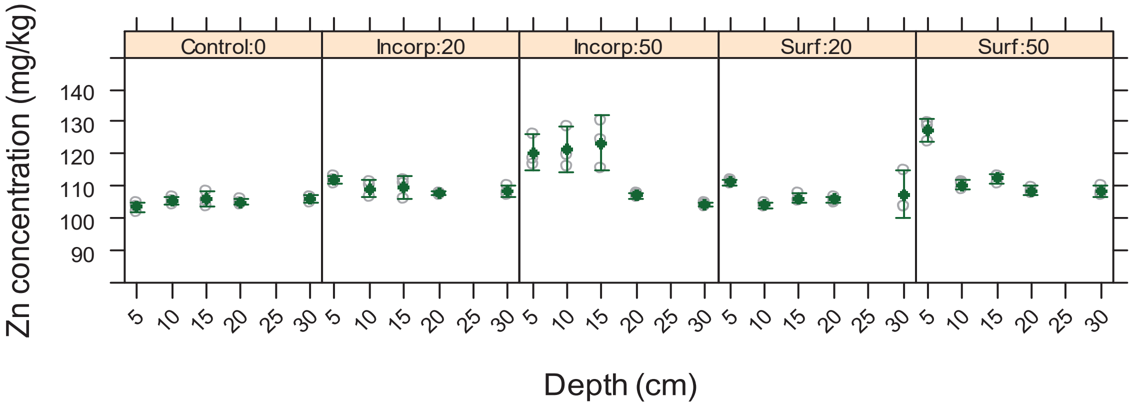
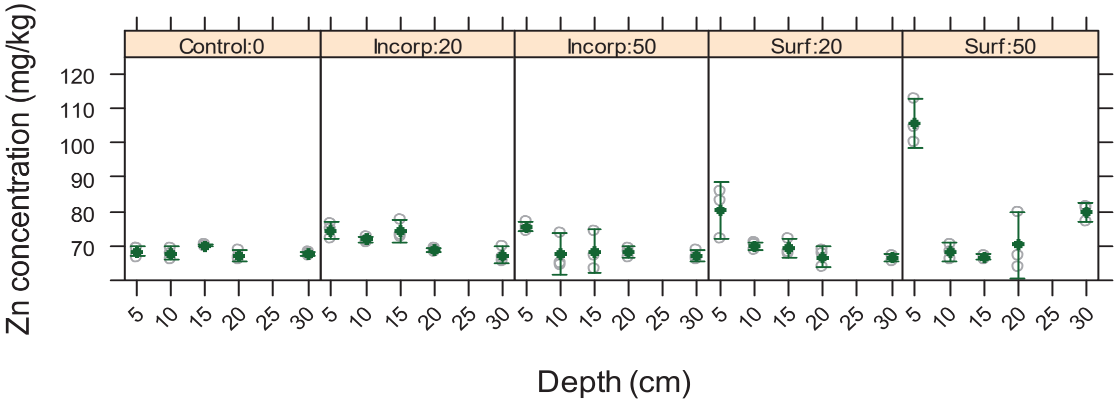
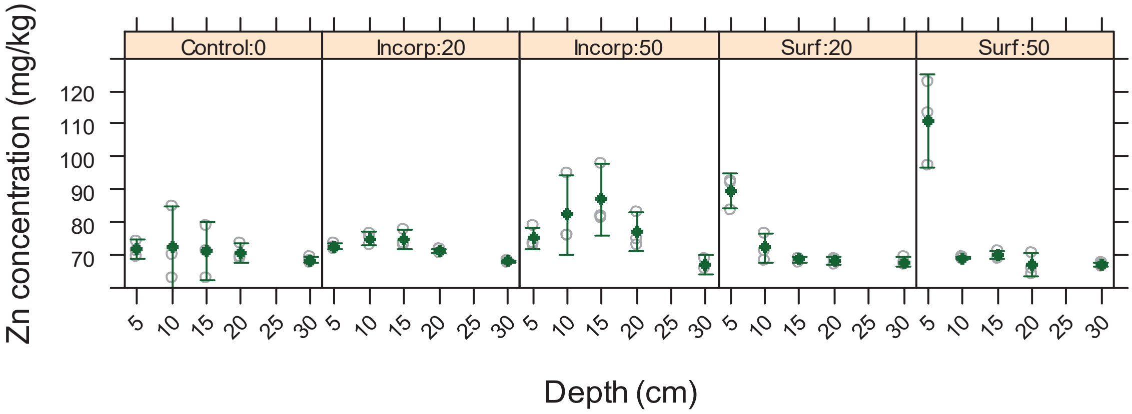


18 month

Figure B.3.20. Zn concentration in C2 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



6 month



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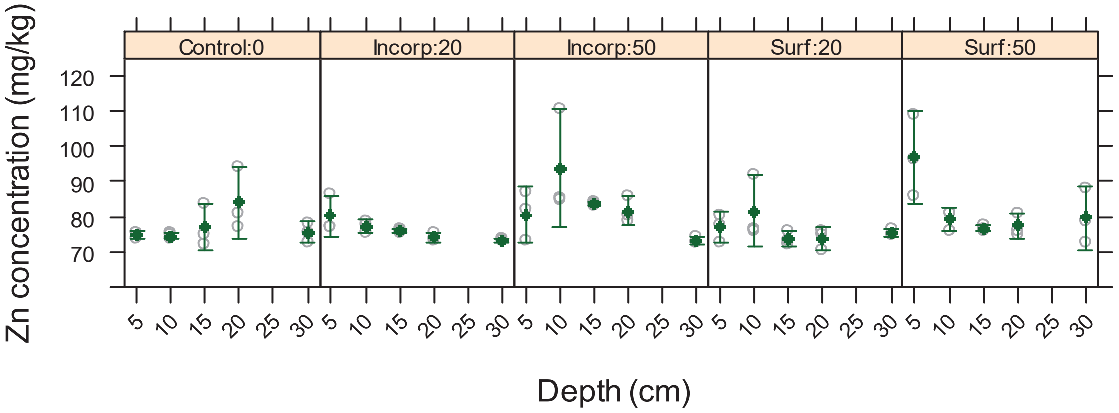
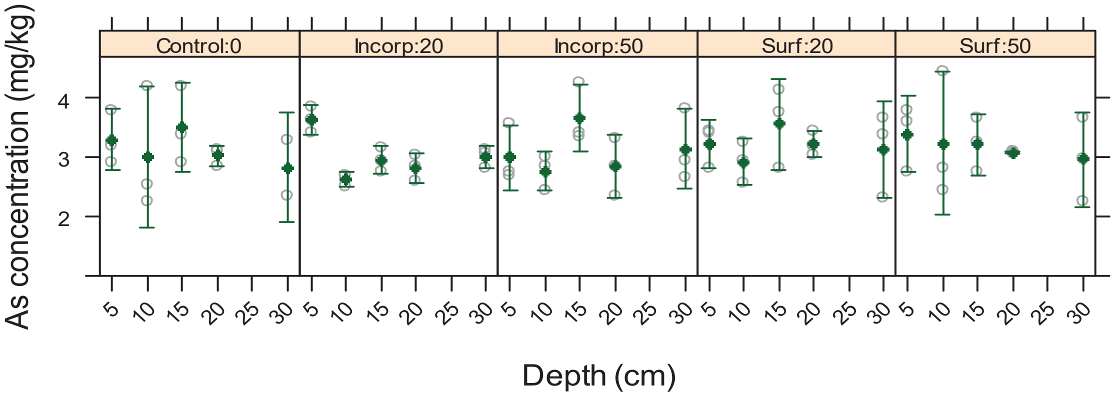


18 month

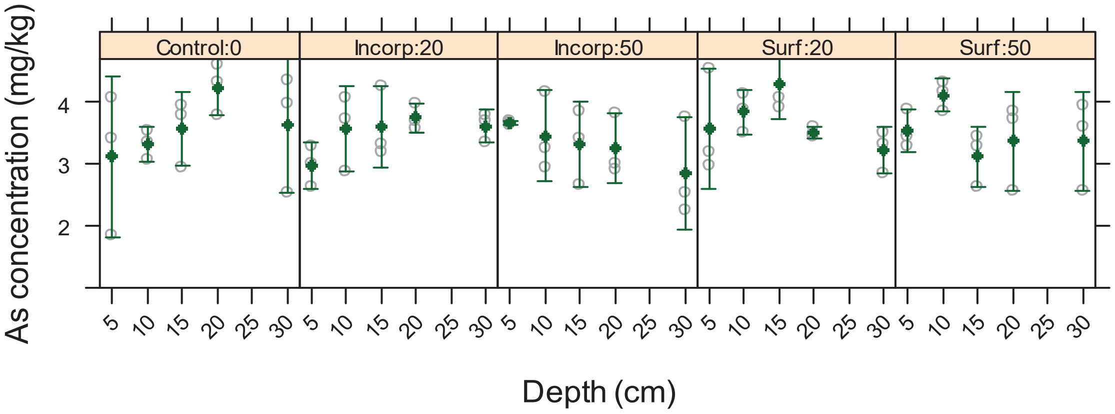
Figure B.3.21. Zn concentration in C3 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals

Appendix B4

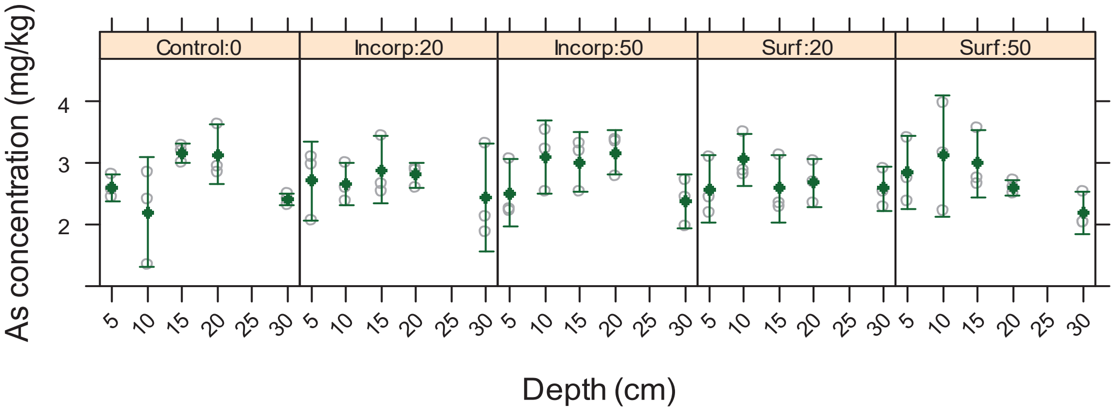
Changes of metal and metalloid concentrations and distribution in organic soil (OM)



6 month

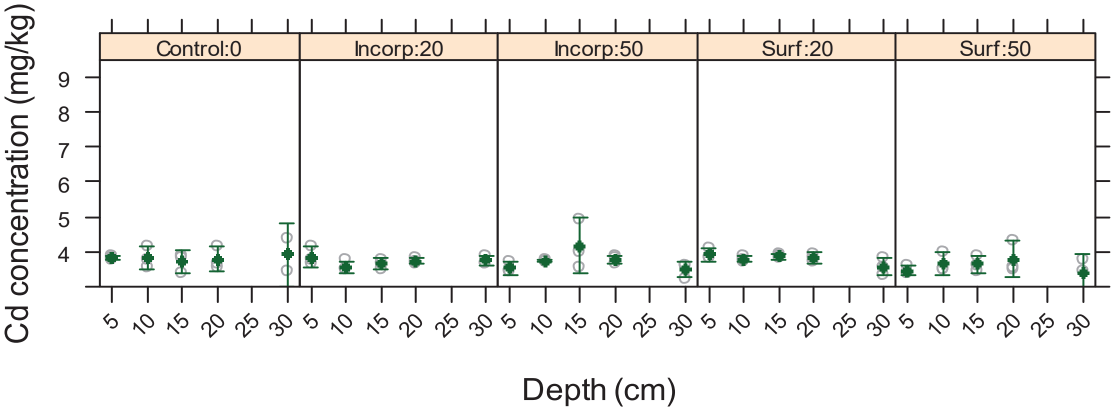


12 month

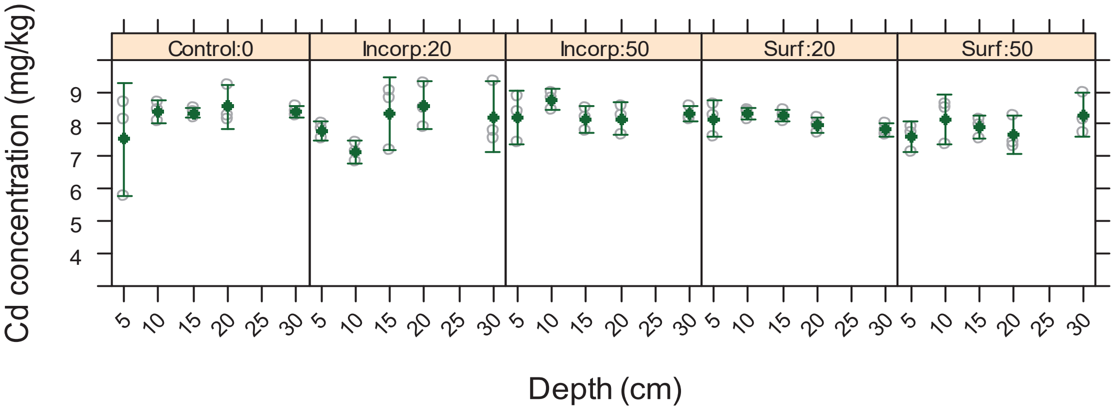


16 month

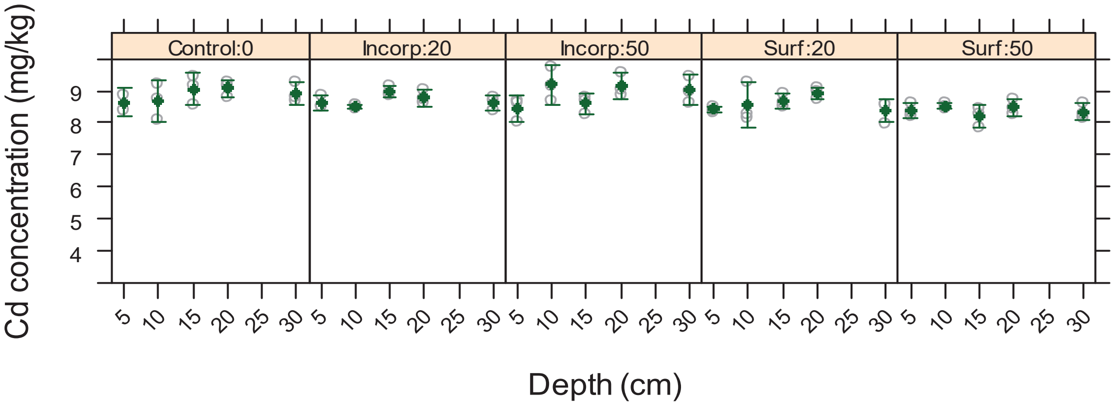
Figure B.4.1. As concentration in OM1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



