THE UNIVERSITY of ADELAIDE

Assessing Natural and Management-Induced Patterns of Herbicide Sorption and Risks in Catchments: A *Soil Landscape Modeling* Approach

A thesis submitted to the University of Adelaide in fulfillment of the requirements for the degree of Doctor of Philosophy in Science

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Abstract

The overall aim of this thesis was to study the natural and landscape-induced patterns of herbicide sorption and risks of leaching and off-site transport of herbicides in an intensively managed orchard system. The questions for this thesis were: a) How can contour-derived digital elevation models be enhanced? b) To what extent do topographic and management factors influence the distribution of soil properties in an apple orchard? c) How do landscape topography, soil properties and land management factors influence the spatial distribution of diuron sorption affinity? and d) How is the fate of diuron influenced by the spatial variability of soil and key fate properties?

The objectives of this thesis were: a) to determine whether a 'smoothing' algorithm can enhance the accuracy of a contour-derived digital elevation model; b) to evaluate the role of topography and management practises in predicting the distribution of soil properties using a soil-landscape modeling approach; c) to evaluate the effects of topography, soil properties and management practises on the sorption affinity of diuron; and d) to assess the integrated effect of topography, management practises and herbicide sorption on the leaching potential of diuron in a spatially variable landscape using the Leaching Estimation and Chemistry Model (LEACHM) and surface runoff using the Organization for Economic Cooperation and Development (OECD) model.

A study site in the Mount Lofty Ranges, South Australia, was selected for its wide variation in landscape and soil properties under intensive horticultural management. The site was a section of an apple orchard with a strong texture contrast soil and landform with a relief difference of 50 m. The accuracy of digital elevation models (DEMs) of the site was first evaluated. Then the relationship between terrain

parameters and critical soil properties that were easily determined in the field (e.g. soil colour and texture) was determined. A strong relationship was found and therefore the experiment was expanded to take into account the effects of management and terrain on soil properties that influence pesticide sorption, such as total organic carbon, soil pH, electrical conductivity, clay content, and soil texture. Sorption of the herbicide diuron was determined on the soil through traditional laboratory and chemometric analyses using mid-infrared (MIR) spectroscopy. A strong correlation was found between diuron sorption coefficient values determined by traditional laboratory methods and those predicted using MIR spectroscopy (R^2 = 0.79) .

Then, the determination of the effects of terrain properties and management practises on diuron sorption distribution was evaluated within the context of soil-landscape analysis and geostatistical mapping. Soil properties varied significantly between alley and tree line regions and among different establishment ages of the orchard trees. Unique spatial patterns for soil properties, particularly total organic carbon (TOC), occurred within zones of the orchard. The variability in spatial distribution of the soil properties was reflected in the amount of diuron sorbed to the different soils. In the tree-line, where the soil was kept bare, diuron sorption affinity was significantly 16% lower than in the alley, where sod strips protected the soil surface all year round.

Finally, leaching of diuron was estimated using LEACHM and the potential for surface runoff of diuron was determined using the OECD model. Management practises, the level of TOC and slope were found to influence leaching and runoff potential of diuron.

The findings imply that, for intensively managed horticultural operations on complex landscapes, the influence of terrain on the distribution of soil properties and *consequently on diuron sorption affinity was masked by management factors. Assessments of sorption distribution and, therefore, the environmental fate of pesticides must include stratification strategies based on management factors. The leaching estimation also suggests variable risk of diuron for mobility based on management and TOC. Therefore, a differential herbicide and pesticide application or management regime might need to be observed to minimise off-site impact of pesticides.*

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Declaration

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Publications and Conference Papers and Presentations arising from this thesis

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Conference Presentation

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You have only to ask the cattle, for them to instruct you, and the birds of the sky, for them to inform you. The creeping things of earth will give you lessons, and the fish of the sea provide you an explanation: there is not one such creature but will know that the hand of God has arranged things like this! In his hand is the soul of every living thing and the breath of every human being!

Job 12: 7-10

I. Introduction

1. Research background

The interrelated processes of retention (most commonly referred to as sorption), transformation and transport govern the behavior of pesticides, once applied in an agricultural environment. Sorption is the result of the interaction between the pesticide molecules and the soil particle surface. The degree to which a pesticide is sorbed to soil is controlled by many factors including characteristics of the pesticides and of the soil. The amount of organic carbon in the soil is often the primary soil component controlling pesticide sorption. The process of transformation depends largely on the chemical and physical nature of the pesticides. Transformation occurs through abiotic (e.g. hydrolysis, photolysis) and biotic (e.g. microbrial degradation) processes. More often, this process is linked with the amount of biological activity, which is in turn influenced by organic matter content, soil moisture and temperature. Pesticide transport, on the other hand, is driven by numerous factors including, but not limited to, topography, weather and the chemical and physical properties of the pesticide. These parameters and the complex interrelationship that occurs in the environment make prediction of off-site transport of pesticides challenging. Moreover, due to the complexity of these interrelated processes and factors as well as the large spatial variability in the environment, measurement and analysis have to be done using samples over an extensive area. However, the first steps in understanding pesticide behavior entail the measurement of these parameters with some degree of certainty and pinpointing which processes are important.

In this research, a soil-landscape analysis technique was employed to map the spatial distribution of key soil properties and the sorption affinity of diuron in a 5.6 ha apple orchard. This included a digital terrain analysis to assess and enhance the accuracy of elevation models derived from readily available topographic maps. Finally a leaching simulation was performed using the Leaching Estimation and Chemistry Model (LEACHM) integrating the observed spatial variability of the key parameters that dictate the fate diuron in an intensively managed apple orchard.

The questions for this thesis were: a) How can contour-derived digital elevation models be enhanced for a complex landscape in Mt. Lofty Ranges, South Australia? b) To what extent do topographic and management factors influence the distribution of soil properties in an apple orchard in Mt. Lofty Ranges, South Australia? c) How do landscape topography, soil properties and land management factors influence the spatial distribution of diuron sorption affinity? and d) How is the fate of diuron influenced by the spatial variability of soil and sorption properties?

2. Research objectives

The objectives of the project were: a) to determine whether a 'smoothing' algorithm can enhance the accuracy of a contour-derived digital elevation mode for a complex landscape in Mt. Lofty Ranges, South Australia; b) to evaluate the role of topography and management practises in predicting the distribution of soil properties in an apple orchard using a soil-landscape modeling approach; c) to evaluate the effects of topography, soil properties and management practises on the sorption affinity of diuron; and d) to assess the integrated effect of topography, management practises and herbicide sorption on the leaching potential of diuron in a spatially variable landscape using LEACHM and the Organization for Economic Cooperation and Development (OECD) surface transport models.

3. Thesis structure

This thesis is composed of eight chapters. Some of the chapters contained here are either published or submitted to journals for publication or manuscript in preparation for submission. Chapter II briefly outlines the processes and factors that determine the environmental fate of pesticides, and the current approaches to model this process. It also summarizes the status of global pesticide use with a slight focus on environmental issues of pesticide use. This is followed by an outline and examples of pesticide fate modeling. The chapter ends with a short description of previous and current attempts to use soil-landscape analysis in modeling the fate of pesticides focusing on the role of the spatial variability of soil, specifically soil organic carbon, and topographic properties in estimating the distribution of sorption properties of pesticides.

Chapters III to VII are the research components of this thesis. Several hypotheses were tested and these chapters included results of these experiments. The research focused on an intensively managed apple orchard in the Mount Lofty Ranges (MLR), South Australia. Chapter III considered the question: Can topographically-derived digital elevation models (DEM) be enhanced? The use of existing smoothing algorithms was investigated to determine their effectiveness to improve the quality of a DEM derived from contour data. Chapters IV and V used the enhanced DEM to predict the distribution of soil properties for an intensively managed orchard, and discussed the question: In the context of off-site movement of pesticides, what controls the spatial distribution of soil properties in an intensively managed apple orchard? Classical statistics and geostatistical analysis were used to model the spatial distribution of soil properties. In Chapter VI, I expanded the spatial analysis to assess the sorption affinity of a commonly used herbicide, diuron. A similar question to the previous chapter was posed but this time I focused my analysis on diuron sorption affinity (K_d). In addition, I validated the use of a new technique called mid-infrared partial least squares (MIR-PLS) to predict diuron K_d. In Chapter VII, a deterministic research tool called LEACHM was used to estimate the leaching of diuron in a spatially variable landscape. Then an OECD pesticide transport model was used to estimate pesticide transport in surface runoff. I tried to answer the question: How does the variability of key leaching parameters affect the fate of diuron? Conclusion and some recommendation for future research are presented in the last chapter.

II. Literature Overview

(N.B. Only a broad overview is given here as specific literature reviews are incorporated in the chapters of this thesis)

1. Pesticides and the modern agricultural production

The first recorded use of pesticide was in the mid 1800s when sulfur dust was used to prevent the growth of powdery mildew in grapes. Reliance on pesticide and other external farm inputs increased as monocultural production system and area also increased. Productivity had to be maintained and ultimately increased as labor became expensive and land resources scarce. The pesticide industry became an integral part of agricultural production. The 2001 global pesticide use is estimated at 2.2 million tons with an equivalent investment cost of about US$32B (Donaldson et al., 2004). Herbicides are the largest contributor to this amount (~36% of pesticide use), followed by insecticides and fungicides, which account for about 25% and 10% of the total pesticide use worldwide, respectively. The remainder of pesticide usage is composed of nematicides, rodenticides, molluscicides and other pesticides (Kiely et al., 2004).

Australia's agricultural sector, which contributes about 3% to national GDP (OECD, 2008), relies considerably upon pesticide use. Though a substantial area of the total Australian landmass is devoted to agriculture (DCC, 2008), agricultural production is constrained by fragile and infertile soils and limited water supply, and its sustainability depends on considerable management input (NLWRA, 2001) including the use of pesticides.

Pesticide may be defined as any substance used to control, kill, attract or repel a pest or disease (USEPA, 2007). Pesticides vary in physico-chemical properties and classes that target plant, animal and microbial pests and diseases. Pesticides can persist in the environment and potentially harm other non-targeted species, including humans, depending on their properties. The problem can be further exacerbated by improper handling and misuse (Eddleston and Bateman, 2007).

2. Threat of pesticides to the environment

Despite the advances in pesticide technology and agriculture, traces of pesticides and its by-products are sometime detected in the surrounding environment. The potential risk of pesticides to the environment and human health is attributed to the "leaky" nature of agricultural landscapes (Harris, 2002) or any other ecological landscapes. Pesticides applied in agriculture have been detected in both ground- and surface-water either in their original forms or as the degradation product. If the pesticides are toxic, water quality suffers, harming the environment and potentially human health. As a result, numerous monitoring and research activities are carried out in different parts of the world providing information on pesticide behaviour and fate most specifically in aquatic ecosystems. The study by Cessna et al (2001) showed that a number of pesticides were detected, although only in trace amounts, in water samples collected in South Saskatchewan River in Canada as a result of herbicide application in flood-irrigated forage production areas. Similar observations were made in Lourens River in South Africa where endosulfan, deltamethrin, azinphos-methyl, chlorpyrifos and procymidone were detected after a notable rainfall event (Dabrowski et al., 2002) in surrounding farming area. In the Central Valley, California, 52 out of 70 sediment samples tested positive for pyrethroid, an insecticide extensively used in orchards and vegetables farmlots in the region (Weston et al., 2004). Linuron and pendemethalin, two active ingredients present in commonly applied herbicides, were also detected above the EU limit of 0.1 μg L^{-1} in a small Northern Italian creek near Bologna (Gardi, 2001).

Although the industry has adopted more environment-friendly pesticide application schemes, serious concerns remain about the continued decline of both surface and ground water quality due to nutrient loading and migration of pesticides from agricultural fields (Kookana et al., 2005; Kookana and Aylmore, 1994; Kookana et al., 1998; OECD, 2008; Radcliffe, 2002; Salama and Kookana, 2001). For example, the report by the 2006 Australian State of the Environment Committee, indicates that the world-renowned Great Barrier Reef Marine Park is under great threat from elevated levels of nutrients, sediments and pesticides draining from agricultural and pastoral areas (Beeton et al., 2006). In a 3-year study in the Mount Lofty Ranges Region, South Australia, chlorpyrifos concentrations in surface runoff were found more than ten times the environmental guideline value (0.01 μg L^{-1}) in the 2007 and 2009 sampling year (Oliver et al., 2011).

3. Mathematical modeling of pesticide fate

The factors governing and the processes involved in pesticide migration are complex and varied. Currently, there is no better way to facilitate quick and inexpensive assessment of the impact of pesticides to the environment than through the use of computer simulations or modeling. A model is defined as "an object or concept designed according to a structural, functional or logical analogy to a corresponding origin in the real world" (Mirsal, 2004). Modeling is beneficial in predicting pesticide migration because it helps assess dissipation time, mobility and persistence of pesticides in soil environments, and it aids in determining management schemes for rational pesticide use (Wagenet and Rao, 1990).

Over the last 50 years, numerous modeling approaches have been developed. The tools have been varied and may be categorised as either empirical or simple models and physical process or complex models (Ghadiri and Rose, 1992). Modeling approaches can also be categorised based on their function (either for research, management, screening, or instructional purposes (Wagenet and Rao, 1990), input parameters (either deterministic and mechanistic or functional (Ghadiri and Rose, 1992)) or scales (either lumped or distributed). Table II.a. presents some examples of tools used for modeling pesticide behaviour in the environment and their classification based on purpose.

The Behavioral Assessment Model (BAM), developed by Jury et al. (1983), was able to assess the relative fate (volatilisation, leaching and degradation) of a number of trace organic chemicals in soil (Jury et al., 1984). A pesticide version of the Leaching Estimations and Chemistry Model (LEACHM), LEACHP, has been used by Sarmah (1998) to simulate the fate of three sulfonylurea residues under low rainfall conditions in a southern Australian agricultural soil. The Pesticide Root Zone Model (PRZM), developed in the early 1980s, has been used to simulate aldicarb behaviour including: interactions in surface runoff, advection in percolating water, molecular diffusion, dispersion, uptake by plants, sorption to soil, and biological and chemical degradation (Carsel et al., 1985).

Table II.a. Examples of simulation models used to predict pesticide behaviour classified according to purpose (Wagenet and Rao, 1990).

Purpose/Classfication	Model
Screening	Behavior Assessment Model (BAM)
Research	Leaching Estimation and Chemistry Model (LEACHM); Numerical Solution to CDE
Management	Pesticide Root Zone Model (PRZM); Chemicals, Runoff and Erosion from Agricultural Management Systems (CREAMS)
Instructional	Chemical Movement in Layered Soil (CMLS); Method of Saturated zone Solute Estimation (MOUSE)

As mentioned earlier, the temporal and spatial variability of both environmental and soil properties are important aspect of modeling pesticide migration. It has been shown in many studies that soil and environmental properties vary across time and space (Addiscott and Mirza, 1998). Gaultier et al. (2006), for instance, showed that soil organic matter content, pH and carbonate varied within (horizontally) and across (vertically) the soil profile. This variability affects the behavior of pesticides in soils.

Another approach in modeling pesticide migration, stochastic modeling, has integrated spatial and temporal variability of the soil and environmental properties. This approach assumes that soil-water system processes can only be defined in statistical terms due to uncertainty. Recent work on stochastic modeling done by Lindahl et al. (2005), and Schriever and Liess (2007) has shown successful results. Results from stochastic modeling predict the migration of a phenoxyacetic acid pesticide MCPA, in a small catchment in the south of Sweden were highly comparable to the measured MCPA concentrations in the surface waters (Lindahl et al., 2005). A stochastic modeling approach was also used for regional Europe to predict runoff inputs and to map ecological risk of agricultural pesticides at a regional scale (Schriever and Liess, 2007).

4. Soil-landscape analysis in assessing pesticide fate

The fate of pesticide is influenced by soil variability, which in turn, is influenced by landscape factors (Liu et al., 2002). Soil variability that is influenced by landscape factors is best studied at the landscape level. This is the emphasis of soil landscape analysis – the science that deals with patterns and distribution of soils in landscapes (Hole and Campbell, 1985). Soil landscape analysis thus becomes potentially important in observing, delineating, and often mapping pesticide behavioural properties (e.g. sorption and leaching) in landscapes.

The concept of using soil landscape analysis to assess pesticide fate is relatively new. Novak et al (1997) was the first to evaluate the effect of landscape position on the sorption of atrazine to soil. Atrazine sorption affinity, which was largely affected by soil organic carbon content, was greatest in soils found in low lying areas compared with soils from an upland shoulder slope. They further concluded that the distribution of field-scale atrazine sorption was best predicted based on landscape position. Later, Farenhorst et al. (2001) also found high sorption affinity of 2,4-D in lower landscape positions that had high organic matter content. Sorption and mineralization of atrazine and alachlor were also assessed in a small field in South Dakota (Liu et al., 2002). The research found that herbicides had different sorption and mineralization rates in soils from different positions in the landscape.

Further studies explored the use of digital terrain analysis to model sorption of pesticides, focusing mainly on one herbicide, 2,4-D. Landscape or topographic parameters, like slope, aspect and curvatures, were successfully used to differentiate distribution of 2,4-D sorption between conventional-till and no-till agricultural fields (Farenhorst et l., 2003). Landscape positions were used to segment a hummocky landscape in a Manitoba cereal-oilseed crop system in order to predict 2,4-D sorption in subsurface soils (Gaultier et al., 2006). More recently, Farenhorst et al (Farenhorst et al., 2008) found that 2,4-D sorption was halved in soils found in upper slopes. The study also found significant correlation of herbicide sorption with compounded topographic index (CTI) gradient and some curvature parameters.

Previous studies on soil-landscape analysis in assessing pesticide fate have only been done in limited areas using limited pesticides. However, it's merit extends beyond gently rolling landscapes and a small breadth of organic chemicals that are used in agricultural production systems.

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CHAPTER III

Quality Assessment of a Topographically Derived High-Resolution Digital Elevation Model of a South Australian Sloping Landscape

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Quality Assessment of a Topographically Derived High-Resolution Digital Elevation Model of a South Australian Sloping Landscape

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III. Quality Assessment of a Topographically Derived High-Resolution Digital Elevation Model of a South Australian Sloping Landscape

Abstract

Digital elevation models (DEMs) are important inputs in many spatial applications, such as land use planning and soil-landscape modeling. For informed decision-making to take place, it is essential that the DEM be of high accuracy and to achieve this, plausibility or smoothing algorithms are often employed to enhance accuracy. DEM's derived from fine scale topographic data are often used in field and catchment scale hydrologic investigations. However, the accuracy of these DEMS are almost never assessed.

We generated DEMs from existing contour topographic information and interferometric synthetic aperture radar (IfSAR). We assessed the error in elevation and terrain models from the DEMs by comparison with a high-resolution real-time kinematic GPS survey. We further investigated whether plausibility algorithms enhanced the quality of the resulting DEMs.

Results showed that the contour-derived DEM underestimated the 'true' elevation with a root mean square error (RMSE) of 3.0 – 4.0 m. The analysis of the DEM also revealed the effect of contour biasing on geomorphological parameters such as slope and curvatures. Smoothing of the contour-derived DEM increased the accuracy of terrain attributes.

Keywords: Contour elevation, smoothing algorithm, accuracy assessment, geomorphological variables

1. Introduction

A digital elevation model (DEM) is a digital representation of elevation information, often arranged in regularly spaced grids embodied as raster sets in a geographic information system (GIS). Accurate elevation models are fundamental data sets for management and research in many scientific disciplines; including meteorology, geomorphology, hydrology and ecology, and are essential component of GIS databases (Hutchinson, 1989). Topography influences energy and material flow between atmosphere, biosphere and pedosphere and thus influences almost all ecological and geomorphological processes (Ostendorf, 1993; Ostendorf, 2011 #2011). Additionally, the spatial variability of a DEM is often used as a surrogate measure of the spatial variability of the various biophysical and geochemical processes occurring at all scales (Moore et al., 1991). Using DEMs for quantification and delineation of geomorphological attributes (e.g. slope and aspect, catchment boundary, drainage networks), and other topographic parameters is a trivial exercise applied routinelyin hydrological and environmental modeling (e.g. solar radiation).

DEMs can be generated with different methods and at different scales. A global 30 m DEM (GDEM) was first released in 2009 using the Advanced Spaceborne Thermal Emission and Reflection Radiometer (ASTER) instrument on board the Terra satellite (http://asterweb.jpl.nasa.gov/). The ASTER GDEM covers the majority of the terrestrial earth and provides a good source of global elevation data. However, the exact accuracy of the data is unknown especially in areas of high and complex relief and land cover. Another global elevation model was generated during the 2000 Shuttle Radar Topography Mission (SRTM) at 90 m resolution.

However, there are known inaccuracies in both of these datasets. A study conducted by Hirt et al. (2010) revealed that the Australian GEODATA DEM 9S contained height errors of up to 100 m in rugged terrain, the CGIAR-CSI SRTM lacked assessment for drainage accuracy, and the ASTER GDEM contained methodological acquisition artifacts.

Frequently, elevation data with a very high spatial resolution (e.g. < 25 m) is required for field and catchment scale hydrological investigations (Gessler et al., 2009). Such detailed elevation models can be generated using airborne LIDAR, ground-based topographic surveys or photogrammetry (Clarke et al., 1983). Photogrammetry is the most commonly applied since it is the least expensive as most contour data have now been converted to digital format. Contour data are interpolated to create the raster DEM which often becomes the prinicipal DEM data. Strategically, topographic data is available at fine scales (e.g. 1:10,000 scale) for many intensively used land areas. Except for flat terrain, manually derived contour data is the best available source of information for elevation models.

Nevertheless, DEMs generated from topographic data are not immune to errors. The high number of processing steps (e.g., photogrammetric interpretation, digitization, interpolation) (Oksanen and Sarjakoski, 2005), the method of data generation and the interpolation procedure (Fisher and Tate, 2007) can all produce errors. Hence, the accuracy of DEMs need to be actively assessed prior to use in analysis.

To enhance the quality of topographically-derived DEM, several techniques can be applied. One technique employs error reduction algorithms (Hengl et al., 2004) which include spurious pit removal or filtering and neighborhood analysis, which are often collectively known as smoothing algorithms. Employing these algorithms has become a standard operating procedure in DEM generation. However, there is a need to assess if these algorithms in fact increase the accuracy of the DEM (Wechsler, 2007) or simply improve the aesthetic quality of the maps. Furthermore, appropriate techniques may have to be employed to prevent error propagation in subsequent analyses. The assessment of DEMs derived from topographic data is also limited. Often, analyses are done in spatial resolution of 30 m but elevation data with finer spatial resolution (e.g. < 25 m) is often sought in most field and catchment scale hydrological investigations (Gessler et al., 2009). Assessment of the accuracy of high resolution DEMs generated from the interpolation and smoothing procedures of topographic data therefore needs to be done.

The objective of this research was to examine the accuracy of high resolution (5 m) digital elevation and terrain models derived from contour datasets digitized from topographic maps for a complex landscape in the Mount Lofty Ranges (MLR) region of South Australia. We also determined the effectiveness of a smoothing algorithm to improve the accuracy of digital elevation and terrain models. The interferometric synthetic aperture radar (IFSAR) DEM (Intermap, Englewood, CO) was also analyzed to assess how the contour-derived DEM compared with commercially available elevation data.

2. Methodology

2.1. Study site

A hilly area located within the Mt. Lofty Ranges (MLR) region (30 km east of Adelaide, South Australia) was selected for this study (Fig. III.a). The subcatchment has a relief of about 100 m, an area of approximately 65 ha and a Mediterranean climate with mean maximum and minimum temperatures of 12°C and 5°C during winter (June-August) and 26°C and 14°C during summer (December-February), respectively. The subcatchment has a mixed use but is planted primarily to apples. It is bounded by Plummers Road in the north to northeast direction, by Hewletts Road in the south, and by Mawson Road in the west.

2.2. Digital elevation models

Topographic maps (1:10,000 and 1:50,000) in digital format were obtained from the South Australian Department of Environment and Heritage (DEH) (metadata of both data available online at www.asdd.sa.gov.au). Both maps were derived photogrametrically from aerial photography and surveyed control points (bench marks). The maps were then scanned and converted to GIS formats. The 1:10,000 map had a contour interval of 5 m. The 1:50,000 map had a contour interval of 10 m.

Several DEMs were generated as a result of this study, all with a resolution of 5 m. The first pair of DEMs were from the interpolated 1:10,000 and 1:50,000 topographic maps and referred here to as raw10K and raw50K, respectively. These DEMs were interpolated using the 'Topo to Raster' tool (ANUDEM) with drainage enforcement and sink filling in ArcGIS 10.0 (ESRI, Redlands, CA).

The second pair of DEMs were generated from the raw10K and raw50K DEM with a smoothing algorithm and are referred to here as smooth10K and smooth50K. The smoothing algorithm was a 3 x 3 low pass filter (mean) which reduced the impact of outliers by local averaging (Brown and Bara, 1994).

Another DEM dataset was included in this study to evaluate a commercially available, high resolution, remotely-sensed DEM. The DEM – an interferometric synthetic aperture radar terrain model – was obtained from Intermap (Englewood, CO) through Apogee Imaging International (Lobethal, South Australia) and is referred to here as IfSAR. The dataset has a reported accuracy of 2 m. The concepts of acquisition, data manipulation and application are summarized by Richards (2007). All of the DEMs utilized in this study are listed in Table III.a. and are all projected to Geocentric Datum of Australia 1994 (GDA94) Zone 54.

2.3 Field evaluation data

Two sets of field evaluation data were collected in the winter-spring season (July-September) of 2010. The first set of data was collected in the 65 ha subcatchment (marked by the blue boundary in Fig. III.a). Firstly, one hundred and seventy four (174) elevation points were obtained along three creek lines at regular intervals (every 10 m) and throughout the subcatchment in random locations using a real-time kinematic GPS (RTK-GPS). This dataset was used to validate the point elevation of DEM for the whole subcatchment. Secondly, we obtained dense elevation data in a 5.6 ha subarea (marked by the black boundary in Fig. III.a) within the subcatchment using RTK GPS. The survey in the subarea generated elevation data approximately every 2 m as it passed through the alleys of the apple orchard. Each alley transect was 5 m wide. The dense elevation data were then used to generate a DEM for the subarea using the 'Topo to Raster' tool (ANUDEM). This dataset, hereinafter referred to as rtk, was used to validate the elevation, slope and curvature parameters for the subarea. The RTK-GPS system, mounted on an all-terrain vehicle (5 kph speed), was set to record data points every 3 s to gather the dataset used for the subarea. All survey campaigns were done in winter-spring season (August-October) when vegetation cover was substantially low (apple trees shed leaves during the winter months) to reduce the effect of canopy interception of GPS signals. Days following a heavy rain were also avoided to reduce the effect of moisture on GPS signals. We used EPOCH 10 L1 GPS receivers (Spectra Precision, Westminster, CO) attached to a Reckon data collector. The system was comprised of a base station, which was tied to a bench mark, and a roving station that gathered the survey point measurements. Horizontal and vertical precision during the survey was set to 10 cm. Post processing was done using Spectra Precision Survey Office software (Spectra Precision, Westminster, CO).

2.4 Analysis

Differences in elevation data (or spot heights) were analyzed for the subcatchment using the various DEMs (raw10K, raw50K, smooth10K, smooth50K, and IfSAR) with the point elevation obtained through RTK-GPS. Geomorphological terrain models (slope, plan and profile curvatures) were analyzed using a subarea dataset (Table III.b). We removed any edge effects (raster cells on the edge of the survey area with fewer neighboring cells) by creating an inward buffer of 10 m.

The following quantitative error descriptors were used: bias, mean absolute error (MAE), and root mean square error (RMSE). Bias is the average deviation of the topographically-derived and remotely-sensed DEM from the reference DEM (i.e. rtk). Bias was calculated using the equation:

$$Bias = \frac{1}{n-1}\sum_{i=1}^{n}(X_i - R_i)$$,

where X_i is the observed measurement at *i*th location, R_i is the reference measurement at the ith location, and *n* is the number of samples (in this case the number of raster cells which is 174 for the elevation data points; and 1208 for the subarea).

Mean absolute error (MAE) measures the closeness of the topographic and remotely-sensed DEM to the reference DEM, and was calculated using the equation:

$$MAE = \frac{1}{n-1}\sum_{i=1}^{n}\left|X_i - R_i\right|$$.

Root mean square error is used here as a measure of accuracy which is used to distinguish between DEM (Wise, 2000). RMSE was calculated using the equation:

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}(X_i - R_i)^2}{n-1}}.$$

3. Results

3.1 Interpolation and smoothing of DEM

The contour lines reveal some breaks and overlapping (Fig. III.a). These features are common throughout this data set and the 1:50,000 contour map due to manual digitization. These anomalies can be treated as sources of inaccuracy for the interpolated DEM. For example, broken contour lines can create a void in the interpolation procedure between elevation data points. A careful investigation of the contour data also revealed an unexplained anomaly in the south central part of the site. A polygon was inadvertently created along the stream and connected to one of the contour lines, which can also cause anomalous sinks or pits in the resulting DEM. However, this was avoided in our study site due to the interpolation procedure. The 'Topo to Raster' interpolation tool incorporates a drainage enforcement algorithm that removes spurious sinks (Hutchinson, 1988; ESRI, 2011).

