Journal of Hazardous Materials 217–218 (2012) 398–405

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

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

Beng P. Umali[a,b], Danielle P. Oliver[a,c], Bertram Ostendorf[a,*], Sean Forrester[c], David J. Chittleborough[a], John L. Hutson[d], Rai S. Kookana[c]

[a] School of Earth and Environmental Sciences, University of Adelaide, Urrbrae, 5064 South Australia, Australia
[b] Cavite State University, Indang, 4122 Cavite, Philippines
[c] CSIRO Land and Water, Water for a Healthy Country National Research Flagship, Urrbrae, 5064 South Australia, Australia
[d] School of the Environment, Flinders University, GPO Box 2100, Adelaide 5001, South Australia, Australia

ARTICLE INFO

Article history:
Received 18 November 2011
Received in revised form 11 February 2012
Accepted 17 March 2012
Available online 26 March 2012

Keywords:
Diuron
MIR-PLS prediction
Soil-landscape analysis
Apple orchard
Spatial variability

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 practices 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 pesticides to soils was not only affected by soil properties and terrain attributes but also by management regime.

© 2012 Elsevier B.V. All rights reserved.

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 [1,2]. 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. [3] mapped the distribution of imazethapyr (a herbicide used in soybean production) sorption based on soil pH variability. Later on, Farenhorst et al. [4] 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 [4,5]. 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 practices 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 [6]. Thus, management practices 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

* Corresponding author at: DX650-DP614 Davies Bldg., Waite Campus, PMB 1, Glen Osmond, South Australia 5064, Australia. Tel.: +61 8 8303 7317; fax: +61 8 8303 6717.
E-mail addresses: danni.oliver@csiro.au (D.P. Oliver), bertram.ostendorf@adelaide.edu.au (B. Ostendorf), sean.forrester@csiro.au (S. Forrester), david.chittleborough@adelaide.edu.au (D.J. Chittleborough), john.hutson@flinders.edu.au (J.L. Hutson), rai.kookana@csiro.au (R.S. Kookana).

0304-3894/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2012.03.050

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 [7] but also pesticide sorption affinity [8]. This technique is a robust, multivariate statistical tool for quantitative analysis of mid-infrared (400–4000 cm^{-1}) spectral data [9]. 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 [10]. 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 [11]. As a widely used and persistent herbicide (DT_{50} = 75–100 d), it has been detected in runoff, tile drain water [12], river systems [13] and enclosed seawater [14]. Diuron is moderately hydrophobic and its behavior in soil is said to be influenced by soil organic carbon [15]. Giacomazzi and Cochet [10] wrote a comprehensive review on the behavior 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 practices (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 [16] and are classified as Petroferric, Melanic-Vertic, Red-Yellow Chromosols [17], 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 (2860 trees per ha); B – planted in 1980, Royal Gala variety, 4.5 m × 2 m spacing (1110 trees per ha); C – planted in 1960, Jonathan and Granny Smith varieties, 4.5 m × 2 m spacing (1110 trees per ha); D – planted in 1960, inter-row of Jonathan-Granny Smith and Pink Lady varieties, 4.5 m × 2 m spacing (1110 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 1 [6]. 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, μS 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 [18] obtained in digital format from the Department of Environment and Natural Resources of South Australia (DENR-SA). The DEM was smoothed [19] 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 [20]. Wetness index (WI) is a gauge used to characterize spatial distribution of surface saturation [21]. A more detailed explanation and calculation of these parameters is given in Wilson and Gallant [20].

Table 1
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[a], μS cm^{-1}	Alley	5.20	5.96b	6.59
	Tree line	5.08	5.77a	6.98
% Clay content (<0.002 mm)	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 ([a] 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).