6 month

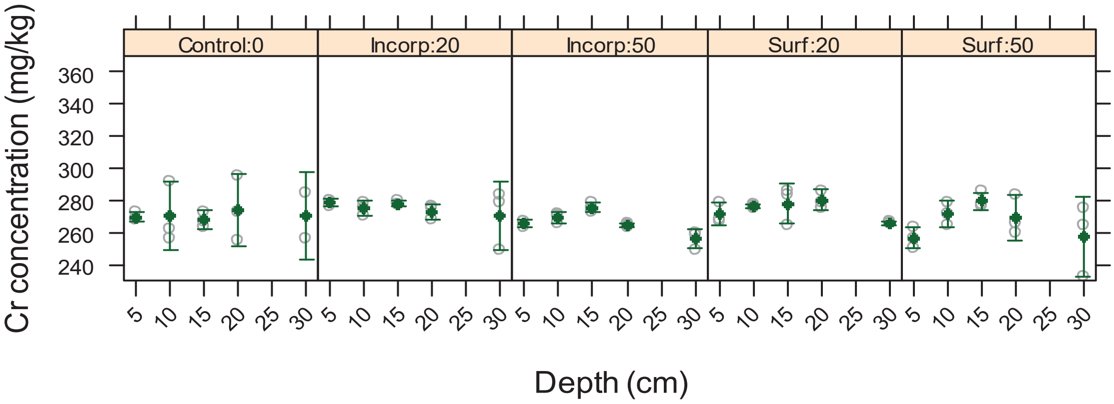


12 month

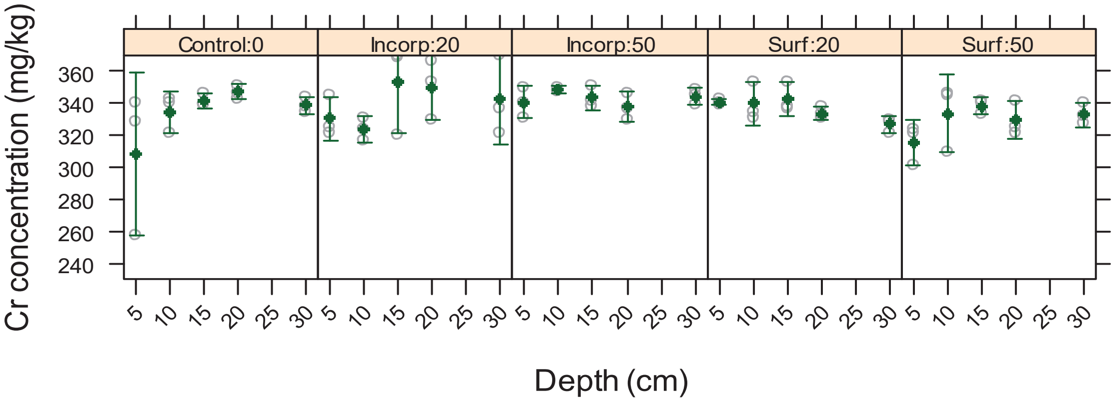


18 month

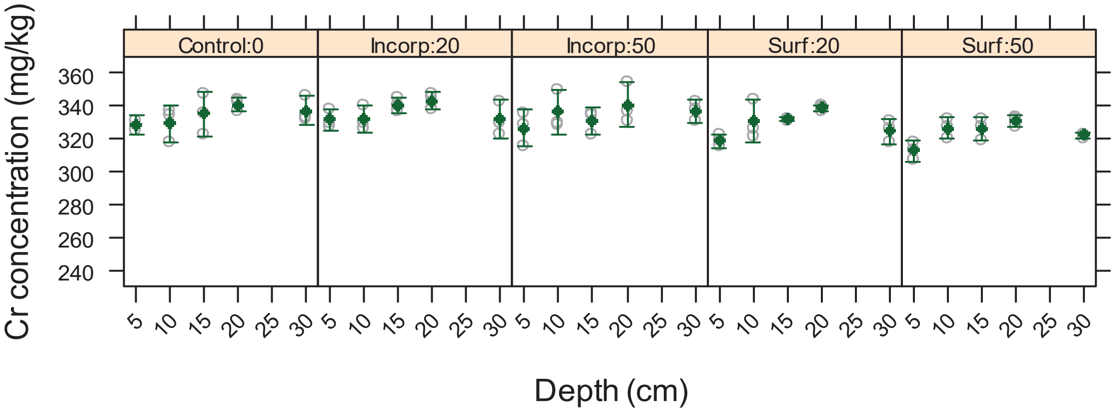
Figure B.4.2. Cd concentration in OM1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



6 month

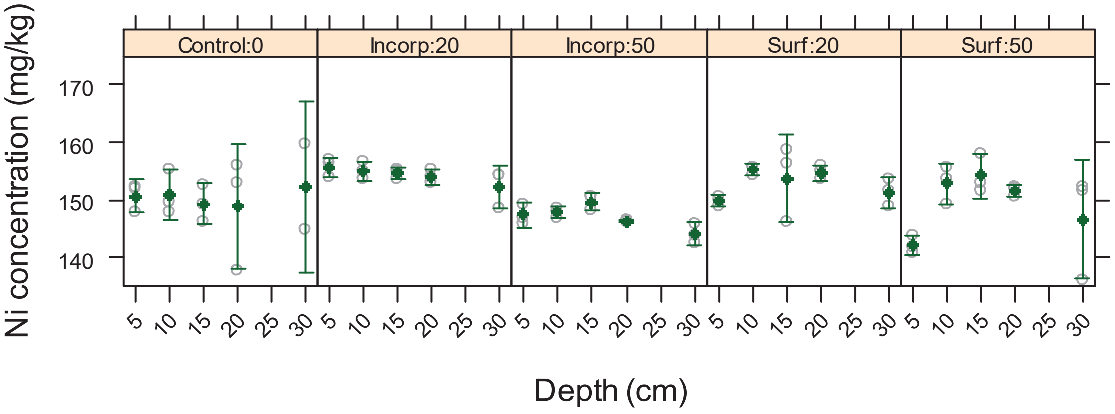


12 month

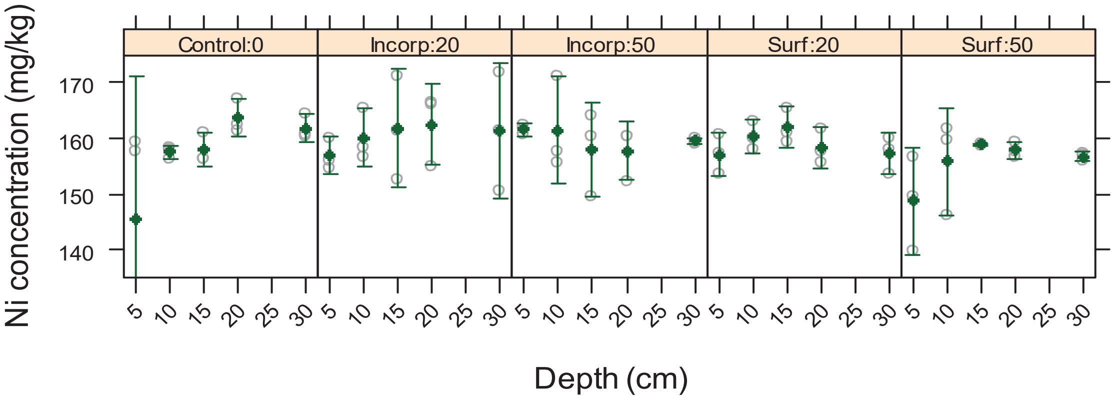


18 month

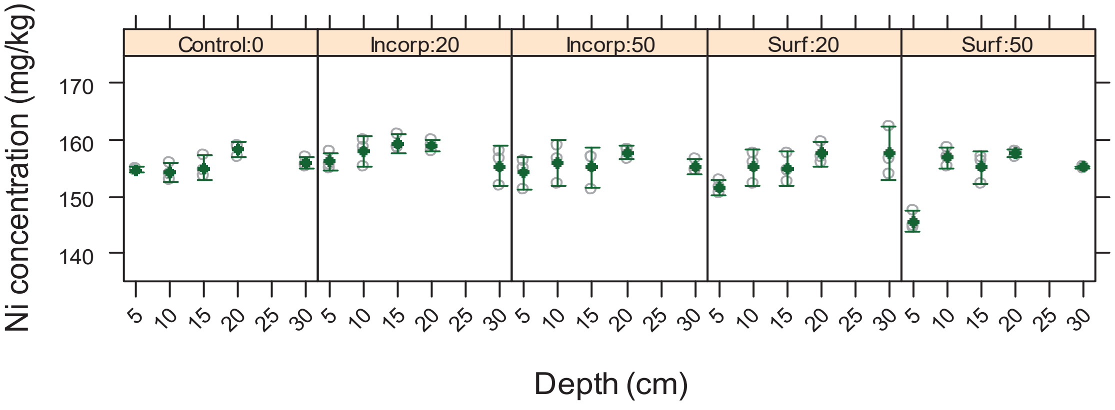
Figure B.4.3. Cr concentration in OM1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



6 month

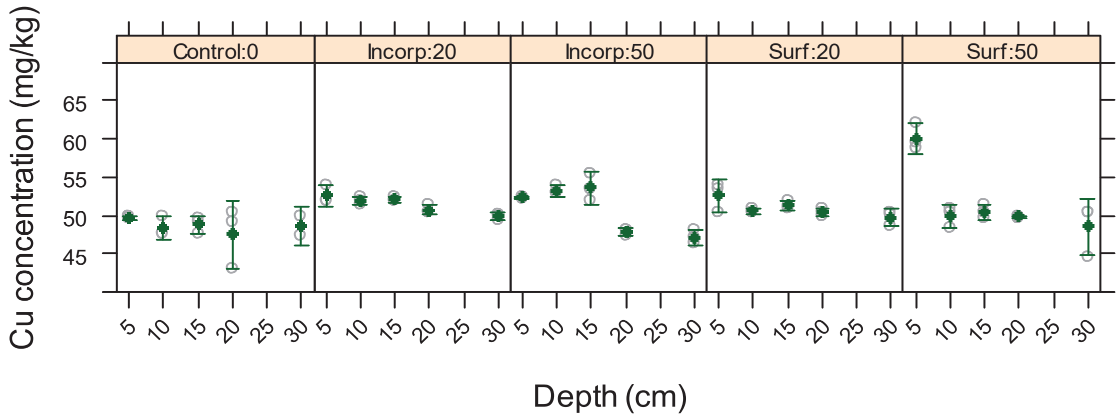


12 month

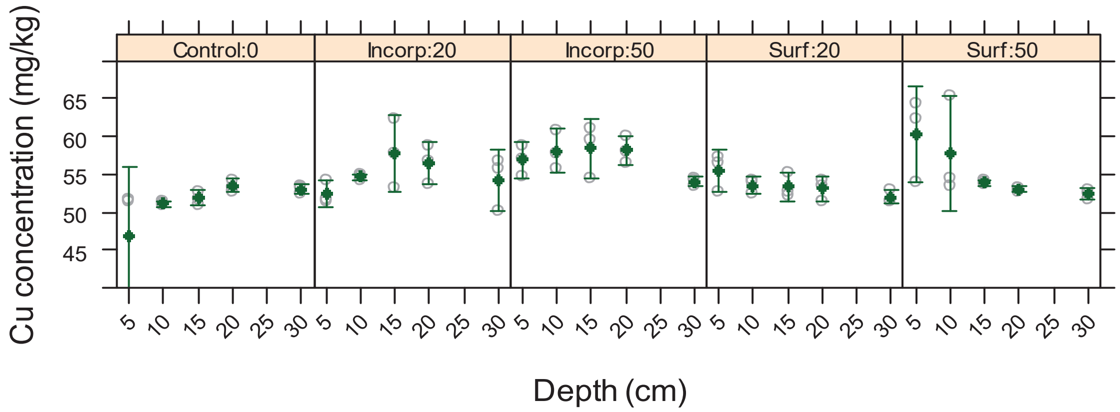


18 month

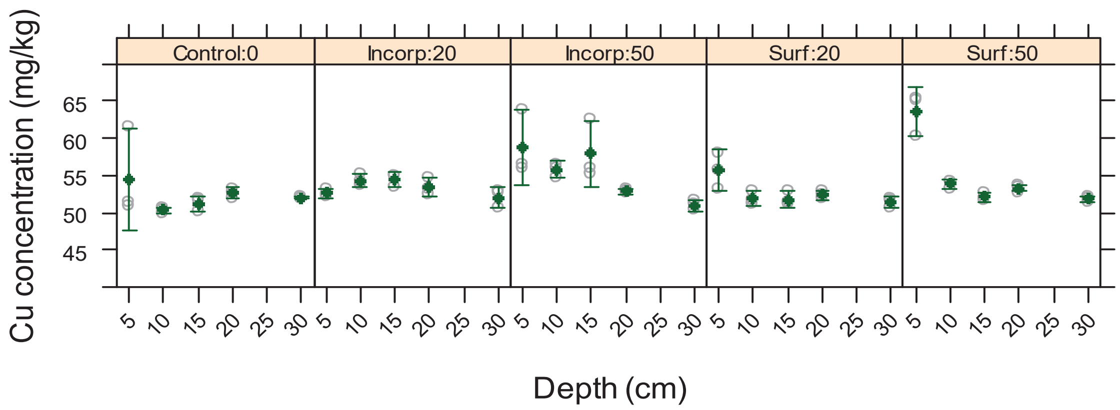
Figure B.4.4. Ni concentration in OM1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



