PESTICIDE REMEDIATION OF IRRIGATION TAILWATER ON AUSTRALIAN COTTON FARMS: COMPOSTED GIN TRASH AS A PESTICIDE SORPTION MEDIUM

by

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STATEMENT OF ORIGINALITY

The material in this thesis is the original work of the author unless otherwise stated. No part of this study has been previously accepted for the award of any other degree or diploma in any university.

Mitchell Burns

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LIST OF SYMBOLS

ADI	Average Daily Intake (mg kg^{-1} bodyweight)
APVMA	Australian Pesticides and Veterinary Medicines Authority
BMP	Best Management Practices
c	Concentration in suspension
C_{aq}(ti)	Concentration in solution at time step ti (μg L^{-1})
C_{aq}(t0)	Initial pesticide concentration (μg L^{-1})
C_{aq}^{deq}	Concentration of pesticide in solution at desorption equilibrium (μg mL^{-1})
C_{aq}^{eq}	Concentration of pesticide in solution at sorption equilibrium (μg mL^{-1})
C_e	Equilibrium solution concentration (mg L^{-1})
C_s	Concentration on soil phase (μg g^{-1})
C_s^{deq}	Pesticide remaining sorbed at desorption equilibrium (μg g^{-1})
C_s^{eq}	Mass of sorbed pesticide at sorption equilibrium (μg mL^{-1})
DCA	3,4-dichlorophenylaniline
DCPMU	N'-(3,4-dichlorophenyl)-N,N-methylurea
DCPU	N'-3,4-dichlorophenylurea
D_h	Hydrodynamic dispersion coefficient
D_p	Diffusion potential
d_p	Particle diameter
EC	Emulsified concentrate
F_{OC}	Soil organic carbon fraction
GABA	Gamma-aminobutyric acid
GM	Genetically modified
IPM	Integrated Pest Management
K_d	Partition constant (L Kg^{-1}; mL g^{-1})
K_{des}	Desorption coefficient (μg mL^{-1})
K_f	Freundlich sorption coefficient ($\mu g^{1-1/n}(cm^3)^{1/n}g^{-1}$)
K_f^{des}	Freundlich desorption coefficient ($\mu g^{1-1/n}(cm^3)^{1/n}g^{-1}$)
K_{OC}	Soil organic carbon partition coefficient (mL g^{-1})
K_{ow}	Octanol:water partition coefficient
LC50	Concentration that kills 50% of the test population
LD50	Dosage of chemical that kills 50% of the test population
LOEL	Lowest Observable Effects Level

m_0	Initial mass of pesticide (µg)
m_{aq}^{des}	Mass of pesticide desorbed at desorption equilibrium (µg)
m_{aq}^{deq}	Mass of pesticide in solution at desorption equilibrium (µg)
m_{gt}	Mass of composted cotton gin trash (g)
m_p	Mass of pesticide (g)
m_s	Mass of soil (g)
m_{aq}^{ads}	Mass of pesticide sorbed at sorption equilibrium (µg)
m_s^{eq}	Mass of sorbed pesticide at equilibrium (µg)
μ_w	Viscosity
n	Freundlich regression constant
NOEL	No Observable Effects Level
NRA	National Registration Authority for Agricultural and Veterinary Chemicals
OC	Organic carbon
φ	Soil porosity
pKa	Acid dissociation constant
PSII	Photo system II
QldEPA	Queensland Environmental Protection Agency
ρ_b	Soil bulk density
RCII	Reaction centre II
s_m	Colloidal amount deposited per unit mass of the porous matrix
S_{ti}	Percentage of substance sorbed (%)
SPCC	State Pollution Control Commission
T	Temperature
t	Unit time
USEPA	United States Environmental Protection Agency
V	Volume (mL; L)
V_T	Volume of aqueous phase during desorption kinetics (mL)
v_p	Average particle velocity
z	Length of transporting column

PAPER I: LITERATURE REVIEW

Review: Fate and remediation of pesticides in irrigation tailwater of Australian cotton farms

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ABSTRACT

Pesticides are widely used in the Australian cotton industry to control organisms, such as insects and weeds that are liable to reduce the economic value of a cotton crop. A pesticide's toxicity toward target organisms is unique. However, once applied to a cotton field pesticides are subject to a variety of processes that influence their persistence and fate in the environment. Modes of pesticide transport include volatilisation, runoff and leaching, all of which, as well as the degradation processes, are significantly influenced by soil sorption which has been identified to have ramifications with soil organic carbon content. Processes of degradation, such as photochemical, chemical and microbiological, provide a means by which pesticides may dissipate in the natural environment, with the principal outcome being reduced risk of exposure. However, many of these processes may produce more potent compounds, *in lieu* of the parent compound.