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 [22]. 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) [8,23]. 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}) was 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 4000–500 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 [24]. 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 K_d 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 Holm's method [25] 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 [26] 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 ($K_d^{\text{soil\_alley}}$, $K_d^{\text{soil\_treeline}}$), terrain parameters ($K_d^{\text{terr\_alley}}$, $K_d^{\text{terr\_treeline}}$), and the combination of soil and terrain variables ($K_d^{\text{soilterr\_alley}}$, $K_d^{\text{soilterr\_treeline}}$). 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 standardized 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 [24] 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 [27] 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 K_d 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. 1. 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. 2). The SECV is a measure of the size of the probable error occurring in the model prediction. Forouzangohar et al. [8] 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

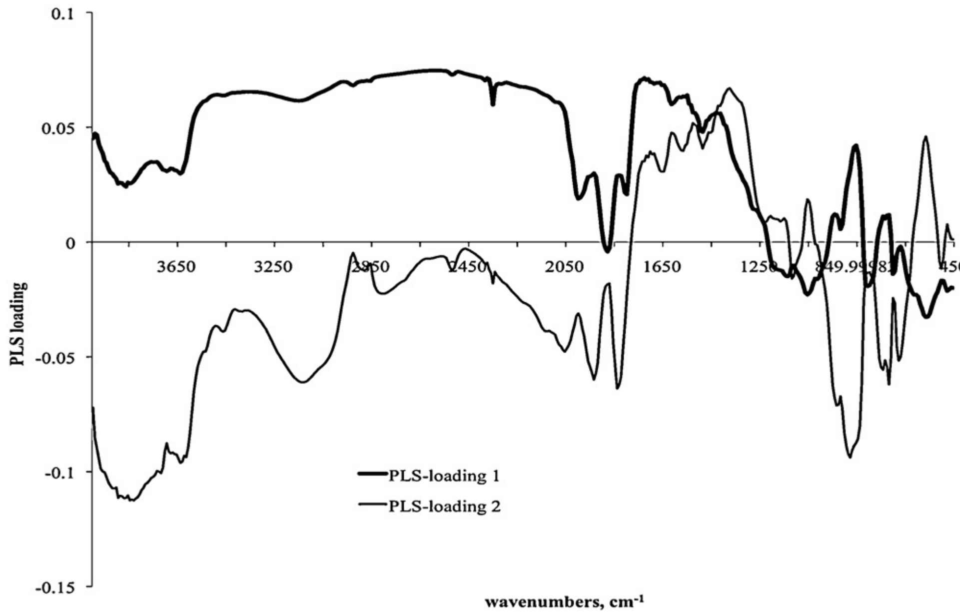

Fig. 1. Partial least squares (PLS) loadings weight of the first two factors used in the regression model.

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 1), which followed Gaussian distribution at $p < 0.05$.

3.2. Relationship of diuron K_d 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 2). 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 practices), the effect of slope on TOC was masked [6]. These observations necessitated the development of regression model and kriging estimation unique for alley and for tree-line soils.

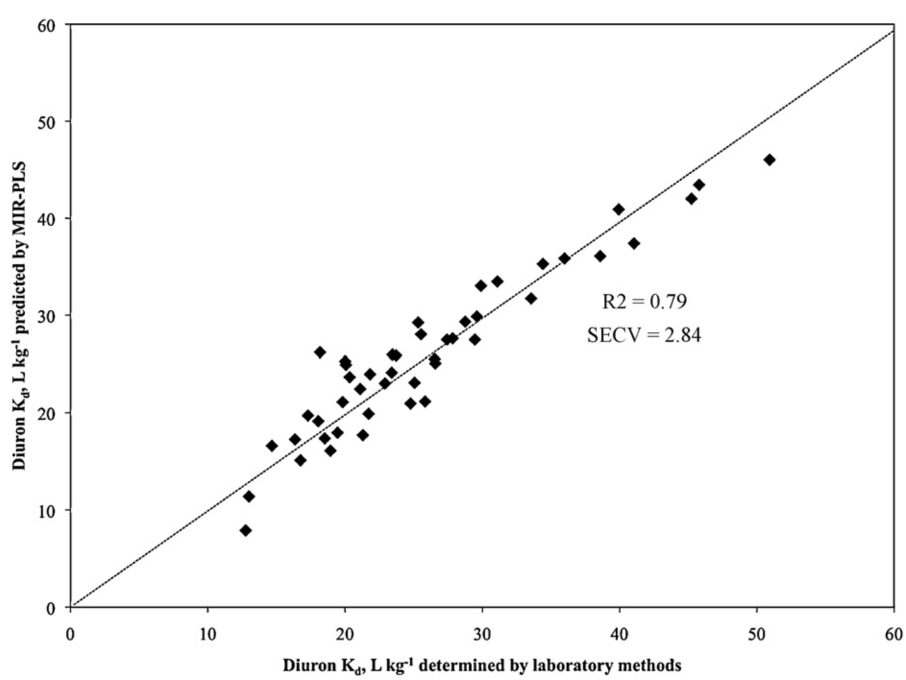

Fig. 2. Relationship between diuron K_d values predicted using MIR-PLS and those determined on the subset ($n = 46$; 4 outliers were removed) of samples using the traditional batch sorption techniques (dotted line is the 1 is to 1 line; SECV is standard error of the cross-validation). MIR-PLS – mid-infrared partial least squares technique.