6 month

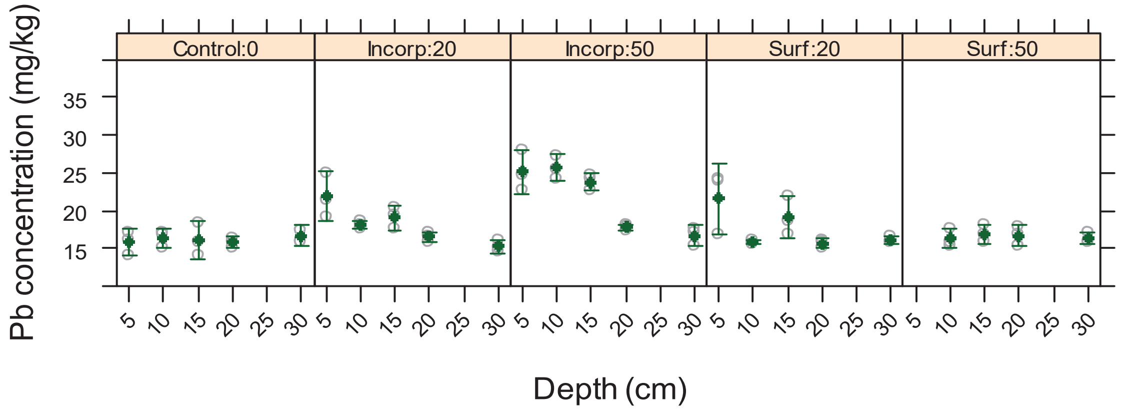


12 month

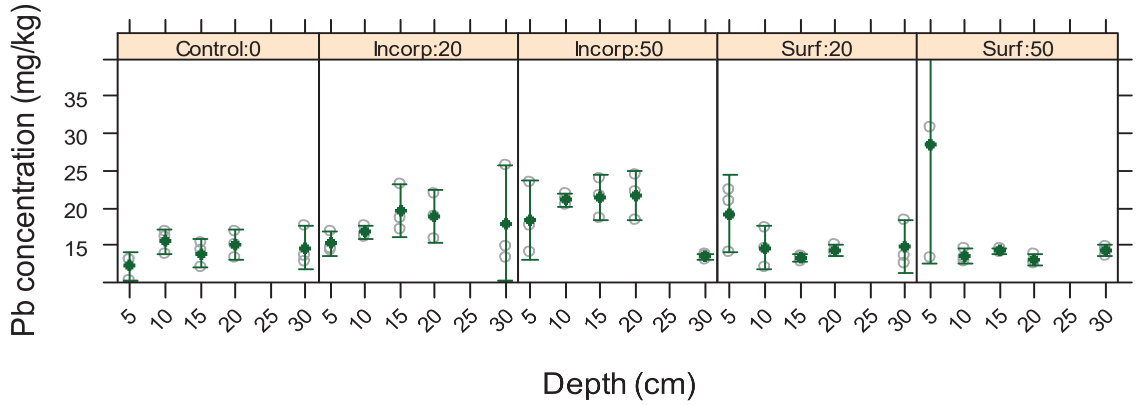


18 month

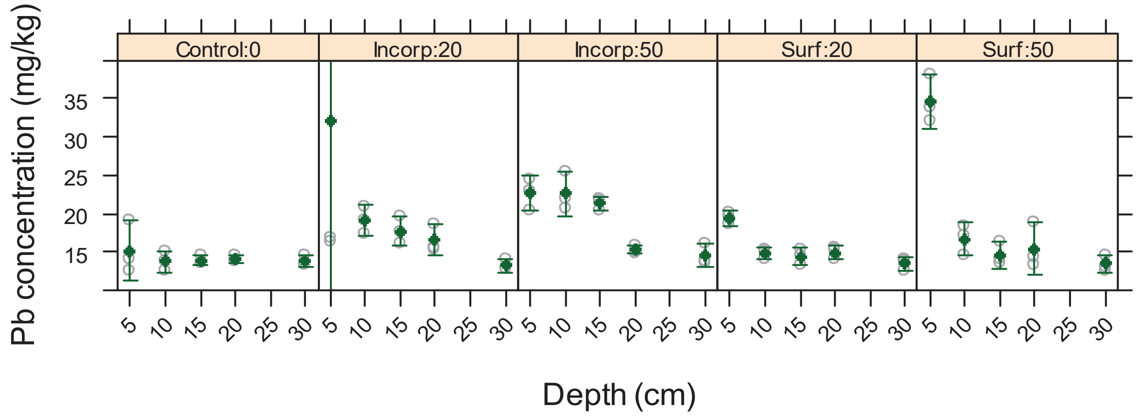
Figure B.4.5. Cu concentration in OM1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



6 month

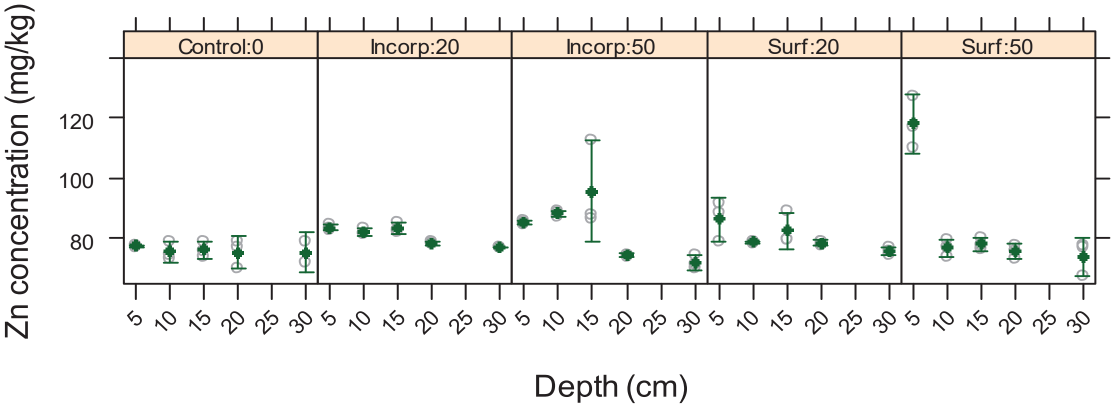


12 month

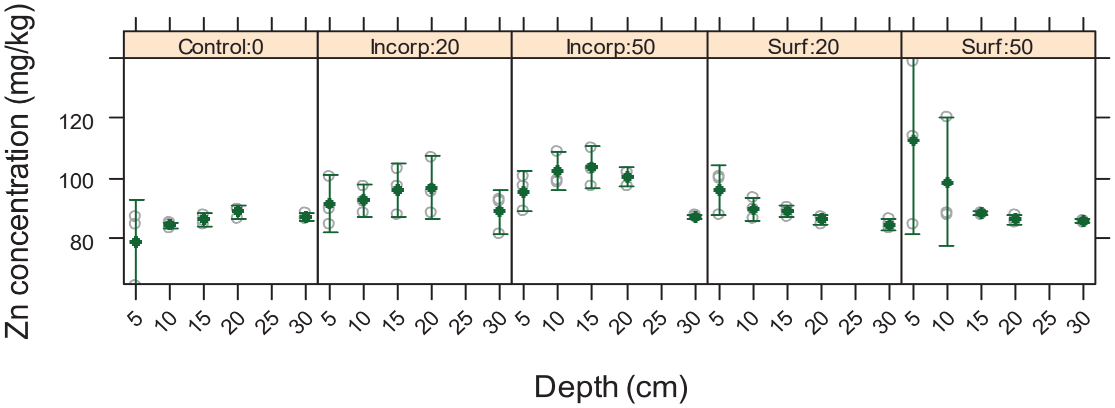


18 month

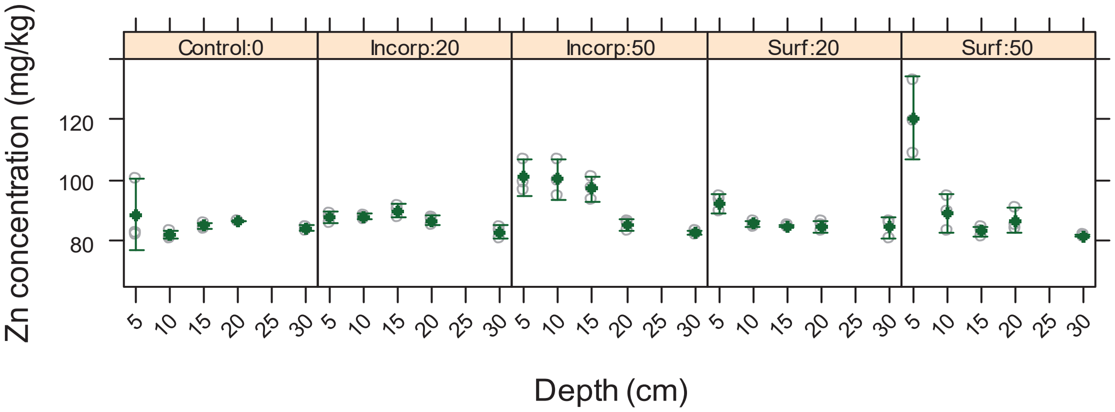
Figure B.4.6. Pb concentration in OM1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals



6 month



12 month



18 month

Figure B.4.7. Zn concentration in OM1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha^{-1} = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals

Appendix B5

Changes of soil EC, pH and TOC after 6 month MWOO application to ten NSW soils

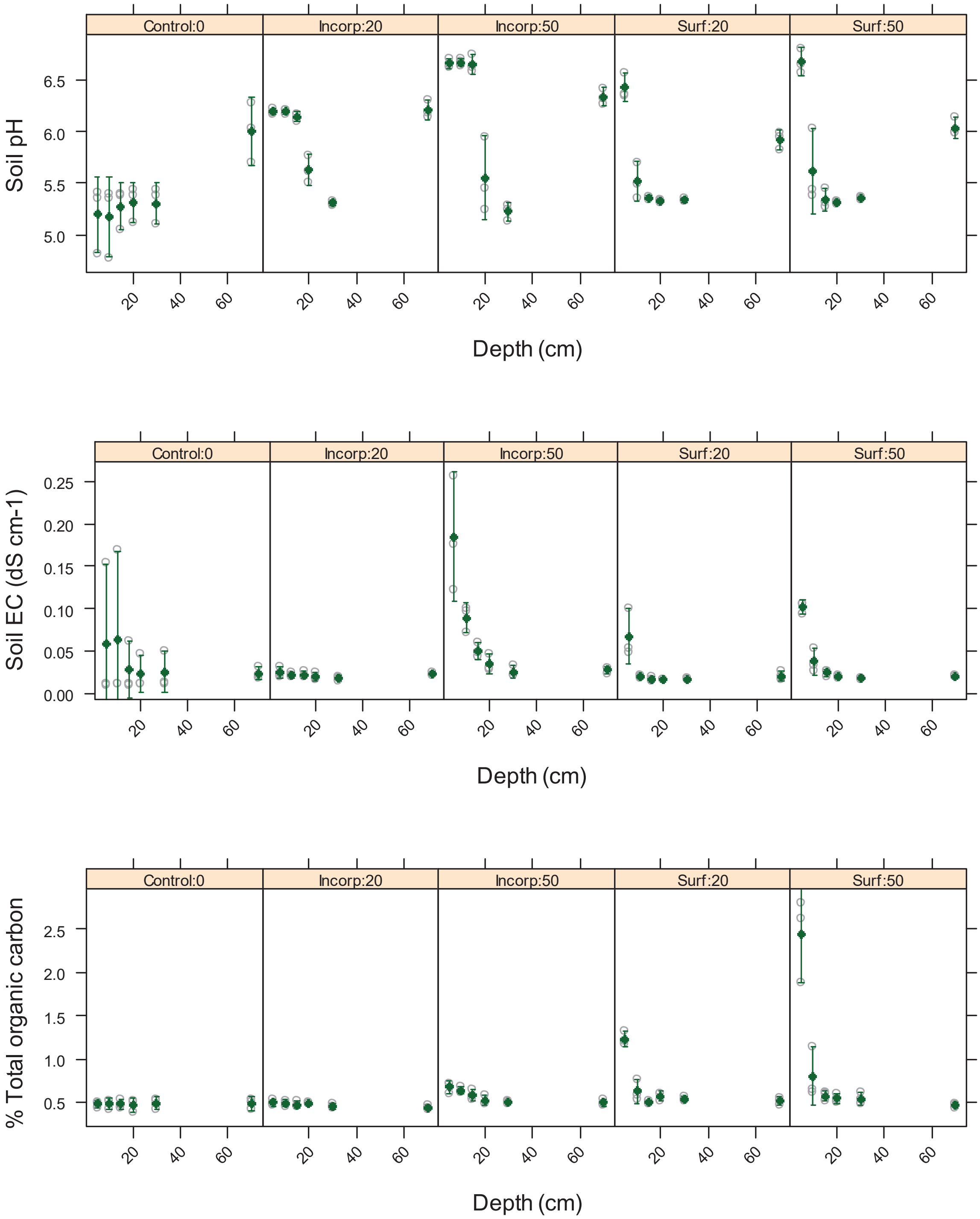


Figure B.1. Soil pH, EC and TOC in S1 after 6 month following MWOO application

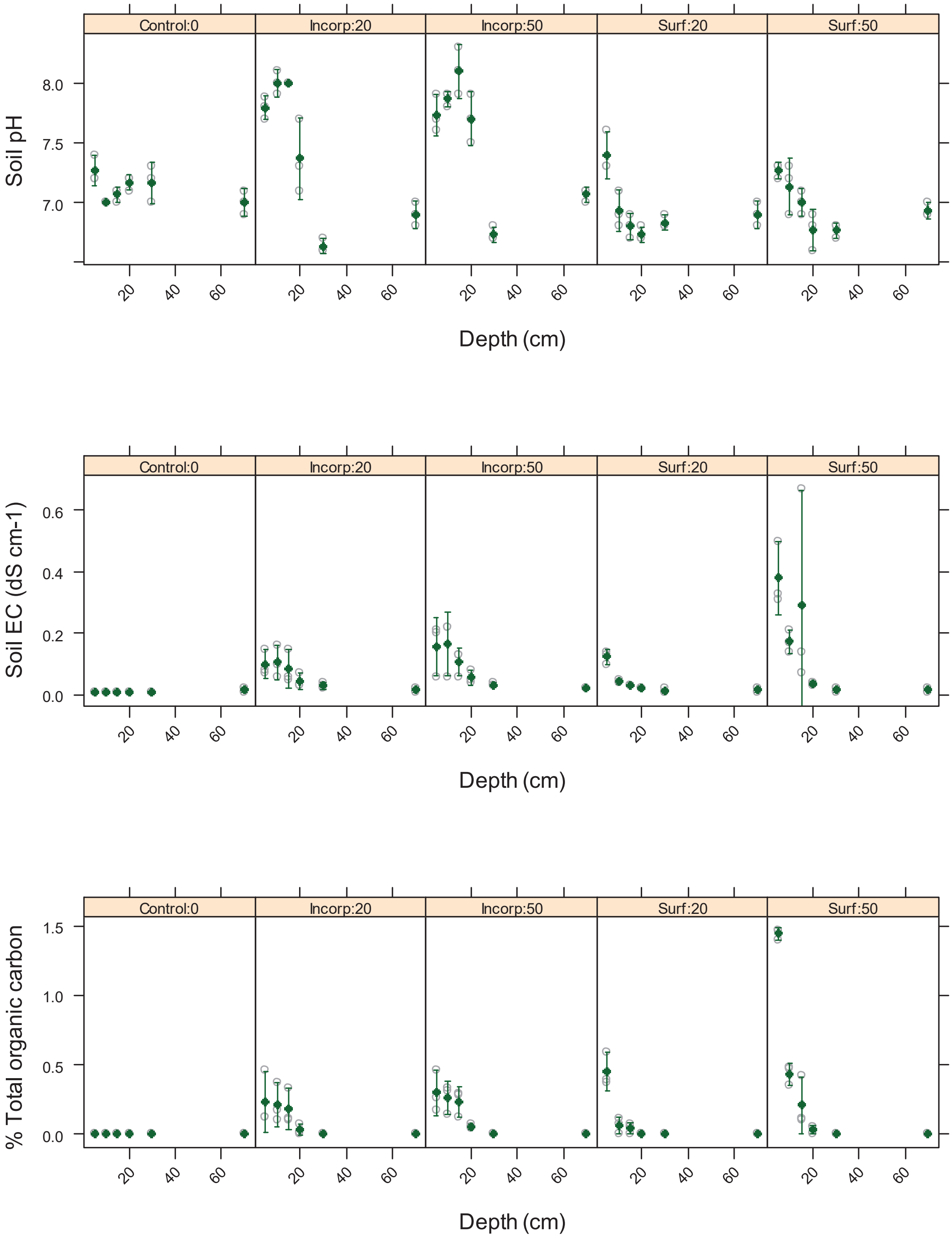


Figure B.2. Soil pH, EC and TOC in S2 after 6 month following MWOO application

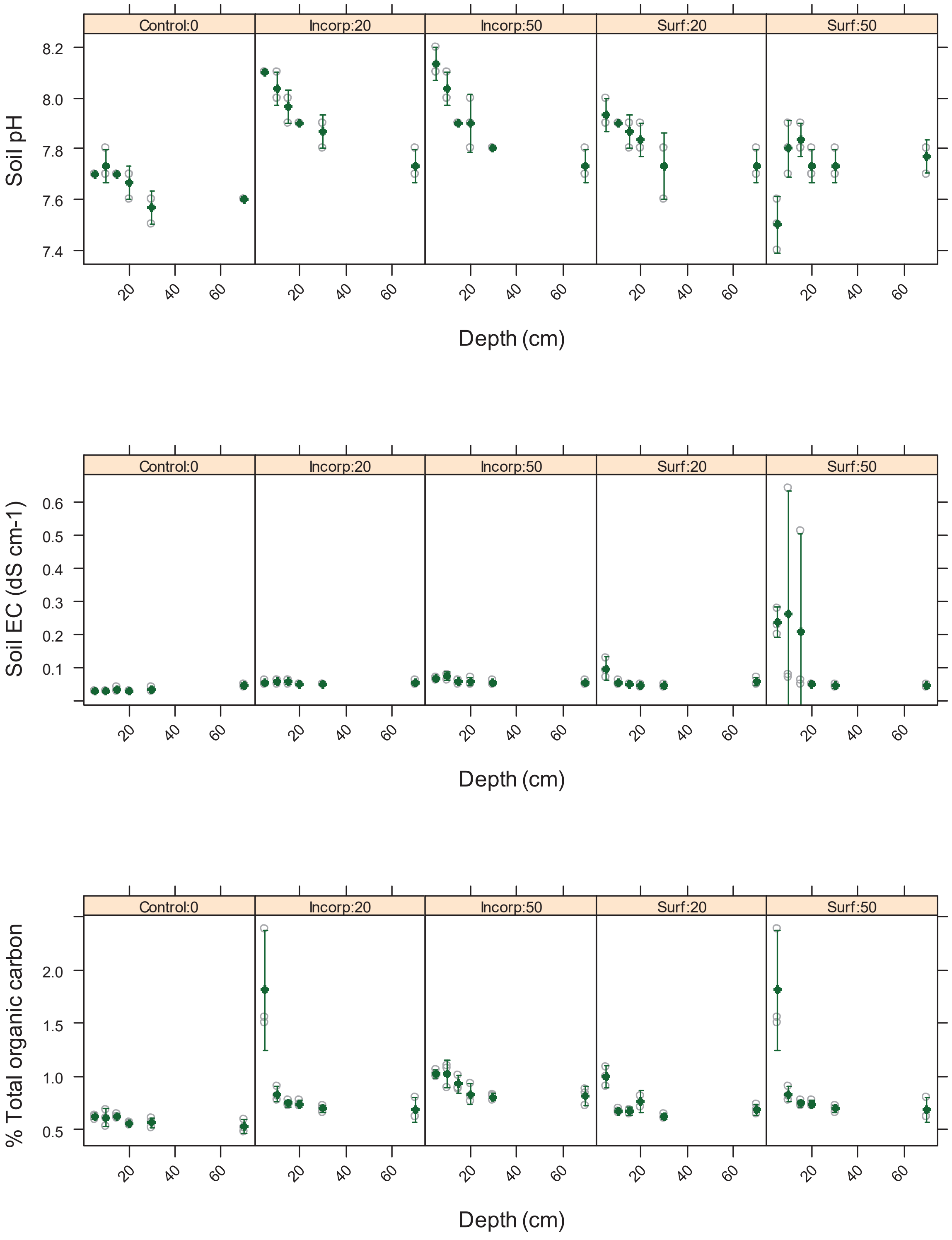


Figure B.3. Soil pH, EC and TOC in S3 after 6 month following MWOO application

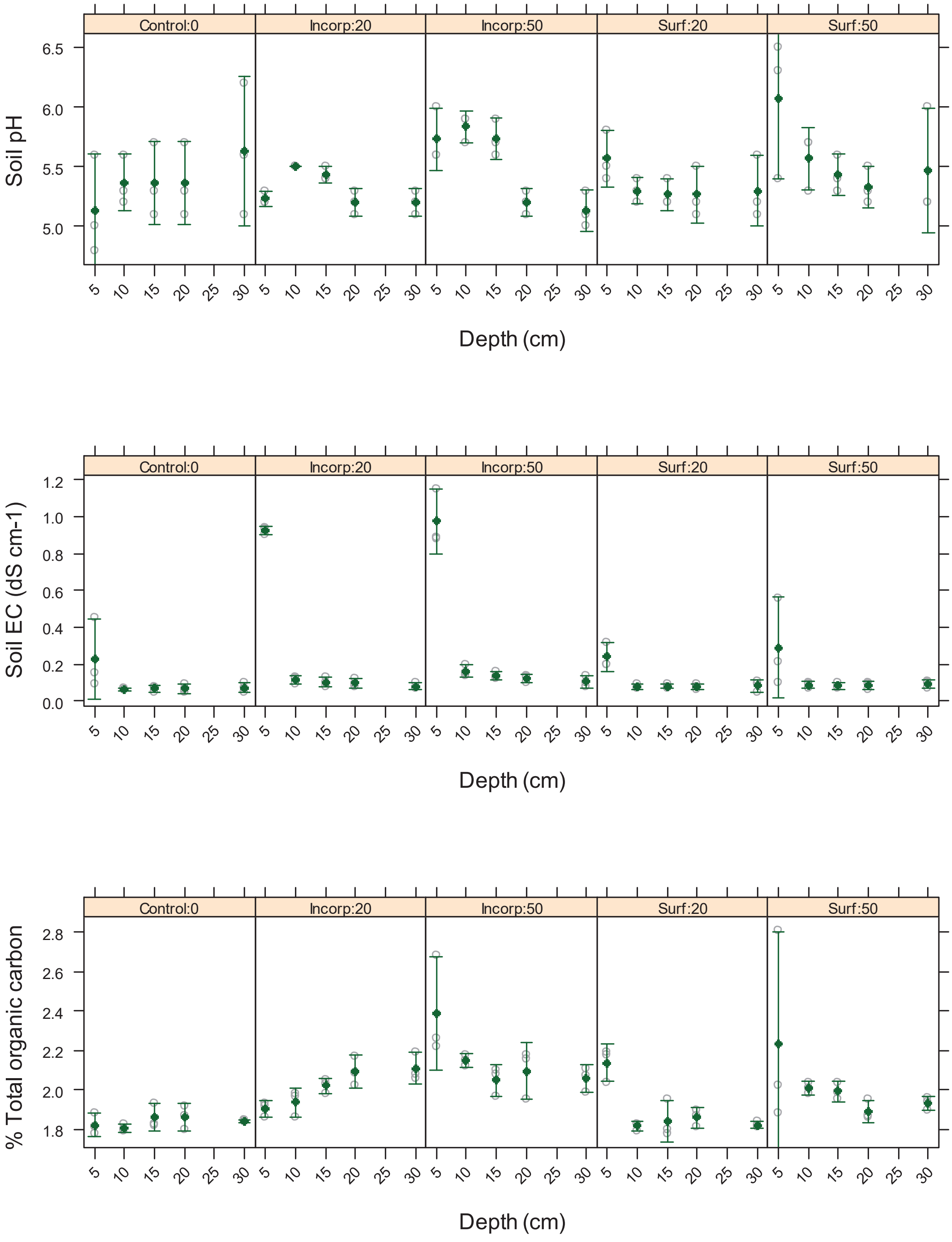


Figure B.4. Soil pH, EC and TOC in SL1 after 6 month following MWOO application

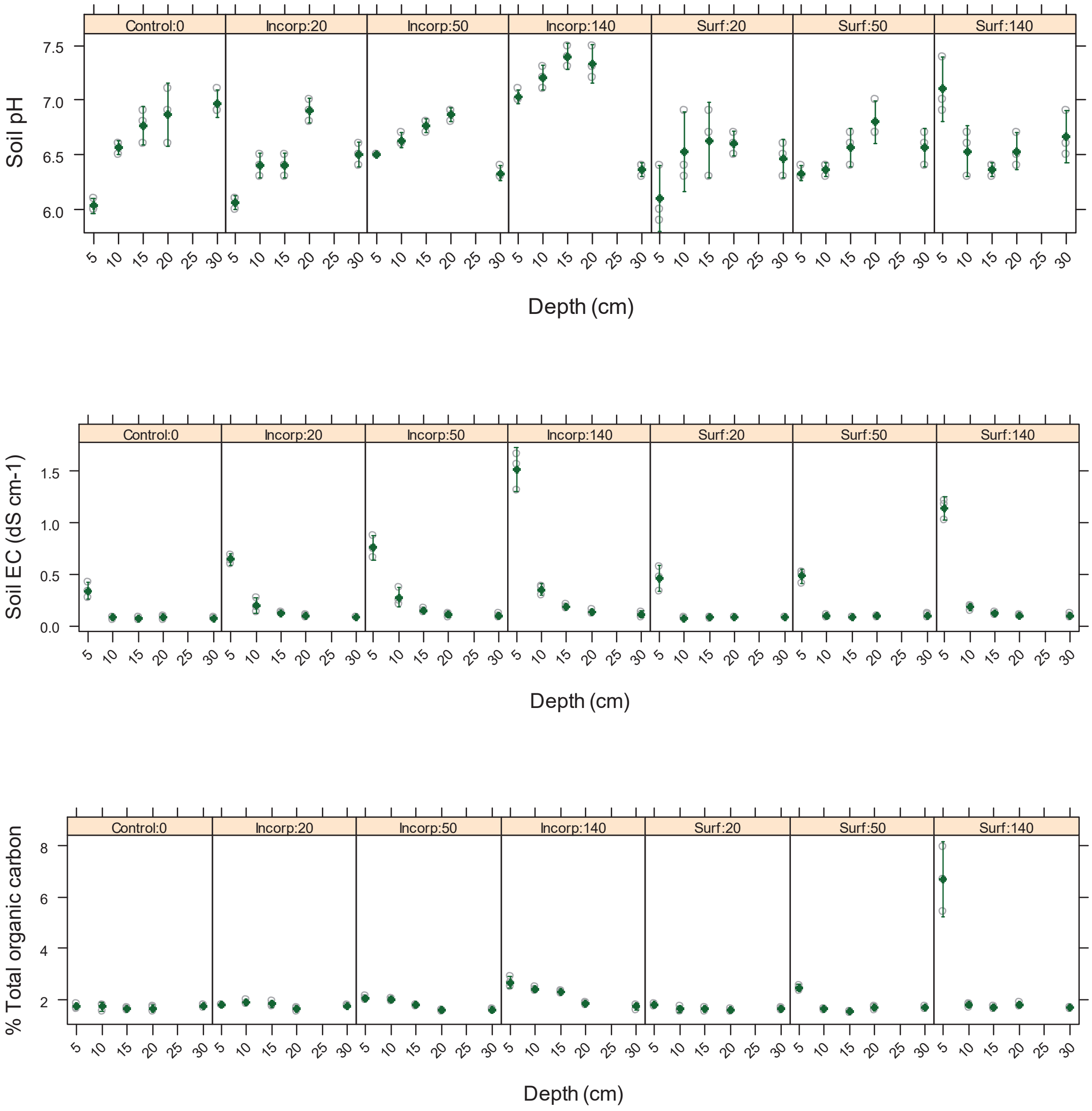


Figure B.5. Soil pH, EC and TOC in SL2 after 6 month following MWOO application

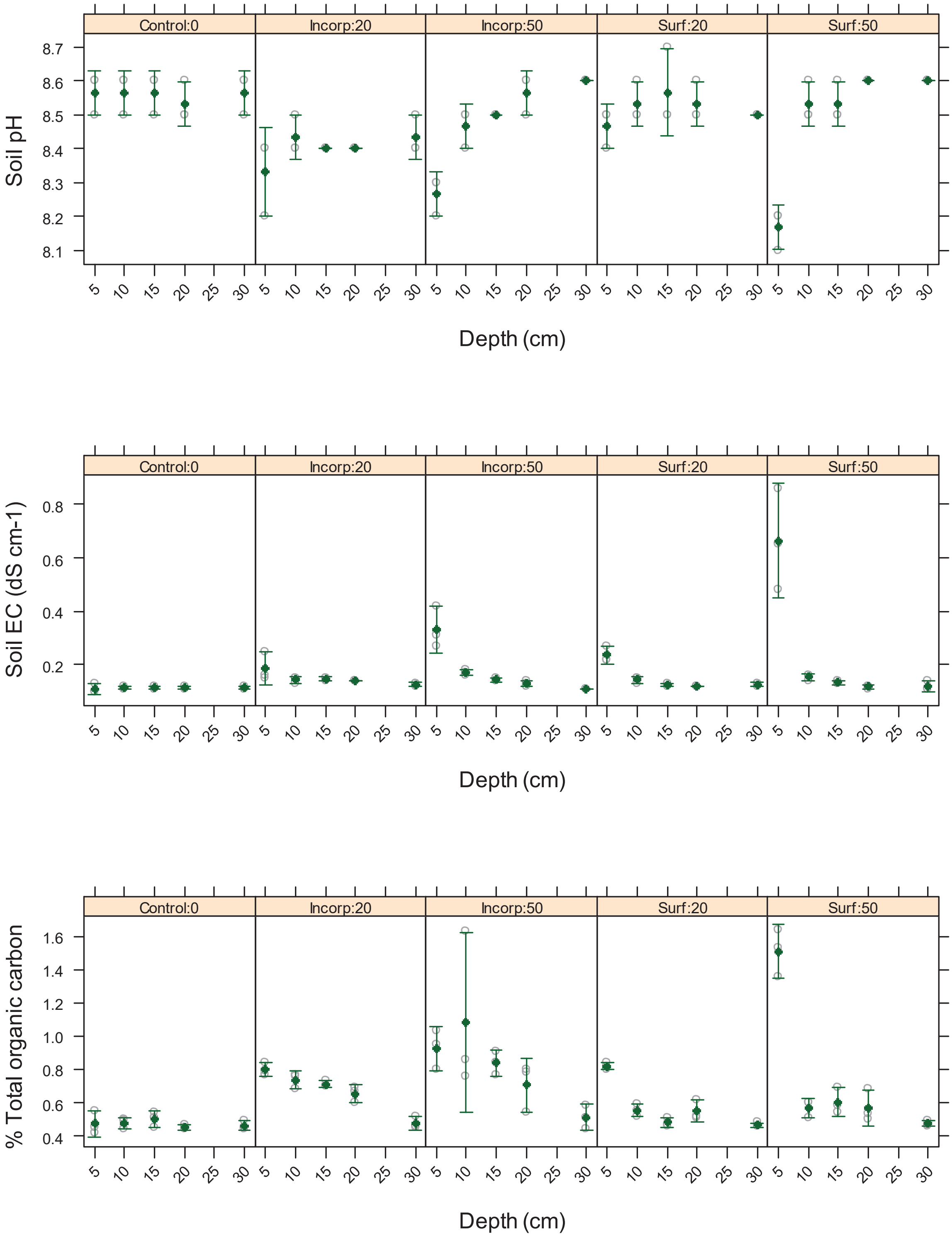


Figure B.6. Soil pH, EC and TOC in SL3 after 6 month following MWOO application

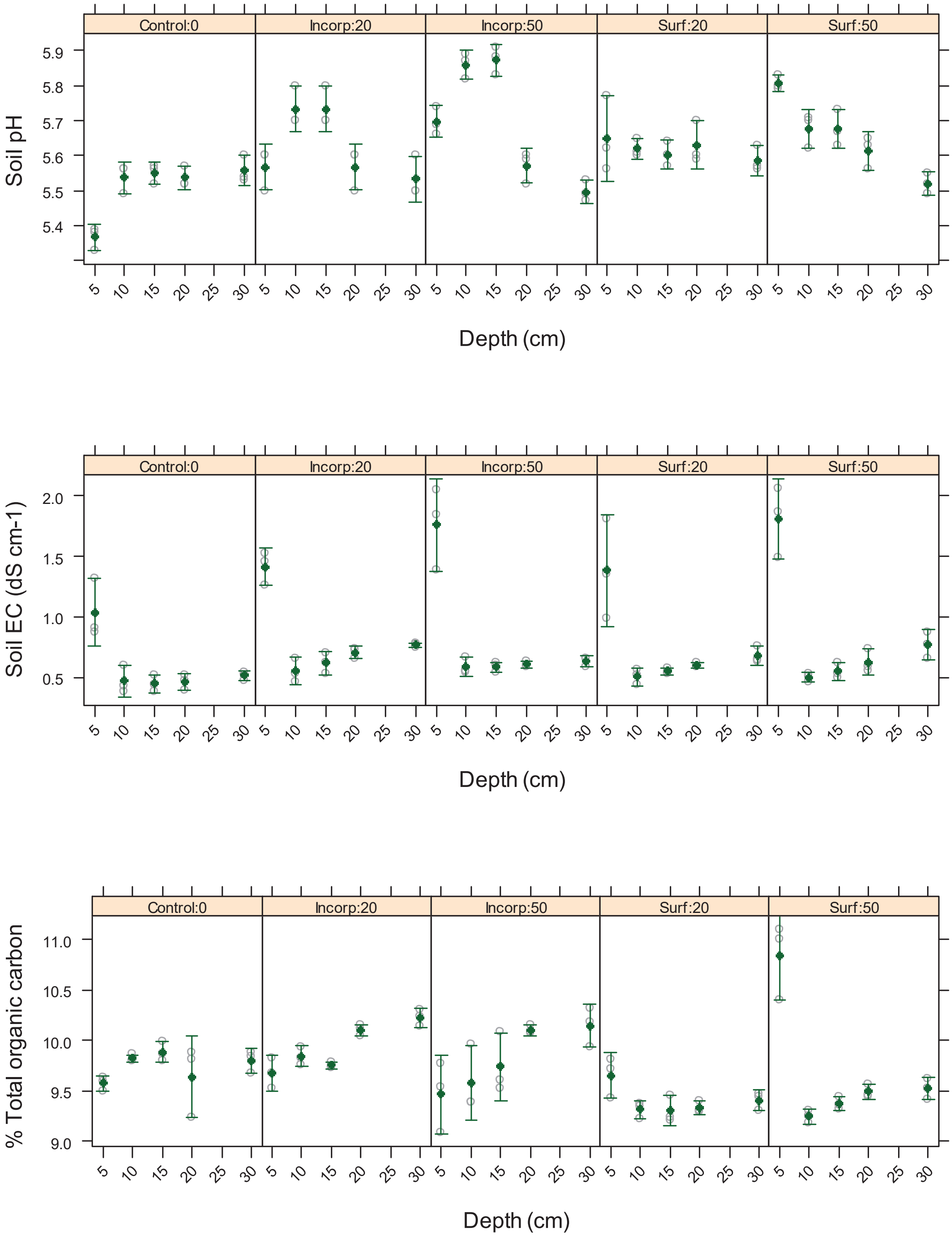


Figure B.7. Soil pH, EC and TOC in OM1 after 6 month following MWOO application

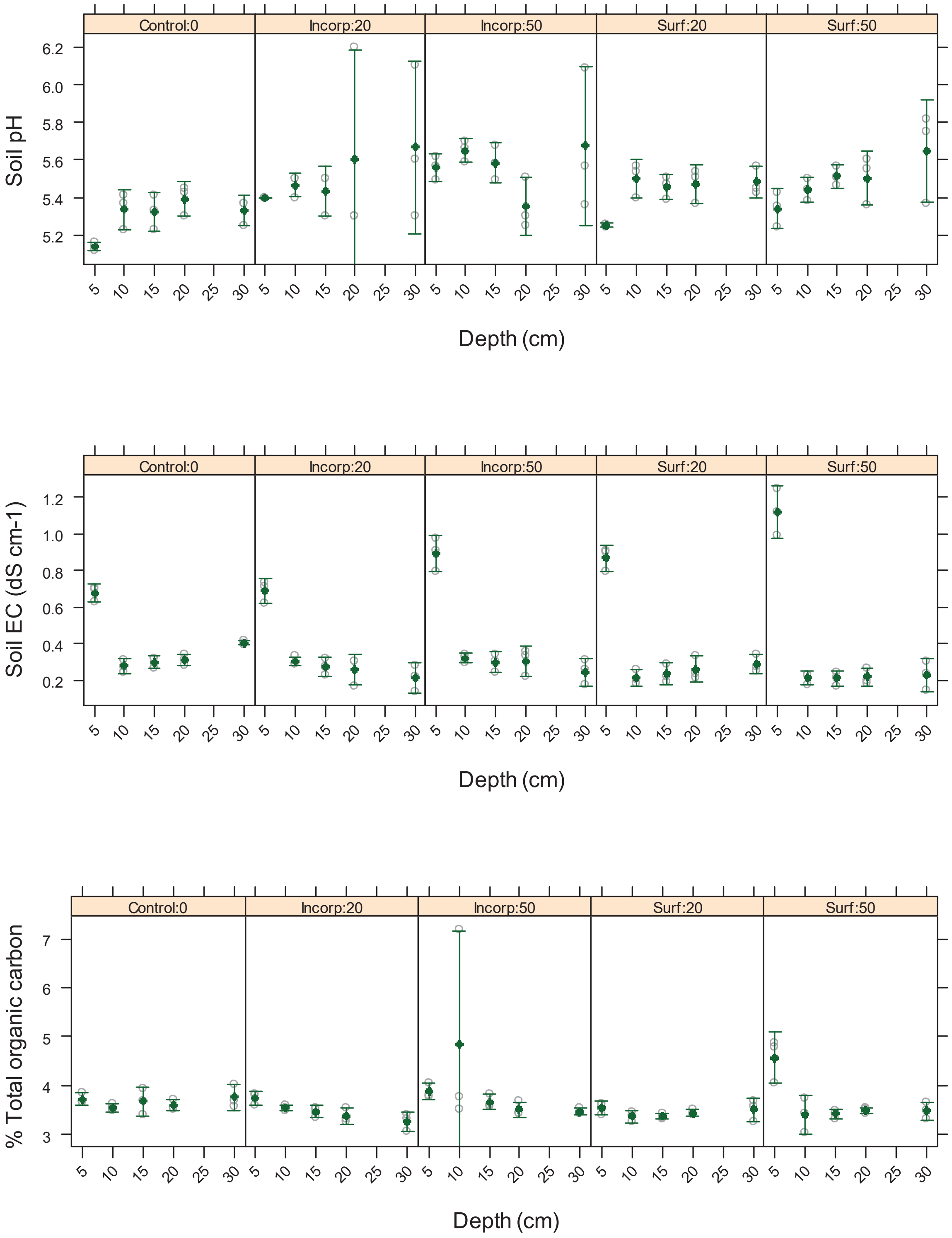


Figure B.8. Soil pH, EC and TOC in C1 after 6 month following MWOO application

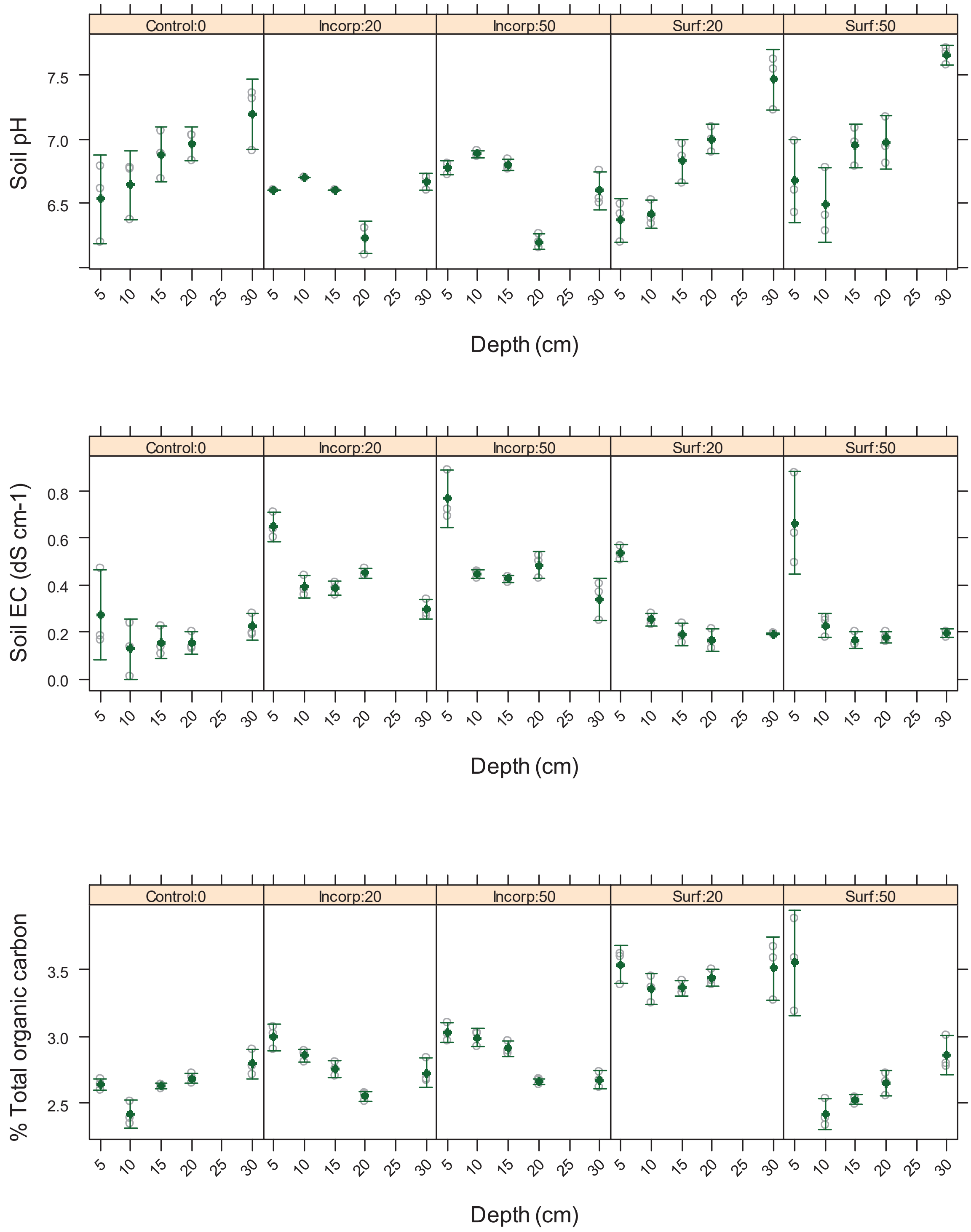


Figure B.9. Soil pH, EC and TOC in C2 after 6 month following MWOO application

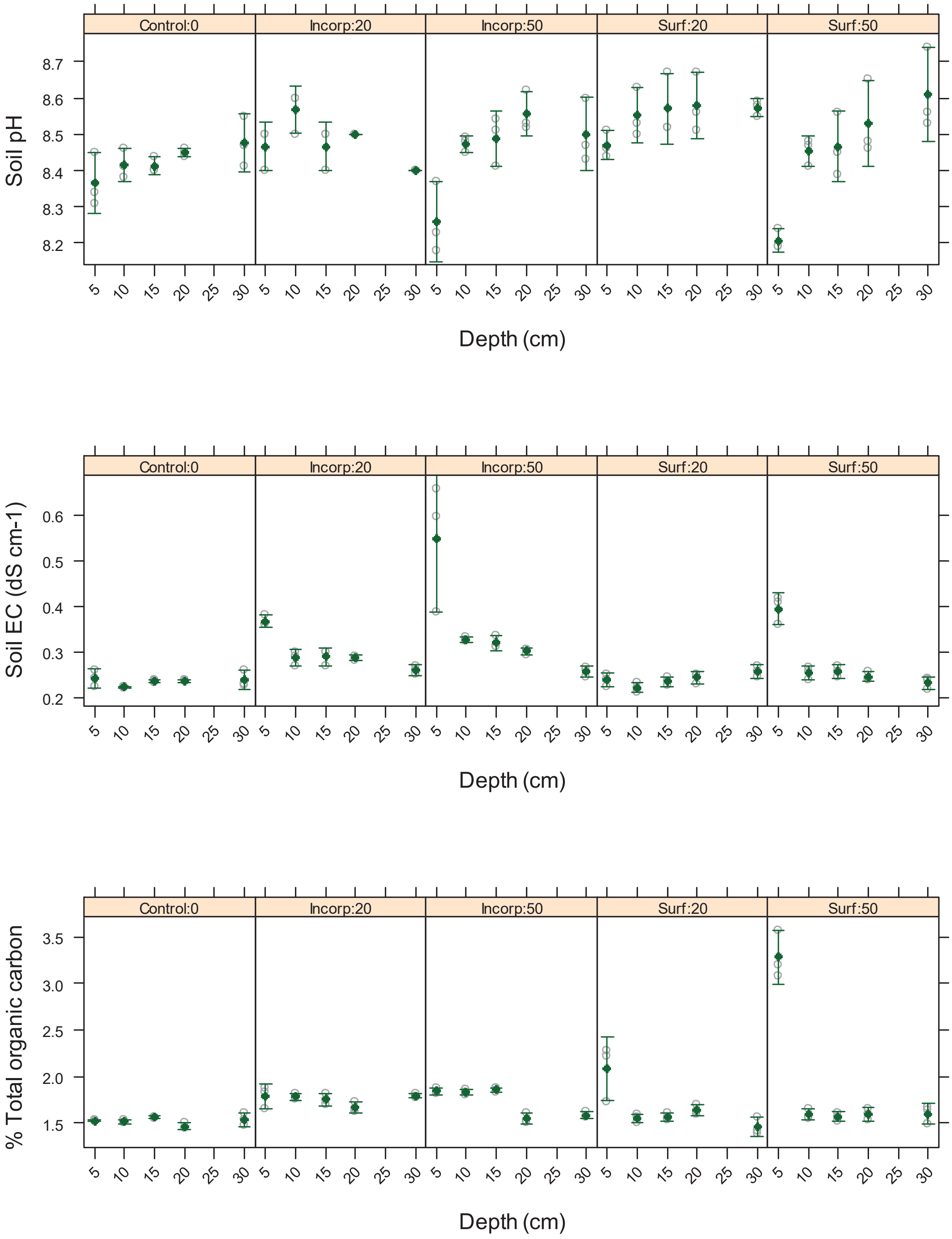


Figure B.10. Soil pH, EC and TOC in C3 after 6 month following MWOO application

Appendix C

Comparison of metal and metalloid concentrations in four fractions in MWOO and sandy loam and clay soils following MWOO application over time

Table C.1. Mean concentration of six metals (mg kg^{-1}) in four fractions in MWOO

Element	Fraction				Total	% Recovery
	EXCH	REDU	OXI	RES		
As	1.05 ± 0.03	1.09 ± 0.05	1.61 ± 0.03	1.28 ± 0.20	4.63 ± 1.01	108.85
Cd	0.29 ± 0.03	1.11 ± 0.04	0.20 ± 0.33	0.03 ± 0.01	1.25 ± 0.07	131.47
Cr	1.63 ± 0.02	3.30 ± 0.04	22.75 ± 0.04	46.78 ± 0.48	86.69 ± 1.57	85.90
Cu	11.65 ± 0.03	16.81 ± 0.06	158.63 ± 0.23	14.90 ± 1.58	157.02 ± 4.64	128.65
Ni	3.45 ± 0.1	1.90 ± 0.01	7.88 ± 0.09	9.30 ± 0.03	31.41 ± 6.45	87.66
Pb	12.72 ± 0.46	61.41 ± 1.73	112.39 ± 4.09	83.25 ± 5.17	326.31 ± 3.78	82.67
Zn	88.87 ± 6.10	149.80 ± 3.16	41.54 ± 1.98	46.42 ± 2.30	374.05 ± 7.45	87.32

EXCH = exchangeable fraction; REDU = reducible fraction, OXI = oxidizable fraction; RES = residual fraction, <dl = below detection limit. Values reported mean ± standard error

Table C.2. Mean concentration of six metals (mg kg^{-1}) in the fractions of controls and MWOO amended soils following six month MWOO application