As a result of limited dissipation, the exposure of contaminated runoff to non-target organisms on cotton farms is prominent. These problems have led to the development of best management practices and sounder environmental policy to combat the issue, an outcome also being the possible development of cost-effective remediation technologies designed to remove or limit the entrainment of pesticides into runoff. Methods exhibited on cotton farms include physical containment of storm runoff and irrigation tailwater, and the possible utilisation of binding media to reduce exposure. This paper reviews information on the transport and dissipation mechanisms of the pesticides diuron, endosulfan and fipronil on irrigated cotton farms of Australia. It also reviews the current and developing technologies designed to reduce risk of exposure to non-target organisms, with special reference to the possible use of gin trash as a potential remediation sorption medium.

Key words: pesticide, diuron, endosulfan, fipronil, cotton, sorption, environmental fate, persistence, transport, tailwater, gin trash, remediation.

I. INTRODUCTION

A pesticide is any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest. The term "pest" encapsulates living entities that are liable to reducing the value of a cash crop. Pesticides are principally hydrophobic organic substances.

They are frequently used by the Australian cotton industry to protect cotton from a variety of pests, such as insects and weeds.

It is important to recognise that pesticides are toxic to a range of non-target biota, such as humans, aquatic and terrestrial organisms. The principal concern for pesticides is post-application off-site migration. Subsequently, farm runoff has been identified to be toxic to many organisms (Gouy, Dur, Calvet, Belamie & Chaplain, 1999; Muschal & Warne, 2003; Rose, Crossan & Kennedy, 2005a). Runoff is attained either from storm or flood irrigation regimes employed on cotton farms. The water derived at the end of the field is called "tailwater" and is often the focus when controlling off-site movement of pesticides. Contaminated tailwater is often exposed to a variety of wildlife, including humans and may be inadvertently discharged into rivers during intense storm events (Gouy *et al.*, 1999). The current means of research are to limit off-site migration by managing irrigation tailwater, however the technologies employed are few, and in some cases inefficient.

The goal of pesticide science is to be able to predict the environmental impact of a pesticide before it is released into the environment (Hornsby, Wauchope & Herner, 1996). It was therefore advised by Kookana, Baskaran & Naidu (1998) that fate and behaviour of pesticides be adequately understood to minimise the impacts, not only on the local environment but also to humans.

The purpose of this review is to highlight the extent which pesticides are being employed in Australia, with special reference to the cotton industry. From this, three pesticides, diuron, endosulfan and fipronil, largely used in Australian cotton production, will be characterised and their fate in the environment examined. Their fate in the environment will be assessed through the identification and characterisation of degradation pathways undertaken by the focus pesticides in the soil environment and the ability for such pesticides to be translocated off-site via hydrological processes exhibited on cotton farms. Further, some insight to remediation methods currently available for utilisation on cotton farms and an assessment to the potential utilisation of gin trash as a remediator will be presented. Further, identification of limitations in the literature will provide the surrogate to future research to supplement this review.

II. PESTICIDES AND THE AUSTRALIAN COTTON INDUSTRY

Pests, inclusive of weeds and insects, impose major constraints on production of many crops worldwide through direct yield reductions, damage in storage and costs associated with control measures (Kookana *et al.*, 1998; Fitt, Wilson, Mensah & Daly, 2004). The various control measures range from the use of organic and inorganic chemicals (herbicides and insecticides) to biological methods. The common means of pest control involves the use of synthetic organic chemicals, which their subsequent use dramatically increased since World War II because of their cost-effectiveness, ubiquity in application and overall sterling reputation in efficiently achieving the desired outcome of control (Kookana *et al.*, 1998). Prior to the 1980's, however, weed control was achieved through conventional tillage practices. In recent times, however, there has been a large implementation of minimum tillage practices which are seen to benefit soil quality by reducing erosion and compaction, and increasing soil organic matter. Subsequently, the primary mechanism by which weeds were controlled was deemed bad practice and the dependence and demand for herbicides increased substantially (Kookana *et al.*, 1998).

The use of synthetic organic pesticides has contributed significantly towards the increase in global food production. It has been estimated that Australia alone has benefited from their use, in the range of $4-5 billion per annum, however even after pesticide application financial losses due to weeds is estimated to be about $3.3 billion (Combellack, 1989; as cited by Kookana *et al*., 1998). Although the financial benefits are substantial, their impacts on the environment are well known, notably toward aquatic ecosystems (Rose *et al.*, 2005a; Rose, Sanchez-Bayo, Crossan & Kennedy, 2005b; Shivaramaiah, Sanchez-Bayo, Al-Rifai & Kennedy, 2005).