Table 2
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[a]	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[a]	***−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 ([a]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.

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. 1). Also, previous work on solid-state ^{13}C nuclear magnetic resonance spectroscopy suggested that certain carbon functional groups influence diuron sorption [15].

Other factors aside from TOC, may affect diuron K_d affinity. In a recent study, Stork et al. [12] 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 such as diuron, may be indirectly affected by other soil properties such as pH and cation exchange capacity [28]. The negative correlation ($p < 0.05$) of diuron K_d with pH_w was noted by Gaillardon et al. [29] who attributed this to the interaction of diuron molecules with cationic species such as 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 such as diuron, K_d is normally positively correlated with clay content [30] 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 [31] 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 2). 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 3. 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 3). 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. 3). The effect of terrain on sorption properties cannot be overemphasized but should be considered as shown here and in other earlier works [4,5]. The implication of this is that the fate of a non-ionic herbicide, such as diuron, may be determined by hydrological processes, especially events that induce surface runoff. Stork et al. [12] 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. 3). 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. 4). The alley, where sod strips were maintained, also had significantly higher ($p < 0.05$) TOC than the tree line, which may explain the greater sorption of diuron (Table 1).

The establishment of sod strips in the alley and a sod-free tree line in apple orchard management is a common practice in the MLR and other apple growing areas [32] 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

Table 3
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[a], 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[a], 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 ([a]log-transformed data); MeanC, mean curvature, SCA, specific catchment area; WI, wetness index.

* All models $p < 0.001$

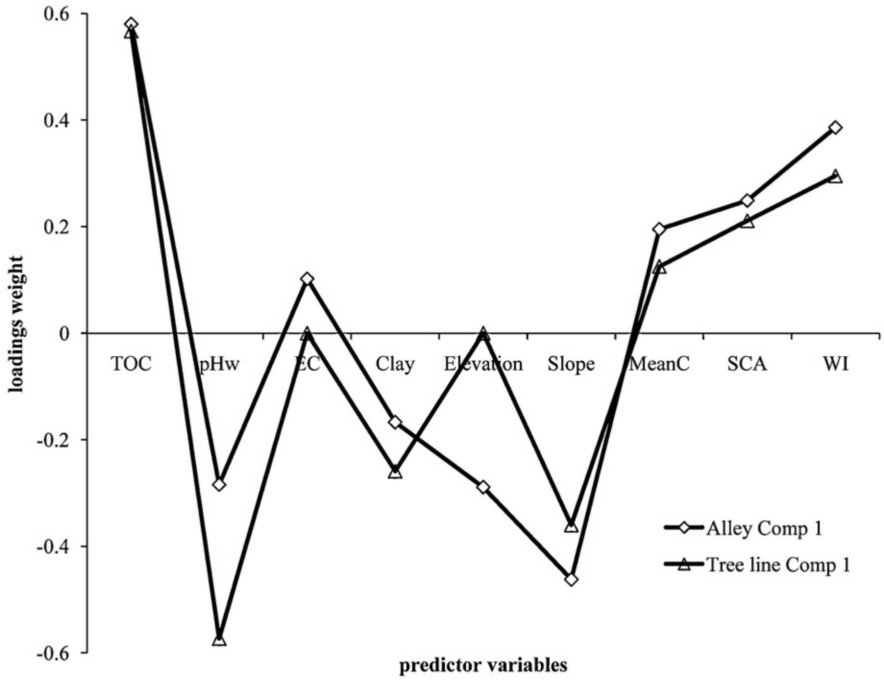

Fig. 3. Loadings weight of the first factor for alley and tree-line of the partial least squares (PLS) regression using soil and terrain variables as predictors.

reducing pesticide offsite movement. This was evidenced in zone A (Figs. 4 and 5) 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 [33]. 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. 5).