Soil	**Treatment**	**Fraction**				**Total**	**% Recovery**
		EXCH	**REDU**	**OXI**	**RES**		
				As			
Sandy loam	**Control**	0.08 ± 0.06a	0.44 ± 0.04a	3.77 ± 0.18a	42.83 ± 3.84a	53.56 ± 6.25a	87.97
	50 t ha^{-1}	0.48 ± 0.1b	0.65 ± 0.12a	4.20 ± 0.21a	45.63 ± 4.19a	56.65 ± 1.27a	89.93
Clay	**Control**	<dl	<dl	0.05 ± 0.04a	2.40 ± 0.23a	2.11 ± 0.51a	115.45
	50 t ha^{-1}	0.01 ± 0.03	<dl	0.15 ± 0.02a	2.50 ± 0.16a	1.99 ± 0.83a	110.88
				Cr			
Sandy loam	**Control**	<dl	<dl	1.75 ± 0.03a	13.76 ± 0.20a	18.74 ± 1.01a	82.79
	50 t ha^{-1}	<dl	<dl	2.74 ± 0.03b	13.61 ± 0.05a	20.02 ± 2.43a	82.87
Clay	**Control**	<dl	0.54 ± 0.04a	20.49 ± 0.33a	116.76 ± 0.28a	195.02 ± 6.97a	78.72
	50 t ha^{-1}	<dl	0.26 ± 0.01b	19.50 ± 0.43a	123.6 ± 0.60b	185.86 ± 12.04b	77.13
				Cu			
Sandy loam	**Control**	0.09 ± 0.02a	0.64 ± 0.04a	0.79 ± 0.04a	9.25 ± 0.48a	13.70 ± 0.57a	84.73
	50 t ha^{-1}	0.29 ± 0.11a	1.34 ± 0.15b	2.78 ± 0.47b	11.46 ± 0.39b	16.33 ± 2.38b	97.16
Clay	**Control**	0.12 ± 0.03a	1.10 ± 0.06a	5.25 ± 0.23a	29.81 ± 1.58a	43.03 ± 0.73a	84.28
	50 t ha^{-1}	0.07 ± 0.02a	1.03 ± 0.1a	6.24 ± 0.22 a	32.90 ± 2.29a	47.08 ± 4.28a	95.87
				Ni			
Sandy loam	**Control**	0.08 ± 0.0a	<dl	0.07 ± 0.0a	4.05 ± 0.28a	4.95 ± 0.30a	84.69
	50 t ha^{-1}	0.13 ± 0.02a	0.07 ± 0.12	0.30 ± 0.04b	3.66 ± 0.09a	5.10 ± 1.47a	80.46
Clay	**Control**	3.11 ± 0.72a	17.54 ± 0.46a	17.22 ± 1.73a	65.98 ± 3.42a	126.45 ± 5.17a	82.12
	50 t ha^{-1}	2.18 ± 0.20a	17.12 ± 0.24a	19.21 ± 0.66a	67.13 ± 4.84a	123.90 ± 6.62a	85.26
				Pb			
Sandy loam	**Control**	0.07 ± 0.02a	1.46 ± 0.10a	1.00 ± 0.16a	7.80 ± 0.98a	10.66 ± 0.30a	96.78
	50 t ha^{-1}	0.20 ± 0.07a	5.18 ± 0.17b	2.23 ± 0.38b	8.51 ± 1.96a	14.80 ± 3.17b	118.14
Clay	**Control**	0.01 ± 0.03	0.09 ± 0.15a	0.43 ± 0.08a	3.55 ± 0.11a	4.31 ± 0.51a	94.50
	50 t ha^{-1}	<dl	1.76 ± 0.61b	1.84 ± 0.40b	6.96 ± 1.02a	8.91 ± 2.70 b	118.51
				Zn			
Sandy loam	**Control**	0.36 ± 0.11a	<dl	0.21 ± 0.14a	18.77 ± 1.29a	17.38 ± 0.89a	108.43
	50 t ha^{-1}	2.78 ± 0.42b	1.99 ± 0.33	3.45 ± 0.44b	23.92 ± 0.68b	24.02 ± 3.98b	115.52
Clay	**Control**	2.93 ± 1.57a	5.33 ± 0.27a	9.26 ± 0.39a	61.67 ± 3.10a	98.79 ± 2.64a	80.14
	50 t ha^{-1}	1.85 ± 0.28b	12.06 ± 3.46b	11.85 ± 0.74b	65.21 ± 3.24a	96.12 ± 8.25a	85.70

EXCH = exchangeable fraction; REDU = reducible fraction, OXI = oxidizable fraction; RES = residual fraction, values at the same column followed by the same letter are not significantly different at $P < 0.05$. <dl = below detection limit. Values reported mean ± standard error