The Australian cotton industry generates over $1.5 billion per year in export revenue (Cotton Australia, 2006). Much of Australia's cotton is produced in NSW under irrigation, with water derived from the Murray-Darling River catchment (Raupach, Briggs, Ford, Leys, Muschal, Cooper & Edge, 2001; Cotton Australia, 2006). The cotton industry has been recognised as one of the largest users of chemicals in Australian agriculture (Kookana *et al.*, 1998; Kennedy, Sanchez-Bayo, Kimber, Hugo & Ahmad, 2001; Fitt *et al.*, 2004; Rose *et al.*, 2005b), and has subsequently caused serious environmental problems, notably in contamination of surface water bodies, which are exposed to various forms of biota (Agassi, Letey, Farmer & Clark, 1995; Kennedy *et al.*, 2001; Muschal & Warne, 2003) and more recently groundwater reservoirs (Accinelli, Vicari, Pisa & Catizone, 2002; Landry, Dousset &

Andreux, 2006). In 1985, the NSW State Pollution Control Commission (SPCC) recognised this potential, notably in cotton production areas associated with inland water bodies of North-Western NSW (Muschal & Warne, 2003; Shivaramaiah *et al.*, 2005). Such rivers commit to supplying water to irrigation regimes, livestock watering, and general domestic use. They are becoming increasingly designated for environmental flows and licensing schemes have been introduced to limit degradation and promote sustainable use of water resources (Muschal & Warne, 2003). This has seen farmers resort to recycling tailwater, as water becomes increasingly viewed as a finite resource and to limit off-site movement of pesticide contaminated water (Cotton Australia, 2006).

An increasing view has been adopted by the wider international community that agricultural practices must exhibit minimal environmental impacts for enhanced market vigour (Muschal & Warne, 2003). This has provided the incentive that governments and industry practice environmental conservation in order to protect lucrative export markets by virtue of maintaining a 'clean and green' image in practice while retaining profitability (Nett & Hendley, 2002; Muschal & Warne, 2003). In light of these recognitions, the cotton industry has developed several strategies aimed at significantly reducing the amount of chemicals used in practice (Kennedy *et al.*, 2001). Such strategies include Best Management Practices (BMP), Integrated Pest Management (IPM) (Yee & Ferguson, 1996; Fitt *et al.*, 2004), and recognition and ratification of international standards (such as ISO). Inline with these developments, significant research has gone into the development of new technologies aimed at reducing the use and overall impact of pesticides. Such technologies include genetically modified (GM) insect-resistant cotton (e.g. Ingard and Bollgard®), construction of on-farm holding dams to collect contaminated runoff (Kennedy *et al.*, 2001; Cotton Australia, 2006), and bioremediation through constructed wetlands and subsurface filtration (Rose *et al.*, 2005a; Rose *et al.*, 2005b). All of these technologies have been developed to work, to some extent, hand-in-hand by way of yielding a cumulative reduction in pesticide use and overall environmental impact such that manifested in devised strategies and legislations.

In summary, although some technologies exist, pesticides are adopted in cotton production to control problem pests. This indicated a characteristic dependence on chemicals in order to enhance the quality of yields. The outcomes of pesticide use have been revealed to have significant environmental implications recognised at the international level. Such recognitions have provided the incentives and spawned the development of technologies to limit environmental impacts and enhance crop vigour in international markets.

III. CHEMISTRY OF THREE PESTICIDES

Diuron, endosulfan, and fipronil are three pesticides frequently used in irrigated cotton production. Diuron is a herbicide used to control a wide variety of annual and perennial broadleaf and grassy weeds; and endosulfan and fipronil are broad spectrum insecticides (Tomlin, 1997). The chemistry of these compounds invokes variable environmental and selective outcomes. This section of the review will discuss the chemical and physical properties exhibited by these compounds and provide an insight to their selectivity based on their mode of action and uses in cotton production.