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. 5). 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

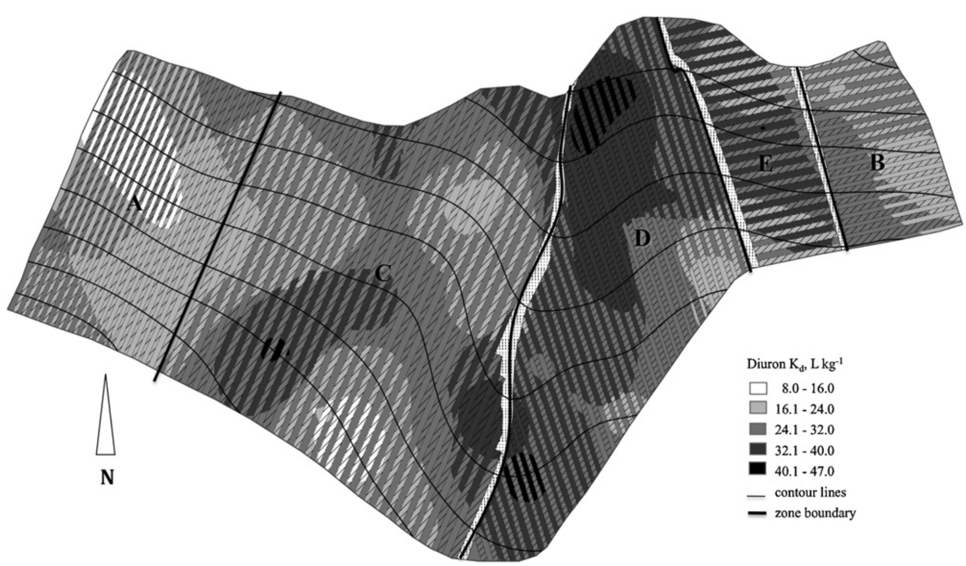

Fig. 4. Interpolated map of diuron K_d for the study site (dotted area is access road, hatched area is tree line, the rest is alley; letters are zone designations). (A) Planted in 2006, Pink Lady variety, 3.5 m × 1 m spacing (2860 trees per ha); (B) planted in 1980, Royal Gala variety, 4.5 m × 2 m spacing (1110 trees per ha); (C) planted in 1960, Jonathan and Granny Smith varieties, 4.5 m × 2 m spacing (1110 trees per ha); (D) planted in 1960, inter-row of Jonathan-Granny Smith and Pink Lady varieties, 4.5 m × 2 m spacing (1110 trees per ha); and (E) planted in 1960, Jonathan and Granny Smith varieties, 5 m × 4 m spacing (500 trees per ha).