Table C.3. Mean concentration of six metals (mg kg^{-1}) in the fractions of controls and MWOO amended soils following 12 month MWOO application

Soil	**Treatment**	**Fraction**				**Total**	**% Recovery**
		EXCH	**REDU**	**OXI**	**RES**		
				As			
Sandy loam	**Control**	0.11 ± 0.0a	0.83 ± 0.06a	4.34 ± 0.15a	41.12 ± 1.86a	52.13 ± 6.25a	89.04
	50 t ha^{-1}	0.60 ± 0.1b	0.95 ± 0.08a	4.27 ± 0.22a	48.24 ± 3.53a	64.99 ± 1.27a	83.19
Clay	**Control**	<dl	0.13 ± 0.02a	0.53 ± 0.02a	1.50 ± 0.04a	1.90 ± 0.51a	113.74
	50 t ha^{-1}	<dl	0.12 ± 0.00a	0.55 ± 0.00a	1.68 ± 0.15a	2.39 ± 0.83a	98.26
				Cr			
Sandy loam	**Control**	<dl	0.09 ± 0.01a	2.22 ± 0.04a	15.19 ± 0.67a	21.56 ± 1.01a	81.20
	50 t ha^{-1}	<dl	0.11 ± 0.02a	2.50 ± 0.11a	17.36 ± 0.98a	21.34 ± 2.43a	93.56
Clay	**Control**	0.01 ± 0.01a	0.44 ± 0.09a	19.56 ± 0.51a	112.71 ± 7.71 a	161.90 ± 6.97a	81.99
	50 t ha^{-1}	0.03 ± 0.00a	0.42 ± 0.06a	20.79 ± 0.35a	127.06 ± 2.01a	183.73 ± 12.04b	80.72
				Cu			
Sandy loam	**Control**	0.34 ± 0.02a	1.30 ± 0.24a	1.38 ± 0.04a	11.43 ± 0.28a	13.98 ± 0.57a	103.32
	50 t ha^{-1}	1.05 ± 0.29a	2.28 ± 0.47a	3.16 ± 0.47b	12.60 ± 0.31b	17.47 ± 2.38b	109.35
Clay	**Control**	0.77 ± 0.14a	1.70 ± 0.13a	6.49 ± 0.44a	29.80 ± 1.88a	46.6 ± 0.73a	83.12
	50 t ha^{-1}	1.00 ± 0.12a	1.28 ± 0.13a	7.62 ± 0.74 a	36.56 ± 1.06b	51.25 ± 4.28a	90.68
				Ni			
Sandy loam	**Control**	0.13 ± 0.01a	0.07 ± 0.00a	0.60 ± 0.02a	5.69 ± 0.23a	8.07 ± 0.30a	80.58
	50 t ha^{-1}	0.33 ± 0.1a	0.21 ± 0.01b	0.69 ± 0.00b	5.72 ± 0.20a	7.98 ± 1.47a	87.23
Clay	**Control**	3.92 ± 0.22a	19.20 ± 0.47a	13.40 ± 0.04a	66.34 ± 3.87a	134.21 ± 5.17a	81.40
	50 t ha^{-1}	2.99 ± 0.29a	18.30 ± 0.70a	15.68 ± 0.35a	71.95 ± 0.66a	126.70 ± 6.62a	94.01
				Pb			
Sandy loam	**Control**	0.15 ± 0.03a	1.88 ± 0.07a	0.88 ± 0.02a	5.71 ± 0.09a	8.32 ± 0.30a	103.53
	50 t ha^{-1}	0.28± 0.04a	4.95 ± 0.14b	1.96 ± 0.21b	8.31 ± 0.31b	15.32 ± 3.17b	101.17
Clay	**Control**	<dl	0.25 ± 0.01a	0.83 ± 0.21a	3.13 ± 0.31a	3.95 ± 0.51a	106.65
	50 t ha^{-1}	<dl	2.13 ± 0.28b	2.21 ± 0.24b	7.24 ± 0.46b	12.09 ± 2.70 b	105.40
				Zn			
Sandy loam	**Control**	0.17 ± 0.03a	<dl	0.27 ± 0.02a	19.42 ± 1.29a	20.03 ± 0.89a	99.18
	50 t ha^{-1}	3.01 ± 0.48b	1.66 ± 0.10	2.63 ± 0.17b	21.15 ± 0.68a	29.90 ± 3.98b	95.18
Clay	**Control**	1.13 ± 0.21a	4.89 ± 0.32a	8.45 ± 0.64a	54.73 ± 3.94a	86.21 ± 2.64a	80.30
	50 t ha^{-1}	2.61 ± 0.25b	11.48 ± 0.27b	10.76 ± 0.27b	62.67 ± 0.86a	94.53 ± 8.25a	85.37