(1) Chemical and physical properties

The chemical structures of diuron, endosulfan and fipronil are shown in Fig. 1 A-C and selected chemical and physical properties are shown in Table 1. It is important to note the functional groups exhibited on these compounds. Diuron exhibits the higher degree of polarity due to its urea functional group (indicated by the dashed box) (Fig. 1A) which accounts for its greater solubility in water (Table 1) over the insecticides endosulfan (Fig. 1B) and fipronil (Fig. 1C) (Roy, Gaillardon & Montfort, 2000). Other important attributes include the highly stable chlorinated aromatic ring functional group (McMurray, 2000). Endosulfan and fipronil appear to lack polarity which is reflected by their low solubilities (Table 1) (Tomlin, 1997). The important features to note for endosulfan are the extensively chlorinated cyclohexane (indicated by the dashed box) and the sulfite (SO_3) functional group, which the latter, as will be revealed in a later section, is the site of profound degradation reactions. Fipronil exhibits slightly greater solubility over endosulfan (Table 1), where the combined action of the trifluoromethyl and sulfinyl functional groups would exhibit some degree of polarity. The phenylpyrazole functional group in fipronil (indicated by the dashed box) is quite stable. All of these pesticides evoke a preference for the organic phase over water, as all the octanol:water partition coefficients (K_{OW}) are greater than one (Table 1). Overall, these pesticides exhibit a wide range of variability in their chemical and physical properties.

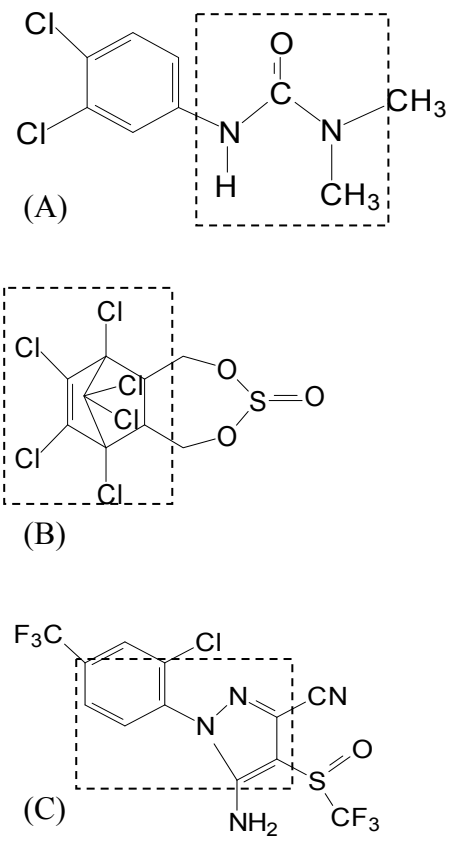


Fig. 1. Chemical structures of (A) diuron, (B) endosulfan, and (C) fipronil (from Tomlin, 1997). Dashed boxes indicate important features outlined in the text.

Table 1. Selected chemical and physical properties of diuron, endosulfan and fipronil (data from Tomlin, 1997).

Property	Diuron	Endosulfan	Fipronil
IUPAC Name	3-(3,4-dichlorophenyl)-1,1-dimethylurea	(1,4,5,6,7,7-hexachloro-8,9,10-trinorborn-5-en-2,3-ylenebismethylene) sulfite	(R,S)-5-amino-1-(2,6-dichloro-α,α,α-trifluoro-*p*-tolyl)-4-trifluoromethyl-sulfinylpyrazole-3-carbonitrile
CAS No.	330-54-1	115-29-7	120068-37-3
Chemical class	Phenylurea	Chlorinated cyclodiene	Phenylpyrazole
Composition		Mixture of two stereoisomers, α-endosulfan and β-endosulfan	
Vapour pressure (mPa)	1.1 x 10^{-3} (at 25°C)	0.83 (2:1 mixture of α- and β-isomers at 20 °C)	3.7 x 10^{-3} (at 20 °C)
logK_{OW}	2.85	α- = 4.74 β- = 4.79	4.0
Solubility in water (mg/L)	36.4	α- = 0.32 (at 22 °C) β- = 0.33 (at 22 °C)	2.2

(2) Application, Modes of Action, and Toxicity of Diuron, Endosulfan and Fipronil

Pesticides are developed to control pests. Their use generally coincides with crop growth, applied at rates able to protect the commodity. Put simply, before a pesticide induces any beneficial effect they are absorbed and translocated within the target, to induce death or desiccation, the finer details of which are beyond the scope of this review. In principle, no single pesticide functions as an insecticide and herbicide. They are, however, selective in that they achieve the desired outcome by altering the functioning of vital chemical attributes manifested in the normal functioning of the target pest. This section of the review will briefly describe the application recommendations, modes of action and toxicity exhibited by diuron, endosulfan and fipronil.