The interpolated DEMs (raw10K and raw50K) and their corresponding smooth versions (smooth10K and smooth50K) are presented in Fig. III.b. The interpolation, using 'Topo to Raster' tool, created a sink-free DEM of the study site. Some artifacts were created that may be due to bias imposed by the high data point density along the contour during the interpolation. This was observed when histograms of the DEM were investigated (Fig. III.c). Contour bias, in this case, is a phenomenon wherein input contours created distortion in the terrain models. The histogram of the DEM showed increased occurrence of elevation close to the contour interval (5 m for 1:10,000 and 10 m for 1:50,000 topographic maps) (Fig. III.c). Contour bias was more pronounced in the 1:50,000 DEM than in the 1:10,000 DEM. A similar anomaly was documented in the United States Geological Survey (USGS) DEM derived from contour data, and this anomaly was referred to as a 'ghost' artifact (Guth, 1999) brought about by "over-representation of elevation equal to the digitized contour" (Fisher and Tate, 2007). We speculate that this anomaly has not been reported for high resolution DEMs derived from fine scale topographic maps because topographic maps are usually used to generate coarse resolution DEMs, and because there is little awareness of this form of error.

The effect of the smoothing algorithm was difficult to notice in the DEM output. However, their corresponding histograms revealed that the over-representation of elevation close to the original contour was reduced. This over-representation is observable as peaks in the DEM histogram, and these peaks were substantially minimized through smoothing of the raw10K and raw50K DEMs (Fig. III.c). To show the effect of this phenomenon (contour biasing) in using the raw (un-smoothed) DEM to derive other terrain variables, we computed profile curvature (ProfC) surface model. The unsmooth DEM created an unrealistic ProfC surface model compared with the smooth DEM (Fig. III.d). This emphasized the importance of interrogating DEM quality.

3.2 Validation of subcatchment elevation

The IfSAR DEM overestimated elevation at the sampled locations with a bias of -0.2 m, but with an RMSE value of 2.6 m (Table III.c.). Among the different DEMs, IfSAR had the lowest bias, MAE and RMSE at -0.2 m, 2.0 m and 2.6 m, respectively. The raw50K DEM had the highest bias, MAE and RMSE at 2.0 m, 3.4 m and 4.0 m, respectively. The smoothing algorithm enhanced the topographically-derived DEM minimally in both scales (1:10,000 and 1:50,000). Nevertheless, the smooth10K had a comparable MAE and RMSE (2.4 and 3.0 m respectively) to the IfSAR DEM.

3.3 Quality of rtk DEM

The survey using the RTK-GPS instrument generated a dataset for a 5.6 ha subarea. The horizontal and vertical accuracy of the survey was 0.5 m. The accuracy is lower than the spot height survey (0.10 m) due to complexity of the terrain where the dense points were collected (i.e. in the subarea). Some transects fell short of the 0.5 m accuracy limit and were culled from the dataset. The final post-processed dataset was comprised of 5,629 points.

The interpolated DEM had 1,208 pixels (5 m size) (bounded by effective DEM area polygon in Fig. III.e). The mean elevation was 516.1 m with a very small bias of 0.1 m and RMSE of 0.7 m (Table III.d) against the RTK-GPS point measurements. We assume that, given the low bias and RMSE values, the resulting rtk DEM was the "true" elevation model of the sub area and hence was used as the basis of comparison for the DEMs under investigation (i.e. topographically derived DEM).

3.4 Assessment of topographically derived DEM

The assessment of topographically-derived and the IfSAR DEM was done using the rtk DEM as a reference. Three statistical parameters were calculated: bias, MAE and RMSE. The summary of the statistical analyses performed on the different DEM sources, including residuals, is summarized in Figures 6 and 7.

In terms of elevation, the IfSAR DEM, as expected, had the lowest bias, MAE and RMSE (0.91 m, 1.08 m and 1.49 m, respectively). All DEMs generated from the contour data overestimated elevation. The unsmooth 1:50,000 DEM (raw50K) had the highest bias and RSME (-2.63 m, and 2.89 m respectively). The smooth 1:10,000 DEM (smooth10K) also overestimated elevation for the subarea (bias = -1.30 m), but had a relatively low RMSE (1.73 m). In addition, the subarea DEM analysis of elevation showed all generated DEM were highly correlated with rtk DEM (R^2 = 0.99) (Fig. III.f).

In terms of slope, raw50K DEM had the highest RMSE value at 3.26 °. The smooth50K had the smallest bias (0.10 °) and the smooth10K DEM had the lowest RMSE (0.26 °) (Fig. III.f). All DEM have slightly overestimated the curvature parameter PlanC. The bias of all DEMs were within the range of -0.02 to -0.10 ° m^{-1} (Fig. III.f). Finally, for the profile curvature parameter (ProfC), all DEM had negligible bias. The IfSAR and smooth10K DEM were almost identical with the rtk DEM having only 0.26 and 0.28 ° m^{-1} RMSE values, respectively (Fig. III.f).

The analysis of the residuals also revealed the effect of contour bias in DEMs generated from topographic data. The resulting geomorphological parameters had greater residuals as the measurements approached the digitized contour (Fig. III.f). This was prominently observed in DEMs derived from the 1:50,000 data.

The correlation of the DEM in terms of slope and curvature parameters also showed varying results (Fig. III.g). In terms of slope, IfSAR was most highly correlated with rtk (R^2 = 0.74) followed closely by the smooth10K DEM (R^2 = 0.70). The least correlated was r10K (R^2 = 0.56). In terms of PlanC, smooth50K had the highest correlation with rtk (R^2 = 0.48). In terms of ProfC, the smooth10K was highly correlated with rtk DEM (R^2 = 0.85).

4. Discussion

In this study, we characterized the errors of DEMs generated from topographic data and compared these with a remotely-sensed DEM (IfSAR) and a validation DEM (derived from RTK-GPS). The results in this study can be summarized into three main points. Firstly, DEMs derived from various datasets exhibited different levels of accuracy. The DEMs derived from topographic datasets revealed the effect of contour bias in surface models like slope and curvature. This finding was not surprising, but demonstrates that this form of bias is common, and stresses the need for care when utilizing this and other DEMs derived from topographic datasets for subsequent analysis (Wise, 2000). The correlation analyses also suggest that although the elevation models appeared almost identical, the resulting terrain models derived from different sources vary independent of its inherent accuracy but dependent on how the elevation is distributed in the elevation model. Geomorphological parameters calculated from IfSAR were not necessarily more correct compared to those calculated from contour-derived DEM. In fact, smooth10K, which was derived from fine scale topographic map (1:10,000), was found to be more accurate for the study site. This is perhaps not surprising, as the study area contains many steep slopes, and a known limitation of the IfSAR DEM is its reduced accuracy in areas with high slope (> 10 °) (Intermap, 2010). This work highlights the need to carefully consider the choice of DEM for the topography of site and to be aware of the limitations of the different DEMs. Given this limitation and the costs involved in acquiring the IfSAR dataset, its use is not encouraged in the type of terrain where this study was performed.

Secondly, DEMs derived from topographic data were enhanced using a simple smoothing algorithm. The resulting DEMs approximated the 'real' shape of the topography more closely than the un-smoothed DEMs, and in one case (smooth10k) were even higher accuracy than the IfSAR DEM.

Finally, the high correlation in elevation data between the rtk DEM and the rest of the DEMs indicated that all elevation data sources (topographic maps and the remotely sensed DEM) were quite reliable. However, this reliability is limited because the shapes of the landscape that were generated from these data sources vary. While elevation information corresponds in all models, marked differences in slope and curvature parameters exist. Therefore, interpretations based on the derived parameters need to be treated with care. The smoothing algorithm enhanced the quality of the DEMs and terrain models and therefore should be employed whenever DEMs are generated from topographic elevation sources similar to those used in this study (e.g. slope and curvatures).

5. Conclusion

In this study, we have shown the relative accuracy of DEM derived from fine scale contour data, which have the most common source of elevation data. Contour-derived and the IfSAR DEMs corresponded reasonably well with the validation data. However, derived parameters, like slope and curvature, were more strongly influenced by DEM source and the use (or absense) of smoothing. This potential error needs to be considered when these topographic variables are used as surrogates for biophysical landscape conditions in environmental models. The inaccuracy may be due to the unknown reliability of the elevation data as well as the limitations of the interpolation procedure employed.

Most importantly, we have also shown that through a simple smoothing algorithm, DEMs derived from contour data can be enhanced to increase accuracy of elevation and consequently landscape shape. Additionally, this study has demonstrated the need to assess the quality of all DEMs derived from topographic data sources. This assessment need not be time consuming or onerous. We recomend a simple analysis of the DEM histogram and the investigation of derived topographic parameters (e.g. slope and curvature).

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Table III.a. Digital elevation model datasets used in this study, all using 5 m pixel.

DEM	Description
raw10K	Interpolated 1:10000 contour data using '*Topo to Raster*' tool in ArcMAP 10.0;
raw50K	Interpolated 1:10000 contour data using '*Topo to Raster*' tool in ArcMAP 10.0
smooth10K	Smoothing algorithms (filter and focal mean statistics) employed in raw10K DEM
smooth50K	Smoothing algorithms (filter and focal mean statistics) employed in raw50K DEM
ifsar	Sourced from Intermap, a digital terrain model derived from surface models where vegetation and land surface cover have been digitally removed
rtk	interpolated spot heights that have been collected for a subarea using real-time kinematic global positioning system (RTK-GPS) using '*Topo to Raster*' tool in ArcMAP 10.0

Table III.b. Terrain parameters calculated in this study.

Attribute	Description
Slope, °	change of elevation with horizontal distance
Plan curvature (PlanC), ° m^{-1}	a measure of topographic convergence and divergence
Profile curvature (ProfC), ° m^{-1}	a measure of flow acceleration or deceleration

Table III.c. Summary statistics of spot heights (m) derived from different elevation sources.

Statistics (n=1208)	Value (m)
Min	495.4
1st Quartile	509.4
Mean	516.1
Median	515.9
3rd Quartile	523.2
Max	537.3
Bias	-0.1
MAE	0.5
RMSE	0.7

MAE – mean absolute error; RMSE – root means square error

Table III.d. Quality of DEM derived from interpolated real-time kinematic GPS survey for the subarea.

Statistics	rtk	raw10K (smooth10K)	raw50K (smooth50K)	ifsar
Min	471.4	468.1 (468.4)	470.6 (470.4)	470.1
1st Quartile	508.7	505.4 (506.2)	505.9 (506.2)	508.7
Mean	524.2	522.3 (522.5)	522.2 (522.3)	524.4
Median	526.1	523.4 (523.6)	522.4 (522.7)	525.5
3rd Quartile	538.2	538.5 (538.6)	539.6 (540.1)	540.2
Max	559.7	560.3 (560.0)	560.4 (560.2)	562.1
Bias		1.9 (1.7)	2.0 (1.9)	-0.2
MAE		2.6 (2.4)	3.4 (3.3)	2.0
RMSE		3.1 (3.0)	4.0 (3.9)	2.6

raw10K – interpolated 1:10,000 topographic map; raw50K – interpolated 1:50,000 topographic map; smooth10K – smooth 1:10000; smooth50K – smooth 1:50,000; ifsar – interferometric synthetic aperture radar; MAE – mean absolute error; RMSE – root means square error; PlanC – plan curvature; ProfC – profile curvature

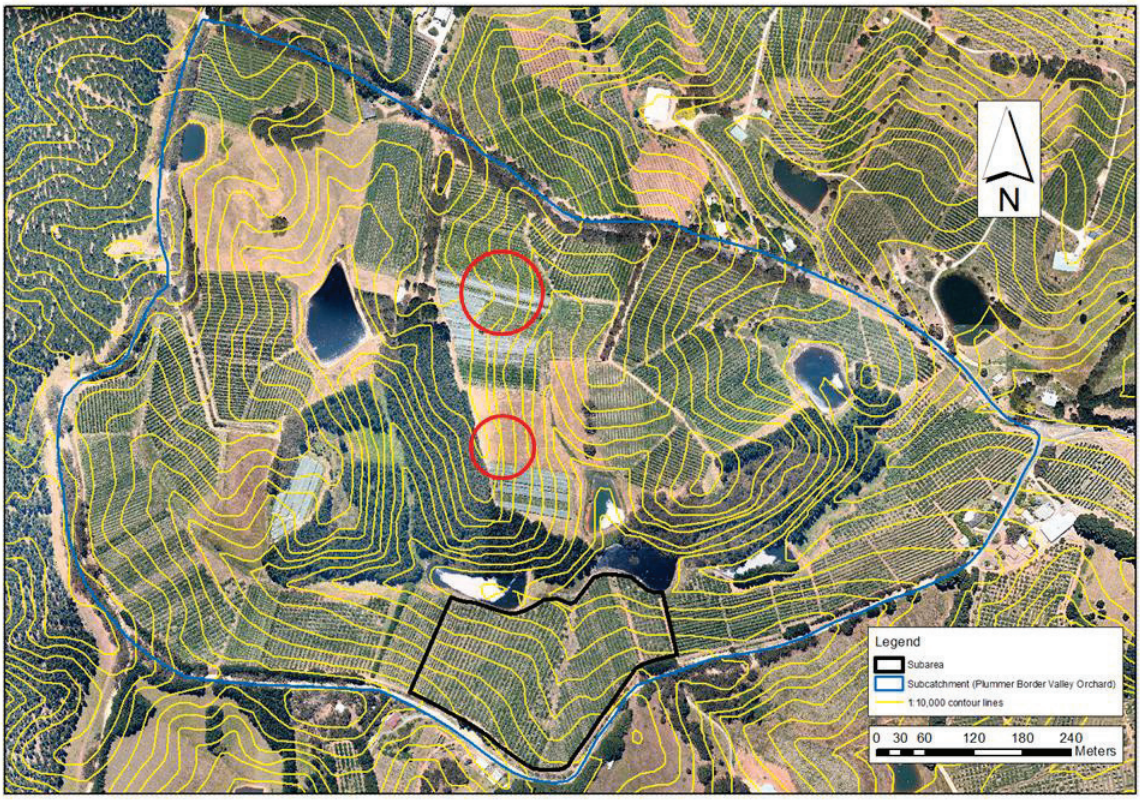


Figure III.a. Location of the study site (Red circles mark broken and overlapping contour lines. Aerial photograph taken 26 December 2009 is from www.nearmap.com available under Creative Commons Attribution Shar e Alike license).

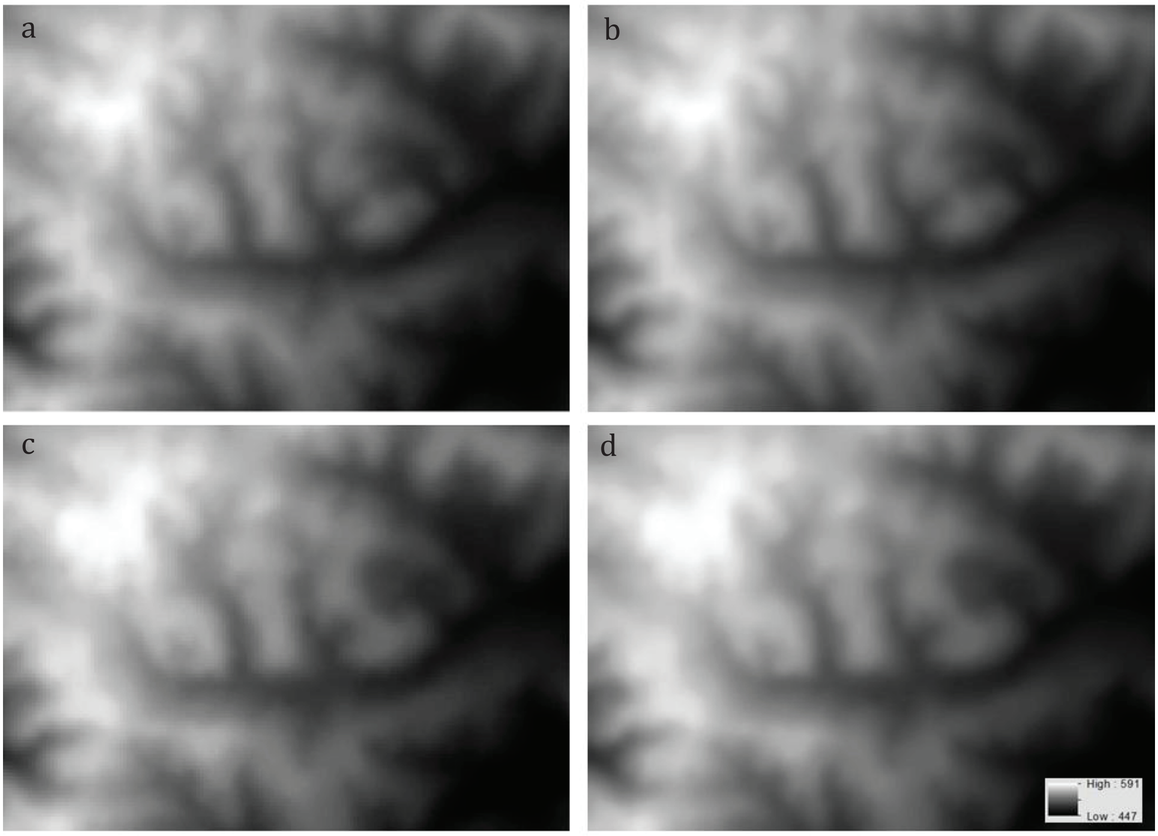
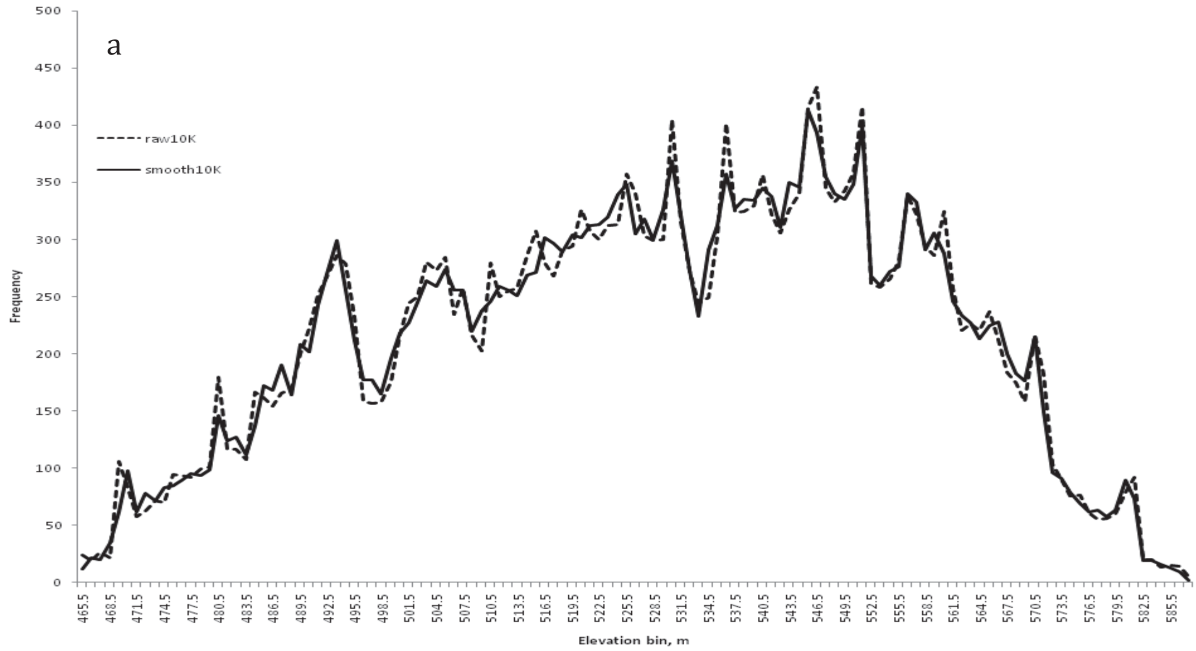


Figure III.b. DEM of the site (a - raw10K, b - smooth10K, c - raw50K, d - smooth50K).

raw10K – DEM derived from 1:10,000 DEM by 'Topo to Raster' interpolation; smooth10K – smooth raw10K; raw50K – DEM derived from 1:50,000 DEM by 'Topo to Raster' interpolation; smooth50K – smooth raw50K.



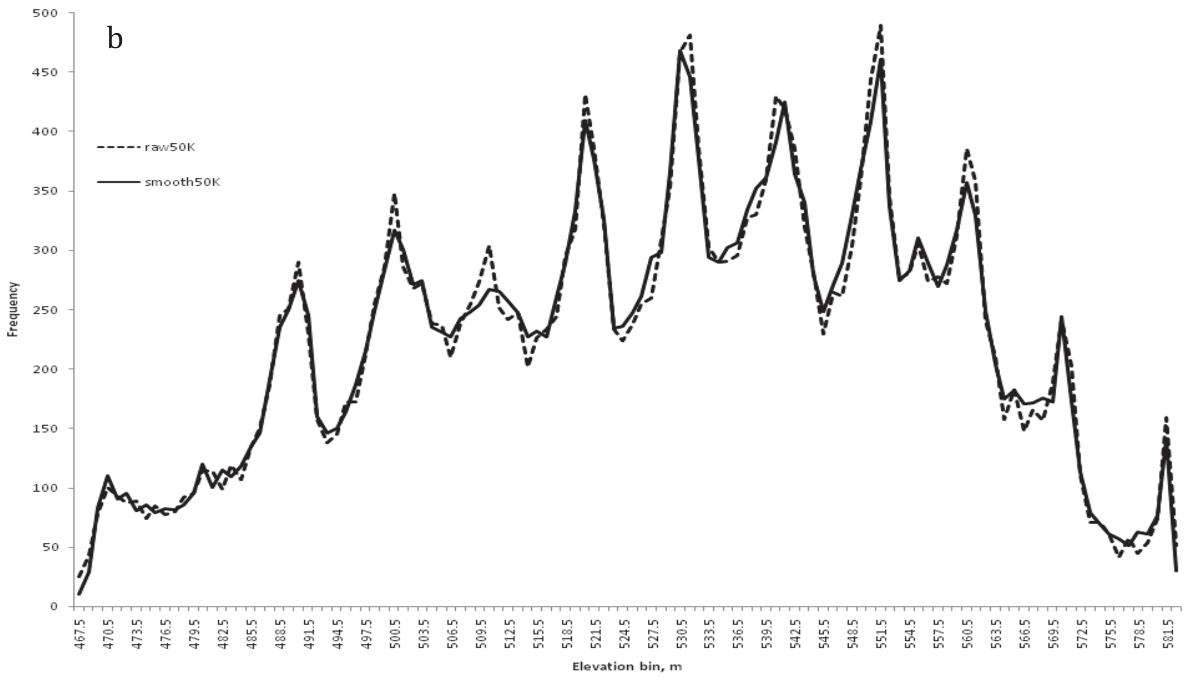


Figure III.c. Histograms of contour-derived DEM from (a) 1:10,000 and (b) 1:50,000 topographic maps.

(raw10K – DEM derived from 1:10,000 DEM by 'Topo to Raster' interpolation; smooth10K – smooth raw10K; raw50K – DEM derived from 1:50,000 DEM by 'Topo to Raster' interpolation; smooth50K – smooth raw50K)

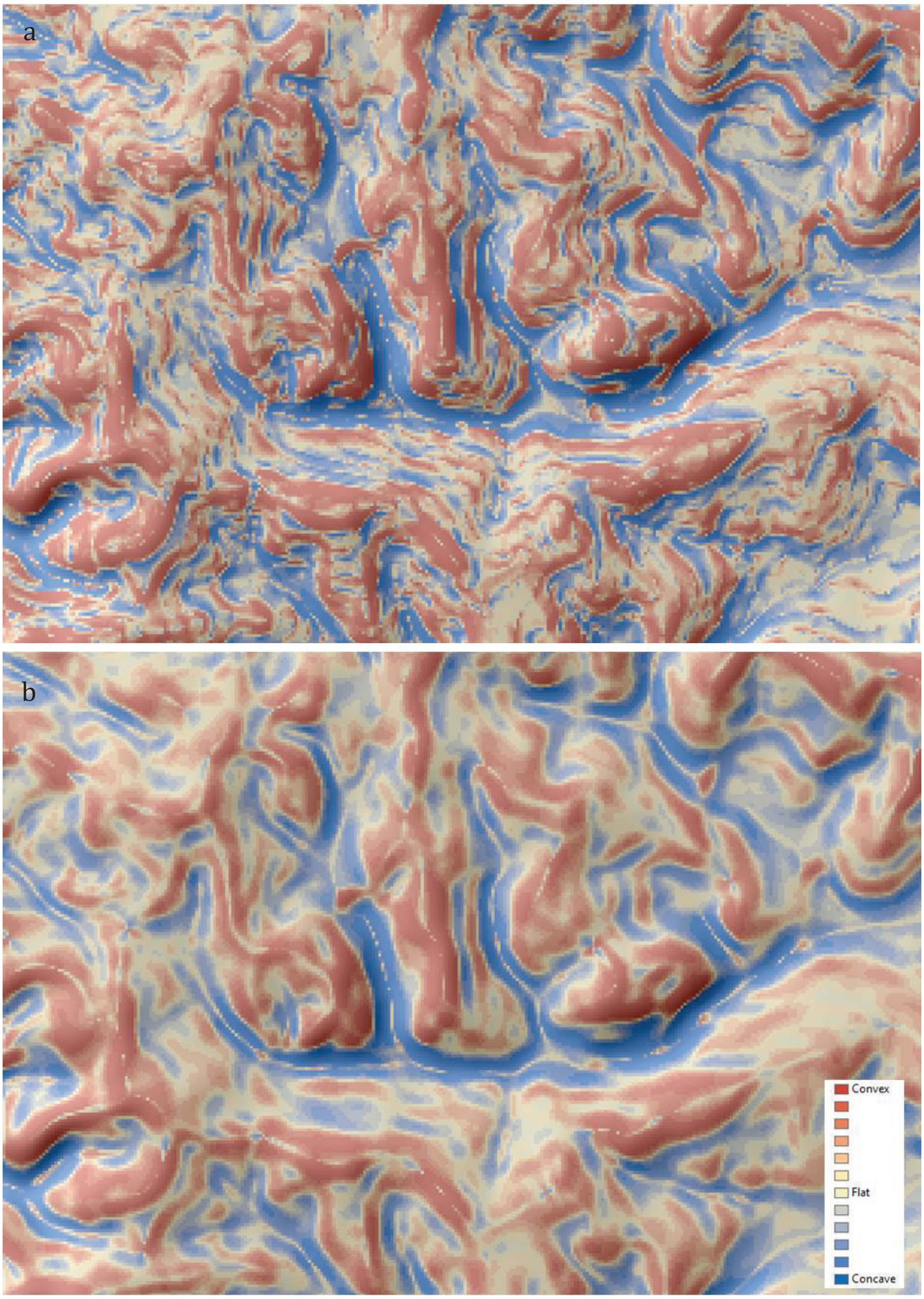


Figure III.d. Profile curvature of unsmooth (a) and smooth (b) DEM derived from 1:10,000 contour data (pixel size = 5 m).