EXCH = exchangeable fraction; REDU = reducible fraction, OXI = oxidizable fraction; RES = residual fraction, values at the same column followed by the same letter are not significantly different at $P < 0.05$. <dl = below detection limit. Values reported ± standard error

Table C.4. Mean concentration of six metals (mg kg^{-1}) in the fractions of controls and MWOO amended soils following 18 month MWOO application

Soil	Treatment	Fraction				Total	% Recovery
		EXCH	REDU	OXI	RES		
				As			
Sandy loam	**Control**	0.09 ± 0.01a	0.68 ± 0.09a	4.12 ± 0.18a	45.82 ± 1.68a	48.03 ± 6.25a	105.60
	50 t ha^{-1}	0.75 ± 0.09b	0.86 ± 0.13a	4.42 ± 0.29a	35.97 ± 2.51a	54.36 ± 1.27a	80.98
Clay	**Control**	<dl	0.10 ± 0.01	0.39 ± 0.01a	2.26 ± 0.13a	2.30 ± 0.51a	120.30
	50 t ha^{-1}	<dl	<dl	0.44 ± 0.00b	2.39 ± 0.13a	2.30 ± 0.83a	94.34
				Cr			
Sandy loam	**Control**	<dl	0.18 ± 0.11a	1.25± 0.10a	16.32 ± 0.65a	22.75 ± 1.01a	78.04
	50 t ha^{-1}	0.02 ± 0.01	0.22 ± 0.05a	1.93 ± 0.19b	17.13 ± 0.98a	26.86 ± 2.43a	71.92
Clay	**Control**	0.06 ± 0.02a	0.46 ± 0.01a	21.86 ± 1.07a	142.47 ± 4.26a	200.68 ± 6.97a	90.38
	50 t ha^{-1}	0.04 ± 0.00a	0.36 ± 0.03b	19.95 ± 0.42a	142.38 ± 0.38a	213.25 ± 12.04b	83.98
				Cu			
Sandy loam	**Control**	0.27 ± 0.02a	1.89 ± 0.18a	0.67 ± 0.08a	11.79 ± 0.44a	13.70 ± 0.57a	111.07
	50 t ha^{-1}	0.49 ± 0.07a	2.58 ± 0.15a	2.97 ± 0.44b	11.94 ± 1.12a	19.13 ± 2.38b	94.08
Clay	**Control**	0.36 ± 0.03a	1.62 ± 0.36a	5.99 ± 0.60a	37.33 ± 1.58a	52.34 ± 0.73a	86.57
	50 t ha^{-1}	0.40 ± 0.09a	1.18 ± 0.04a	5.84 ± 0.18 a	37.86 ± 1.16a	54.69 ± 4.28a	82.84
				Ni			
Sandy loam	**Control**	0.10 ± 0.01a	0.63 ± 0.01a	0.62 ± 0.04a	6.03 ± 0.32a	8.38 ± 0.30a	82.42
	50 t ha^{-1}	0.26 ± 0.06a	0.44 ± 0.20a	0.32 ± 0.05b	5.77 ± 0.13a	8.25 ± 1.47a	80.60
Clay	**Control**	5.44 ± 0.18a	21.12 ± 1.20a	14.36 ± 1.56a	83.55 ± 2.69a	132.48 ± 5.17a	94.12
	50 t ha^{-1}	3.97± 0.07b	19.48 ± 0.70a	14.72 ± 0.35a	77.54 ± 3.20a	135.45 ± 6.62a	85.43
				Pb			
Sandy loam	**Control**	0.07 ± 0.01a	1.56 ± 0.65a	0.90 ± 0.04a	6.00 ± 0.09a	7.97 ± 0.30a	107.18
	50 t ha^{-1}	0.46 ± 0.10a	5.46 ± 0.49b	1.88 ± 0.06b	6.94 ± 0.61a	15.54 ± 3.17b	95.68
Clay	**Control**	<dl	0.21 ± 0.01a	0.68 ± 0.05a	3.84 ± 0.25a	4.95 ± 0.51a	96.30
	50 t ha^{-1}	<dl	1.62 ± 0.05b	2.37 ± 0.03b	6.69 ± 0.21b	12.09 ± 2.70 b	88.39
				Zn			
Sandy loam	**Control**	0.52 ± 0.03a	0.35 ± 0.03a	0.48 ± 0.04a	20.06± 0.92a	25.03 ± 0.89a	85.64
	50 t ha^{-1}	5.82 ± 0.83b	1.99 ± 0.25b	3.09 ± 0.21b	21.86 ± 0.73a	33.02 ± 3.98b	99.29
Clay	**Control**	1.84 ± 0.12a	5.28 ± 0.59a	10.63 ± 1.03a	78.42 ± 5.82a	111.56 ± 2.64a	86.21
	50 t ha^{-1}	3.09 ± 0.07b	13.29 ± 0.99b	12.08 ± 0.26a	72.15 ± 1.91a	127.74 ± 8.25a	80.40

EXCH = exchangeable fraction; REDU = reducible fraction, OXI = oxidizable fraction; RES = residual fraction, values at the same column followed by the same letter are not significantly different at $P < 0.05$. <dl = below detection limit. Values reported ± standard error

Appendix D

Changes of metal and metalloid concentrations in three extractants following MWOO application and comparison of the four fractions after sequential extraction

Table D1. Mean concentration of seven metals (mg kg^{-1}) in soil solution over 48 hours in controls and MWOO amended soils leached by deionized water, $CaCl_2$ and EDTA

Extractant	Treatment	Time (h)								
		0	0.5	1	2	4	8	16	24	48
As										
H_2O	**Control**	0	0.03 ± 0.0	0.03 ± 0.0	0.04 ± 0.0	0.04 ± 0.003	0.04 ± 0.0	0.05 ± 0.0	0.06 ± 0.001	0.04 ± 0.0
	MWOO treated	0	0.05 ± 0.001	0.06 ± 0.001	0.07 ± 0.0	0.09 ± 0.008	0. 11 ± 0.001	0. 11 ± 0.0	0. 11 ± 0.0	0. 10 ± 0.001
$CaCl_2$	**Control**	0	0.003 ± 0.0003	0.007 ± 0.0003	0. 013 ± 0.0003	0. 01 ± 0.0	0. 013 ± 0.0003	0. 013 ± 0.0003	0. 013 ± 0.0007	0. 01 ± 0.0006
	MWOO treated	0	0.03 ± 0.0	0. 03 ± 0.0	0. 03 ± 0.0	0. 03 ± 0.0	0. 037 ± 0.0007	0. 03 ± 0.0	0. 037 ± 0.0003	0. 033 ± 0.0003
EDTA	**Control**	0	0.024 ± 0.002	0.024 ± 0.0	0. 25 ± 0.0	2.9 ± 0.0	3.4 ± 0.001	4.0 ± 0.001	4.3 ± 0.002	5.0 ± 0.001
	MWOO treated	0	0. 27 ± 0.003	0. 37 ± 0.001	0. 43 ± 0.002	0. 46 ± 0.002	0. 57 ± 0.001	0. 81 ± 0.002	0. 99 ± 0.01	1.0 ± 0.006
Cd										
H_2O	**Control**	0	0. 0005 ± 0.0	0.0005 ± 0.0	0.0005 ± 0.0	0.0005 ± 0.0	0.0005 ± 0.0	0.0005 ± 0.0	0.0006 ± 6.67E-05	0.0005 ± 0.0
	MWOO treated	0	0.001 ± 0.0001	0.005 ± 3E-05	0.001 ± 0.0	0.001 ± 0.0	0.005 ± 0.0	0.003 ± 3.3E-05	0. 001 ± 5.77E-05	0.002 ± 8.82E-05
$CaCl_2$	**Control**	0	0.002 ± 0.0	0.002 ± 0.0	0.002 ± 0.0	0.002 ± 0.0	0.0005 ± 0.0	0.002 ± 0.0	0.002 ± 0.0	0.002 ± 0.0
	MWOO treated	0	0.004 ± 3E-05	0.004 ± 0.0	0.004 ± 3E-05	0.004 ± 3E-05	0.001 ± 0.0001	0.004 ± 3E-05	0.004 ± 0.0	0.004 ± 3.33E-05
EDTA	**Control**	0	0.002 ± 0.0	0.0023 ± 3.3E-05	0.002 ± 3E-05	0.003 ± 3E-05	0.0027 ± 3.3E-05	0.002 ± 3E-05	0.0027 ± 3.3E-05	0.003 ± 0.0
	MWOO treated	0	0.018 ± 8E-05	0. 0267 ± 0.006	0. 03 ± 6E-04	0. 021 ± 0.0004	0. 031 ± 0.0002	0. 029 ± 0.0003	0. 0347 ± 0.0005	0. 05067 ± 0.001
Cr										
H_2O	**Control**	0	0. 005 ± 0.0	0. 007 ± 0.0003	0. 020 ± 0.0	0. 01 ± 0.002	0.013 ± 0.0009	0.027 ± 0.0003	0.053 ± 0.002	0. 013 ± 0.0003
	MWOO treated	0	0. 027 ± 0.0003	0.037 ± 0.0007	0. 033 ± 0.0003	0. 05 ± 0.003	0. 04 ± 0.0006	0. 047 ± 0.0003	0. 053 ± 0.0009	0. 050 ± 0.0006

$CaCl_2$	**Control**	0	0.005 ± 0.0	0. 005 ± 0.0	0. 07 ± 0.0007	0. 005 ± 0.0	0. 005 ± 0.0	0. 005 ± 0.0	0.005 ± 0.0	0. 003 ± 0.0003
	MWOO treated	0	0.02 ± 0.0	0. 020 ± 0.0006	0. 17 ± 0.0003	0. 013 ± 0.0003	0. 027 ± 0.0003	0. 02 ± 0.0	0.020 ± 0.0	0. 023 ± 0.0003
EDTA	**Control**	0	0.02 ± 0.0	0. 023 ± 0.0003	0. 3 ± 3E-04	0. 04 ± 0.0	0. 07 ± 0.0003	0. 09 ± 0.0	0. 10 ± 0.0003	0. 13 ± 0.0003
	MWOO treated	0	0.073 ± 0.002	1.2 ± 0.0006	1.4 ± 7E-04	0. 157 ± 0.001	0. 18 ± 0.0008	0. 21 ± 0.0003	0.3 ± 0.004	0.3 ± 0.001
Cu										
H_2O	**Control**	0	0. 093 ± 0.0007	0. 063 ± 0.002	0. 16 ± 0.006	0. 110 ± 0.008	0. 15 ± 0.003	0. 1 ± 0.0006	0. 283 ± 0.01	0.09 ± 0.0009
	MWOO treated	0	0. 25 ± 0.0007	0.3 ± 0.002	0. 28 ± 0.001	0. 3 ± 0.027	0. 32 ± 0.003	0. 24 ± 0.0	0. 637 ± 0.03	0. 38 ± 0.001
$CaCl_2$	**Control**	0	0. 05 ± 0.0006	0.013 ± 0.0003	0. 043 ± 0.0003	0. 063 ± 0.002	0.053 ± 0.0003	0.03 ± 0.0006	0. 05 ± 0.001	0. 04 ± 0.0006
	MWOO treated	0	0. 16 ± 0.001	0. 14 ± 0. 003	0.13 ± 0.0009	0. 137 ± 0.0003	0. 16 ± 0.0009	0. 12 ± 0.001	0. 14 ± 0.001	0. 14 ± 0.0007
EDTA	**Control**	0	0. 71 ± 0.001	0. 64 ± 0.001	0. 74 ± 0.003	0. 8 ± 0.002	0. 9 ± 0.004	0. 98 ± 0.001	1.0 ± 0.003	1.1 ± 0.001
	MWOO treated	0	1.2 ± 0.02	2.0 ± 0.02	1.9 ± 0.008	2.1 ± 0.01	2.3 ± 0.01	2.3 ± 0.002	3.0 ± 0.04	3.0 ± 0.01
Ni										
H_2O	**Control**		0.03 ± 0.001	0. 03 ± 0.002	0. 09 ± 0.002	0. 04 ± 0.003	0.16 ± 0.01	0.08 ± 0.001	0.17 ± 0.007	0.16 ± 0.006
	MWOO treated	0	0. 06 ± 0.001	0. 08 ± 0.005	0. 11 ± 0.005	0. 3 ± 0.01	0.1 ± 0.001	0.1 ± 0.001	0.13 ± 0.004	0.11 ± 0.001
$CaCl_2$	**Control**	0	0. 023 ± 0.0003	0. 04 ± 0.003	0. 04 ± 0.0	0. 047 ± 0.0007	0.083 ± 0.0009	0.06 ± 0.0	0.067 ± 0.0003	0.1 ± 0.001
	MWOO treated	0	0. 04 ± 0.0	0. 023 ± 0.0003	0. 043 ± 0.0003	0. 043 ± 0.0003	0.073 ± 0.0003	0.05 ± 0.006	0.053 ± 0.0009	0.11 ± 0.005
EDTA	**Control**	0	0. 073 ± 0.0007	0. 043 ± 0.0003	0. 07 ± 3E-04	0.08 ± 0.0003	0.09 ± 0.0003	0.097 ± 0.000	0.1 ± 0.001	0.14 ± 0.003
	MWOO treated	0	0. 15 ± 0.004	0. 21 ± 0.002	0. 24 ± 0.002	0.29 ± 0.002	0.28 ± 0.001	0.29 ± 0.0009	0.34 ± 0.004	0.4 ± 0.001
Pb										
H_2O	**Control**	0	0.01 ± 0.0	0.01 ± 0.0006	0.017 ± 0.0003	0.02 ± 0.001	0.043 ± 0.001	0.04 ± 0.001	0.097 ± 0.003	0.17 ± 0.006