(a) Application

Pesticides are chosen based on their selective nature by which they act on a specific pest. Their selectivity also indirectly encapsulates a variety of other organisms inclusive of humans. Recognition of this has spawned, in line with environmental policy, the development of procedures by which pesticides must be applied in cotton production, with explicit reference to their potency and fugacity (mobility) in the natural environment. These recommendations include modes, rates and timing of application.

Diuron is a soil applied pre-emergent herbicide which functions as a photosynthesis inhibitor (Gooddy, Chilton & Harrison, 2002). It is dispensed in Australia as a 500 g L^{-1} or 900 g kg^{-1} of active diuron component (Farrell & Johnson, 2005). It is recommended that a solution mixture be applied by a dual seeding-herbicide cultivator to moist soil at a depth of no more than 5 cm and at a rate of 1.8-3.5 L ha^{-1} of active component upon cotton seeding per season (Farrell & Johnson, 2005). Cotton seeds are recommended to be placed well below the treated soil zone to limit interaction with the applied herbicide. This is the case because diuron exhibits no selectivity towards different plants; hence its application is prescribed such that drift does not occur and at times where leaching through the soil is minimal (Farrell & Johnson, 2005).

Endosulfan is a broad spectrum insecticide. It is dispensed in Australia as an emulsifiable concentrate (EC) containing 350 g L^{-1} of active endosulfan ingredient and 640 g L^{-1} hydrocarbon solvent (Farrell & Johnson, 2005). The mixture is prepared as a solution with water. It is applied aerially using a crop duster or specialised tractor using a boom spray, for application to the soil and foliage where water acts as the carrier. The recommended application rate in cotton production is 2.1 L ha^{-1} of endosulfan active ingredient and is

recommended to coincide with egg-hatching of caterpillars or at the first sign of infestation (Farrell & Johnson, 2005). Application, however, is limited to a total of 2205 g ha^{-1} of active ingredient application per season, where irrigation tailwater and up to 25 mm of rainfall can be captured on farm (Farrell & Johnson, 2005). This is reduced to 1470 g ha^{-1} of active ingredient where irrigation tailwater and up to 25 mm of rainfall cannot be captured on farm (Farrell & Johnson, 2005). Repeated applications must be carried out at 5-10 day intervals for effective control over a growing season. Application has been reduced compared to the 1990's and is restricted where drift may be prominent, i.e. high winds, and the subsequent mode of application is also restricted during growing season, as Fig. 2 reveals.

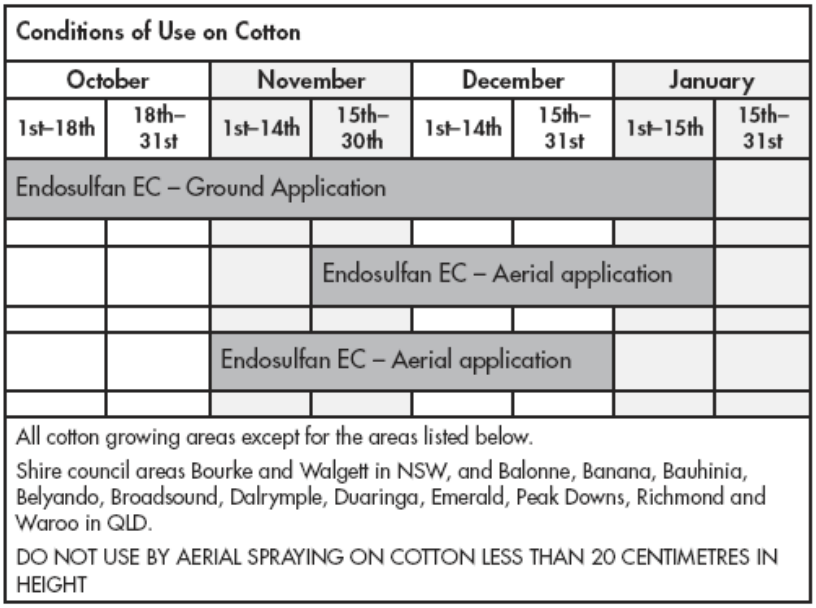


Fig. 2. In season mode of application recommendations for endosulfan (from Farrell & Johnson, 2005).

Fipronil is a broad spectrum insecticide. It is dispensed in Australia as a 200 g L^{-1} active fipronil component (Farrell & Johnson, 2005; APVMA, 2006). The compound is prepared as a solution and may be applied aerially or directly to the soil surface using a boom spray. The recommended application rate for cotton production ranges from 0.0625 to 0.125 L ha^{-1} of active ingredient, where water is the carrier (Farrell & Johnson, 2005). Application is restricted where drift may be prominent (Farrell & Johnson, 2005; APVMA, 2006).