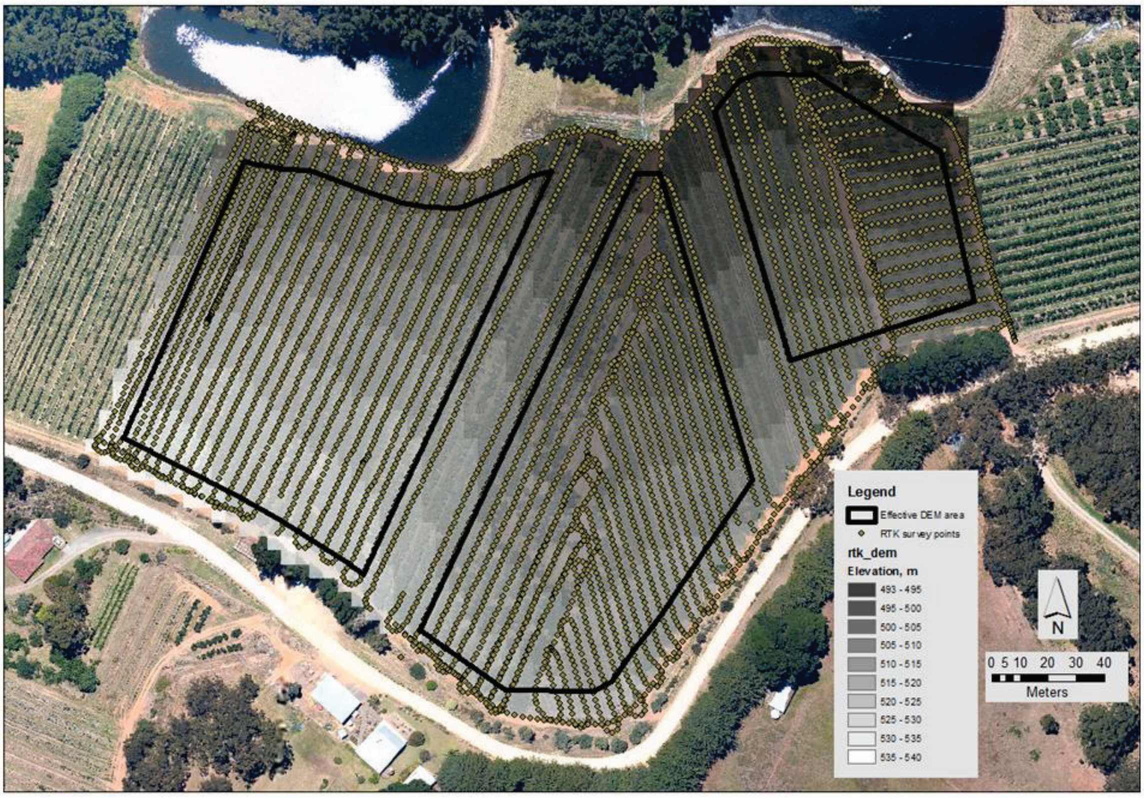
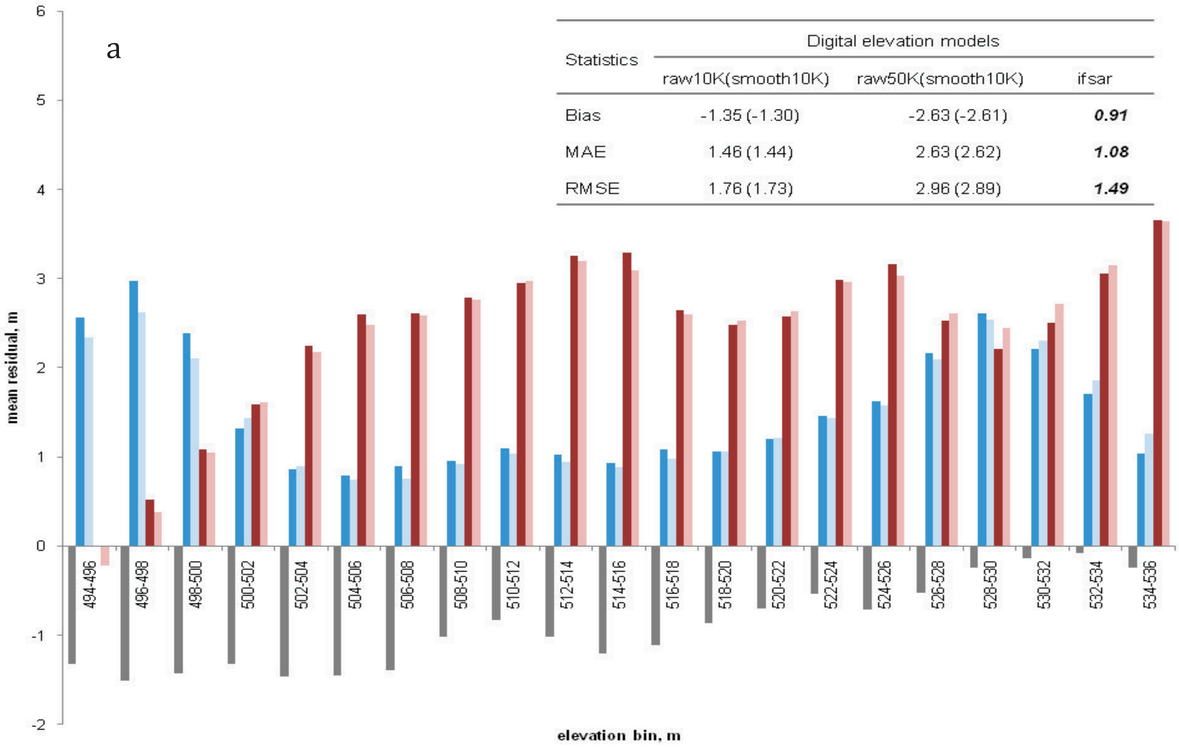
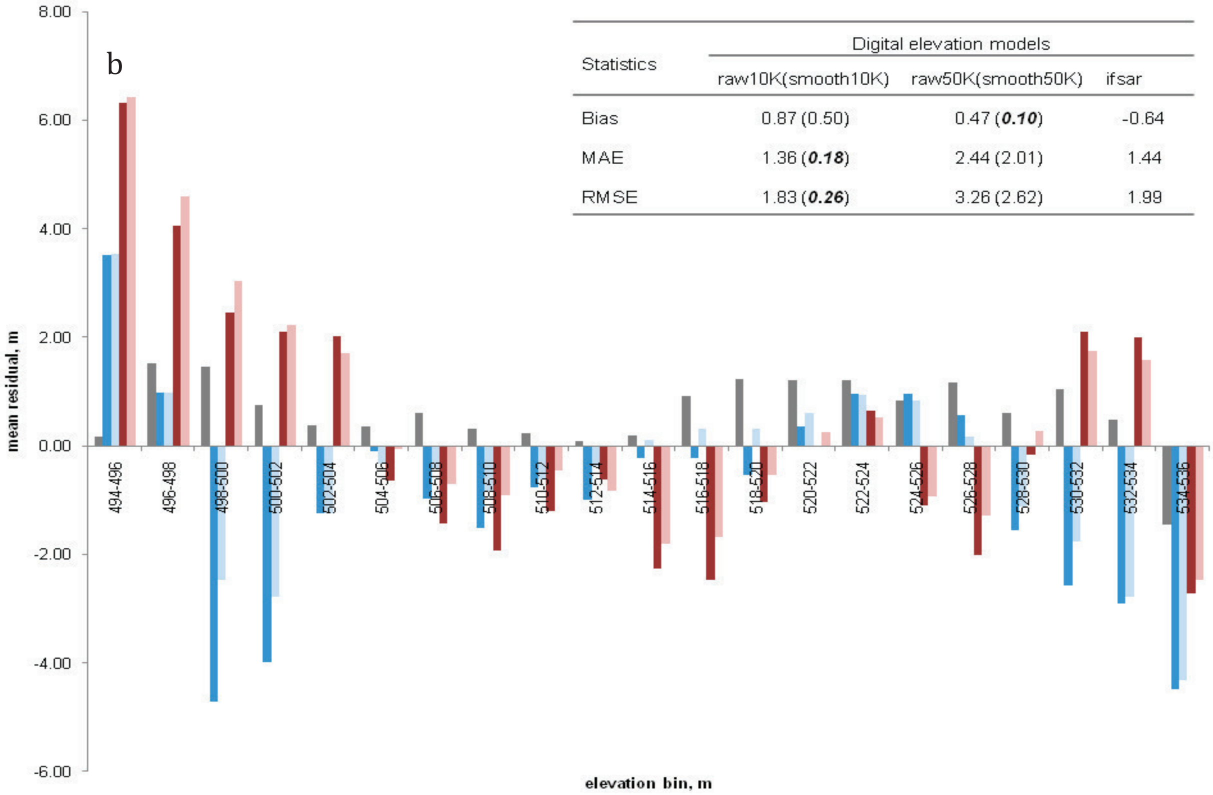


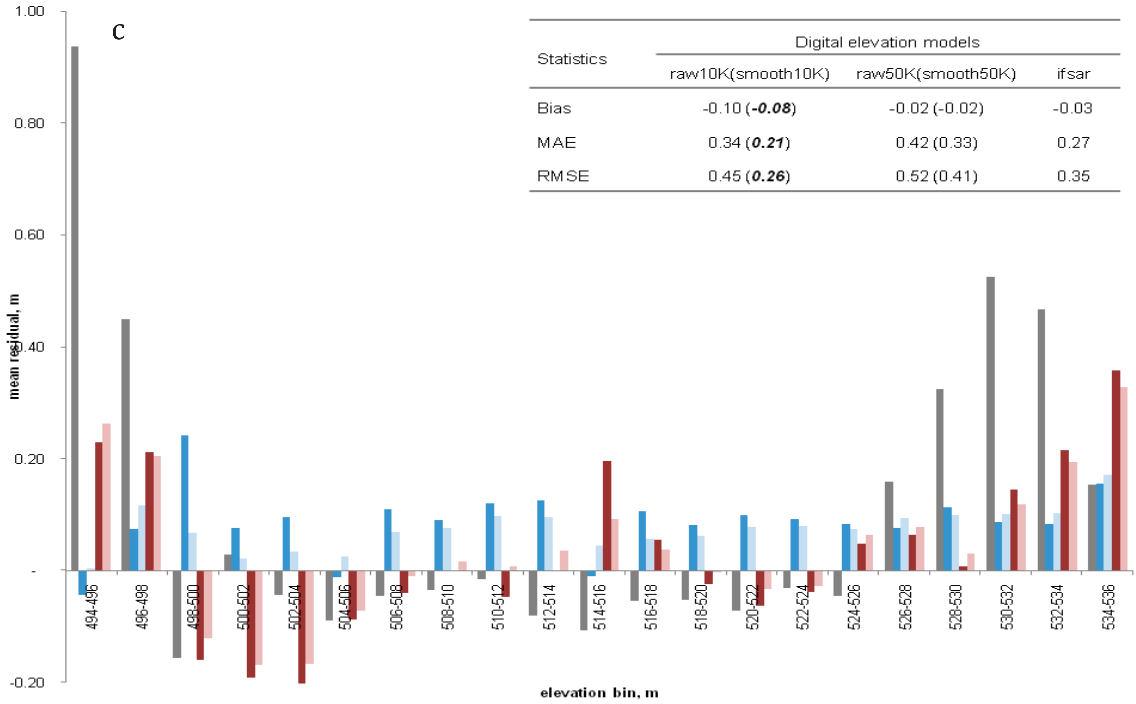
Figure III.e. Survey points and digital elevation model from real-time kinematic global positioning system (RTK-GPS) survey.



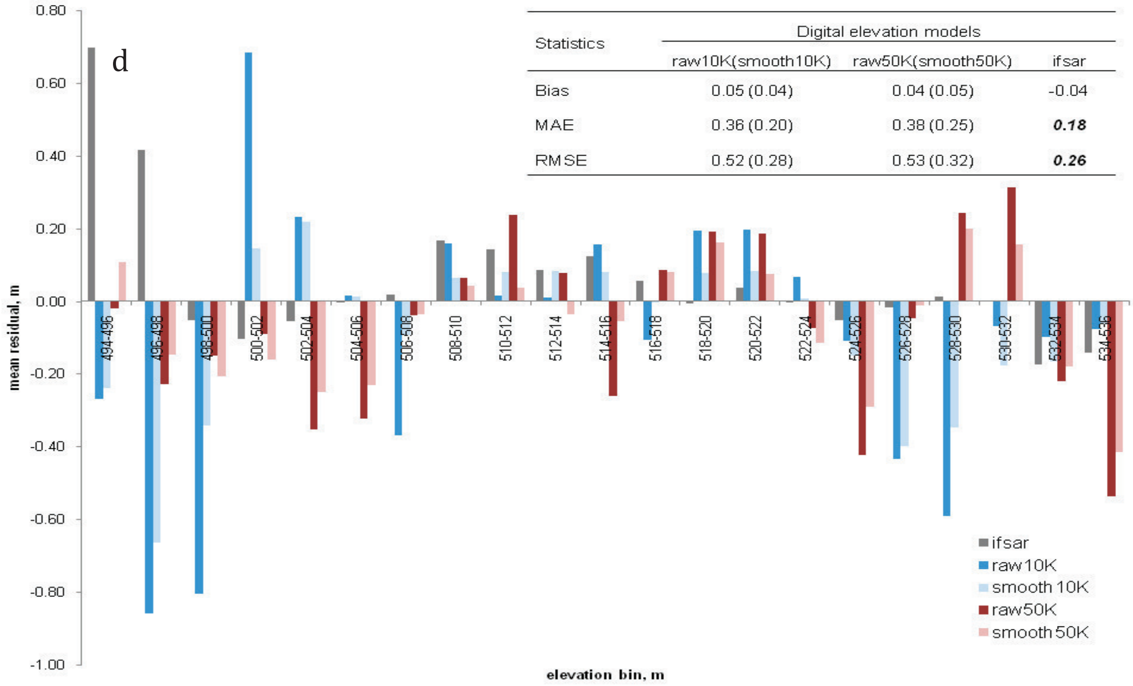
Statistics	Digital elevation models		
	raw10K(smooth10K)	raw50K(smooth10K)	ifsar
Bias	-1.35 (-1.30)	-2.63 (-2.61)	***0.91***
MAE	1.46 (1.44)	2.63 (2.62)	***1.08***
RMSE	1.76 (1.73)	2.96 (2.89)	***1.49***



Statistics	Digital elevation models		
	raw10K(smooth10K)	raw50K(smooth50K)	ifsar
Bias	0.87 (0.50)	0.47 (***0.10***)	-0.64
MAE	1.36 (***0.18***)	2.44 (2.01)	1.44
RMSE	1.83 (***0.26***)	3.26 (2.62)	1.99



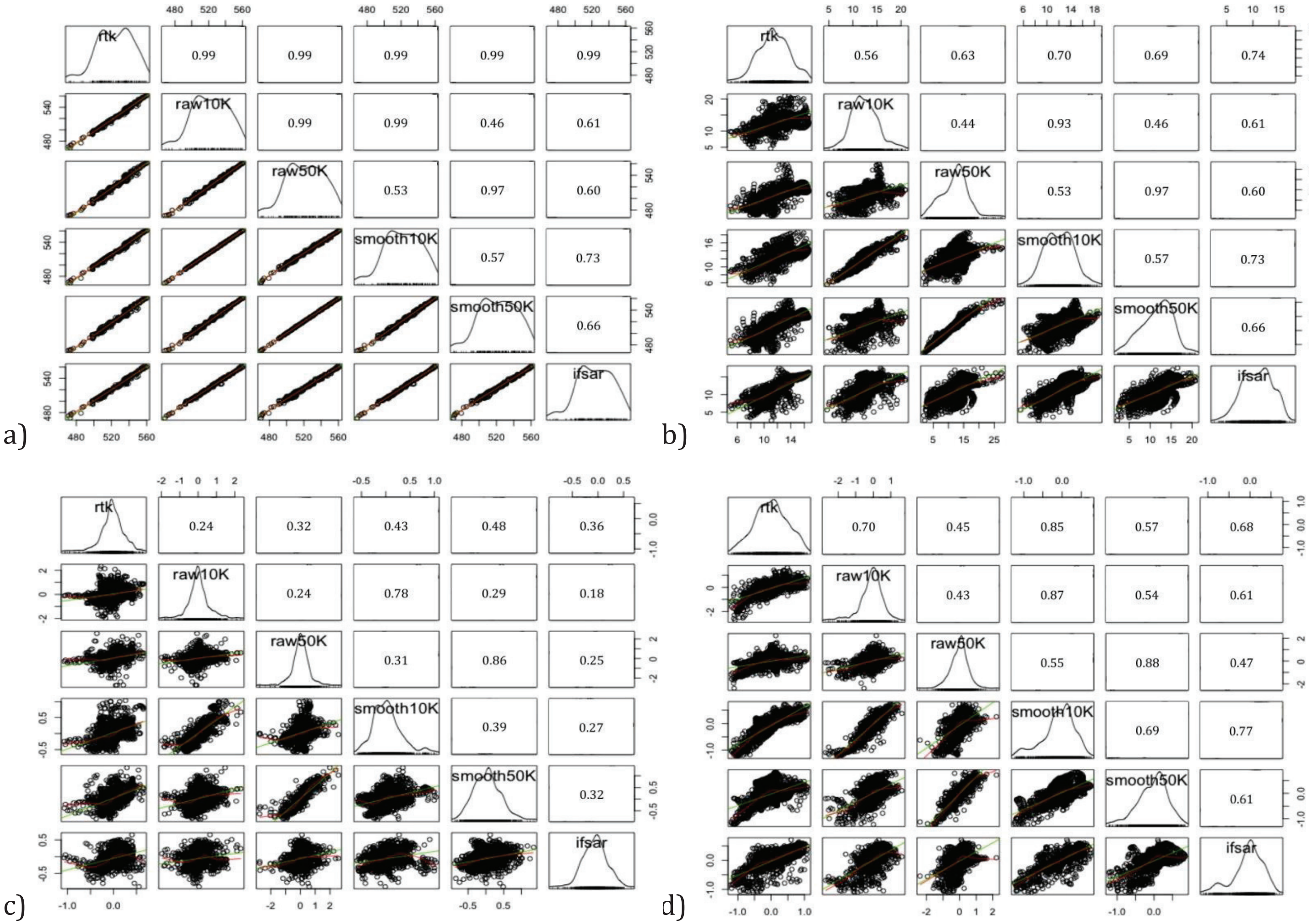
Statistics	Digital elevation models		
	raw10K(smooth10K)	raw50K(smooth50K)	ifsar
Bias	-0.10 (***-0.08***)	-0.02 (-0.02)	-0.03
MAE	0.34 (***0.21***)	0.42 (0.33)	0.27
RMSE	0.45 (***0.26***)	0.52 (0.41)	0.35



Statistics	Digital elevation models		
	raw10K(smooth10K)	raw50K(smooth50K)	ifsar
Bias	0.05 (0.04)	0.04 (0.05)	-0.04
MAE	0.36 (0.20)	0.38 (0.25)	***0.18***
RMSE	0.52 (0.28)	0.53 (0.32)	***0.26***

Figure III.f. Residuals of the (a) elevation, (b) slope, (c) plan curvature, and (d) profile curvature for each DEM against rtk DEM.

(raw10K – DEM derived from 1:10,000 DEM by 'Topo to Raster' interpolation; smooth10K – smooth raw10K; raw50K – DEM derived from 1:50,000 DEM by 'Topo to Raster' interpolation; smooth50K – smooth raw50K)



(rtk – real time kinematic; raw10K – interpolated 1:10,000 topographic map; raw50K – interpolated 1:50,000 topographic map; smooth10K – smooth 1:10,000; smooth50K – smooth 1:50,000; ifsar – interferometric synthetic aperture radar (n = 1,208 pixels).

Figure III.g. Scatterplots and correlation coefficient values of digital elevation models (a) elevation, (b) Slope, (c) plan curvature, and d) profile curvature) from different sources.

CHAPTER IV

Spatial heterogeneity of soil properties to predict pesticide movement

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of the thesis held in the University of Adelaide Library.

CHAPTER V

Effect of terrain and management on the spatial variability of soil properties in an apple orchard

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V. Effect of terrain and management on the spatial variability of soil properties in an apple orchard

Abstract

Soil variability has implications in farm workability, nutrient and pesticide management, and sustainability. The aims of this study were to investigate how management practises and topography influence the variability of key soil properties and to test the efficacy of various analytical techniques for predictive high resolution soil mapping. We measured properties of soils sampled in an intensively managed orchard in the Adelaide Hills, South Australia using a stratified sampling design for alleys and tree-lines in order to distinguish potential management effects (extrinsic factors) from effects of natural soil variability (intrinsic factors). Key soil properties were determined using standard techniques and predictions using mid-infrared partial least-squares (MIR-PLS). Total organic carbon and electrical conductivity (EC) were significantly lower in the tree-line than in the alley. The distribution of coarse fraction (>2mm) was also very different between tree-line and alley, most likely because of ripping during orchard establishment. Terrain parameters had varying effect on distribution of soil properties. The degree of correlation between soil properties and terrain parameters was influenced by the different management regimes in the alley and the tree-line. Within-field management practises impose marked short-range variability in soil properties. Soil sampling for risk assessment of *pesticide movement must consider both the spatial variability of soil properties between tree-lines and alleys and the influence of terrain.*

Keywords

Soil-landscape analysis; managed apple orchard

1. Introduction

The variability of soil properties has a profound, but often unrecognized, effect on the economic and environmental aspects of agricultural production. Soil variability has implications in farm workability (Kværnø, 2007), nutrient management (Stenger et al., 2002; Liu et al., 2009), and sustainability (Patzold et al., 2008; Van de Wauw et al., 2008). The spatial variability of soil properties is invariably influenced by changes in topography, and this variability affects the transport and storage of water within the soil profile (Mulla and McBratney, 2000; Ahuja et al., 2002). Topographic gradients characterise the shape of the land surface thereby dictating the distribution of soil chemical and physical properties (Moore et al., 1991).

Numerous research studies have reported the relevance, often the primacy, of topography in determining the variability of soil properties. Moore et al. (1993) attributed variability of key soil chemical and physical properties to slope, wetness index, aspect and to some extent plan curvature in a study in north-eastern Colorado, USA. Similarly, McKenzie and Ryan (1999) used plan curvature, dispersal area and related environmental variables to predict soil depth, total phosphorus and total carbon in an alpine and sub-alpine mountain site in New South Wales, Australia. Also, Gessler et al., (2000) attributed soil carbon, depth of A-horizon and net primary productivity in a hillslope catena to slope and flow accumulation. Takata et al., (2007) reported that the distribution of potential mineralizable carbon and soil organic carbon were predicted using elevation and mean curvature as independent variables. More recently, Hattar et al. (2010) explained that the distribution of total carbonates and organic matter in the Levant (an arid region in the East Mediterranean), were primarily influenced by hillslope position, steepness and topographic shape properties.

Studies on spatial variability of soil properties are most often conducted in homogenous fields or landscapes such as arid zones (Hattar et al., 2010), forests, pasture areas and broadacre cropping (e.g. grain and oilseed production, but there is a paucity of reports on soil variability in intensively managed, non-homogenous fields such as orchards. Profitability and environmental sustainability of small-orchard enterprises is highly influenced by nutrient and pesticide distribution in the landscape (Aggelopoulou et al., 2011). With respect to soil chemistry, organic carbon, pH, electrical conductivity and texture of the surface horizons often exert a dominant effect on nutrient availability, pesticide sorption (Kookana et al., 1998) and overall ecosystem services (Simon et al., 2010). In this paper we attempt to quantify the spatial structure of these soil properties, determine the effect of management practises on this spatial structure in a heterogeneous landscape, and explore a suitable interpolation technique for un-sampled location. Numerous spatial interpolation or prediction methods are available for a wide range of soil properties. One is digital soil-terrain modelling (Bishop and Minasny, 2006) which emanated from Jenny's equation of soil formation (Jenny, 1941) and employs regression. This approach requires reliable model parameter data, for example elevation. Moreover, the statistical relationship of the variables also needs to be established. Another approach is geostatistics (Goovaerts, 1999; McBratney et al., 2003; Webster and Oliver, 2007) whereby the spatial coordinates of properties are used to describe their spatial structure as well as predict the values at unsampled locations. The most common geostatistical method is ordinary kriging (Webster and Oliver, 2007) and has been used extensively to predict the distribution of a variety soil properties. Other geostatistical and hybrid approaches are available and readers are encouraged to read Webster and Oliver (2007) and Hengl (2009).

The objectives of this study were therefore to (i) measure the spatial variability of surface soil properties in an intensively managed apple orchard (ii) determine the effects of topography and management practises on the distribution of soil properties and iii) determine an appropriate approach for the spatial prediction of soil properties. We quantify the spatial structure of soil properties in an apple orchard, compare how this structure varies from alley to tree-line, and predict the distribution of soil properties using regression and geostatistical approaches.

2. Materials and methods

2.1. Site description and general methodological approach

The study site, situated in the central Mount Lofty Ranges 30 km east of Adelaide, South Australia (34°54.918"S 138°48.107"E), lies within the Onkaparinga Catchment and was planted to apples of various varieties in the early 1950s. The subcatchment is hilly with mean elevation of 513 m, maximum slope of 30° and mean slope of 13°. The area has a Mediterranean climate with mean maximum and minimum temperatures of 12°C and 5°C during winter and 26°C and 14°C during summer, respectively. The soils have a xeric moisture regime. The mean monthly rainfall from 1970 to 2000 in the winter months (June-August) was approximately 150 mm and in the summer months (December to February) was 32 mm. The soils in the site developed from Proterozoic shales, siltstones and metasandstones (Hall et al., 2009) and are classified as Petroferric, Melanic-Vertic, Red-Yellow Chromosols. Profiles on the upper slopes are thin, moderately gravelly and silty. The size of the study site is 5.6 ha (Fig. V.a). The site is dominated by one soil type, Red-Yellow Chromosols (Isbell, 2002) (The Australian Soil Classification). Soils of this type occur on about 60% of the entire Mt. Lofty Ranges region.

2.2. DEM and DTM Generation

A digital elevation model (DEM) was generated from 5-m contour and drainage maps both of which were obtained in digital format from the state mapping agency. The Topo to Grid interpolator in ArcMAP 10® (Environmental

Systems Research Institute, 2010) was used to create a 5 m gridded DEM, which was further enhanced using error-reduction algorithms (Hengl et al., 2004a).

Eight key terrain parameters (Table V.a) were calculated in a GIS environment using ArcMAP 10® and Terrain Analysis System or TAS (Lindsay, 2005). All DEM data were converted to TAS format. First and second derivatives of the DEM were estimated using the finite difference method (Wilson and Gallant, 2000) with the D∞ flow routing algorithm. This algorithm is recommended for high-resolution DEM, with the advantage of reducing bias caused by overestimation of grid alignment upslope area (Tarboton, 1997). The resulting terrain models were converted back to ArcMap format for spatial sampling and analysis. The resulting digital terrain models are presented in Fig. V.b.

2.3. Apple orchard management

The orchard was established in the 1950s. Trees were planted at high density (~450 trees per hectare). Tree-lines, 2 to 4 m wide, run either across or along the slope. Alleys, 2.5 m wide divide the tree-lines. A small portion, concentrated mainly on the western section of the study site, had been replanted in 2006. Ripping to a depth of about 1 m along the tree-lines was carried out during establishment to break up the top of the dense B horizon. Sod strips were laid out in the alleys (between tree-lines) using various grass species such as *Festuca sp.* (dwarf fescue), *Pennisetum purpurium* (napier) and *Hordeum hystrix* (barley grass). Native grasses are also encouraged along the alleys. Clippings from mowing were used as mulch to minimise moisture loss in the tree-lines, most importantly during replanting and in elevated and sloping areas. Herbicides are also periodically applied. Fertiliser is applied through localised fertigation. Irrigation is localised using sprinklers raised less than 0.3 m above the ground from a series of lines laid out along the tree-line. Thinned biomass (fruits, leaves and small branches) is left under the trees whereas mown grasses are left where they are cut (normally on alleys). Mulching and herbicide application along the tree-line is undertaken to reduce competition for nutrient and water. Sod strips in the alleys serve as cover to reduce impact of farm machinery and to act as buffer for soil erosion and material loses.

2.4. Soil sampling and analysis

One thousand soil samples were collected from one hundred paired locations (2 x 100) randomly selected from an area of 5.6 ha within the subcatchment. Each location was referenced on the ground using a handheld high-sensitivity GPS. A pair location corresponds to one sampling point from the tree-line and one sampling point from the alley. At each sampling point, a 0.25 m^2 area, 5 subsamples were taken – one at each corner and one at the center. Soil sampling in alleys was carried out in such a way that compacted zones from farm machinery tracks were avoided. The top 10 cm of soil was sampled with an auger. Samples were air-dried, passed through a 2mm sieve, composited and analysed. Total organic carbon (TOC, %) and clay (%) were all determined by diffuse reflectance infrared Fourier-transform (DRIFT) spectroscopy and models derived from partial least-squares regression (Janik and Skjemstad, 1995; Janik et al., 1998). Prior to scanning, samples were pulverised to ~0.1mm (Janik and Skjemstad, 1995).

The predictions were calibrated by analysing a sub-set (10%) of samples using traditional wet chemistry techniques. Total carbon was determined by high temperature combustion in an atmosphere of oxygen using a Leco CNS-2000 (Matejovic, 1997). Inorganic C was determined by reacting the sample with acid in a sealed container and measuring the pressure increase with a pressure transducer (Sherrod et al., 2002). Total organic carbon was calculated by subtracting the inorganic carbon from the total carbon. The proportion of clay was determined using the pipette method (Day, 1965). The coefficient of determination (R^2) between the prediction and the calibration data sets was 0.93 and 0.98 for TOC and clay (%), respectively.

Electrical conductivity (EC) was measured in 1:5 soil suspensions using an Orion 150 EC meter with 2 cell constants and calibrated using standard solutions. Soil pH_w was measured in 1:1 soil:H_2O suspension. Proportion of coarse fraction (>2mm, mostly stones and pebbles) was determined gravimetrically. Soil EC, pH_w and coarse fraction were all determined in the laboratory for all soil samples.

2.5. Statistical Analysis

All measured and predicted soil properties were analysed for normality using the Shapiro-Wilks test. Means of variables for each sampling location were analysed for significant differences at 0.05 level of confidence using the Welch Modified two-sample t-test. Pearson's product-moment coefficients (r) were computed in order to determine significant associations between soil properties and terrain parameters listed in Table V.a.

Spatial autocorrelation of soil properties were calculated through semi-variogram modelling using VESPER (Minasny et al., 2005). The calculations used the equation:

$$\hat{\gamma}(h) = \frac{1}{N(h)} \sum_{i=1}^{N(h)} \left[z(x_i) - z(x_i + h) \right]^2$$

The analysis, a local variogram calculation, used a maximum lag size of 300 m divided into 15 lag distance classes. Model fitting was based on root mean square error (RMSE) and the Akaike Information Criteria as reported by VESPER. Among the soil properties, only EC was log transformed to approximate a normal distribution. Spatial autocorrelation was evaluated using the nugget:sill ratio (Cambardella et al., 1994).