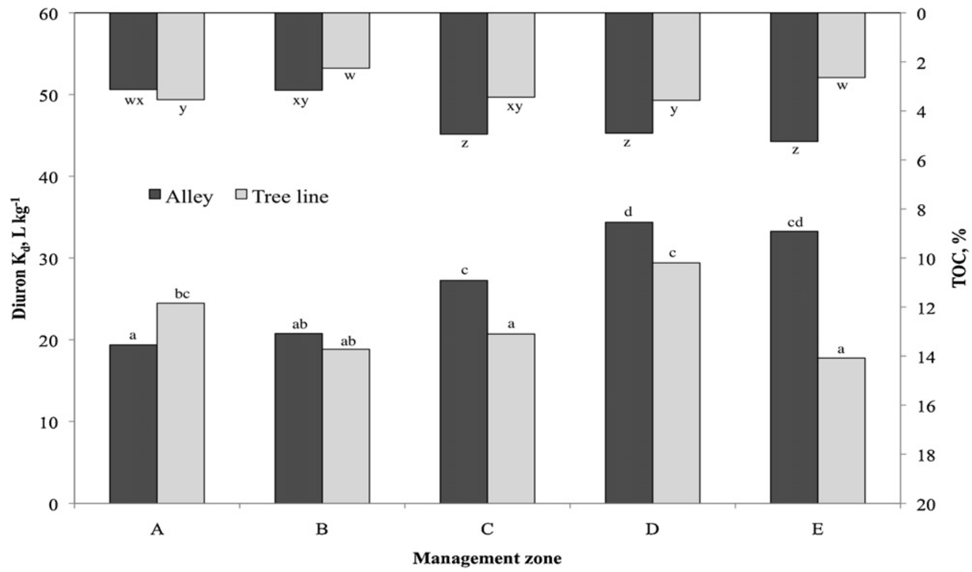

Fig. 5. Means of diuron K_d (lower data, L kg^{-1}) and total organic carbon (upper data, %) in the different management zones and sampling locations. (A) Planted in 2006, Pink Lady variety, 3.5 m × 1 m spacing (2860 trees per ha); (B) planted in 1980, Royal Gala variety, 4.5 m × 2 m spacing (1110 trees per ha); (C) planted in 1960, Jonathan and Granny Smith varieties, 4.5 m × 2 m spacing (1110 trees per ha); (D) planted in 1960, inter-row of Jonathan-Granny Smith and Pink Lady varieties, 4.5 m × 2 m spacing (1110 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 $p < 0.05$.

capacity, soil nutrient levels, water holding capacity [33] as well as sorbing pesticides. Finally, we suggest that growers ensure that the risk for offsite movement of pesticides is avoided by management practices 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 diuron. 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 practices 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.

Acknowledgements

We thank Jenny Anderson of CSIRO Land and Water for the technical support in the conduct of the batch sorption experiment, Dr. Mohsen Forouzangohar of the University of Melbourne for his advice on MIR-PLS, Dr. Ronald Smernik for providing valuable comments to the manuscript, and the Department of Environment and Natural Resources – South Australia for providing the topographic data. The lead author thanks the Australian Centre for International Agricultural Research (ACIAR) for funding through the John Allwright Fellowship.

References

[1] C. Wesseling, R. McConnell, T. Partanen, C. Hogstedt, Agricultural pesticide use in developing countries: health effects and research needs, Int. J. Health Serv. 27 (1997) 273–308.

[2] R.J. Gilliom, J.E. Barbash, C.G. Crawford, P.A. Hamilton, J.D. Martin, N. Nakagaki, L.H. Nowell, J.C. Scott, P.E. Stackelberg, G.P. Thelin, D.M. Wolock, The quality of our nation's waters-Pesticides in the nation's streams and ground water, 1992–2001, in: U.S. Geological Survey Circular 1291, U.S. Geological Survey, 2006, 2006, pp. 172.

[3] R.S. Oliveira, W.C. Koskinen, F.A. Ferreira, B.R. Khakural, D.J. Mulla, P.J. Robert, Spatial variability of imazethapyr sorption in soil, Weed Sci. 47 (1999) 243–248.

[4] A. Farenhorst, S.K. Papiernik, I. Saiyed, P. Messing, K.D. Stephens, J.A. Schumacher, D.A. Lobb, S. Li, M.J. Lindstrom, T.E. Schumacher, Herbicide sorption coefficients in relation to soil properties and terrain attributes on a cultivated prairie, J. Environ. Qual. 37 (2008) 1201.

[5] A. Farenhorst, I.V. Florinsky, C.M. Monreal, D. Muc, Evaluating the use of digital terrain modelling for quantifying the spatial variability of 2,4-D sorption by soil within agricultural landscapes, Can. J. Soil Sci. 83 (2003) 557–564.

[6] B.P. Umali, D.P. Oliver, S.T. Forrester, D.J. Chittleborough, J.L. Hutson, R.S. Kookana, B.F. Ostendorf, The effect of terrain and management on the spatial variability of soil properties in an apple orchard, Catena (2012).

[7] L.J. Janik, J.O. Skjemstad, Characterization and analysis of soils using mid-infrared partial least-squares. II. Correlations with some laboratory data, Aust. J. Soil Res. 33 (1995) 637–650.

[8] M. Forouzangohar, R.S. Kookana, S.T. Forrester, R.J. Smernik, D.J. Chittleborough, Midinfrared spectroscopy and chemometrics to predict diuron sorption coefficients in soils, Environ. Sci. Technol. 42 (2008) 3283–3288.

[9] D.M. Haaland, E.V. Thomas, Partial least-squares methods for spectral analyses. 2. Application to simulated and glass spectral data, Anal. Chem. 60 (1988) 1202–1208.

[10] S. Giacomazzi, N. Cochet, Environmental impact of diuron transformation: a review, Chemosphere 56 (2004) 1021–1032.

[11] K.H. Bowmer, W. Kort, A. Scott, G. McCorkelle, M. Thomas, Pesticide monitoring in the irrigation areas of South-western New South Wales, Australia 1990–1995, in: CSIRO Land and Water, 1998.