Overall, application procedures vary between pesticides, with recommendations devised based on their potential to cause environmental harm.

(b) Modes of action

Upon application to the target medium, the actions of pesticides become apparent. The modes of action exhibited by pesticides are variable, with insecticides acting on insects and herbicides acting on weeds. The mode of action exhibited by pesticides is diverse and complex, the explicit details will not be discussed.

Once in the soil, diuron is absorbed by plant roots and translocated. The active component functions by retarding the photosynthetic process through binding to specific sites within the plant's chloroplasts. Specifically, diuron binds at the secondary quinone binding site of reaction centre II (RCII) exhibited in the photosystem II (PSII) apparatus (Zer & Ohad, 1995). There it retards, but does not prevent, the degradation of RCII-D1, D2 and CP43 proteins, manifested in tryptic reactions (Zer & Ohad, 1995). Tryptic reactions are catalysed by the enzyme trypsin which acts by breaking peptide bonds exhibited in proteins (Zer & Ohad, 1995). The resultant degradation of proteins is the prerequisite in a series of chain reactions that yield glucose ($C_6H_{12}O_6$), the principal carbohydrate utilised by plants as a source of chemical energy (Zer & Ohad, 1995; Knox, Ladiges, Evans & Saint, 2001). By retarding the photosynthetic yield of chemical energy results in a slow starvation of the plant and desiccation is induced (Zer & Ohad, 1995). There is no available data to suggest weed resistance toward diuron, explaining its success and continued use as a herbicide in Australian cotton production.

Fipronil and endosulfan both act on gamma-aminobutyric acid (GABA) receptors, the principal nerve transmitter of insects (Bloomquist, 1993; Hainzl & Casida, 1996; Le Corronc, Alix & Hue, 2002; Bloomquist, 2003). Furthermore, biological studies have revealed that fipronil interferes with the passage of chloride ions through the GABA-regulated chloride channel, thereby disrupting the central nervous system, while at sufficient concentrations death may be induced (Bloomquist, 1993; Hainzl & Casida, 1996; Tomlin, 1997; Fenet, Beltran, Gadji, Cooper & Coste, 2001; Le Corronc *et al.*, 2002; Ying & Kookana, 2002; Bloomquist, 2003). Subsequently, it is active against a variety of soil and foliar insects such as rice grasshopper, rice skippers, vine weevil, termites and black ants in agricultural, forestry, and pastoral zones as well as urban environments (Ying & Kookana, 2002). A distinct advantage of fipronil, as Le Corroc *et al*. (2002) revealed, is that it is one of the most selective of the insecticidal blockers of the GABA-gated chloride channel with a favourable safety factor between insects and mammals, compared to endosulfan. Consequently, fipronil's profound toxicity has been attributed to the trifluoromethylsulfinyl functional group that is not present in any other agrochemical, such as endosulfan. Furthermore, endosulfan has exhibited resistance in some insects (e.g. *Drosophilia*) as a consequence of alteration in the GABA

receptor (Le Corronc *et al.*, 2002; Bloomquist, 2003), and there is little evidence to suggest resistance toward fipronil.

(c) Toxicity

Diuron, endosulfan and fipronil are applied at variable times in the growing season to control problem pests. Through spray-drift or runoff, such pesticides may end up in waterways or surface waterbodies and subsequent exposure to humans and various other forms of biota is prominent (Peterson & Batley, 1993).

Diuron is slightly toxic to mammals. The oral dosage of chemical that kills 50% of the test population (LD50) in rats is 3400 mg kg^{-1}. However, the dermal LD50 is lower for rats at 2000 mg kg^{-1} (EXTOXNET, 1996a). Diuron is slightly toxic to birds where bobwhite quail exhibited a dietary concentration that killed 50% of the test population (LC50) of 1730 mg L^{-1}; Japanese quail, ring-necked pheasant and mallard ducks have an LC50 greater than 5000 mg L^{-1} (EXTOXNET, 1996a). Diuron is moderately toxic to fish and even more toxic to aquatic invertebrates with LC50 values ranging from 4.3 mg L^{-1} to 42 mg L^{-1} in fish, and from 1 mg L^{-1} to 2.5 mg L^{-1} for aquatic invertebrates (EXTOXNET, 1996a). Furthermore, diuron is non-toxic to bees (EXTOXNET, 1996a). The only reported human case of acute, oral exposure to diuron produced no significant symptoms or toxicity (EXTOXNET, 1996a).