2.6. Regression and geostatistical prediction of soil property distribution

Three approaches were used to predict the spatial distribution of soil properties within the apple orchard. Moreover, two sets of predictions were made, one for alley and one for tree-line samples because of differences in spatial structure and variability. The first approach was multiple linear regression using the terrain parameters as explanatory variables. Regressions employed were all in the first order form. Key model parameters were selected using stepwise (forward and backward) Akaike Information Criteria (Akaike, 1974) in the statistical software R. The second approach was ordinary kriging (Goovaerts, 1999; Webster and Oliver, 2007) to predict the distribution of soil properties utilizing the spatial coordinates and ultimately the spatial dependence of the soil properties across all sampling points. Using the semi-variance model parameters generated in the spatial autocorrelation analysis, prediction maps were generated for each of the soil properties. The third approach was regression-krigging model C (Odeh et al., 1995; Hengl et al., 2004b). This approach utilised the regression output of the first approach to create spatial predictions of soil properties using the significant model parameters as predictors. Residuals at sample locations were also used to obtain a kriged spatial estimate (using ordinary kriging) of the prediction error. Finally, the two spatial predictions were added to give an estimate of the distribution of the soil properties. A more detailed explanation of this procedure can be found in Hengl et al. (2004b) and Herbst et al. (2006). All analyses were performed at a 5 m raster resolution.

To examine model accuracy, jack-knife validation was carried out by partitioning the sample set into training (80%) and validation (20%) data sets. Samples in each set were identified randomly. The three approaches stated earlier (regression, ordinary kriging and regression kriging) were applied to the training set for the alley and tree-line samples. Spatial predictions based on these models were sampled on points where the validation set was located and the residuals were computed. The predicted and measured soil properties in these sampling locations were compared. Mean absolute error (MAE) and root mean square error (RMSE) were computed as comparative parameters for each model. They were calculated using the equation:

$$MAE = \frac{1}{n}\sum_{i=1}^{n}\left|e_i\right|$$

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}e_i^2},$$

where e_i is the residual for each soil property under investigation.

Maps of selected soil properties (TOC and coarse fraction) were created using ordinary kriging. To visualise the heterogeneity of soil properties between the alley and tree-line locations, soil properties were interpolated independently in these locations and overlaid.

3. Results

3.1. Variability of soil properties

The range of variability of soil properties within and between alleys and tree-lines (Table V.b) was wide regardless of sampling location. For instance, clay content and pH_w had little variability (CV < 15%), however, coarse fraction, EC and TOC showed moderate (CV = 15-35%) to high variability (CV > 35%). Mean TOC and EC values were significantly greater in soils from the alleys than those from the tree-lines but coarse fraction was significantly greater in soils from the tree-lines than those from the alleys. The level of variability also increased from moderate in soils collected in alleys to high in soils collected in tree-lines for EC.

3.2. Univariate spatial dependence analysis of soil properties

The results of the variogram modelling show that the spatial structure varied between sample locations and among soil properties (Fig. V.c). For example, the nugget:sill ratio of TOC increased from 0.28 in the alley to 1.07 in the tree-line and in a similar manner for clay content and coarse fraction. This means that the spatial structure of TOC, clay and coarse fraction was greater in the alley than in the tree-line. The reverse was true for pH_w and EC which had weaker spatial structure in the alley than in the tree-line. We also observed that in the alley, coarse fraction had the highest spatial structure and EC had the lowest whereas in the tree-line, pH_w had the strongest spatial structure and clay content the weakest. The semi-variogram for EC in the tree-line and the coarse fraction in the alley had unbounded forms (range was greater than the maximum variogram distance), in this case, may be limited by the size of the study site.

3.3. Soil landscape analysis and modelling

The soil properties for both alley and tree-line samples were influenced, albeit minimally, by most terrain parameters (Fig. V.d). TOC in the alley was significantly correlated with slope and STCI. In the tree-lines, TOC was significantly correlated ($p<0.05$) with the same terrain parameters as well as elevation and ProfC. Soil pH_w in the alley was correlated ($p<0.05$) with elevation, PlanC, TanC, STCI and WI. In the tree-line, pH_w was correlated with slope, RSP and STCI. Soil EC in the alley was correlated ($p<0.05$) with SCA, RSP and STCI, whereas in tree-line, it was correlated with elevation, slope, ProfC and WI. For clay content, the topographic variables that showed significant correlation ($p<0.05$) were elevation, PlanC, TanC, SCA, RSP, STCI and WI in the alleys. The same parameters, except elevation, were correlated with clay content in the tree-line. Coarse fraction in the alley was correlated with elevation, slope, ProfC, TanC and WI. In the treeline, coarse fraction was correlated with elevation and ProfC.

The level of correlation also changed based on sampling location (tree-line vs. alley). For instance, the r for TOC and slope was -0.54 and -0.29 in alleys and tree-lines, respectively. The value of r for the association between coarse fraction and elevation was 0.69 in the alley but 0.60 in the tree-line. Over the whole landscape segment, the correlation was moderate and sometimes weak: r-values ranged from |0.01| to |0.69|. This level of correlation was expected and is not unusual in soil-landscape studies (Moore et al., 1993; Garten et al., 2007).

3.4. Prediction of soil properties

To determine the appropriate interpolation procedure for the spatial distribution of soil properties, regression, ordinary kriging and regression-kriging model C were employed. Owing to the weak correlation between the explanatory variables and the dependent variables, most soil-landscape models had weak R^2 values (Table V.c). On the other hand, the model R^2 values for TOC in the tree-line was 0.41 0.51 and for coarse fraction in the alley. The stepwise regression also revealed which terrain variables were significant in predicting the distribution of soil properties. The significance of the terrain variables also varied from alley and tree-line locations. The model parameters for the distribution of soil pH_w, for instance, include elevation, TanC, ProfC, SCA and RSP in the alley. In the tree-line, model parameters were PlanC, TanC, SCA and RSP.

A summary of the model MAE and RMSE is presented in Table V.d. Of the soil properties studied, only the distribution of the coarse fraction in the alley was accurately predicted by regression, which had the minimum RMSE at 4.79 owing to the high correlation of coarse fraction with model parameters (elevation, slope, TanC and WI). The other soil properties were more accurately predicted by ordinary kriging. Regression and regression kriging had high MAE and RMSE which we attribute to the low correlation of regression model parameters with soil properties. However, regression kriging had lower MAE and RMSE than regression, which indicate improved prediction highlighting the benefit of residual kriging. Kriged maps were created for TOC and coarse fraction (Fig. V.e) assuming that there were clear boundaries between the alley and the tree-line for each of the soil properties. Based on field observations, the grower follow strict orchard floor management whereby the tree-lines are kept free from ground cover vegetation (grasses or weeds) and sod strips are maintained in the alley.

4. Discussion

Previous studies conducted reveal the behaviour of soil spatial structure and variability in natural vegetation areas and in monoculture farms. The present study describes the distribution of some soil properties in a heterogeneously-managed orchard. We found that the distribution of soil properties in the site was affected more by orchard floor management than by terrain properties. The low levels of TOC in the tree-line was attributed to the periodic application of herbicide products that prohibited ground cover growth. Both the proportion, and the spatial structure of TOC (Fig. V.c) in the tree-lines were significantly lower in soils collected in the tree-line. We also observed that TOC levels were lower in the western side, where replanting took place in 2006, compared with the rest of the study area (Fig. V.e). However, the tree line in the western side had relatively higher proportion of TOC compared with the alley. This is most likely caused by addition of trimmed biomass, now discontinued, after the original trees were removed and while the new stocks were growing. Similarly, Hipps and Samuelson (1991) found that organic carbon, along with other key soil nutrients, were significantly lower in bare soils where herbicide was applied than in grassed areas of an apple orchard. Soil organic carbon was also lower in cultivated lands than in the adjacent restored grassland in a study in Saskatchewan, Canada (Nelson et al., 2008).

More evidence of management practice altering soil patterns is provided by the variability of coarse fraction. The significantly higher amount of coarse fraction in the tree-lines compared with alleys is most likely the result of ripping during orchard establishment. Ripping may have resulted in the incorporation of coarse materials from B and C horizons into the surface horizon. Hydraulic properties of the soil, especially the rate of infiltration (Brakensiek and Rawls, 1994) will have been altered.

The results of the topographic analysis also indicate that within-field management practises altered the distribution of some soil properties in the apple orchard landscape. Correlations between terrain parameters and soil properties differed markedly between alley and tree-line samples (Fig. V.d). Correlations were either enhanced or moderated as evidenced by, for example, non-significant to highly significant positive correlations between TOC and elevation in the alley and tree-line, respectively. Empirically, under natural conditions, TOC is expected to show negative correlation with elevation (Manning et al., 2001) due to higher moisture contents and therefore organic matter accumulation, in lower lying areas. This is not the case in the tree-line, probably because of management practises. The association of coarse fraction and elevation was lower in the tree-line than in the alley. Similar trends in association (either reduced or enhanced) were observed for other soil variables. These observations imply a masking effect of management practises on soil distribution. This masking effect renders the distribution of soil properties more complex and sometimes unpredictable. Other management-related factors, such as age of trees, variable irrigation scheme and varietal management regimes, which were not considered in this study, are envisaged to further explain this variability.

Guo et al. (2009) found that for a hilly area in South-Western China, soil organic matter is negatively correlated with slope and elevation by about 50% and to WI by only 30%. However, we observed that TOC was not affected by WI and elevation in the alleys but positively correlated with elevation in the tree-line. The only plausible explanation for this is the constant addition of mulch material in the tree-line on elevated sites in order to reduce soil erosion and reduce the impact of pesticide on neighboring bodies of water (rivers and dams). This was supported by the grower during a follow-up interview. Organic carbon is an important parameter in predicting environmental fate and behaviour of pesticides (Wauchope et al., 2002). A direct link between sorption properties of organic herbicides and soil organic carbon has also been established (Coquet and Barriuso, 2002). Farenhorst et al. (2008) found that integrating soil and topographic properties can best model the distribution of 2,4-D sorption which has weak soil sorption capacity. The spatial structure and distribution of TOC in this kind of landscape implies that pesticide risk assessment and models should accommodate the spatial variability of soil parameters caused by management practises in order to improve accuracy and reliability.

The geostatistical prediction show that ordinary kriging provide good results for modelling the distribution of soil properties. This was expected, and due to the low correlation of the terrain parameters with soil properties, regression kriging did not show better predictions than ordinary kriging. This suggests that variogram analysis and kriging work well for our study site considering the heterogeneity of soil properties that have been brought about by existing management regimes.

5. Conclusion and Recommendation

The degree by which terrain affected the distribution of soil properties investigated here varied between the alley and the tree-line. Ordinary kriging interpolation also reveal the masked extent to which orchard floor management influenced the distribution of soil properties. This rendered the orchard soil to have a distinct spatial pattern.

This study also shows that soil sampling in this type of landuse should be stratified. There is clear spatial heterogeneity of soil properties and that management history adds to the complexity, yet in a systematic and predictable way. The spatial prediction of soil properties is important in order to identify zones or pockets that are critical in terms of material dissipation or accumulation.

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Table V.a. Terrain parameters calculated in this study.

Attribute	Description	Formula (reference)
Slope, °	rate of change of elevation	$\sqrt{z_x^2 + z_y^2}$ (Wilson and Gallant, 2000)
Plan curvature (PlanC), ° m^{-1}	horizontal curvature, a measure of topographic convergence and divergence	$\frac{z_{xx} z_y^2 - 2z_{xy} z_x z_y + z_{yy} z_x^2}{p^{3/2}}$ (Wilson and Gallant, 2000)
Profile curvature (ProfC), ° m^{-1}	vertical curvature, a measure of flow acceleration or deceleration	$\frac{z_{xx} z_x^2 + 2z_{xy} z_x z_y + z_{yy} z_y^2}{q^{3/2}}$ (Wilson and Gallant, 2000)
Tangential curvature (TanC), ° m^{-1}	a measure of flow convergence and divergence	$\frac{z_{xx} z_y^2 - 2z_{xy} z_x z_y + z_{yy} z_x^2}{pq^{1/2}}$ (Wilson and Gallant, 2000)
Specific catchment area (SCA), $m^2 m^{-1}$	the ratio of the area upslope of a contour segment that contributes flow to that segment and the length of that segment	A/l (Wilson and Gallant, 2000)
Sediment transport capacity index (STCI)	equivalent to RUSLE Length-Slope factor	$\left(\frac{SCA}{22.13}\right)^{0.6} \times \left(\frac{sin\beta}{0.0896}\right)^{1.3}$ (Burrough and McDonnell, 1998)
Relative stream power (RSP)	an index of erosive power of overland flow	$SCA \times tan\beta$ (Moore et al., 1993)
Wetness index (WI)	characterise spatial distribution of surface saturation	$\ln(SCA/tan\beta)$ (Beven and Kirkby, 1979)

notations: z_n corresponds to each grid in a 3x3 grid matrix, clockwise from top right, with h as grid size;

$z_x = \frac{z_2 - z_6}{2h}$, $z_y = \frac{z_8 - z_4}{2h}$, $z_{xx} = \frac{z_2 - 2z_9 + z_6}{h^2}$, $z_{yy} = \frac{z_8 - 2z_9 + z_4}{h^2}$, $z_{xy} = \frac{-z_7 + z_1 + z_5 - z_3}{4h^2}$, $p = z_x^2 + z_y^2$, $q = p + 1$, $\beta =$ arctan $(slope)$. All formula from Wilson and Gallant (2000) and Moore et al. (1993)

Table V.b. Summary statistics of properties for soils sampled in alleys and in tree lines.

Variable	Sampling location	Min	Max	Mean§	Median	SD	Skew-ness	CV
TOC, %	alley	2.2	6.9	4.5a	4.7	1.1	-0.1	24.3
	tree line	1.5	5.5	3.4b	3.4	0.8	0.0	23.1
pH (1:1 H_2O)	alley	6.1	7.5	6.9	6.9	0.3	-0.5	4.7
	tree line	5.4	7.6	6.9	7.1	0.5	-1.2	6.4
EC, $\mu S\ cm^{-1}$	alley	181.8	729.1	404.6a	378.7	118.6	0.6	29.3
	tree line	160.9	1071.6	339.3b	328.8	124.9	2.5	36.8
Clay, %	alley	16.1	33.8	23.3	22.9	3.7	0.6	15.7
	tree line	16.7	35.7	23.1	22.8	3.5	0.5	14.9
Coarse fraction, %	alley	7.4	47.2	30.6b	31.2	8.7	-0.4	28.3
	tree line	15.9	50.4	35.0a	35.6	7.7	-0.3	21.9

TOC – total organic carbon; EC – electrical conductivity

§ means of variables for each sampling location followed by different letters are significantly different at 0.05 level of confidence using Welch Modified two sample t-test.

Table V.c. Summary table of model parameters for soils properties using stepwise linear regression with Akaikie Information Criterion.

Location	Soil property	Intercept	Elevation	Slope	PlanC	ProfC	TanC	SCA	RSP	WI	STCI	Model R^2	p-value
Alley	TOC, % (df=78)	7.54		-0.23								0.30	<0.001
	pH_w (df=74)	0.17	0.01		-0.10	0.36		0.0039	-0.01			0.21	<0.01
	EC, $\mu S\ cm^{-1}$ (df=73)	2098.56		-53.59			214.10	2.03	-14.10	239.94	75.26	0.20	<0.05
	Clay, % (df=74)	43.95			-7.40		32.16	0.13	-0.36	-4.26		0.32	<0.001
	Coarse Fraction, % (df=75)	-348.11	0.63	1.14			-24.62			7.11		0.51	<0.001
Tree line	TOC, % (df=75)	-13.08	0.03				-1.19		0.07		-0.28	0.41	<0.001
	pHw (df=75)	7.18			-0.46		2.35	0.01	-0.05			0.19	<0.01
	EC, $\mu S\ cm^{-1}$ (df=73)	-2168.64	3.94	51.49	-165.02		707.24	3.57			70.62	0.32	<0.001
	Clay, % (df=74)	35.44			-5.99		28.51	0.08	-0.23	-2.38		0.21	<0.01
	Coarse Fraction, % (df=77)	-195.81	0.41		-1.57					3.61		0.33	<0.001

EC – electrical conductivity; PlanC – plan curvature, ° m^{-1}; ProfC – profile curvature, ° m^{-1}; TanC – tangential curvature, ° m^{-1}; RSP – relative stream power; SCA – specific catchment area, m^2m^{-1}; STCI – sediment transport capacity index; TOC – total organic carbon, % WI – wetness index.

Table V.d. Results of the jack-knife validation of the three prediction models

	Alley					Tree line				
	TOC (%)	pH_w	EC, $\mu S\ cm^{-1}$	Clay (%)	Coarse Fraction (%)	TOC (%)	pH_w	EC, $\mu S\ cm^{-1}$	Clay (%)	Coarse Fraction (%)
MAE[1]										
Regression	0.67	0.23	98.31	2.86	3.68	0.62	0.29	66.74	2.71	5.73
Ordinary Kriging	0.37	0.17	65.33	1.67	3.76	0.48	0.11	29.26	2.62	3.71
Regression Kriging	0.52	0.21	88.03	2.97	3.75	0.63	0.21	65.02	2.57	4.85
RMSE[2]										
Regression	0.79	0.27	114.29	3.64	4.79	0.72	0.35	95.56	3.12	6.99
Ordinary Kriging	0.46	0.22	79.56	2.28	5.12	0.54	0.14	36.95	3.00	4.37
Regression-kriging	0.64	0.25	105.02	3.63	4.86	0.73	0.27	94.64	2.94	6.65

EC – electrical conductivity, $\mu S\ cm^{-1}$; PlanC – plan curvature, ° m^{-1}; ProfC – profile curvature, ° m^{-1}; TanC – tangential curvature, ° m^{-1}; RSP – relative stream power; SCA – specific catchment area, $m^2 m^{-1}$; STCI – sediment transport capacity index; TOC – total organic carbon, % WI – wetness index.

TOC – total organic carbon; WI – wetness index.

[1]MAE – mean absolute error

[2] RMSE – root mean square error

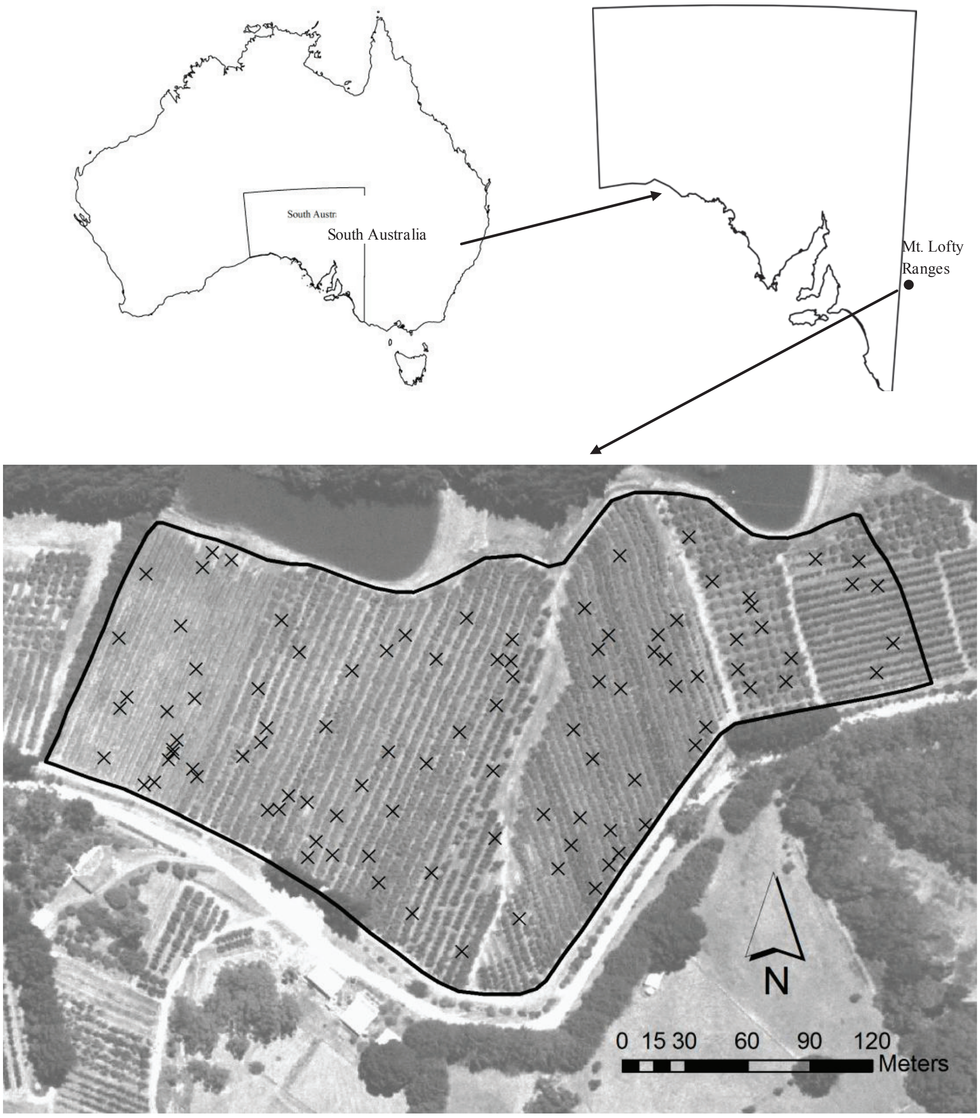

Figure V.a. Location map of the study site (Each × represents a sampling location of two samples, one in the alley and one in the tree line).

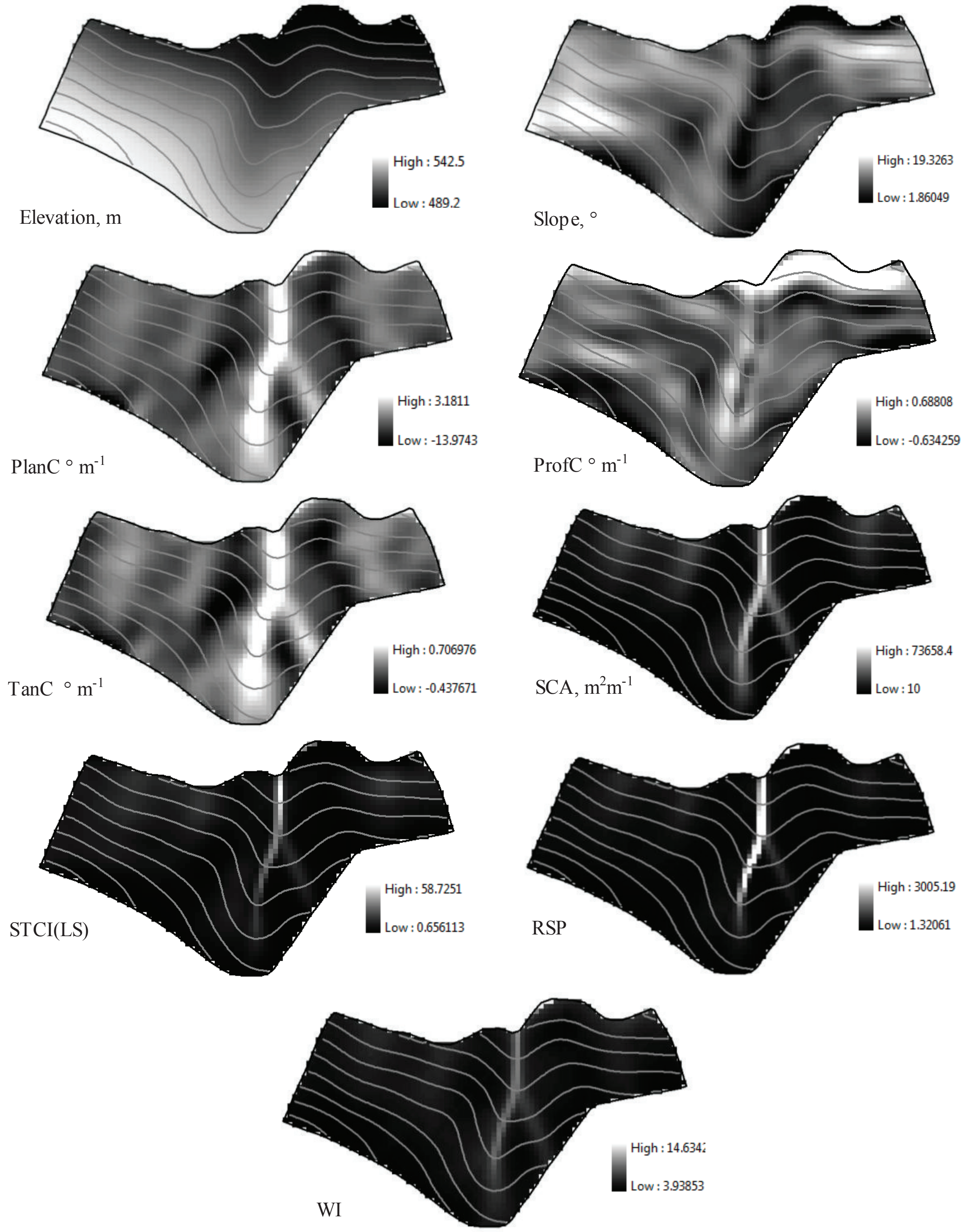

Figure V.b. Digital terrain models generated from topographic and drainage maps of the study site (contour lines in gray are from 490 m at the top right to 540 m at the bottom left). PlanC – plan curvature; ProfC – profile curvature; TanC – tangential curvature; RSP – relative stream power; SCA – specific catchment area, m^2m^{-1}; STCI – sediment transport capacity index; WI - wetness index).

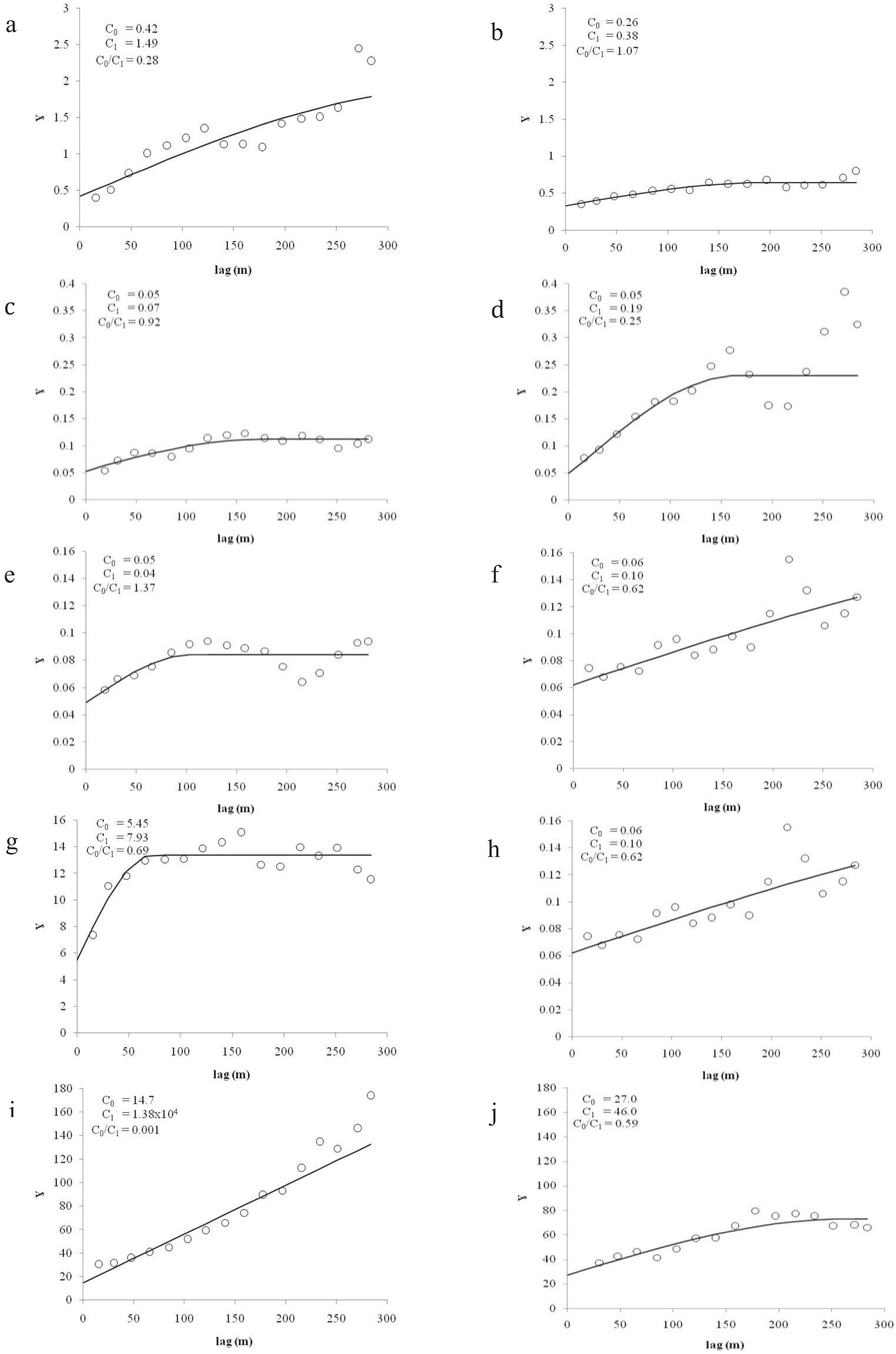

Figure V.c. Variograms of total organic carbon (%) in the alley (a) and tree line (b), pH_W in the alley (c) and tree line (d), log normal electrical conductivity in the alley (e) and tree line (f), per cent clay in the alley (g) and tree line (h), and per cent coarse fraction in the alley (i) and tree line (j).