[12] P.R. Stork, F.R. Bennett, M.J. Bell, The environmental fate of diuron under a conventional production regime in a sugarcane farm during the plant cane phase, Pest Manag. Sci. 64 (2008) 954–963.

[13] B. Meyer, J.Y. Pailler, C. Guignard, L. Hoffmann, A. Krein, Concentrations of dissolved herbicides and pharmaceuticals in a small river in Luxembourg, Environ. Monit. Assess. (2010) 1–20.

[14] K. Martinez, I. Ferrer, M.D. Hernando, A.R. Fernandez-Alba, R.M. Marce, F. Borrull, D. Barcello, Occurrence of antifouling biocides in the Spanish Mediterranean marine environment, Environ. Technol. 22 (2001) 543–552.

[15] A.G. Ahangar, R.J. Smernik, R.S. Kookana, D.J. Chittleborough, Clear effects of soil organic matter chemistry, as determined by NMR spectroscopy, on the sorption of diuron, Chemosphere 70 (2008) 1153–1160.
[16] J.A.S. Hall, D.J. Maschmedt, N.B. Billing, The Soils of Southern South Australia, Department of Water, Land, Biodiversity Conservation, Government of South Australia, Adelaide, South Australia, 2009.
[17] R.F. Isbell, The Australian Soil Classification, CSIRO Publishing, Melbourne, Victoria, 2002.
[18] M.F. Hutchinson, A new procedure for gridding elevation and stream line data with automatic removal of spurious pits, J. Hydrol. 106 (1989) 211–232.
[19] T. Hengl, S. Gruber, D.P. Shrestha, Reduction of errors in digital terrain parameters used in soil-landscape modelling, Int. J. Appl. Earth Obs. Geoinf. 5 (2004) 97–112.
[20] J.P. Wilson, J.C. Gallant, Terrain Analysis: Principles and Applications, Wiley, New York, 2000.
[21] K.J. Beven, M.J. Kirkby, Physically based, variable contributing area model of basin hydrology, Hydrol. Sci. Bull. Sci. Hydrol. 24 (1979) 43–69.
[22] OECD., Guideline for Testing Chemicals 106: Adsorption/Desorption Using a Batch Equilibrium Method, OECD Publications, Paris, 2000.
[23] D.P. Oliver, R.S. Kookana, B. Quintana, Sorption of pesticides in tropical and temperate soils from Australia and the Philippines, J. Agric. Food Chem. 53 (2005) 6420–6425.
[24] P. Geladi, B.R. Kowalski, Partial least-squares regression: a tutorial, Anal. Chim. Acta 185 (1986) 1–17.
[25] S. Holm, A simple sequentially rejective multiple test procedure, Scand. J. Stat. 6 (1979) 65–70.
[26] J. Fox, Effect displays in R for generalised linear models, J. Stat. Softw. 8 (2003) 1–27.
[27] B. Minasny, A.B. McBratney, B.M. Whelan, Vesper v1. 6, Australian Centre for Precision Agriculture, The University of Sydney, NSW, 2005.
[28] K.N. Reddy, M. Singh, A.K. Alva, Sorption and desorption of diuron and norflurazon in Florida citrus soils, Water Air Soil Pollut. 64 (1992) 487–494.
[29] P. Gaillardon, R. Calvet, J.C. Gaudry, Adsorption de quelques phénylurées herbicides par des acides humiques, Weed Res. 20 (1980) 201–204.
[30] L.C. Liu, H. Cibesvia, F.K.S. Koo, Adsorption of ametryne and diuron by soils, Weed Sci. 18 (1970) 470.
[31] R. Celis, H. De Jonge, L.W. De Jonge, M. Real, M.C. Hermosin, J. Cornejo, The role of mineral and organic components in phenanthrene and dibenzofuran sorption by soil, Eur. J. Soil Sci. 57 (2006) 308–319.
[32] E.J. Hogue, G.H. Neilsen, Orchard floor vegetation management, Hortic. Rev. 9 (1987) 377–430.
[33] J.A. Baldock, J.O. Skjemstad, Soil organic carbon/soil organic matter, in: K.I. Peverill, L.A. Sparrow, D.J. Reuter (Eds.), Soil Analysis: An Interpretation Manual, CSIRO Publishing, Collingwood, Victoria, 1999, pp. 159–170.