Toxicology varies between the isomers of endosulfan, with α-endosulfan being more toxic than β-endosulfan. Its toxicity, however, is often reported collectively as endosulfan (EXTOXNET, 1996b; Marshall & Rutherford, 2002). Endosulfan is highly toxic, with reported oral LD50 values ranging from 18 to 160 mg kg^{-1} in rats, 7.36 mg kg^{-1} in mice, and 77 mg kg^{-1} in dogs (EXTOXNET, 1996b). Endosulfan exhibits high to moderate toxicity to bird species, with LD50 values in mallards ranging 31 to 243 mg kg^{-1}, and in pheasants ranging from 80 to greater than 320 mg kg^{-1} (EXTOXNET, 1996b). Endosulfan is very toxic to aquatic organisms. For four fish species, LC50 values were reported for rainbow trout, 1.5 μg L^{-1}; fathead minnow, 1.4 μg L^{-1}; channel catfish, 1.5 μg L^{-1}; and bluegill sunfish, 1.2 μg L^{-1} (EXTOXNET, 1996b). For two aquatic invertebrates, scuds and stoneflies, the LC50 values were 5.8 μg L^{-1} and 3.3 μg L^{-1} respectively (EXTOXNET, 1996b). Furthermore, endosulfan is moderately toxic to bees; however it is non-toxic to parasitic wasps and lady bird beetles and some mites (EXTOXNET, 1996b).

Endosulfan has exhibited predominant toxicological effect following acute exposure in humans, the result being over stimulation of the central nervous system (Queensland Health, 2001; Marshall & Rutherford, 2002). Toxicity may be attained by ingestion, skin contact, or

inhalation. Lethal poisoning in humans has been reported after ingestion of endosulfan, with the lowest reported dose being 35 mg kg^{-1} bodyweight (Queensland Health, 2001; Marshall & Rutherford, 2002). An Average Daily Intake (ADI) of 0.006 mg kg^{-1} day^{-1} has been set for endosulfan by a number of regulatory agencies, which is based on a No Observable Effect Level (NOEL) with an application of 100-fold inter- and intra-species safety factor (Queensland Health, 2001; Marshall & Rutherford, 2002).

Fipronil application can impact non-target aquatic organisms. Fipronil is acutely toxic to red swamp crayfish (LC50 = 14.3 mg L^{-1}) and white river crayfish (LC50 = 19.5 mg L^{-1}) (Schlenk, Huggett, Allgood, Bennett, Rimoldi, Beeler, Block, Holder, Hovinga & Bedient, 2001), adult grass shrimp (LC50 = 0.32 mg L^{-1}) (Key, Chung, Opatkiewicz, Wirth & Fulton, 2003), and the estuarine copepod (LC50 = 6.8 mg L^{-1}) (Chandler, Cary, Volz, Walse, Ferry & Klosterhaus, 2004). It is very toxic to freshwater bluegill sunfish (LC 50 = 0.083 mg L^{-1}) and rainbow trout (LC50 = 0.246 mg L^{-1}) (USEPA, 1996). Moderate toxicity has been shown for small mammals with LD50 of 10 mg L^{-1} reported for rats (USEPA, 1996). Fipronil is also toxic to birds with no observable effects reported for mallards or bobwhite quail at concentrations of 1000 mg L^{-1} and 10 mg L^{-1} respectively (USEPA, 1996). No data on human deaths have been found for fipronil, however being a neuro-inhibitor, it is likely to exhibit similar outcomes to that of endosulfan.

It has been shown that herbicides and insecticides exhibit unique modes of action, with diuron functioning as a photosynthesis inhibitor in plants, and endosulfan and fipronil acting as neuro-transmitter inhibitors in insects. The outcomes of their toxicity towards a target have also been shown to exhibit adverse implications toward non-target organisms, inclusive of humans, when applied to the natural environment. The recognition of toxicity posed to non-target organisms by diuron, endosulfan and fipronil, with reference to their mobility, has spawned the development of application recommendations, with criteria being devised specifically for cotton production as well as other agricultural practices.

IV. PERSISTENCE AND ENVIRONMENTAL FATE

Once applied to the environment, the fate of pesticides is controlled by many processes. Organic pesticides are widely considered to pose risks to human and ecological health. They are principally mineralized by microbial metabolism, photochemical degradation, or surface-catalysed reaction into inorganic compounds such as carbon dioxide, or ammonia (Baer &

Calvet, 1999; Jacobson, Dousset, Guichard, Baveye & Andreux, 2005). Kookana *et al*. (1998) conveniently defined the unique environmental attributes that dictate the persistence and fate of a pesticide in a diagram (Fig. 3). As Fig. 3 suggests, degradation generally encapsulates biotic and abiotic transformation, and a variety of transport and immobilisation mechanisms (Schnoor, 1992; Scheunert, 1993; Kookana *et al.*, 1998).