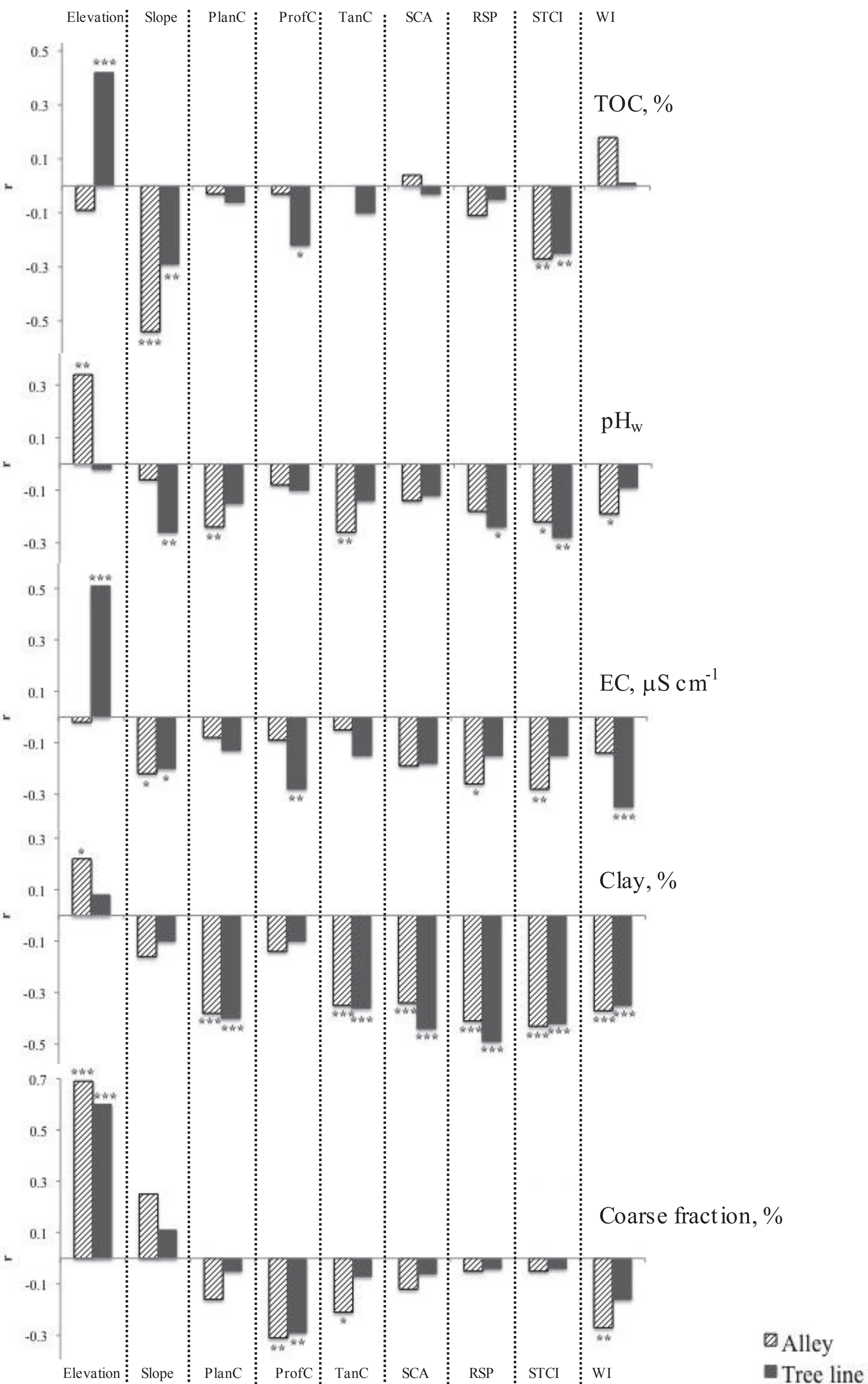

Figure V.d. Pearson correlation coefficients of soil properties and terrain parameters.

PlanC – plan curvature; ProfC – profile curvature; TanC – tangential curvature; RSP – relative stream power; SCA – specific catchment area, m^{2}m^{-1}; STCI – sediment transport capacity index; WI - wetness index) *** $p < 0.001$ ** $p < 0.01$ * $p < 0.05$

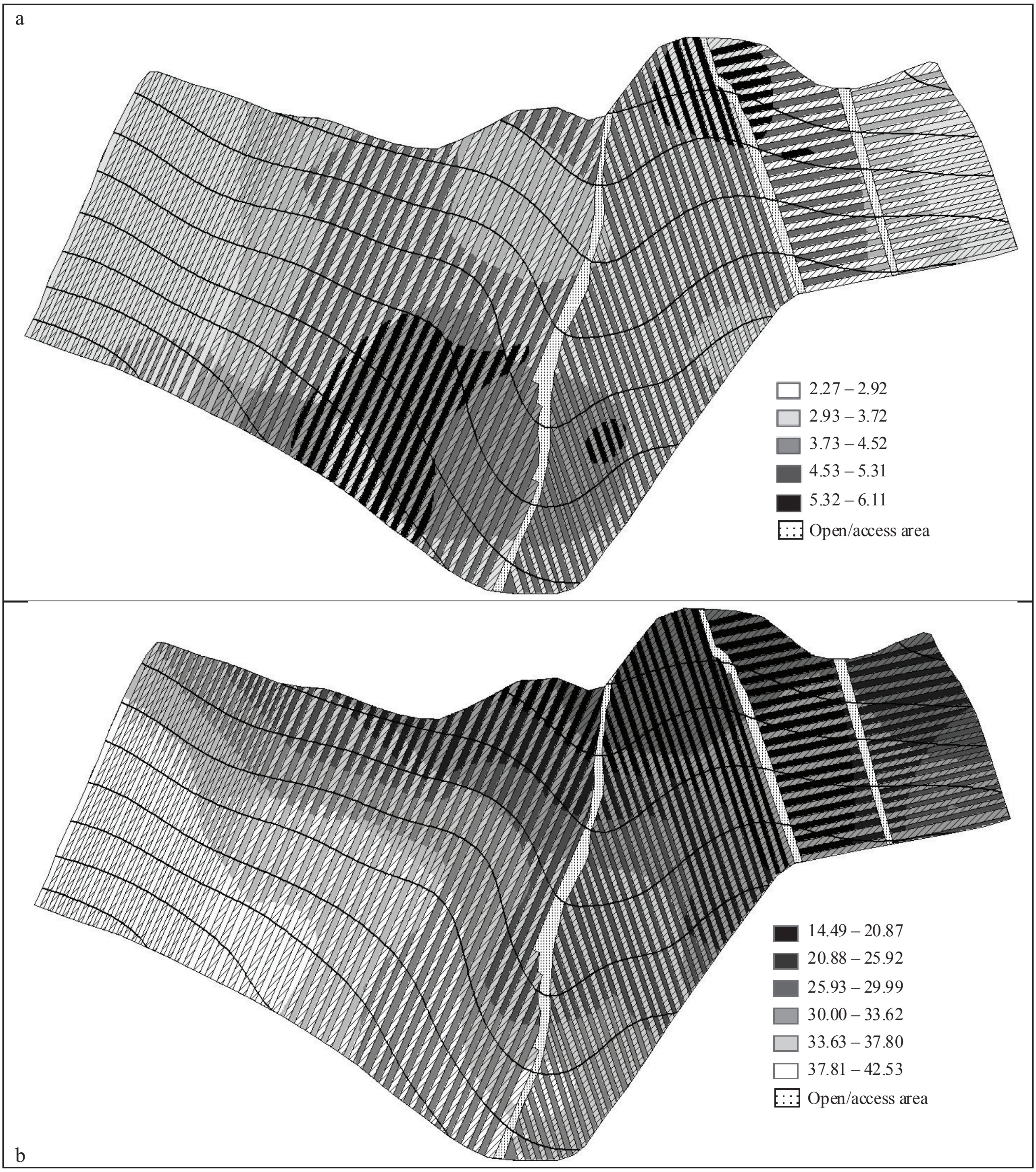

Figure V.e. Predicted map of total organic carbon (a), and coarse fraction (b), of the study site using ordinary kriging (both properties are in %; hatched area is the tree line, the rest is alley; contour lines at 5 m interval from 490 m in the top right to 540 m in the bottom left).

CHAPTER VI

Spatial distribution of diuron sorption affinity as affected by soil, terrain and management practices in an intensively manged apple orchard

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VI. Spatial distribution of diuron sorption affinity as affected by soil, terrain and management practises in an intensively managed apple orchard

Abstract

We investigated how the sorption affinity of diuron (3'-(3,4-dichlorophenyl)-1,1-dimenthyl-urea), a moderately hydrophobic herbicide, is affected by soil properties, topography and management practises in an intensively managed orchard system. Soil-landscape analysis was carried out in an apple orchard which had a strong texture contrast soil and a landform with relief difference of 50 m. Diuron sorption (K_d) affinity was successfully predicted (R^2 = 0.79; $p < 0.001$) using a mid-infrared – partial least squares model and calibrated against measured data using a conventional batch sorption technique.

Soil and terrain properties explained 75% of the variance of diuron K_d with TOC, pH_w, slope and WI as key variables. Mean diuron K_d values were also significantly different ($p < 0.05$) between alley and tree line and between the different management zones. Soil in the tree line generally had lower sorption capacity for diuron than soil in the alleys. Younger stands, which were found to have lower TOC than in the older stands, also had lower diuron K_d values. In intensively managed orchards, sorption affinity of herbicides is influenced not only by soil properties and terrain attributes but also by the management regimes.

Keywords

diuron, MIR-PLS prediction, soil-landscape analysis, apple orchard, spatial variability

1. Introduction

Agricultural pesticides continue to contribute to the emergence of environmental and health risks. Active parent compounds and by-products have contaminated, in some cases, both soil and water ecosystems near, or even several kilometers away from, vineyards, orchards and key agricultural production areas (Wesseling et al., 1997; Gilliom et al., 2006). Assessing the risk and predicting the impact and movement of pesticides is critical for informing both policy makers and growers.

Soil and topography are among the many factors that affect the behavior of pesticides and likelihood of off-site transport. Oliveira et al. (1999) mapped the distribution of imazethapyr (a herbicide used in soybean production) sorption based on soil pH variability. Later on, Farenhorst et al. (2008) demonstrated the association of 2,4-D sorption, soil organic matter and slope position, in which the greatest sorption was found in lower landscape positions with higher soil organic matter. More recently, topographic analysis in mapping the distribution of soil properties and processes (or soil-landscape modeling) has become increasingly used to assess the movement and behavior of agricultural pesticides at the landscape level. For instance, it was found that predicting the spatial distribution of 2,4-D sorption using soil properties was enhanced by about 20% after incorporating terrain parameters (Farenhorst et al., 2003; Farenhorst et al., 2008). There is evidence that spatial estimates of pesticide sorption can be enhanced by reliable and easily accessible digital elevation data in combination with terrain attributes derived from these data. There is also an increased recognition that spatial factors influence the distribution of pesticide sorption. However, little is known about how within-field management practises interact with natural biophysical variability in order to mitigate pesticide offsite impacts. In a heterogeneously managed hilly orchard, for instance, the effect of topography on soil distribution is masked by the long-term differential management in the alley and tree line (Umali et al., 2012). Thus, management practises affect soil variability and hence have the potential to influence pesticide sorption characteristics.

However, mapping of the spatial distribution of pesticide sorption relies on a spatially adequate and representative set of soil samples. This makes it necessary to explore new techniques that reduce soil and pesticide analysis costs without compromising prediction accuracy. Recently, a mid-infrared spectroscopy coupled with partial least squares (MIR-PLS) technique was successfully used to predict not only key soil properties (Janik and Skjemstad, 1995) but also pesticide sorption affinity (Forouzangohar et al., 2008). This technique is a robust, multivariate statistical tool for quantitative analysis of mid-infrared (400–4,000 cm^{-1}) spectral data (Haaland and Thomas, 1988). Applying these techniques has the potential to assist the process of elucidating the spatial distribution of pesticide sorption.

Diuron (3’-(3,4-dichlorophenyl)-1,1-dimenthyl-urea) is a non-selective, systemic herbicide that blocks electron transport at photosystem II (Giacomazzi and Cochet, 2004). It is non-ionic, moderately soluble in water (42 mg L^{-1}) and breaks down to several derivatives. In Australia, it is used in irrigated and horticultural production areas (Bowmer et al., 1998). As a widely used and persistent herbicide (DT_{50} = 75-100 d), it has been detected in runoff, tile drain water (Stork et al., 2008), river systems (Meyer et al., 2010) and enclosed seawater (Martinez et al., 2001). Diuron is moderately hydrophobic and its behaviour in soil is said to be influenced by soil organic carbon (Ahangar et al., 2008). Giacomazzi and Cochet (2004) wrote a comprehensive review on the behaviour and the environmental effects of diuron.

The aim of this study was to investigate how sorption of diuron is affected by soil properties, terrain attributes and within-field management practises (including orchard stand characteristics, age, planting density, etc.) in a 5.6 ha apple orchard in the Mt. Lofty Ranges (MLR), South Australia.

2. Methodology

2.1. Study site, soil sampling and terrain parameterization

The study site is located in the central Mount Lofty Ranges (MLR) which is 30 km east of Adelaide, South Australia (34° 54.918" S 138° 48.107" E). The 5.6 ha orchard is planted to apples of various varieties and was established in the early 1960s. It is hilly with mean elevation of 513 m, maximum slope of 30° and mean slope of 13°. The area has a Mediterranean climate with long-term (50 y) average maximum and minimum temperatures of 12°C and 5°C during winter months and 26°C and 14°C during summer months, respectively, and a xeric soil moisture regime. The mean monthly rainfall from 1970 to 2000 was approximately 150 mm in the winter and 32 mm in the summer. The soils at the site developed from Proterozoic shales, siltstones and metasandstones (Hall et al., 2009) and are classified as Petroferric, Melanic-Vertic, Red-Yellow Chromosols (Isbell, 2002), which dominate (about 60%) the entire MLR region. Profiles on the upper slopes are thin, moderately gravelly and silty.

The study site (5.6 ha) was divided into five management zones that were unique in at least one of the following characteristics: tree age, variety of apples, and tree spacing or density. These zones were: A - planted in 2006, Pink Lady variety, 3.5 m × 1 m spacing (2,860 trees per ha); B - planted in 1980, Royal Gala variety, 4.5 m × 2 m spacing (1,110 trees per ha); C - planted in 1960, Jonathan and Granny Smith varieties, 4.5 m × 2 m spacing (1,110 trees per ha); D - planted in 1960, inter-row of Jonathan-Granny Smith and Pink Lady varieties, 4.5 m × 2 m spacing (1,110 trees per ha); and E - planted in 1960, Jonathan and Granny Smith varieties, 5 m × 4 m spacing (500 trees per ha). Adjacent orchards and orchards throughout region are managed in a similar manner but zones may vary in configuration and size. A stratified random sampling technique was used to collect soil samples. A total of 100 sampling locations were randomly selected across the study site, in effect 20 samples were collected in zone A, 5 in zone B, 32 each in zones C and D and 11 in zone E. The number of samples in each zone was decided based on size and complexity of the terrain. Sampling locations were referenced using a high-sensitivity (~2 m accuracy) global positioning system (GPS) device. Each sampling location corresponded to a pair of sampling units that represented the alley and the tree line. This resulted in 200 (2 × 100) sampling points. In each sampling point, a 0.25 m^2 area was established where 5 soil samples were taken – one at the center and 4 at each corner, which were composited. The samples were air-dried and sieved to < 2 mm. As part of the orchard floor management, sod strips using a variety of grass species were maintained in the alley. In contrast, a clear apple tree understorey was maintained in the tree-line which was mulched only at the establishment phase. Relevant soil properties were determined in a previous study and are summarized in Table VI.a (Umali et al., 2012). For the purpose of this study, properties considered to influence the behavior of diuron sorption were used, namely: total organic carbon (TOC, %); soil pH in 1:1 H_2O suspension (pH_w); electrical conductivity (EC, $\mu S\ cm^{-1}$); and clay (< 0.002 mm) content (Clay, %).

Key terrain parameters were derived from a 5 m digital elevation model (DEM) produced from elevation and drainage datasets (Hutchinson, 1989) obtained in digital format from the Department of Environment and Natural Resources of South Australia (DENR-SA). The DEM was smoothed (Hengl et al., 2004) and sampled using the GPS locations of the sampling points. The terrain variables used in this study were: elevation (Elevation, m), slope (Slope, °), mean curvature (MeanC, $° m^{-1}$), specific catchment area (SCA, $m^2 m^{-1}$), and wetness index (WI). Elevation is the vertical height with reference to mean sea level. Slope is the rate of change of elevation with horizontal distance. Mean curvature (MeanC) describes the flow convergence and relative deceleration of material flow. Specific catchment area (SCA) is the ratio of the area upslope of a contour segment that contributes flow to that segment to the length of that segment (Wilson and Gallant, 2000). Wetness index (WI) is a gauge used to characterize spatial distribution of surface saturation (Beven and Kirkby, 1979). A more detailed explanation and calculation of these parameters is given in Wilson and Gallant (Wilson and Gallant, 2000).

2.2. Diuron sorption determination by mid-infrared spectroscopy

Diuron was used as a test chemical and as a representative of a moderately hydrophobic, neutral pesticide. Due to the cost involved in determining sorption coefficient (K_d) using traditional laboratory techniques, diuron K_d for all soil samples was predicted using a MIR-PLS technique. For this study, the predictions were calibrated by analyzing a sub-set (50 samples) using traditional batch equilibrium method (OECD, 2000). The soils selected for traditional determination of K_d values (reference analysis) were chosen to cover the range of total organic carbon content (1.55-6.97%) found in our study site. In the batch sorption experiment, 25 mL of 2 mg L^{-1} diuron solution was added to 5 g soil (in triplicate). Soils were shaken for 24 h on an end-over-end shaker then centrifuged for 10 min at 3500 *g*. The supernatant was filtered through a 0.45 µm polytetraflouroethylene (PTFE) syringe filter. The concentration of the remaining diuron in the solution was measured using an established protocol for diuron analysis on a high-performance liquid chromatograph (HPLC) (Oliver et al., 2005; Forouzangohar et al., 2008). The Agilent 1100 HPLC was fitted with an Altima HP C18 column (5 µm particle size; 250 mm × 4.6 mm internal diameter). The mobile phase was acetonitrile:water (60:40) with a flow rate of 1 mL min^{-1} and a sample injection volume of 20 µL. The amount of diuron sorbed by soil is the difference between the initial and the final concentration of diuron in the solution after equilibration. Sorption coefficient (K_d) values were calculated as the ratio of diuron sorbed by the soil to that remaining in the solution. Method reproducibility was ensured by routine analysis of blanks and a series of standard diuron solutions.

Losses of diuron on the polypropylene tubes and PTFE syringe filters were tested. Diuron solution with varying concentrations (0.25, 0.45 and 0.95 µg mL^{-1}) were prepared. About 20 mL of each solution was placed in polypropylene tubes (replicated) and shaken along side the batch with soil solution. Another 5 mL of each solution was passed through PTFE syringe filters (replicated). About 6% loss was observed in the polypropylene tubes and none in the filters. Corrections, due to losses of diuron on the polypropylene tubes, were then made to the concentration of diuron remaining in the solution in calculating soil sorption.

To predict diuron K_d values by chemometric analysis, we used the spectral data in the frequency range 4,000-500 cm^{-1} scanned at 8 cm^{-1} resolution using a PerkinElmer Spectrum One FT-IR (PerkinElmer, Wellesley, MA) obtained using 0.1 g of soil placed neatly in a stainless steel sample cup. The spectrometer has a restricted frequency range within the desired spectral region. Samples were prepared for scanning, without dilution, by crushing 10 g of the sample in a vibrating ring mill equipped with a steel puck for 60 s. The MIR data in absorbance units was transformed using baseline offset and linear baseline correction prior to analysis using The Unscramber X (version 10.1 Camo Software, Norway). A principal component analysis (PCA) of the spectral data was first carried out which revealed no potential extreme spectral outliers using Hotelling T^2 statistics at 5% level of significance. The MIR data was then used as the independent variable (in 446 × 50 matrix form) and the laboratory-derived diuron K_d as the response variable (in 1 × 50 matrix) in the partial least squares (PLS) regression [8]. The PLS regression projects the spectral and the response variable to a small number of "latent" variables called PLS loadings (Geladi and Kowalski, 1986). Both data sets were mean centered and given equal weights upon implementation of the regression. Initial PLS regression showed four samples had high leverage and deviated largely from the regression line and were thus removed as outliers. The PLS regression was recalculated without the outliers and a full cross-validation procedure was made to assess model reliability. Using the constructed cross-validated model, diuron K_d was predicted for the rest of the samples along with the samples used in the PLS regression ensuring all sampling points had diuron K_d values from the same data source. The predicted values were then used in subsequent analysis and spatial interpolation.

2.3. Statistics and modeling spatial distribution of diuron Kd values

The distribution of the soils data was analyzed using standard statistical parameters and the Shapiro-Wilks test of normality. Results indicated that EC data for both sampling locations were positively skewed and were log transformed. The Pearson product moment (*r*) was used to assess the level of correlation between diuron K_d and the independent variables (soil properties and terrain parameters). Statistical inferences were done simultaneously for all variables, therefore, the adjusted p-value (*p*) using the Holm's method (Holm, 1979) was used to infer significant correlation between variables. Significant mean difference between alley and tree-line soil properties was determined using the Welch modified test. Effects plots (Fox, 2003) were used to illustrate the effects of zones and sampling location on TOC and diuron K_d. Means of TOC and diuron K_d were plotted in each management zone and sampling location. Least square difference (LSD) values were calculated at $p < 0.05$ for each interaction pair and used to compare mean difference. Soil-landscape modeling of diuron K_d was also done using soil properties ($K_d^{soil\_alley}$, $K_d^{soil\_treeline}$), terrain parameters ($K_d^{terr\_alley}$, $K_d^{terr\_treeline}$), and the combination of soil and terrain variables ($K_d^{soilterr\_alley}$, $K_d^{soilterr\_treeline}$). Because the independent variables had various units, scaling to unit variance was done using the equation:

$$X_{ST} = \frac{(X - \mu)}{\sigma},$$

where X_{ST} is the standardised value, X is the original value, μ is the mean, and σ is the standard deviation. PLS regression models were developed using the nonlinear iterative partial least squares (NIPALS) algorithm (Geladi and Kowalski, 1986) to model diuron sorption affinity in the alley and in the tree-line.

To create a visual spatial interpolation of the diuron K_d, we used the ordinary kriging procedure in ArcMAP 10 (ESRI, Redlands, CA). Semi-variogram analysis performed in Vesper v1.62 (Minasny et al., 2005) showed a spatially autocorrelated diuron K_d. Kriging parameters were set at a maximum lag size of 300 m divided into 15 lag distance classes. The alley and tree line boundaries were first digitized using an orthorectified high-resolution satellite image of the study site. Ordinary kriging of diuron K_d was done on each of the alley and tree line data set. Then the two interpolated maps were overlaid.

3. Results and Discussion

3.1 Prediction of diuron Kd affinity using MIR-PLS model

The PLS regression performed in this study showed that spectral data were useful in inferring sorption properties of our soil samples for diuron. Two of the seven PLS loadings used to generate the MIR-PLS model to predict diuron K_d for all soil samples are presented in Fig. VI.a. Positive peaks corresponding to both clay (near 3550 cm^{-1} and 3650 cm^{-1}) and organic matter (near 2900 cm^{-1})

characterized the first PLS loading. The cumulative explained variance of all seven loadings was 90%. Cross validation showed good agreement between the K_d values for diuron predicted by the MIR technique and those determined by conventional batch equilibrium methodology in the laboratory with $R^2 = 0.79$ ($p < 0.001$) and a standard error of cross-validation (SECV) of 2.84 (Fig. VI.b). The SECV is a measure of the size of the probable error occurring in the model prediction. Forouzangohar et al. (2008) reported an R^2 and SECV of around 0.81 and 2.39, respectively, in recent work on diuron K_d prediction using MIR-PLS. Based on this relationship, the PLS model was used to predict diuron K_d values for the rest of the samples, which was used in subsequent analyses. The mean diuron K_d was 28.3 L kg^{-1} while the minimum and maximum values were 7.9 and 46.2 L kg^{-1}, respectively (Table VI.a), which followed Gaussian distribution at $p < 0.05$.

3.2 Relationship of Diuron Kd with soil properties and terrain parameters

Correlation analysis of diuron K_d with soil and terrain variables revealed that the strength of correlation was different between the alley and the tree-line (Table VI.b). Generally, stronger correlation was observed in the alley than in the tree-line. For instance, the value of r for the association of diuron K_d and TOC in the alley was 0.70 ($p < 0.001$) while in the tree-line was 0.55 ($p < 0.001$). The difference may be explained by low TOC in the tree-line and, thus, low sorption affinities. Also, a stronger negative correlation was observed in the alley ($r = -0.56$; $p < 0.001$) than in the tree-line ($r = -0.35$; $p < 0.01$) for diuron K_d and slope. We argue that this was due to the fact that the negative correlation of TOC and slope was also stronger in the alley ($r = -0.53$; $p < 0.001$) than in the tree-line (r = -0.29; ns). This means that for our site, areas with steep slopes have low TOC but because of the addition of mulch in the tree-line (as a consequence of management practises), the effect of slope on TOC was masked (Umali et al., 2012). These observations necessitated the development of regression model and kriging estimation unique for alley and for tree-line soils.

The effect of TOC on the diuron K_d affinity may also be inferred from the MIR-PLS regression. A positive contribution of organic carbon around 2900 cm^{-1} was revealed by the first PLS loading (Fig. VI.a). Also, previous work on solid-state ^{13}C nuclear magnetic resonance spectroscopy suggested that certain carbon functional groups influence diuron sorption (Ahangar et al., 2008).

Other factors aside from TOC, may affect diuron K_d affinity. In a recent study, Stork et al. (2008) detected more than 70% of diuron and its metabolites in the top 15 cm of soil in the field after application, even at TOC level just less than 1%. It was found that, at low TOC values, the sorption of non-ionic pesticides like diuron, may be indirectly affected by other soil properties such as pH and cation exchange capacity (Reddy et al., 1992). The negative correlation (p < 0.05) of diuron K_d with pH_w was noted by Gaillardon et al. (1980) who attributed this to the interaction of diuron molecules with cationic species like Fe^{3+} and Al^{3+} in humic substances. However, we cannot confirm at this stage whether our samples have high Fe^{3+} and Al^{3+} contents. Unexpectedly, clay content was negatively correlated with diuron K_d. In most circumstances, even for neutral molecules like diuron, K_d is normally positively correlated with clay content (Liu et al., 1970) as an indirect effect of clay and TOC correlation. We found, however, that there is no significant correlation between TOC and clay content for our soil samples. In a related study, it was also found that clay and sorption properties were inversely related (Celis et al., 2006) for two non-ionic organic compounds (phenanthrene and dibenzofuran), but no further explanation was given.

The relationships of diuron K_d with terrain parameters varied depending on sampling location (Table VI.b). Generally, the relationship was stronger in the alleys and weaker or negligible in the tree line. For instance, diuron K_d values were negatively correlated with elevation in the alley (r = -0.35; p < 0.001) but not in the tree line. In terms of slope, the negative correlation with diuron K_d decreased from r = -0.56 (p < 0.001) in the alley to r = -0.35 (p < 0.01) in the tree line. The negative correlation of diuron K_d values with elevation (in the alley) and slope (both alley and tree line) may be due to loss of organic matter and clay from erosion zones.

The result of the soil-landscape modeling is summarized in Table VI.c. Using only either soil properties or terrain variables, the R^2 and RMSEP values were better in the alley than in the tree-line. Moreover, the tree line PLS regression model for diuron K_d using only terrain variables was very poor (R^2 0.09). However, when soil properties and terrain variables were both used as input parameters, the regression models improved by as much as 8× (Table VI.c). PLS loadings indicate that in the first component of the regression models ($K_d^{soilterr\_alley}$ and $K_d^{soilterr\_treeline}$), the greatest relative contribution came from TOC, pH_w, slope and WI (Fig. VI.c). The effect of terrain on sorption properties cannot be overemphasized but should be considered as shown here and in other earlier works (Farenhorst et al., 2003; Farenhorst et al., 2008). The implication of this is that the fate of a non-ionic herbicide, like diuron, may be determined by hydrological processes, especially events that induce surface runoff. Stork et al. (2008) found in a study conducted in a coastal catchment of southeast Queensland that about 0.6% of total diuron loading was detected (including two diuron metabolites) in runoff and had the potential to accumulate in river sediments.