	MWOO treated	0	0.05 ± 0.0007	0.07 ± 0.001	0.057 ± 0.0003	0.07 ± 0.006	0.063 ± 0.0003	0.06 ± 0.001	0.077 ± 0.001	0.14 ± 0.007
$CaCl_2$	**Control**	0	0.037 ± 0.0003	0.017 ± 0.0003	0.047 ± 0.002	0.023 ± 0.0003	0.023 ± 0.0003	0.02 ± 0.0	0.015 ± 0.0	0.027 ± 0.0007
	MWOO treated	0	0.04 ± 0.0006	0.017 ± 0.0003	0.03 ± 0.0006	0.02 ± 0.0	0.023 ± 0.0009	0.017 ± 0.0003	0.004 ± 0.0003	0.013 ± 0.0003
EDTA	**Control**	0	1.1 ± 0.005	1.1 ± 0.003	1.1 ± 0.005	1.2 ± 0.002	1.3 ± 0.006	1.5 ± 0.006	1.4 ± 0.006	1.7 ± 0.006
	MWOO treated	0	3.0 ± 0.09	4.2 ± 0.01	4.1 ± 0.02	4.3 ± 0.04	4.5 ± 0.02	4.7 ± 0.007	6.0 ± 0.07	6.0 ± 0.03
Zn										
H_2O	**Control**	0	0.30 ± 0.003	0.45 ± 0.02	0.61 ± 0.02	0.41 ± 0.006	0.8 ± 0.05	0.35 ± 0.003	0.31 ± 0.05	0.36 ± 0.01
	MWOO treated	0	0.30 ± 0.002	0.68 ± 0.04	0.5 ± 0.02	0.92 ± 0.02	0.40 ± 0.008	0.39 ± 0.004	0. 95 ± 0.05	0.67 ± 0.02
$CaCl_2$	**Control**	0	0.20 ± 0.003	0.56 ± 0.02	0.15 ± 0.001	0.30 ± 0.005	0.25 ± 0.006	0.29 ± 0.001	0.24 ± 0.002	0.28 ± 0.005
	MWOO treated	0	0.71 ± 0.004	0.79 ± 0.008	0.62 ± 0.002	0.79 ± 0.0	0.64 ± 0.004	0.73 ± 0.003	0.61 ± 0.003	0.70 ± 0.004
EDTA	**Control**	0	0.38 ± 0.001	0.24 ± 0.003	0.19 ± 0.003	0.27 ± 0.001	0.24 ± 0.002	0.30 ± 0.004	0.20 ± 0.002	0.30 ± 0.007
	MWOO treated	0	3.8 ± 0.17	6.3 ± 0.04	5.6 ± 0.03	5.5 ± 0.04	5.9 ± 0.02	5.9 ± 0.04	7.3 ± 0.12	7.4 ± 0.06

Values reported mean ± standard error

Table D.2.1 Repeated measures mixed model 3-way ANOVA investigating changes in As concentration in soil solution extracted by different leaching agent, application rate over time

```
                                   Sum Sq Df  F value    Pr(>F)
Application.rate                 0.005047  1  411.643 < 2.2e-16 ***
Extractant                       0.061376  2 2502.994 < 2.2e-16 ***
Time                             0.006538  7   76.177 < 2.2e-16 ***
Application.rate:Extractant      0.005213  2  212.594 < 2.2e-16 ***
Application.rate:Time            0.001699  7   19.797 3.464e-16 ***
Extractant:Time                  0.010329 14   60.177 < 2.2e-16 ***
Application.rate:Extractant:Time 0.002849 14   16.600 < 2.2e-16 ***
Residuals                        0.001177 96
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

Table D.2.2 Repeated measures mixed model 3-way ANOVA investigating changes in Cd concentration in soil solution extracted by different leaching agent, application rate over time

```
                                     Sum Sq Df  F value    Pr(>F)
Application.rate                 3.6451e-05  1 161.0741 < 2.2e-16 ***
Extractant                       6.9108e-05  2 152.6905 < 2.2e-16 ***
Time                             4.1140e-06  7   2.5971  0.016931 *
Application.rate:Extractant      5.6164e-05  2 124.0918 < 2.2e-16 ***
Application.rate:Time            3.6770e-06  7   2.3210  0.031279 *
Extractant:Time                  7.2270e-06 14   2.2812  0.009728 **
Application.rate:Extractant:Time 6.4640e-06 14   2.0401  0.022265 *
Residuals                        2.1725e-05 96
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

Table D.2.3 Repeated measures mixed model 3-way ANOVA investigating changes in Cr concentration in soil solution extracted by different leaching agent, application rate over time

```
                                   Sum Sq Df  F value Pr(>F)
Application.rate                 0.039398  1 477.3044 <2e-16 ***
Extractant                       0.129545  2 784.7090 <2e-16 ***
Time                             0.019826  7  34.3125 <2e-16 ***
Application.rate:Extractant      0.009286  2  56.2475 <2e-16 ***
Application.rate:Time            0.000538  7   0.9312 0.4862
Extractant:Time                  0.018307 14  15.8423 <2e-16 ***
Application.rate:Extractant:Time 0.001995 14   1.7262 0.0626 .
Residuals                        0.007924 96
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

Table D.2.4 Repeated measures mixed model 3-way ANOVA investigating changes in Cu concentration in soil solution extracted by different leaching agent, application rate over time

```
                                  Sum Sq Df   F value    Pr(>F)
Application.rate                 0.35302  1  390.9429 < 2.2e-16 ***
Extractant                       2.30965  2 1278.8750 < 2.2e-16 ***
Time                             0.05372  7    8.4987 4.574e-08 ***
Application.rate:Extractant      0.09004  2   49.8554 1.417e-15 ***
Application.rate:Time            0.01582  7    2.5028 0.0209053 *
Extractant:Time                  0.04344 14    3.4359 0.0001586 ***
Application.rate:Extractant:Time 0.02210 14    1.7482 0.0583504 .
Residuals                        0.08669 96
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

Table D.2.5 Repeated measures mixed model 3-way ANOVA investigating changes in Ni concentration in soil solution extracted by different leaching agent, application rate over time

```
                                   Sum Sq Df F value    Pr(>F)
Application.rate                 0.025269  1 52.8154 9.746e-11 ***
Extractant                       0.085011  2 88.8434 < 2.2e-16 ***
```

```
Time                             0.028501  7  8.5104 4.470e-08 ***
Application.rate:Extractant      0.038404  2 40.1354 2.150e-13 ***
Application.rate:Time            0.004244  7  1.2672 0.2747956    
Extractant:Time                  0.021400 14  3.1950 0.0003764 ***
Application.rate:Extractant:Time 0.012473 14  1.8622 0.0403040 *  
Residuals                        0.045930 96                      
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

Table D.2.6 Repeated measures mixed model 3-way ANOVA investigating changes in Pb concentration in soil solution extracted by different leaching agent, application rate over time

```
                                  Sum Sq Df   F value    Pr(>F)    
Application.rate                 0.25499  1  246.2345 < 2.2e-16 ***
Extractant                       2.76602  2 1335.5267 < 2.2e-16 ***
Time                             0.02214  7    3.0538  0.006041 ** 
Application.rate:Extractant      0.49299  2  238.0311 < 2.2e-16 ***
Application.rate:Time            0.01819  7    2.5095  0.020592 *  
Extractant:Time                  0.03109 14    2.1448  0.015587 *  
Application.rate:Extractant:Time 0.04132 14    2.8503  0.001297 ** 
Residuals                        0.09941 96                        
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

Table D.2.7 Repeated measures mixed model 3-way ANOVA investigating changes in Zn concentration in soil solution extracted by different leaching agent, application rate over time

```
                                  Sum Sq Df  F value Pr(>F)    
Application.rate                 13.0026  1 220.5320 <2e-16 ***
Extractant                        6.3456  2  53.8128 <2e-16 ***
Time                              0.3299  7   0.7993 0.5898    
Application.rate:Extractant       9.6619  2  81.9359 <2e-16 ***
Application.rate:Time             0.3748  7   0.9081 0.5037    
Extractant:Time                   0.5742 14   0.6956 0.7736    
Application.rate:Extractant:Time  1.2807 14   1.5515 0.1077    
Residuals                         5.6602 96                    
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

Table D.3. Mean concentration of six metals and metalloids (mg kg^{-1}) in the fractions of controls and MWOO amended soil residues after leaching with deionized water, CaCl$_2$ and EDTA

Extractant	**Treatment**	**Fraction**				**Total concentration in extracted samples after 48 hours**	**% Recovery**
		EXCH	**REDU**	**OXI**	**RES**		
				As			
H2O	**Control**	0.06 ± 0.0	0.26 ± 0.02	0.64 ± 0.06	37.87 ± 1.68	49.08 ± 1.37	79.13
	50 t ha^{-1}	0.27 ± 0.07	0.41 ± 0.12	1.36 ± 0.30	40.55 ± 1.34	51.63 ± 0.12	82.48
CaCl2	**Control**	0.07 ± 0.009	0.31 ± 0.03	0.71 ± 0.06	37.50 ± 0.74	43.88 ± 2.80	87.94
	50 t ha^{-1}	0.20 ± 0.02	0.27 ± 0.01	0.85 ± 0.12	54.70 ± 14.78	55.35 ± 5.14	100.82
EDTA	**Control**	0.62 ± 0.05	0.27 ± 0.01	0.67 ± 0.01	42.85 ± 4.83	52.35 ± 2.67	84.82
	50 t ha^{-1}	0.65 ± 0.05	0.25 ± 0.02	0.95 ± 0.16	34.22 ± 1.86	43.62 ± 1.46	82.69
				Cr			
H2O	**Control**	< dl	0.04 ± 0.01	0.96 ± 0.08	10.30 ± 0.92	13.40 ± 0.63	84.36
	50 t ha^{-1}	0.02 ± 0.02	0.01 ± 0.02	1.68 ± 0.17	10.33 ± 0.52	12.70 ± 1.12	94.78
CaCl2	**Control**	<dl	0.03 ± 0.009	1.02 ± 0.07	10.81 ± 0.74	13.90 ± 0.35	85.27
	50 t ha^{-1}	0.01 ± 0.01	0.06 ± 0.0	1.26 ± 0.04	9.88 ± 1.37	11.75 ± 0.09	95.33
EDTA	**Control**	0.09 ± 0.01	0.06 ± 0.0	1.02 ±0.05	9.10 ± 0.71	12.58 ± 0.76	81.59
	50 t ha^{-1}	0.12 ± 0.01	0.07 ± 0.01	1.47 ± 0.21	9.92 ± 1.37	12.60 ± 0.74	91.86
				Cu			
H2O	**Control**	0.13 ± 0.01	0.30 ± 0.02	0.58 ± 0.06	7.97 ± 0.40	10.18 ± 0.54	88.19
	50 t ha^{-1}	0.21 ± 0.03	0.43 ± 0.06	2.34 ± 0.56	8.21 ± 0.33	14.02± 0.33	79.81
CaCl2	**Control**	0.15 ± 0.009	0.30 ± 0.02	0.60 ± 0.06	7.50 ± 0.41	9.80 ± 0.67	87.17
	50 t ha^{-1}	0.30 ± 0.07	0.35 ± 0.05	1.90 ± 0.07	6.70 ± 0.30	11.78 ± 0.44	78.47
EDTA	**Control**	0.22 ± 0.01	< dl	0.70 ± 0.03	6.18 ± 0.25	7.50 ± 0.43	94.67
	50 t ha^{-1}	0.28 ± 0.01	< dl	0.88 ± 0.14	6.58 ± 0.74	9.23 ± 0.14	83.81
				Ni			
H2O	**Control**	< dl	0.04 ± 0.01	0.14 ± 0.01	4.0 ± 0.20	4.62 ± 0.34	90.46
	50 t ha^{-1}	0.06 ± 0.04	0.14 ± 0.02	0.35 ± 0.04	3.50 ± 0.13	4.52 ± 0.54	89.51
CaCl2	**Control**	< dl	0.02 ± 0.00	0.12 ± 0.01	3.90 ± 0.30	3.64 ± 0.12	110.89
	50 t ha^{-1}	0.08 ± 0.01	0.10 ± 0.02	0.28 ± 0.01	3.19 ± 0.13	4.05 ± 0.18	90.00
EDTA	**Control**	0.02 ± 0.02	0.01 ± 0.01	0.19 ± 0.01	3.31 ± 0.30	3.25 ± 0.34	108.53
	50 t ha^{-1}	0.11± 0.01	< dl	0.28 ± 0.04	3.58 ± 0.51	4.25 ± 0.46	93.21
				Pb			
H2O	**Control**	0.08 ± 0.01	0.74 ± 0.07	0.90 ± 0.03	4.87 ± 0.05	6.92 ± 0.07	95.10
	50 t ha^{-1}	0.31 ± 0.08	3.5 ± 1.03	3.70 ± 0.80	6.11 ± 0.34	12.42 ± 1.82	109.65
CaCl2	**Control**	0.09 ± 0.01	1.11 ± 0.08	0.88 ± 0.04	4.50 ± 0.21	7.03 ± 0.35	93.51
	50 t ha^{-1}	0.16 ± 0.01	2.23 ± 0.26	2.06 ± 0.22	5.94 ± 1.02	10.50 ± 0.87	99.03
EDTA	**Control**	0.22 ± 0.01	0.13 ± 0.01	0.88 ± 0.01	4.19 ± 0.13	5.35 ± 0.21	101.17
	50 t ha^{-1}	0.32 ± 0.02	0.14 ± 0.009	0.90 ± 0.05	5.05 ± 0.50	6.02 ± 0.86	106.44
				Zn			
H2O	**Control**	0.20 ± 0.04	< dl	0.82 ± 0.25	16.38 ± 1.54	13.50 ± 1.38	128.82

	50 t ha^{-1}	5.41± 1.39	2.37 ± 0.67	1.35 ± 0.15	11.60 ± 0.47	20.90 ± 2.26	99.21
CaCl2	**Control**	0.06 ± 0.06	0.02 ± 0.02	0.48 ± 0.05	12.41 ± 0.75	13.46 ± 0.75	96.35
	50 t ha^{-1}	3.90 ± 0.60	1.26 ± 0.22	1.13 ± 0.13	8.38 ± 0.11	17.34 ± 0.11	84.56
EDTA	**Control**	0.20 ± 0.03	< dl	0.60 ± 0.07	10.40 ± 0.81	13.47 ± 0.81	83.14
	50 t ha^{-1}	0.50 ± 0.04	0.02 ± 0.02	0.84 ± 0.18	11.32 ± 1.40	13.83 ± 2.14	91.66

EXCH = exchangeable fraction; REDU = reducible fraction, OXI = oxidizable fraction; RES = residual fraction, <dl = below detection limit. Values reported mean ± standard error