3.3 Sorption of diuron is affected by differential management between alley and tree line

The kriged map of diuron K_d affinity shows the spatial variability of this property for the study site (Fig. VI.c). In this map, darker region corresponds to higher diuron K_d affinity and lighter region corresponds to lower diuron K_d affinity. The mean diuron K_d value for soils in the alley (28.3 L kg^{-1}) was significantly greater ($p < 0.05$) than for soils in the tree line (23.8 L kg^{-1}; hatched area in Fig. VI.d). The alley, where sod strips are maintained, also had significantly higher ($p < 0.05$) TOC than the tree line, which may explain the greater sorption of diuron (Table VI.a).

The establishment of sod strips in the alley and a sod-free tree line in apple orchard management is a common practise in the MLR and other apple growing areas (Hogue and Neilsen, 1987) since apple trees do not compete well for nutrients and water. However, growers commonly add straw mulch to reduce erosion risk, minimize evaporation and protect newly established trees, but only in the first year of establishment. This can provide soil in the tree line an additional source of organic carbon to which diuron may sorb potentially reducing pesticide offsite movement. This was evidenced in zone A (Figures VI.d and VI.e) where the level of TOC was higher in the tree line than in the alley, presumably as a result of the addition of mulch recently during establishment. In zones B, C, D and E, where there was no subsequent addition of mulch, TOC levels in the tree line were significantly lower ($p < 0.05$) than in the alley. It has been well documented that when a soil is cultivated, the organic carbon decreases significantly (Baldock and Skjemstad, 1999). This data suggests that in the more recently cultivated zones (i.e. zone A cultivated in 2006 and zone B in 1980), the organic carbon content in the alleys has not had sufficient time to increase after cultivation during the orchard establishment. By contrast the zones where cultivation in the alleys last occurred over 40 years ago (i.e. zone C, D and E), TOC under the sod strips increased significantly compared with the tree line. Moreover, the mean TOC in the alley in these zones is approximately 1.7× the mean TOC in zones A and B (Fig. VI.e).

The observed differences in TOC were directly reflected in diuron K_d values, with higher K_d values for the tree line in zone A and higher K_d values for the alley in zones C, D and E (Fig. VI.e). This is most likely due to increased root density under the sod strips in the alleys while tree lines are kept sod-free through application of herbicides.

This data suggests that management of tree crops should include the maintenance of grassed alleys and the continued application of mulch material within the tree lines to increase TOC in soil which would aid in increasing soil structural stability, pH buffering capacity, soil nutrient levels, water holding capacity (Baldock and Skjemstad, 1999) as well as sorbing pesticides. Finally, we suggest that growers ensure that the risk for offsite movement of pesticides is avoided by management practises that take into account the spatial variability of sorption for pesticides.

4. Conclusion

In this study, we used a recently developed technique (MIR-PLS) to predict K_d values for pesticides. The technique allows for quick and less expensive determination of sorption properties thereby facilitating faster assessment of the distribution and potential off-site migration of herbicides and other agro-chemicals.

Soil properties together with terrain parameters influenced the spatial distribution of diuron sorption affinity at our study site. The level of TOC appears to be the parameter that most influences diuron sorption. TOC varied with different stand age and between the alleys and the tree lines within each zone. Slope and WI were also correlated with diuron sorption affinity. Variable soil properties and terrain properties resulted in spatial variability in herbicide sorption affinity.

Management practises were also found to affect the distribution of diuron K_d values, mostly through their effects on TOC levels. The zones (differentiated by variable tree age, density and apple variety) influenced the distribution of soil properties and consequently affected the sorption of diuron. This implies that a differential herbicide or pesticide application or management regime such as extended or continued mulching after establishment might need to be observed to reduce offsite impacts of herbicide applications.

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Table VI.a. Summary statistics of soil properties and diuron K_d determined for soils from alley and tree line.

Variable	Sampling location	Min	Mean	Max
TOC, %	Alley	2.2	4.5b	7.0
	Tree line	1.6	3.4a	5.5
pH_w	Alley	6.10	6.9a	7.5
	Tree line	5.40	7.0a	7.6
EC†, µS cm^{-1}	Alley	5.20	5.96b	6.59
	Tree line	5.08	5.77a	6.98
% Clay content (<0.002mm)	Alley	16.1	23.3a	33.8
	Tree line	16.7	23.1a	35.7
Diuron K_d, L kg^{-1}	Alley	12.6	28.3b	46.2
	Tree line	7.9	23.8a	42.0

TOC – total organic carbon; EC – electrical conductivity († log-transformed data); pH_w – pH 1:1 soil:H_2O. Means within a variable denoted by same letter are not significantly different ($p < 0.05$).

Table VI.b. Correlation matrix of diuron sorption affinity (K_d), soil properties and terrain parameters for alley (in bold) and tree-line (in bold-italics).

	K_d	TOC	pH_w	EC†	Clay	Elevation	Slope	MeanC	SCA	WI
K_d	1	0.70 ***	-0.35 *	0.12	-0.2	-0.35 **	-0.56 ***	0.24	0.3	0.47 ***
TOC	0.55 ***	1	0.07	0.55 ***	0.14	0.09	-0.53 ***	-0.04	0.04	0.18
pH_w	-0.56 ***	-0.08	1	0.27	0.25	0.34 *	-0.06	-0.25	-0.14	-0.19
EC†	-0.07	0.44 ***	0.03	1	0.23	-0.02	-0.20	-0.10	-0.19	-0.14
Clay	-0.25	-0.11	0.10	0.01	1	0.22	-0.16	-0.38 **	-0.34 *	-0.37 **
Elevation	-0.04	-0.42 ***	-0.02	0.50 ***	0.09	1	0.12	-0.17	-0.29	-0.42 ***
Slope	-0.35 **	-0.29	-0.26	0.20	-0.10	0.12	1	0.08	0.72 ***	-0.32 *
MeanC	0.12	-0.10	-0.16	-0.17	-0.38 **	-0.17	0.08	1	-0.1	0.7
SCA	0.20	0.03	-0.12	-0.18	-0.33 *	-0.29	-0.1	0.72 ***	1	0.9 ***
WI	0.29	0.01	-0.09	-0.35 **	-0.35 **	-0.42 ***	-0.32 *	0.7 ***	0.9 ***	1

TOC – total organic carbon, pH_w – pH 1:1 soil:H_2O; EC – electrical conductivity († log-transformed data); MeanC – mean curvature, SCA – specific catchment area; WI – wetness index. $^{***}p < 0.001$ $^{**}p < 0.01$ $^{*}p < 0.05$ where p is the adjusted p-value using Holm's method.

Table VI.c. Soil landscape models for diuron K_d using Partial least squares (PLS) regression.

Model	Model parameter input	No. of components in the PLS*	R^2	RMSEP (L kg^{-1})
$K_d^{soil\_alley}$	TOC, pHw, EC†, Clay	2	0.67	0.57
$K_d^{soil\_treeline}$		2	0.61	0.62
$K_d^{terr\_alley}$	Elevation, Slope, MeanC, SCA, WI	2	0.37	0.78
$K_d^{terr\_treeline}$		2	0.09	0.95
$K_d^{soilterr\_alley}$	TOC, pHw, EC†, Clay, Elevation, Slope, MeanC, SCA, WI	3	0.75	0.54
$K_d^{soilterr\_treeline}$		3	0.73	0.54

RMSEP – root means square error of the prediction; TOC – total organic carbon, pH_w – pH 1:1 soil:H_2O; EC – electrical conductivity († log-transformed data); MeanC – mean curvature, SCA – specific catchment area; WI – wetness index

* all models $p < 0.001$

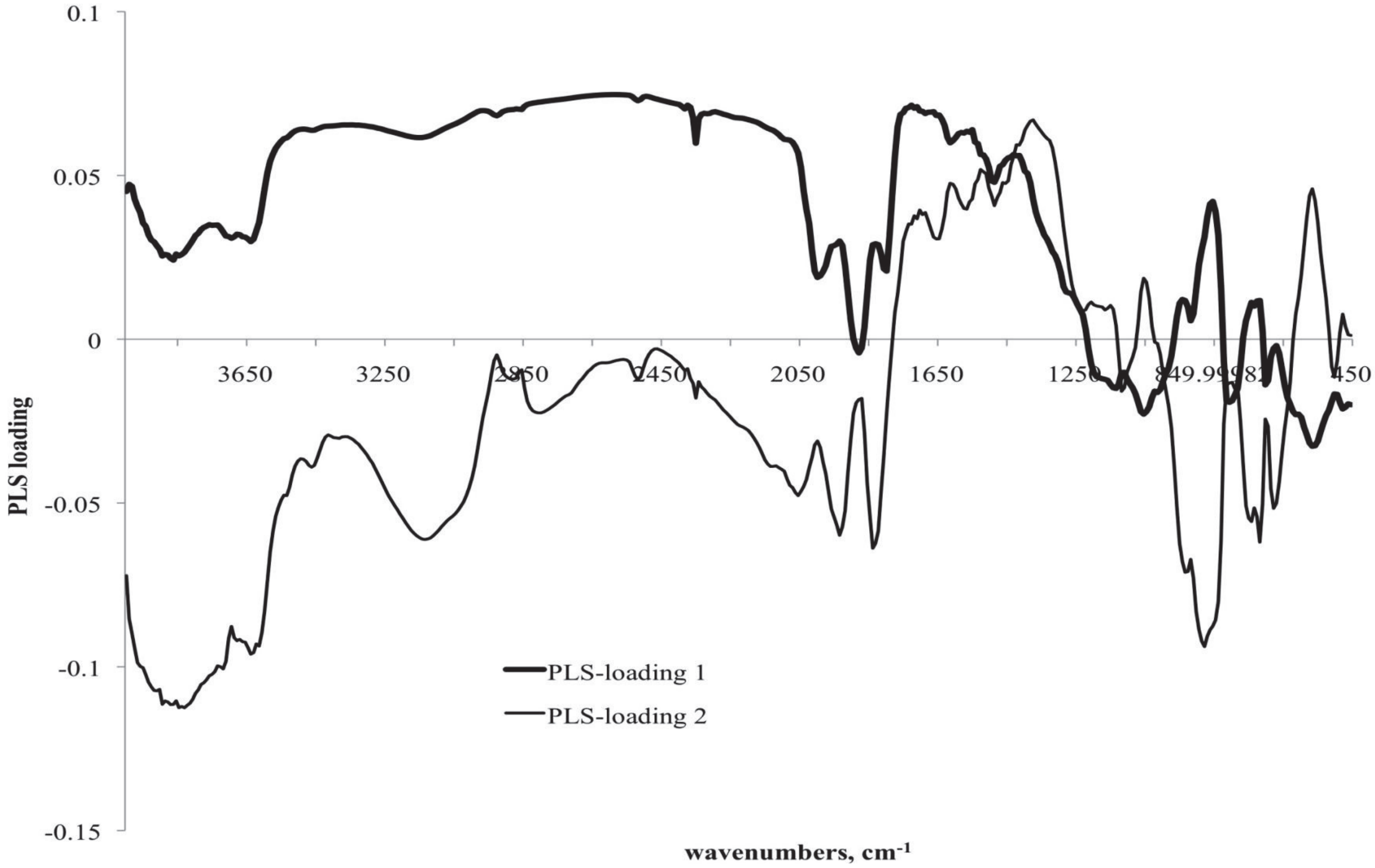


Figure VI.a. Partial Least Squares (PLS) loading weights of the first two factors used in the regression model.

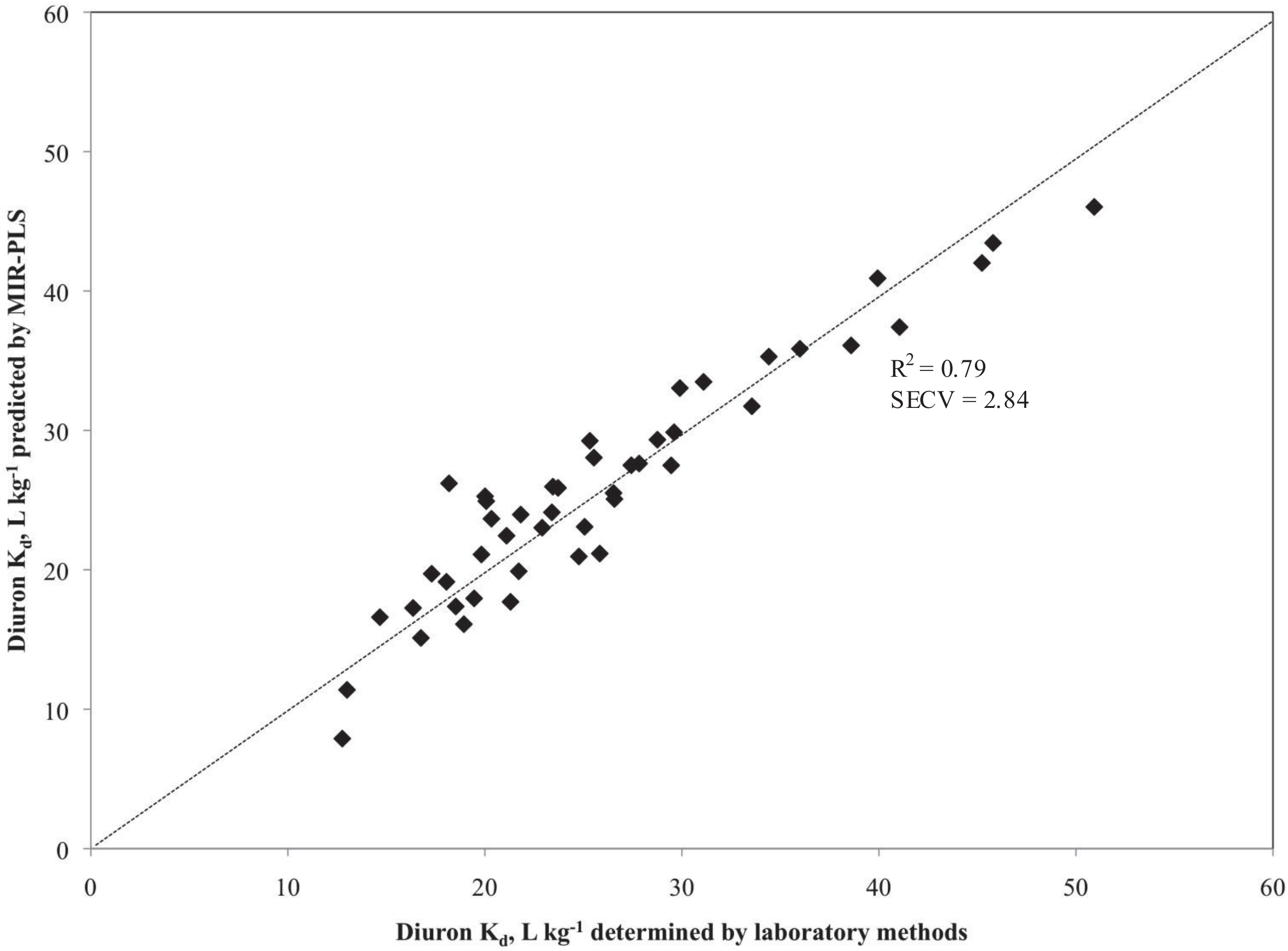


Figure VI.b. Relationship between diuron K_d values predicted using MIR-PLS and those determined on the subset (n=46; 4 outliers were removed) of samples using the traditional batch sorption techniques (dotted line is the 1 is to 1 line; SECV is standard error of the cross-validation). MIR-PLS – mid-infrared partial least squares technique

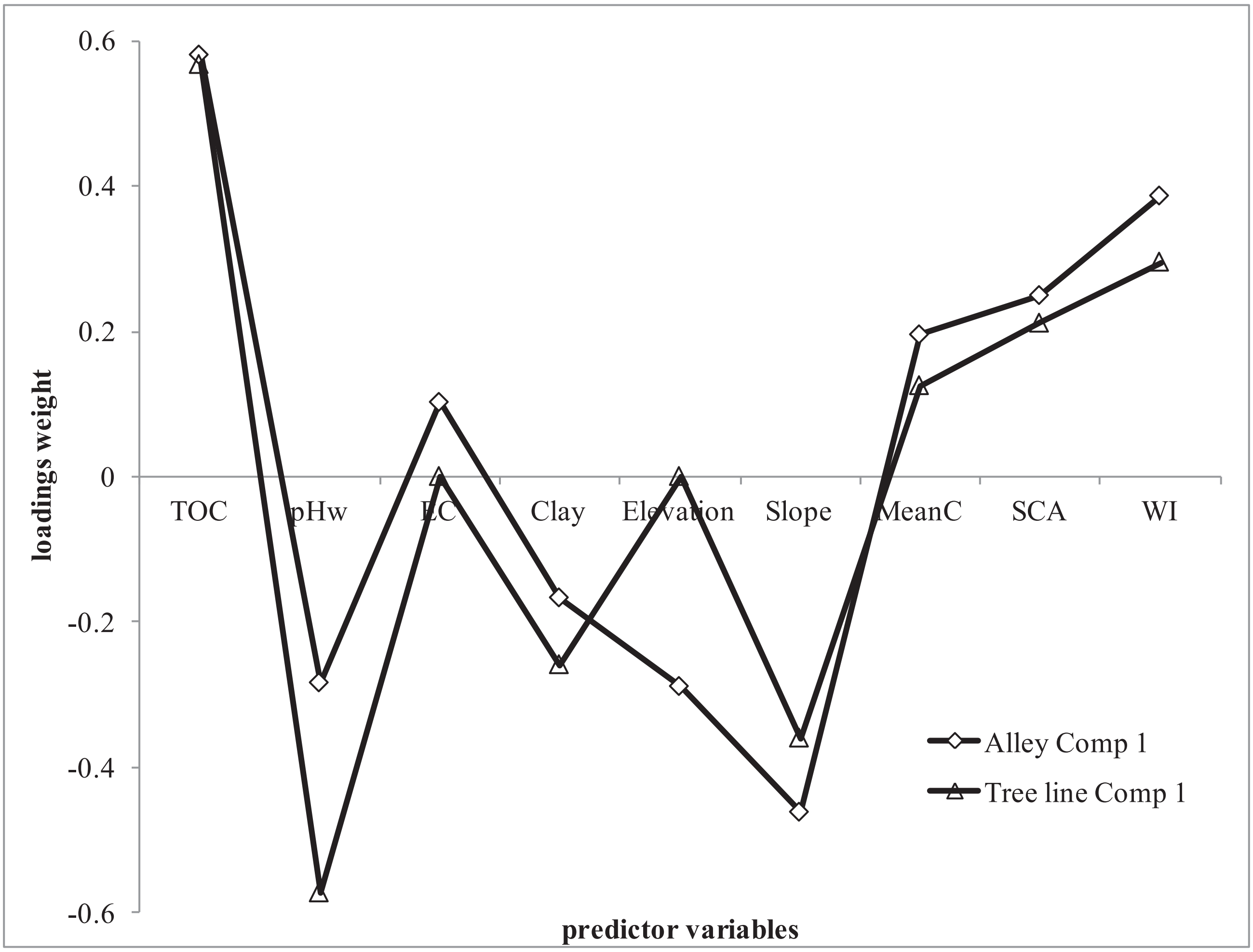
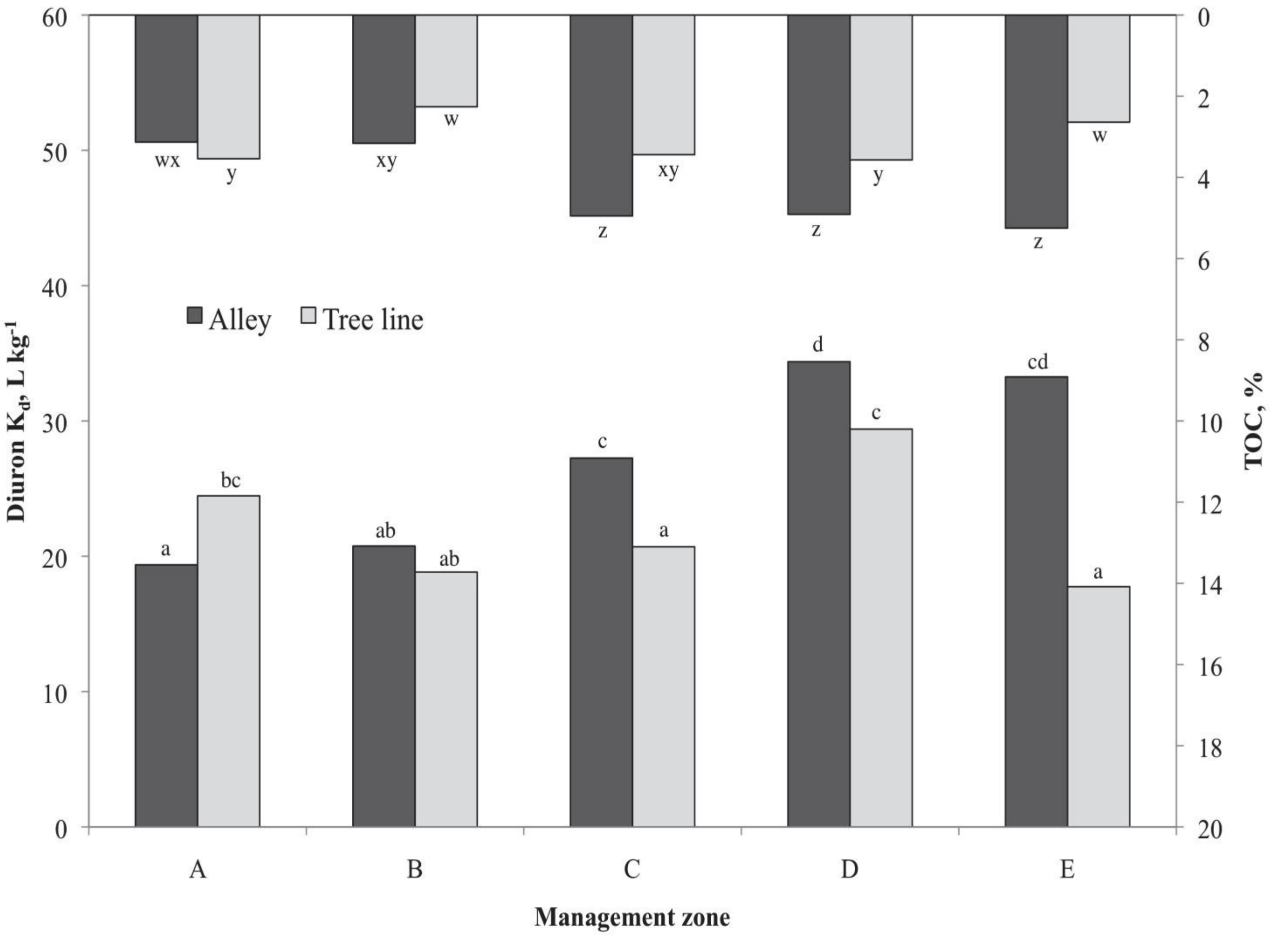


Figure VI.c. Loading weights of the first factor for alley and tree-line of the Partial Least Squares (PLS) regression using soil and terrain variables as predictors.

Figure VI.d. Interpolated map of diuron K_d (kg L^{-1}) for the study site.

(dotted area is access road, hatched area is tree line, the rest is alley; letters are zone designations). A - planted in 2006, Pink Lady variety, 3.5 m × 1 m spacing (2,860 trees per ha); B - planted in 1980, Royal Gala variety, 4.5 m × 2 m spacing (1,110 trees per ha); C - planted in 1960, Jonathan and Granny Smith varieties, 4.5 m × 2 m spacing (1,110 trees per ha); D - planted in 1960, inter-row of Jonathan-Granny Smith and Pink Lady varieties, 4.5 m × 2 m spacing (1,110 trees per ha); and E - planted in 1960, Jonathan and Granny Smith varieties, 5 m × 4 m spacing (500 trees per ha).



A - planted in 2006, Pink Lady variety, 3.5 m × 1 m spacing (2,860 trees per ha); B - planted in 1980, Royal Gala variety, 4.5 m × 2 m spacing (1,110 trees per ha); C - planted in 1960, Jonathan and Granny Smith varieties, 4.5 m × 2 m spacing (1,110 trees per ha); D - planted in 1960, inter-row of Jonathan-Granny Smith and Pink Lady varieties, 4.5 m × 2 m spacing (1,110 trees per ha); and E - planted in 1960, Jonathan and Granny Smith varieties, 5 m × 4 m spacing (500 trees per ha). Means for K_d or TOC denoted with same letter are not significantly different at $p < 0.05$.

Figure VI.e. Means of diuron K_d (lower data, L kg^{-1}) and total organic carbon (upper data, %) in the different management zones and sampling locations.

n for management zones: A = 20; B = 5; C = 32; D = 32; E = 11

CHAPTER VII

Field-scale variability of simulated diuron leaching and surface runoff in an intensively managed apple orchard

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Field-scale variability of simulated diuron leaching and surface runoff in an intensively managed apple orchard

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Prepared and performed simulation, analysed simulation output, wrote manuscript.

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VII. Field-scale variability of simulated diuron leaching and surface runoff in an intensively managed apple orchard

Abstract

The fate of diuron was simulated using the deterministic-mechanistic tool, Leaching Estimation and Chemistry Model (LEACHM). This was done in order to assess the integrated effect of topography, management practices and herbicide sorption on the leaching and surface runoff potential of diuron in a spatially variable landscape. The specific objective was to assess how the observed spatial variability in soil properties and landscape attributes affected the simulated environmental fate of pesticides, represented by diuron as a model compound. The first simulation was performed to determine effect of clay content (17%; 35%), TOC (2%; 6%), irrigation, slope (9°; 17°). The second was made to determine the effect of management zones of different stands. Simulated flux of diuron just below the top 10 cm of the soil (referred to here as Flux) was affected by TOC. Moreover, the simulated amount of diuron that remained in the surface layer (referred to here as Retention) was significantly higher ($p < 0.05$) in soils with 6% TOC. The simulated concentration of diuron dissolved in water draining below the 10 cm layer (referred to here as Loading) also varied depending on zones. As expected, simulated leaching was driven by soil water content. Moreover, varying levels of TOC between management zones resulted to significant differences in mean Retention, Flux and Loading of diuron among these zones. Across the landscape, a 2.7 fold increase in slope was translated *into 4 to 5 fold increase in the simulated Pesticide Runoff calculated using the Organisation for Economic Cooperation and Development (OECD) model. These findings highlight the importance of incorporating the spatial heterogeneity of soil and terrain attributes in the simulation of fate and risk assessment of the test herbicide.*

Keywords: diuron, LEACHP, pesticide transport, spatial heterogeniety, pesticide management zones

1. Introduction

The variability of key field parameters influences both the fate of pesticides in the environment as well as the accuracy by which pesticide transport can be predicted (Coquet and Barriuso, 2002). Parameters like soil properties, cropping system and water regimes vary in time and space. These highly variable input parameters can be incorporated in simulation modeling to quickly and inexpensively assess the behavior of pesticides (Ghadiri and Rose, 1992) within a field or region and across seasons. Advances in computer technology and speed allow various simulation conditions to be run quickly using pesticide fate models.

The variability of soil and topography has been found to greatly affect pesticide fate (Farenhorst et al., 2008). Soil properties are, in turn, influenced by management regimes especially for intensively managed orchard systems (Umali et al., 2012a). However, this variation is often not taken into account during assessment of pesticide transport. The question addressed in this study was: To what extent is the simulated fate of pesticide influenced by the spatial variability of key parameters observed on the study site (Umali et al., 2012b)?

The Leaching Estimation and Chemistry Model (LEACHM) (Hutson, 2003) was applied to heterogeneously managed orchard soils to assess the integrated effect of topography and management practises on the leaching and surface transport potential of diuron. The specific objective of this research was to determine the effect of slope, soil water content, soil parameters and management practises on the simulated fate of diuron in a spatially variable landscape.

2. Methodology

2.1 Study area and diuron

The area is located in an intensively managed apple orchard in the Forest Range (34° 54.918" S 138° 48.107" E) within the central Mount Lofty Ranges (MLR) which is 30 km east of Adelaide, South Australia. The 5.6 ha apple orchard was planted to various varieties and was established in the early 1960s. It is hilly with mean elevation of 513 m, maximum slope of 30° and mean slope of 13°. The area has a Mediterranean climate with long-term (50y) average maximum and minimum temperatures of 12°C and 5°C during winter months (June-August) and 26°C and 14°C during summer months (December-February), respectively, and a xeric soil moisture regime. The mean monthly rainfall from 1970 to 2000 was approximately 150 mm in the winter and 32 mm in the summer. The soils at the site developed from Proterozoic shales, siltstones and metasandstones (Hall et al., 2009) and are classified as Petroferric, Melanic-Vertic, Red-Yellow Chromosols (Isbell, 2002), which dominate (about 60%) the entire MLR region. Profiles on the upper slopes are thin, moderately gravelly and silty.

Apple trees were planted at high density. Tree-lines, 2 to 4 m wide, run either across or along the slope and a 2.5 m wide alleys separated the tree-lines. Ripping to a depth of about 1 m along the tree-lines was carried out during establishment to break up the dense B horizon. Sod strips were laid out in the alleys (between tree-lines) using various grass species such as *Festuca sp.* (dwarf fescue), *Pennisetum purpurium* (napier) and *Hordeum hystrix* (barley grass). Native grasses were also encouraged along the alleys. Clippings from mowing were used as mulch to minimise moisture loss in the tree-lines, most importantly during re-planting and in elevated and sloping areas. Herbicides were also periodically applied. Fertiliser was applied through localised fertigation. Irrigation was localised using sprinklers raised less than 0.3 m above the ground from a series of lines laid out along the tree-line. Thinned biomass (fruits, leaves and small branches) was left under the trees whereas mown grasses were left where they were cut (normally on alleys). Mulching and herbicide application along the tree-line was undertaken to decrease weed competition for nutrients and water. Sod strips in the alleys served as cover to reduce the impact of farm machinery and to act as buffer for soil erosion and material loses.

The study site was subdivided into five management zones that were unique in at least one of the following characteristics: tree age, variety of apple grown, and tree spacing or density (Fig. VII.a). These zones are: A - planted in 2006, Pink Lady variety, 3.5 m × 1 m spacing (2,860 trees per ha); B - planted in 1980, Royal Gala variety, 4.5 m × 2 m spacing (1,110 trees per ha); C - planted in

1960, Jonathan and Granny Smith varieties, 4.5 m × 2 m spacing (1,110 trees per ha); D - planted in 1960, inter-row of Jonathan-Granny Smith and Pink Lady varieties, 4.5 m × 2 m spacing (1,110 trees per ha); and E - planted in 1960, Jonathan and Granny Smith varieties, 5 m × 4 m spacing (500 trees per ha).

Diuron is a phenylurea, non-selective, systemic herbicide that blocks electron transport at photosystem II (Giacomazzi and Cochet, 2004). It is non-ionic, moderately soluble in water (42 mg L^{-1}) (Kidd and James, 1991) and breaks down to several derivatives. It is used primarily to effectively control weeds in many crops and also commonly applied in non-cultivated areas (e.g. in controlling weeds in roads, railways and parks). The environmental fate of diuron has been extensively studied (Giacomazzi and Cochet, 2004) and was found to be persistent in soil and water environments and has been detected in runoff, tile drain water (Stork et al., 2008), river systems (Meyer et al., 2010) and enclosed seawater (Martinez et al., 2001).

2.2 Description of LEACHP

We used the Leaching Estimation and Chemistry Model (LEACHM) (Hutson, 2003), to estimate the concentration of diuron retained in the top 10 cm of soil and flux from this layer. LEACHP is one of a suite of simulation models in LEACHM, and was specifically designed in 1985 to simulate the fate and transport of pesticides. The version used in this modeling was LEACHM 4.0 (2010). The input file contains several sections that define periods of simulation, profile depth, node spacing, output file specification, soil data, crop data, chemical properties and chemical applications, cultivation, weather and irrigation data. Detailed explanations are found in the next sections.

LEACHP, and in general LEACHM, describes water regime and chemistry and transport of solutes in variably saturated soils (Hutson, 2003). LEACHP simulates pesticide displacement, transformation and degradation. One or more segments, of uniform thickness, may comprise a soil horizon. LEACHP has been widely used as a research model. It has been validated using various agrochemicals in various soil types and plant growth conditions (Gallant and Moore, 1993; Dust et al., 2000; Chatupote and Panapitukkul, 2005).

In LEACHP, flux is driven by rainfall, evaporation and transpiration and the boundary conditions are defined at the soil surface (by quantifying rain, irrigation, potential evaporation) and at the lower boundary (fixed matric potential, unit gradient drainage, fixed or variable water table, or zero flux). The rate of water flow may be calculated using either the Richards equation or the Addiscott mobile:immobile capacity concept (Addiscott et al., 1986). Reference evapotranspiration (ET_0) is split into potential evaporation (E_P) and potential transpiration (T_P) using a defined crop cover fraction that varied over the growing season and a crop factor assumed to be 1.

Input parameters required for simulation include: a) daily water input (rainfall or irrigation or both), b) weekly potential evapotranspiration and minimum and maximum temperatures, c) soil physical properties (TOC and soil texture), d) Soil Conservation Service (SCS) curve number (Williams, 1991) and slope e) crop data, f) chemical properties, transformation and degradation rate constants, and application rates.

2.3 Description of the modeling scenario

The first simulations (small simulation) determined the effect of clay and organic carbon contents, irrigation and slope while the second set of simulation (big simulation) determined the effect of management on the simulated fate of diuron. A more detailed discussion of the simulations is given in Sections 2.3.1. and 2.3.2. For both sets of simulations several parameters were constant. These included the simulation period, which was run for 12 years from 1 January 2000 to 31 December 2011. The profile depth was set to 600 mm with a free draining lower boundary condition, which was based on mean depth of soil (surface and subsoil layers) of the area determined through a survey using a soil probe. Water flow was calculated using the Richards' equation (Ross, 1990). Water retention and hydraulic conductivity were estimated by the two-part retentivity Campbell-based function (Campbell, 1974) fitted with data generated using a pedotransfer function. A uniform soil bulk density of 1.29 g cm^{-3} for the top 10 cm of soil was used in the simulation. Diuron was applied once a year on the 23rd January at the rate of 100 mg m^{-2}, which was hypothetical but a realistic (equivalent to 1 kg ha^{-1} of active ingredient) to facilitate percentage calculations of diuron leaching, retention and runoff. It was assumed that no diuron was applied to the site prior to 2000, thus initial profile chemical data was set to 0 for all simulations. Diuron is moderately to highly persistent in soil ranging from 30 d to 365 d (Alva and Singh, 1990). As a conservative estimate, a half-life of 75.5 d was used for the simulation. Two levels of K_{OC} of diuron were used to reflect the mean values derived for soils obtained in the alleys (K_{OC} = 633 L kg^{-1}) and in the tree-line (K_{OC} = 720 L kg^{-1}) (Umali et al., 2012b). These values were calculated by multiplying the measured mean values of K_d and fraction of organic carbon for the site.

The crop growth and root distribution for the alley, which consisted of sod strip and grass, and tree-line, which consisted of the apple trees and cleared areas between trees, were estimated based on literature (Hughes and Gandar, 1993; Neilsen et al., 2000). Various grass species were grown in the sod strip in the alley, therefore we have assigned an estimated rooting depth of 30 cm. Crop cover for the alley was set to 0.8 (from an index of 0 – 1) all year round. For the tree-line, a 60 cm rooting depth was used for the simulation (the maximum soil depth). Although the root system of apples can reach up to 3 m deep (Rogers and Vyvyan, 1934), the effect of drip fertigation and other management practices like root pruning would be expected to limit the bulk of root system to a depth of about 1 m (Neilsen et al., 2000) and root-length density is significantly lower beyond this depth (Hughes and Gandar, 1993). Crop cover for the tree-line region was set to 0.8 during the growing season (from September to May) and 0.2 after harvest (June to August). In Fig. VII.c, the seasonal variability of cover was evident. The orthophotograph taken on August 3, 2010 (middle of winter) shows that cover in the tree-line was very minimal. In the alley at the same time, however, there was a substantial amount of grass cover. Cover in the tree line becomes more pronounced in the summer as shown in the orthophoto taken on January 3, 2011.

Total weekly reference transpiration (ET_0, mm) was derived from the FAO56 reference estimates of the Lenswood Research Centre weather station which was located about 2 km from the orchard (BOM, 2011; www.bom.gov.au/silo).

Water contents at wilting point (-1500k Pa) were also determined using the pressure plate apparatus technique for 74 soil samples randomly selected to check simulated water content at -1500 kPa.

2.3.1. First simulation

The first simulation was done to determine the key soil and environmental parameters that influenced the simulated fate of diuron and to establish the overall water balance. The simulation had two levels of soil clay content (17% and 35%) and two levels of TOC (1% and 6%) that represented the minimum and the maximum values for soils found in the site (Umali et al., 2012a).

Irrigation in the tree-line was also automatically set to trigger each time the matric potential at 300 mm dropped to -60kPa, rewetting the profile to field capacity.

2.3.2. Second simulation

In this simulation, a range of soil properties were used to cover the range of TOC, clay and silt contents of soil collected in the 100 paired sampling locations. These were obtained from previous studies (Umali et al., 2012a; Umali et al., 2012b) and are summarized in Table VII.a. Soil samples were collected in the alley and in the tree-line and across the five management zones within the orchard and 200 input files were created using the sampling location identification (ID) number as file name. One hundred of these files corresponded to the soils found in the tree-line, and 100 input files corresponded to soils found in the alley.

To determine the range of slope where the 100-paired sampling points were located, a 5 m digital elevation model (DEM) was used. Slope was calculated from the DEM and the values for all locations were extracted in ArcMAP 10.0. The range of slope values is summarized in Table VII.a. These values were then encoded in each of the 200 input files for LEACHP simulation.

From the simulations that covered 12 years (2000-2011) data was extracted for certain time periods, which were the wettest year in the last 12 years (2001; 1202.3 mm annual rainfall), the driest year in the last 12 years (2006; 656.6 mm annual rainfall) and the current year (2011, 852.2 mm annual rainfall). In each of these years, three separate months were selected to represent the end of a specified season i.e. end of summer (February), middle of winter (July) and end of spring (November). Forty years of meteorological data showed February and July were the driest and wettest months, respectively (BOM, 2011). A total of nine simulation periods were used and the corresponding total monthly rainfall is presented in Table VII.b.

2.4. LEACHM output simulation parameters: Flux, Retention and Loading

Two leaching parameters were studied in the output simulation, namely a) flux of chemical species (i.e. diuron) (mg m^{-2}) across the lower boundary of the top 10 cm soil (Flux); and b) total amount of chemical (mg m^{-2}) that remained in the top 10 cm soil macro-segment during the time step simulation (Retention). Flux constitutes the amount of the chemical that may be transported in subsurface flow or in groundwater. Retention, on the other hand, constitutes the amount of chemical that remains in the surface soil (0-10cm), a critical layer of the soil profile, and may degrade or move off-site with surface runoff. These two parameters determine the fate of the chemical in soil. These parameters were extracted from the output simulation and were used to assess the fate of diuron in the study site. No validation procedure could be done (due to the continuum of landscape attributes and heterogeneous soil properties) to assess these outputs, however, the main purpose of this paper was to show how spatially variable input parameterization impact simulation outputs.

The concentration of diuron that drained below 10 cm of soil (mg L^{-1}) also was calculated across the study site in all simulation periods by obtaining the ratio of chemical loading (mg m^{-2}) to water fluxes (mm, or L m^{-2}). This gave an approximate estimation of the concentration of diuron that potentially moved in drainage from below the top 10 cm. We determined if there were significant differences in chemical loading between the alley and tree-line regions and among the management zones for a particular simulation period.

2.5. Pesticide runoff simulation using the OECD model

Pesticide runoff was considered to be a significant pathway of diuron behavior in the environment. We used an OECD model (OECD, 1998) that estimated the fraction of diuron transported with runoff (% Pesticide Runoff):

$$\%Runoff = \frac{Q}{P} f_1 f_2 e^{(-\Delta t(\ln 2 / DT_{50soil}))} \times \frac{100}{1+K_d}$$

where Q is the monthly runoff volume (mm) (an output of LEACHP simulation using the Soil Conservation Service curve number approach), P is the monthly rainfall, f_1 is the slope factor using the equation $f_1 = 0.02153 \times slope + 0.00143 \times slope^2$, f_2 is plant interception factor which was simplistically set to 1, Δt is the time in days after application and K_d is soil sorption coefficient of diuron (set to 28 kg L^{-1} for the alley and 24 kg L^{-1} for the tree-line which were mean values taken from Umali et al., 2012b). The parameter Q was obtained from the simulated runoff output of LEACHP. The *slope* factor was obtained from the DEM. Only two slope values (7° and 19°) were used to represent the minimum and maximum slope of the site. For simplicity, an SCS curve number value of 75 was assumed based on the existing land use of the study site (Williams, 1991). The parameter f_1 was therefore 0.22 for 7°slope and 0.92 for 19° slope. Diuron half-life (DT_{50}) was set to 75.5 d similar to the LEACHP simulation. Input parameters of the model were prepared in MS Excel spreadsheets where Pesticide Runoff was calculated for each of the sampling location point. Pesticide Runoff (%) was used as an indicative parameter of the potential runoff risk of diuron.

3. Results and Discussion

3.1. Effects of soil water content and irrigation on simulated Flux and Retention

The simulated soil water regime was compared with rainfall data and field measured soil water contents using capacitance probes installed at the site (Fig. VII.d) for a period of 1 year (December 2010 to November 2011). Owing to the stony condition of the site, a good field calibration of the probe (Sentek Sensor Technologies, Stepney, South Australia) was not achieved. However, trends in soil water fluctuations behaved similarly for the simulated and the measured data. The upward spikes in soil moisture that were observed corresponded with rainfall events.

The effect of irrigation was investigated using a profile in the tree-line with 35% clay content and 6% TOC for simplicity since this represented conditions under which diuron was least likely to be mobile. Two simulations were considered such that one received irrigation each time the matric potential at 300 mm dropped to -60kPa (called 'with irrigation') while the other was not irrigated (called 'no irrigation'). The triggered irrigation in the tree-line provided a soil moisture regime contrasting the alley, which was not irrigated. Flux happened as soon as diuron was applied to the tree-line soils with irrigation (Fig. VII.e). Flux in the tree-line soils with no irrigation peaked only when there was considerably high rainfall (mostly in July of each year). The simulated Flux occurred along the triggered irrigation events. The effect on simulated Retention was also significant. The amount of diuron that remained in the surface soil was twice in the non-irrigated soil than in the irrigated soil. During most of the simulation period, twice as much diuron remained in the top 10 cm soil with no irrigation compared to that with irrigation.

3.2. Effect of clay and organic carbon contents on the simulated Flux and Retention

Simulated Flux over the period was unchanged in soils with 17% and 35% clay content (Fig. VII.f). Simulated Retention was also unchanged in soils with 17% and 35% clay content. This means that for the range of clay content found in the site, the simulated fate of diuron was unaffected. By contrast, the range of TOC found in the study site showed a large effect on the simulated Flux and Retention of diuron (Fig. VII.g). Simulated Flux was 2 to 3 times higher in soils with only 2% TOC than in the soils with 6% TOC in July of each year when soil moisture was sufficiently high for leaching to occur. In drier months, simulated

Retention was almost 50% greater in soils with 6% TOC than in soils with 2% TOC. In the wetter months, however, simulated Retention was only about 20% greater in soils with 6% TOC than in soils with 2% TOC.

3.3. Effect of cropping system/crop cover on the simulated Flux and Retention

Among the input parameters considered in the simulations, cropping system was considered to be a determining factor for assessing the fate of diuron. In this study cropping system constituted crop cover differences in the alley and in the tree-line. The alleys had crop cover all year round provided by the sod strips, while tree-line had crop cover only during growing months (around September to May). However, the effect of crop cover was inferred indirectly through its role in increasing the level of TOC. Because soils in the alley had higher TOC than soils in the tree-line, the simulated chemical Flux in the alley was lower than in the tree-line and the simulated Retention was higher in the alley than in the tree-line.

3.4. Effect of slope on simulated Pesticide Runoff

The rate of Pesticide Runoff (%) may be quickly assessed from the simulated water runoff output of LEACHP. Consequently, the simulated Pesticide Runoff (%) was greater from steep slopes (19°) than from gentle slopes (7°) (Fig. VII.h). Moreover, both the timing of application with soil moisture and the chemical nature of the diuron were also critical in the calculation of Pesticide Runoff. The seasonal trends in the simulated Pesticide Runoff (%) in the alley is shown in Fig. VII.h. Expectedly, a big rainfall event in the beginning of 2000 resulted in a high simulated Pesticide Runoff. Generally, simulated Pesticide Runoff was considerably higher during the wet months (June to August) in each year. In the tree-line, the simulated Pesticide runoff occurred right after pesticide application (Fig. VII.h). During the 12 year simulation period, an increase in slope from 7° to 19° resulted in an increase in the simulated Pesticide Runoff in the alley and in the tree-line.

3.5. Seasonal variability of simulated Flux, Retention and Pesticide Runoff of diuron

The summary statistics of simulated Flux, Retention and Pesticide Runoff for the different particular simulation periods is given in Table VII.c. This data represents the simulated Flux, Retention and Pesticide Runoff for the whole study site using input parameters for each of 200 sampling points. Mean Retention values fluctuated within and between the simulation periods. Mean Retention was higher ($p < 0.05$) in February than in July and November in each of the simulation year periods. The reason was that the pesticide was applied just before February of each year and that due to degradation and leaching, by November of each year most of the chemical leached or degraded. Also, mean Retention was always significantly higher ($p < 0.05$) in the alley than in the tree-line in all simulation periods, which is most likely due to the higher amount of TOC in the alley than in the tree-line (Umali et al., 2012a).

Comparison of mean monthly Flux was significantly higher ($p < 0.05$) in July than in February or November in all simulation years (2001, 2006 and 2011) primarily because rainfall was highest in these periods. The lowest mean Flux ($p < 0.05$) simulated was for November since leaching happened earlier than this period and the next diuron application did not occur until January the next year. However, minimal mean flux was also observed in February 2011 simulation period and we attribute this to low rainfall (only 11.8 mm). Moreover, the long half-life ($t_{1/2}$ = 75.5 d) and high sorption affinity of diuron in soil contributed to its persistence that even six months after application, Flux tended to peak in high rainfall events (e.g. July 2006).

3.6. Effect of management on simulated Flux, Retention and Loading

To determine the effect of management on the simulated Flux and Retention of diuron, LEACHP was run in 200 input files that corresponded to the sampling locations with unique soil and terrain properties and a particular simulation period was chosen (July 2006 – being the month with the highest rainfall). Simulated Flux and Retention values were extracted for that period and analysed in R and the means were compared using least square difference (LSD). The results are show in Table VII.d. During the simulation period, mean simulated Flux was variable among management zones and between alleys and tree-line soils. The alley soils in zones A and B and the tree-line soils in zones B and E had the highest mean simulated Flux. The alley soils in zones C, D and E and the tree-line soils in zone A had the lowest mean simulated Flux. Alley soils in zones C, D and E had higher simulated Retention compared to zones A and B, while in the tree-line, zone E was the lowest while zones A and C were highest. In terms of simulated Loading, the alley soils in zones C, D and E had the lowest value.

In a previous study (Umali et al., 2012b) management zones, differentiated in terms of age and density of tree planting, influenced the distribution of soil properties particularly the level of TOC. This had considerable consequence on sorption behaviour of diuron across the study site wherein old stands (zones C, D and E) with high soil TOC had higher capacity for diuron sorption. In this study, the simulated fate of diuron was also notably influenced by differences in zones particularly for soils found in the alley. For example, alley soils in zones C and D (planted in 1960) which had significantly higher ($p < 0.05$) TOC had significantly lower simulated Flux and Loading ($p < 0.05$) and significantly higher simulated Retention ($p < 0.05$) compared with zone A (planted in 2006).

Differences in the simulated fate of diuron were also observed between the alley and the tree-line soils in the older stands (zones C, D and E). In these zones, the simulated Flux was higher (significantly higher for zone E; $p < 0.05$), the simulated Loading was significantly higher ($p < 0.05$) and the simulated Retention was significantly lower ($p < 0.05$) in the tree-line, which had lower TOC, than in the alley.

4. Conclusion

Among the soil properties investigated, the amount of total organic carbon greatly influenced the simulated fate of diuron for the study site. Diuron remained in the soil surface because of the high level of TOC in specific areas of the study site, particularly in older stands. Moreover, because TOC varied in the landscape, the simulated fate of diuron also varied significantly. Generally for the study site, soils with high TOC had high capacity for retaining diuron while soils with low TOC had high tendency to lose the chemical to leaching. The range of TOC variability that was observed between the alley and tree-line and among the management zones translated to 40-150% differences in the simulated fate of diuron. In terms of the simulated Pesticide Runoff, the greater the slope, the greater the tendency for diuron to move off-site with surface runoff. This suggests that for the study site, which had a highly variable terrain, the risk of diuron transport may vary depending on slope and spatially variable conditions.

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Table VII.a. Summary statistics of selected soil, pesticide and terrain properties in the alley and tree-line regions in the apple orchard used in the LEACHP simulation.

Parameter	Location	Mean	SD	Min	Max
TOC, %	Alley	4.5 b	1.14	2.2	7.0
	Tree-line	3.4a	0.82	1.6	5.5
Clay, %	Alley	23.3	3.73	16.0	33.8
	Tree-line	23.1	3.50	16.7	35.7
Silt, %	Alley	35.5	3.06	28.0	41.0
	Tree-line	34.9	2.95	26.0	41.0
K_{oc}, kg L^{-1}	Alley	633.0a	122.0		
	Tree-line	720.0b	204.0		
Slope °		12.9		7.0	19.0

K_{oc} – organic carbon-normalised sorption coefficient
TOC – total organic carbon
SD – Standard deviation
Means followed by different letters within a given parameter are significantly different at $p < 0.05$.

Table VII.b. Total monthly rainfall for the designated month considered in the simulation (BOM, 2011).

Simulation period	Rainfall (mm)
February 2001	11.8
July 2001	115.7
November 2001	56.0
February 2006	27.6
July 2006	144.2
November 2006	25.6
February 2011	61.5
July 2011	130.5
November 2011	19.7

Table VII.c. Summary statistics of simulated Retention and Flux for alley and tree line (in brackets) (n=100) during three simulation periods.

Simulation		Mean	Min	Max
Parameter	Period			
Retention ($mg\ m^{-2}$)	Feb 2001	130.16 (118.04)*	120.18 (113.46)	137.22 (124.60)
	Feb 2006	***154.47*** (147.83)*	136.17 (135.80)	168.71 (160.25)
	Feb 2011	114.26 (109.39)*	97.30 (97.43)	129.67 (121.47)
	July 2001	81.80 (70.58)*	66.79 (62.18)	91.66 (79.58)
	July 2006	94.99 (90.55)*	75.59 (78.01)	106.34 (100.10)
	July 2011	81.63 (75.47)*	62.19 (61.47)	98.35 (90.10)
	Nov 2001	45.08 (***38.96***)*	31.45 (30.86)	54.00 (47.01)
	Nov 2006	73.79 (67.58)*	55.90 (54.66)	88.61 (80.91)
	Nov 2011	54.17 (48.24) *	35.76 (35.05)	69.69 (62.13)
Flux ($mg\ m^{-2}$)	Feb 2001	0.08 (0.06)	0.03 (0.03)	0.12 (0.10)
	Feb 2006	0.34 (0.32)	0.21 (0.22)	0.52 (0.47)
	Feb 2011	1.71 (1.82)*	1.22 (1.30)	2.93 (2.65)
	July 2001	1.97 (2.15)*	1.40 (1.57)	3.3 (3.0)
	July 2006	2.83 (***3.13***)	1.65 (1.99)	5.72 (4.88)
	July 2011	2.32 (2.34)	1.71 (1.78)	3.60 (3.19)
	Nov 2001	0.20 (0.19)	0.14 (0.14)	0.27 (0.23)
	Nov 2006	0.17 (0.17)	0.12 (0.12)	0.25 (0.23)
	Nov 2011	0.04 (***0.02***)	0.01 (0.01)	0.07 (0.05)

Values in bold and italics face are either lowest or highest mean for each simulation output parameter.
* means between alley and tree-line are significantly different ($p < 0.05$)

Table VII.d. Mean comparison of simulated Flux, Retention and Loading among zones for July 2006; TOC means of zones were put for reference (Umali et al., 2012b).

Management zone	Flux, mg m^{-2}		Retention, mg m^{-2}		Loading, mg L^{-1} ($\times 10^{-2}$)		TOC, %	
	Alley	Tree-line	Alley	Tree-line	Alley	Tree-line	Alley	Tree-line
A (*n*=20)	3.79c	2.96a	87.33a	91.80b	3.40c	2.89b	3.13ab	3.54b
B (*n*=5)	4.22c	3.76c	86.24a	87.02ab	3.55c	3.92c	4.95c	3.43b
C (*n*=32)	2.48a	2.92ab	97.86c	92.16b	2.45a	2.94b	4.91c	3.57b
D (*n*=32)	2.57a	3.00ab	96.94c	91.51ab	2.50a	2.90b	5.25c	2.64a
E (*n*=11)	2.29a	4.16c	98.91c	82.42a	2.34a	3.75c	3.16ab	2.25a

Means followed different letters within each parameter are significantly different at $p < 0.05$. A - planted in 2006, Pink Lady variety, 3.5 m × 1 m spacing (2,860 trees per ha); B - planted in 1980, Royal Gala variety, 4.5 m × 2 m spacing (1,110 trees per ha); C - planted in 1960, Jonathan and Granny Smith varieties, 4.5 m × 2 m spacing (1,110 trees per ha); D - planted in 1960, inter-row of Jonathan-Granny Smith and Pink Lady varieties, 4.5 m × 2 m spacing (1,110 trees per ha); and E - planted in 1960, Jonathan and Granny Smith varieties, 5 m × 4 m spacing (500 trees per ha).

Figure VII.a. An orthophotograph of the study site showing the management zones in capital letters.

A - planted in 2006, Pink Lady variety, 3.5 m × 1 m spacing (2,860 trees per ha); B - planted in 1980, Royal Gala variety, 4.5 m × 2 m spacing (1,110 trees per ha); C - planted in 1960, Jonathan and Granny Smith varieties, 4.5 m × 2 m spacing (1,110 trees per ha); D - planted in 1960, inter-row of Jonathan-Granny Smith and Pink Lady varieties, 4.5 m × 2 m spacing (1,110 trees per ha); and E - planted in 1960, Jonathan and Granny Smith varieties, 5 m × 4 m spacing (500 trees per ha).

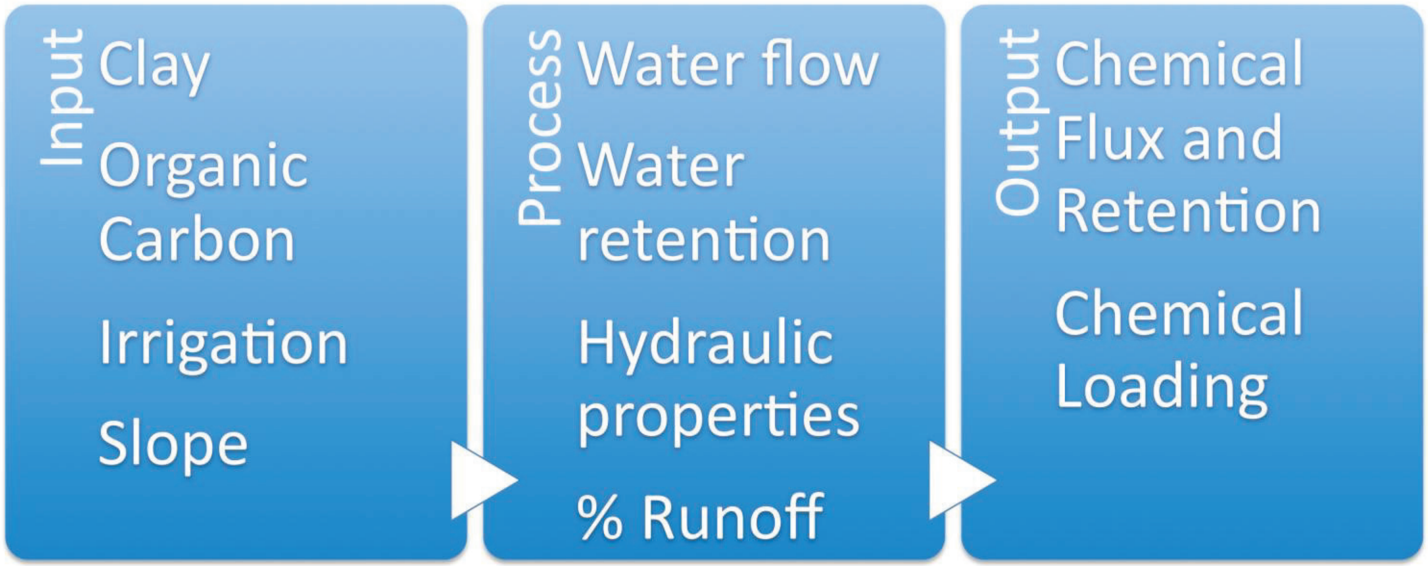

Figure VII. General input-process-output framework of the simulation.

Figure VII. The seasonal variability of cover that show alley and tree-line (Nearmap ortophotos zoomed in on one section of the study site).

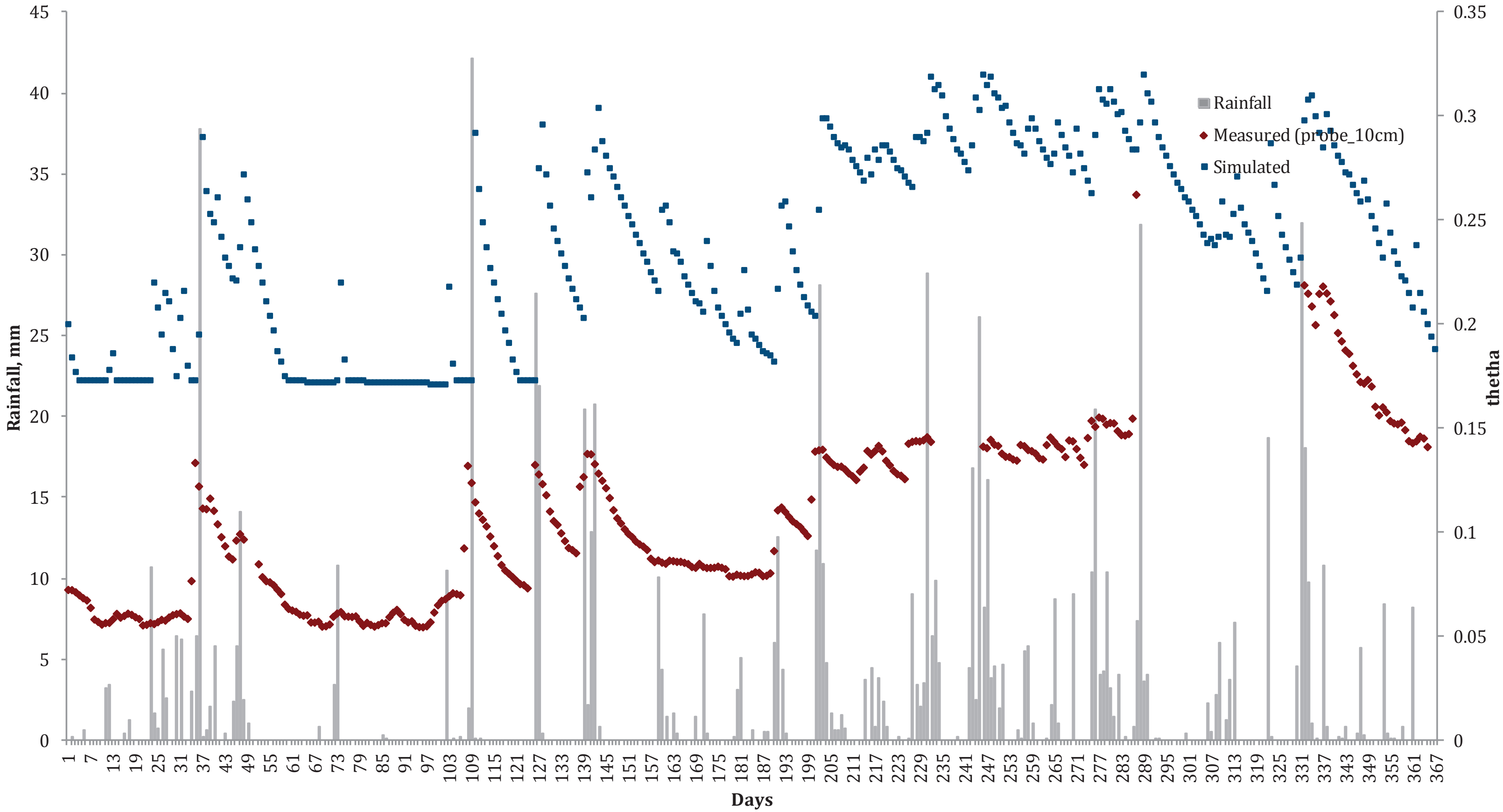

Figure VII. Rainfall and soil water contents simulated using LEACHP and measured using Sentek moisture probe installed in the site at 10 cm depth (December 2010 – November 2011).

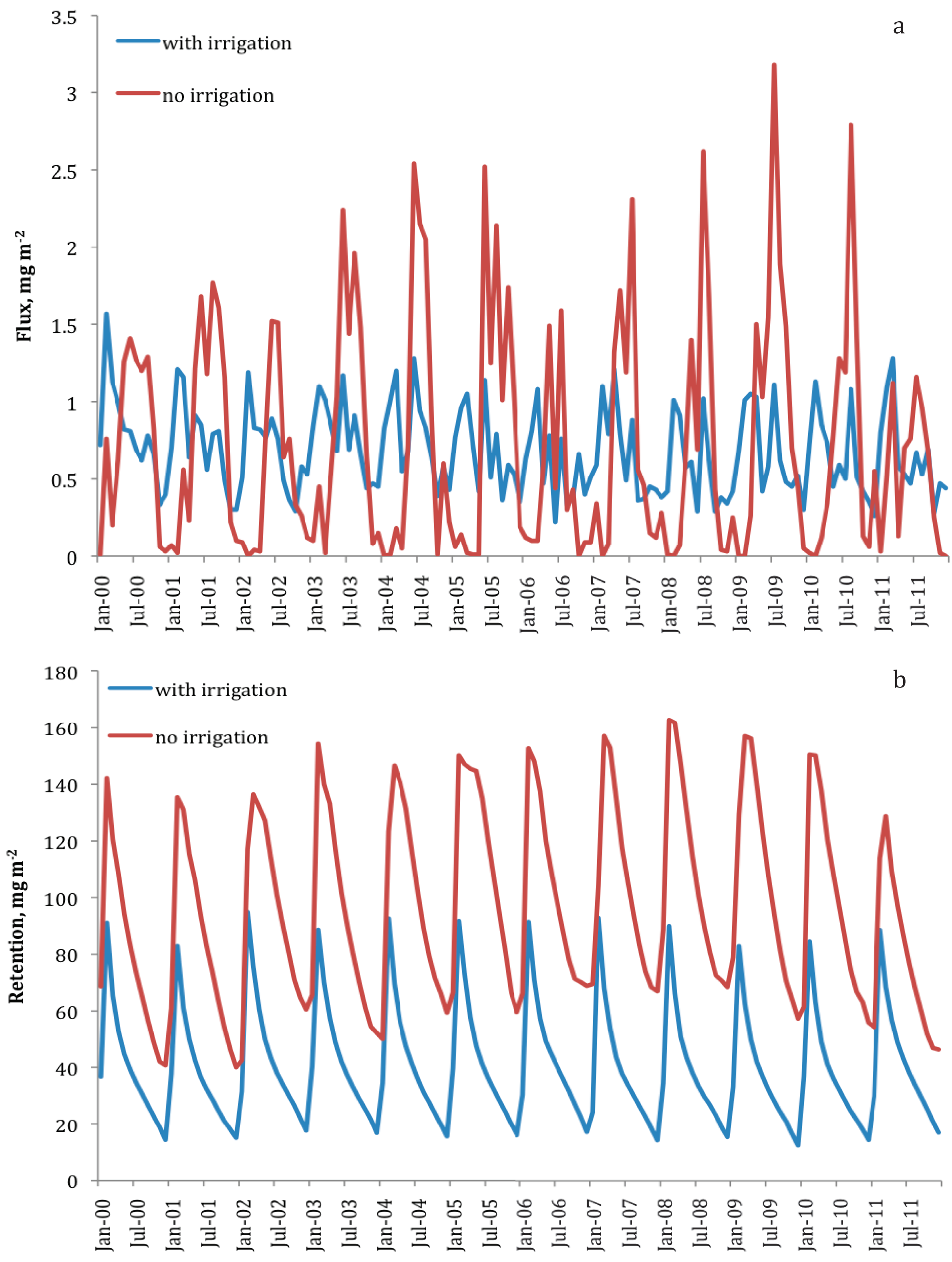

Figure VII. Effect of irrigation on Flux (a) and Retention (b).

(Flux – simulated flux of diuron just from the top 10 cm of soil; Retention – simulated amount of diuron that remained in the surface layer)

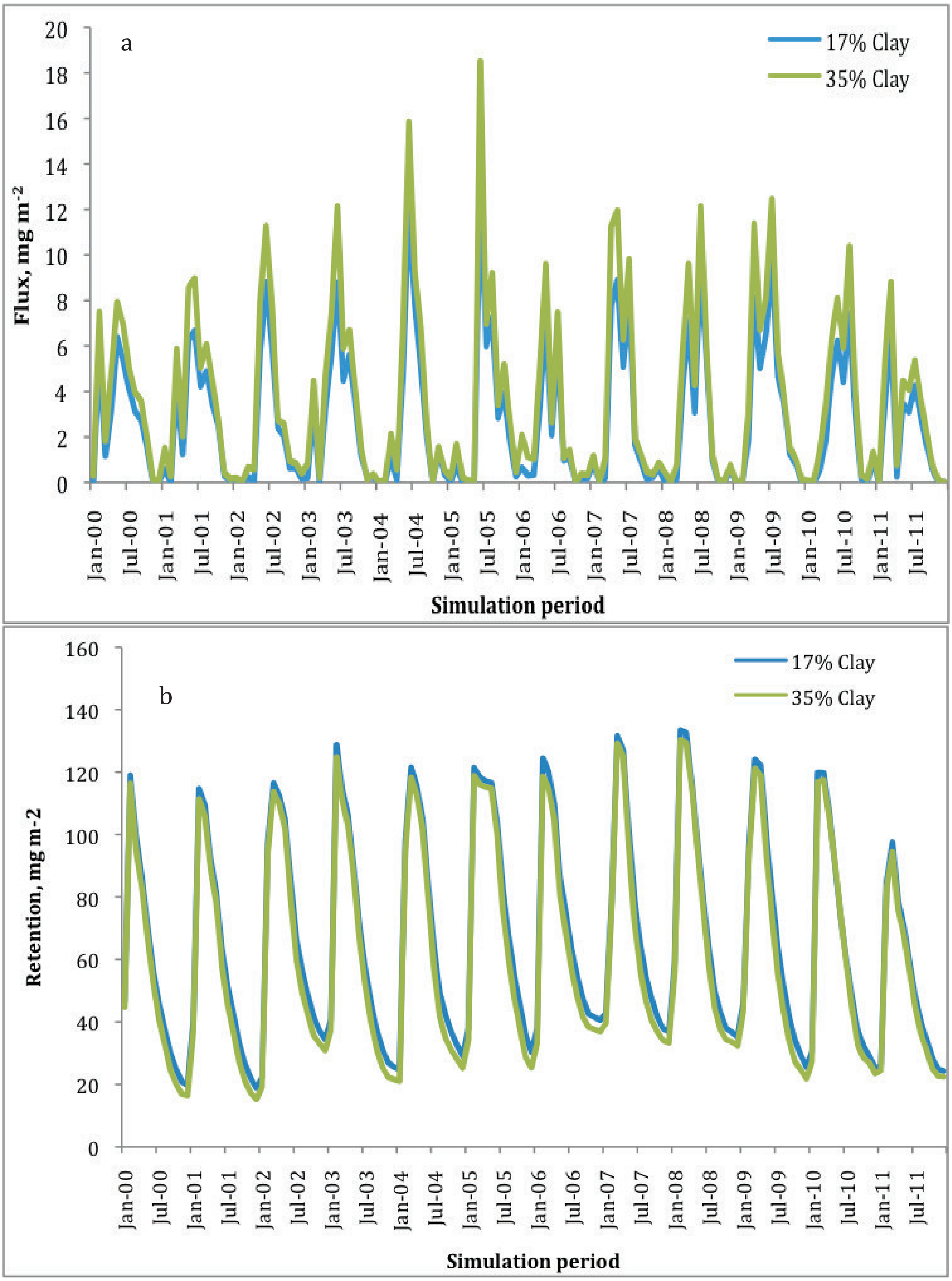

Figure VII. Effect of clay on the simulated Flux (a) and Retention (b) of diuron in the top 10 cm of soils found in alley (no irrigation) using 2 % total organic carbon content.

(Flux – simulated flux of diuron just from the top 10 cm of soil; Retention – simulated amount of diuron that remained in the surface layer)

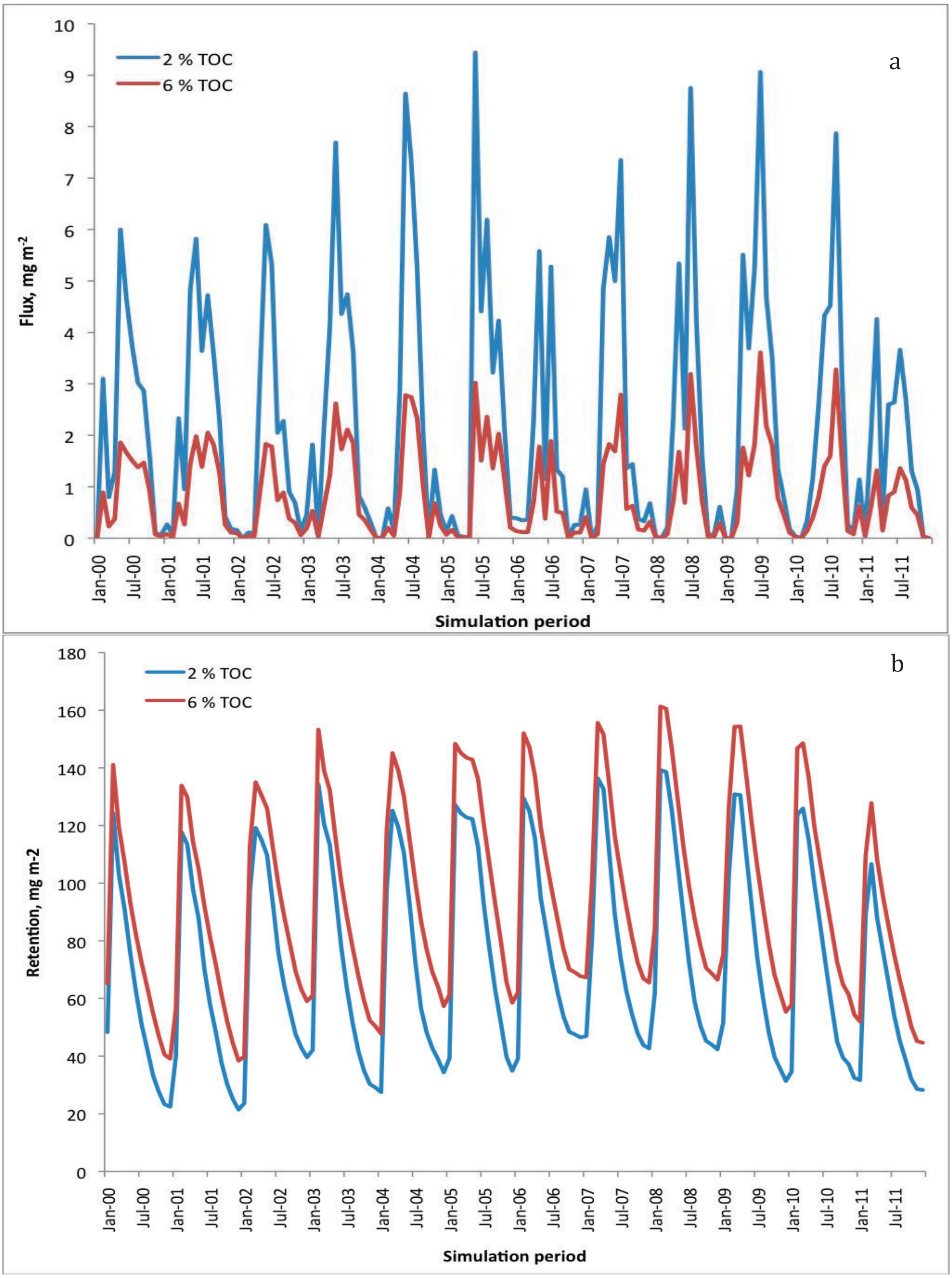

Figure VII. Effect of soil total organic carbon on simulated Flux (a) and Retention (b) of diuron in the top 10 cm of soil found in alley (no irrigation) using 35% clay content.

(Flux – simulated flux of diuron just from the top 10 cm of soil; Retention – simulated amount of diuron that remained in the surface layer)

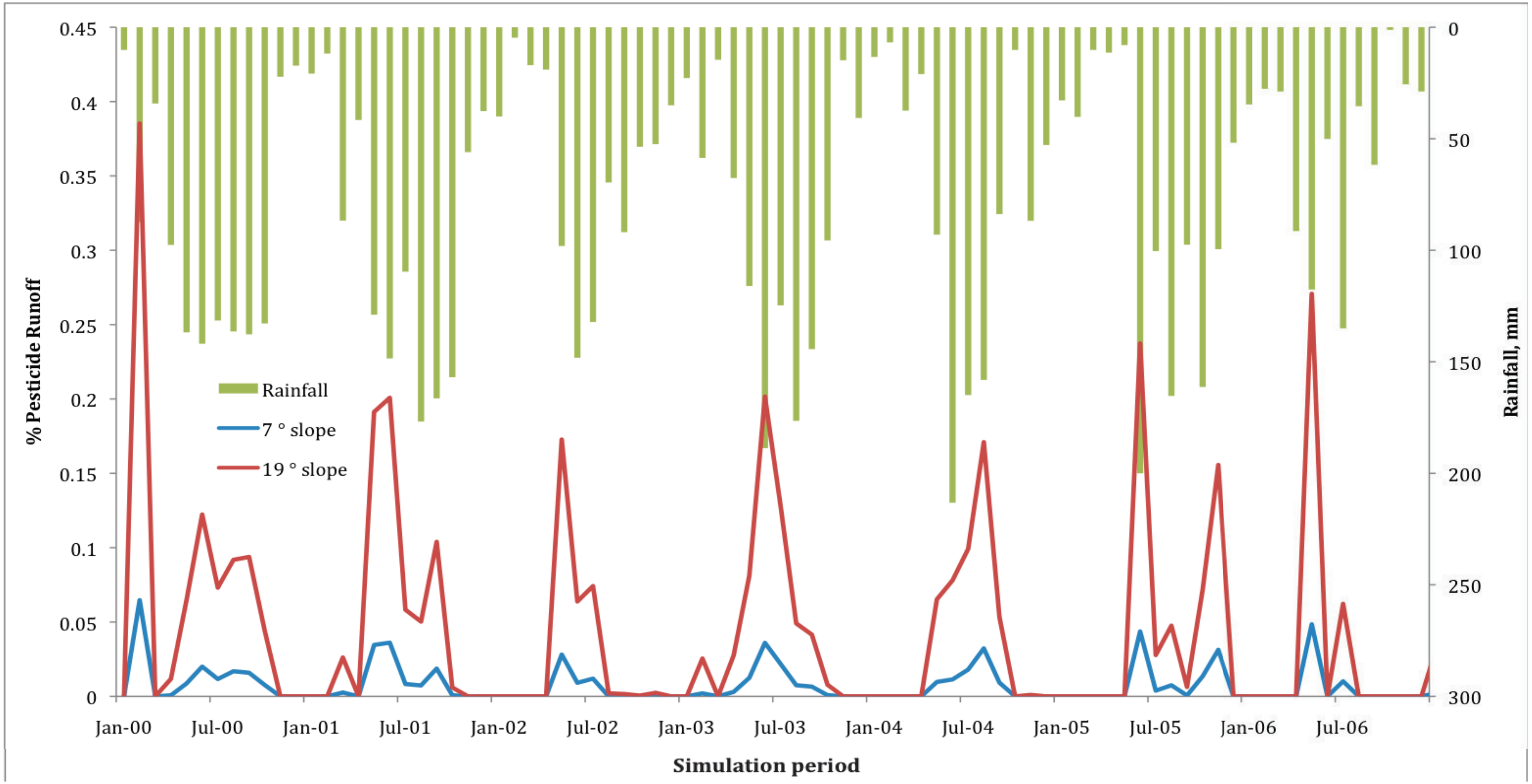

Figure VII. Effect of slope on simulated % Pesticide Runoff in the alley from 2000 to 2006 using 35% clay content and 6% total organic carbon content.

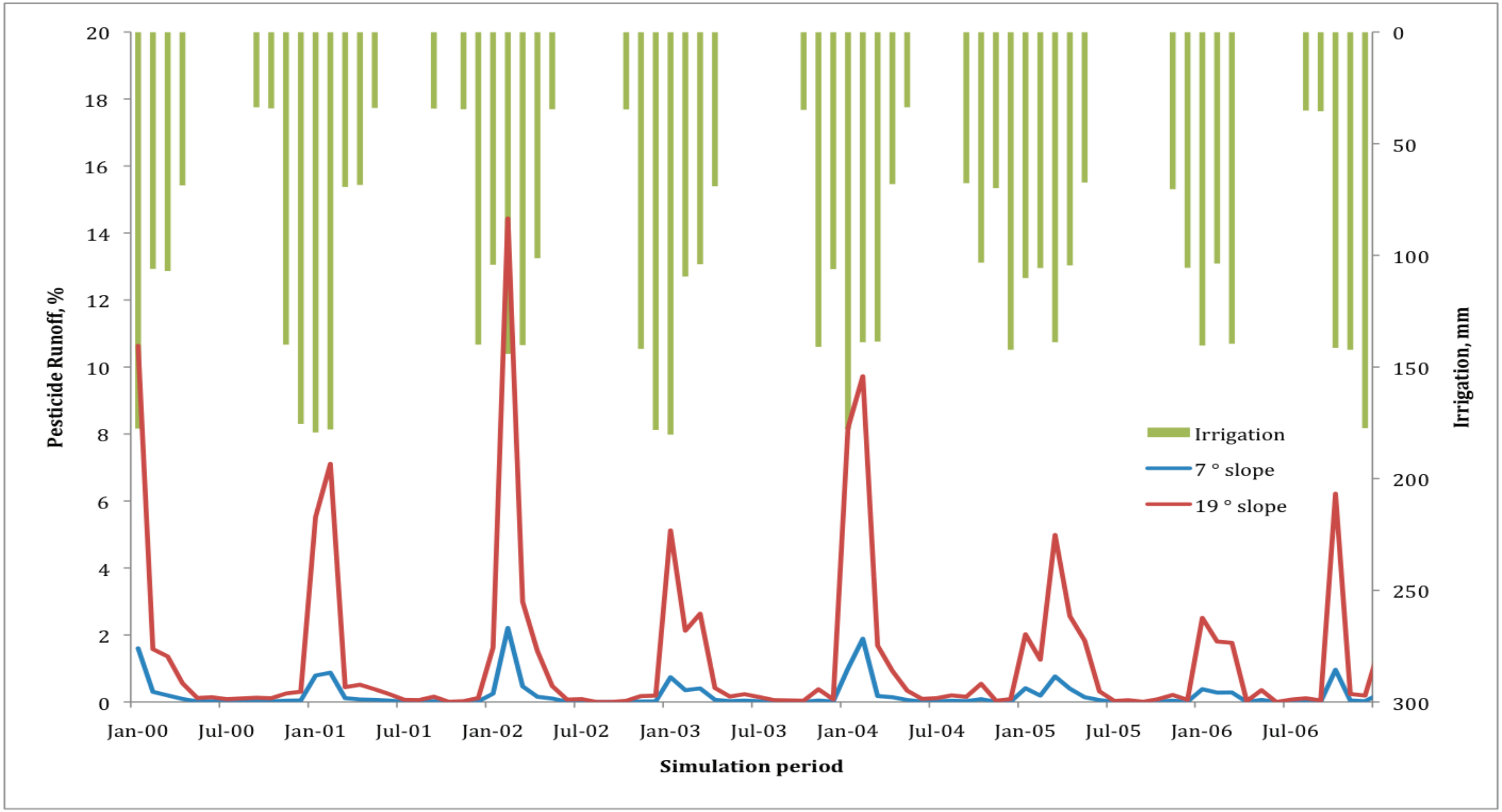

Figure VII. Effect of slope on simulated Pesticide Runoff (%) in the tree-line from 2000 to 2006 using 35% clay content and 6% total organic carbon content.

VIII. Overall Summary, Conclusion and Recommendations

Spatial variability of soil properties and processes along with topography contributes considerably to pesticide movement in orchards, yet very little systematic studies exist that examine causes of variability and hence little practical guidelines exist on how to assess the spatial differences in the fate and risks of off-site movement of pesticides. Assessment tools generally ignore this spatial variability despite wide recognition that soils and associated parameters that influence pesticide movement vary dramatically within landscapes. This thesis has narrowed this gap by the systematic evaluation of the causes of spatial variability of parameters that influence pesticide movement, by testing the usefulness of topographic information to explain natural variability in soil conditions and the differences of anthropogenic factors that influence pesticide sorption.

The overall aim of this thesis was to study the natural and landscape-induced patterns of herbicide sorption and risks of leaching and off-site transport of herbicides in an intensively managed orchard system. The objectives of this thesis were: a) to determine whether a 'smoothing' algorithm can enhance the accuracy of a contour-derived digital elevation model; b) to evaluate the role of topography and management practises in predicting the distribution of soil properties using a soil-landscape modeling approach; c) to evaluate the effects of topography, soil properties and management practises on the sorption affinity of diuron; and d) to assess the integrated effect of topography, management practises and herbicide sorption on the leaching potential of diuron in a spatially variable landscape using the Leaching

Estimation and Chemistry Model (LEACHM) and surface runoff using the Organization for Economic Cooperation and Development (OECD) model.

The salient findings of this research can be summarized as follows:

- Our study showed that the quality of digital elevation models (DEMs) limits the use of simple surrogates for soil landscape analyses. We tested different elevation models against highly precise surveyed elevation points and found that contour-based DEMs performed better than commercially available broad-scale radar products. However, the inaccuracies, which were observed in slope and curvature terrain models derived from countour data, could be reduced using simple smoothing techniques. (Chapter III and Appendix 1).
- Using soil colour as a surrogate of soil organic carbon, which is a major factor in soil sorption of pesticides, an initial assessment of the varying degree of capacity for pesticide sorption was made. Moreover, a strategy to separate the space between the alleys and the tree-line in an apple orchard was needed because of the differences in the spatial variability of soils found in these locations (Chapter IV).
- A key outcome of this thesis was a surprisingly strong systematic influence of management-induced soil variability on herbicide sorption. The spatial variability of soils in the alley were different for soils found in tree-line. Orchard floor management (e.g. keeping the tree-line free from ground cover) influenced the distribution of soil properties. Segmenting an orchard landscape into management zones better explained the variability of soil properties (Chapter V).
- A mid-infrared – partial least squares (MIR–PLS) regression model was developed that incorporated soil organic carbon content, its chemistry as

well mineral matter in soils. The model adequately predicted diuron sorption affinity (K_d) for soils obtained from the apple orchard, this was validated using traditional laboratory techniques. A close agreement was noted between laboratory-determined and and MIR-predicted K_d values. Variability of diuron K_d was found to vary between alleys and tree-lines and among management zones. Terrain variables such as slope and wetness index (WI) were used as predictors for modeling the spatial distribution of diuron K_d (Chapter VI)

- Soil water contents influenced simulated leaching, retention and off-site movement of diuron in the study site. Due to the moderately high persistence of diuron ($t_{1/2}$ = 75 d) the simulations found the chemical remained in the surface soil but potential for leaching and transport was increased later in the year when rainfall events were more frequent and of greater quantity (Chapter VII). More importantly, the distribution of soil organic carbon content, as influenced by management practises, affected the simulated fate of diuron in the study site.

The results of this thesis have potential contributions to a number of areas including topographic analysis, digital terrain analysis in the context of pesticide fate assessment, assessment of pesticide behaviour in managed orchards and pesticide management in variable landscapes. Although, elevation, slope and other terrain parameters were found to influence soil distribution, it was also greatly influenced by existing management practices.

Consequently, the management-induced variability of soil properties was also found important in assessing herbicide sorption. This was shown in

Chapter VI because the sorption property of diuron, the test herbicide used, was dependent on soil organic carbon content. This chapter also provided information on the relative importance of the terrain variables (e.g. elevation and wetness index) in assessing the distribution of diuron sorption. In the last chapter, Chapter VII, it was also found that management practises influenced the simulated fate of diuron. The implication of these findings for farmers is that in order to reduce the risk of off-site movement of diuron, differential herbicide/pesticide application might have to be observed.

The work embodied in this thesis answered a number of questions related to natural and management-induced patterns of herbicide fate using the soil landscape analysis approach, however, I recommend the following areas for future research:

a) The applicability of using surrogates like colour in assessing pesticide fate can be further investigated. This thesis established that colour was related to TOC in one section of the orchard – the alley. A good relationship between TOC and diuron sorption was also established. However, more work needs to be done in order to ascertain these relationships when dealing with soils that have been altered immensely by anthropogenic or extrinsic causes.

b) In addition, a more robust sampling technique could be investigated to better assess the distribution of soils that are found in this kind of landscape. Results of the geostatistical and regression modeling revealed low spatial structure for some of the soil properties in either the alley or the tree-line.

c) Previous studies have also been conducted in mono-cropping systems with gently rolling terrain. Although this study expanded this analysis on a more complex terrain with relief difference of 50 m, analyses made in this thesis were still limited in the land use and geographic region where the soils were taken. Therefore, similar studies are needed on other land uses that are impacted not only by the terrain attributes but also by the management regime employed by the land user.

d) One of the potential extensions of this research work is in identifiying the 'source zones' or hotspots from where pesticide residues are mobilized in surface water or deep drainage, due to the complex interplay of landscape attributes, soil properties and management regimes. The study should be extended to identify the 'source zones' in such systems to allow targeted management of such source zone to minimize any off-site impact of pesticides.

APPENDIX I

DEM and terrain analysis to predict spatial pattern of SOC

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STATEMENT OF AUTHORSHIP

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Beng P. Umali (Candidate)
Analysed and interpreted data, wrote manuscript, presented paper

Certification that the state of contribution is accurate
Signed: ______________ Date: 03/09/2012

Rai S. Kookana
Supervised development of work, provided critical evaluation of the manuscript

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Appendix I. Paper presented during the 19th World Congress of Soils Science, Brisbane, Australia. 1-6 August 2010.

Appendix I. DEM and terrain analysis to predict spatial pattern of SOC

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