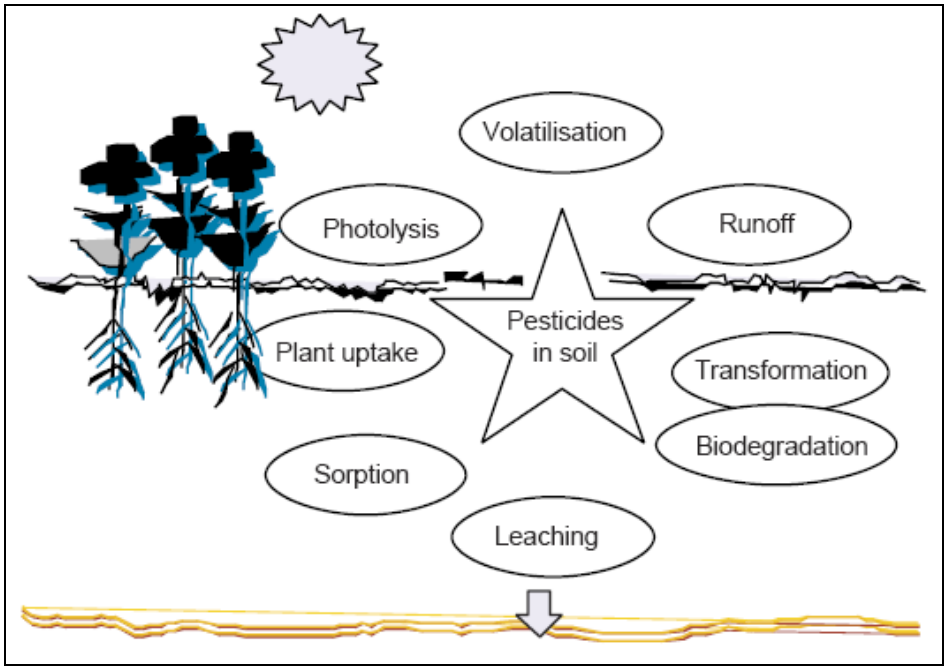


Fig. 3. Various processes determining the fate of pesticides in the environment (from Kookana *et al*. 1998).

The environmental persistence of a pesticide is often quantitatively defined by the respective half-life of a compound exhibited within a defined environment. These are governed by both biotic and abiotic processes. Biotic mechanisms in soil include plant uptake and microbial degradation, whereas chemical and photochemical degradation are abiotic processes. The environmental fate of a pesticide is governed by the various transport processes operating in the environment. These include volatilisation or drift through the atmosphere, leaching through the soil profile to aquifers and entrainment in surfacewater runoff.

The outcome degradation and transport processes results in the production of more potent and persistent compounds, and transference of toxicity to other unrelated areas, respectively. Degradation can be affected by many factors including changes in the physicochemical properties of the chemical and management of the soil through cultivation practices or fallow periods. Additionally, bioavailability of a compound can be reduced

because of complexation or sorption to soil solids. The ability of microbes to degrade a compound depends on its bioavailability, which in turn affects its longevity (Schnoor, 1992; Scheunert, 1993; Jacobson *et al.*, 2005). The literature reflects this by reporting half-life ranges; for example, diuron is considered to be moderately to highly persistent in soil with first-order half-lives ranging from 1 month to 1 year (EXTOXNET, 1996a), endosulfan is moderately persistent in the soil environment with a reported average half-life of 50 days in the field, and fipronil is considered as non-persistent with half-lives ranging from 36 hours (Bobe, Cooper, Coste & Muller, 1998) up to 188 days (Ying & Kookana, 2002) in the field. It is important to note that these half-lives have been derived from soils of different geographical locations, indicating that persistence is dictated by the environmental conditions exhibited by a site (Schnoor, 1992; Kookana *et al.*, 1998; Nkedi-Kizza, Shinde, Savabi, Ouyang & Nieves, 2006).

In light of these revelations, this section reviews the degradation and transport mechanisms that respectively govern the environmental persistence and fate of diuron, endosulfan and fipronil with reference to the main processes operating in the soil environment. The processes include degradation, soil sorption and transport.

(1) Degradation

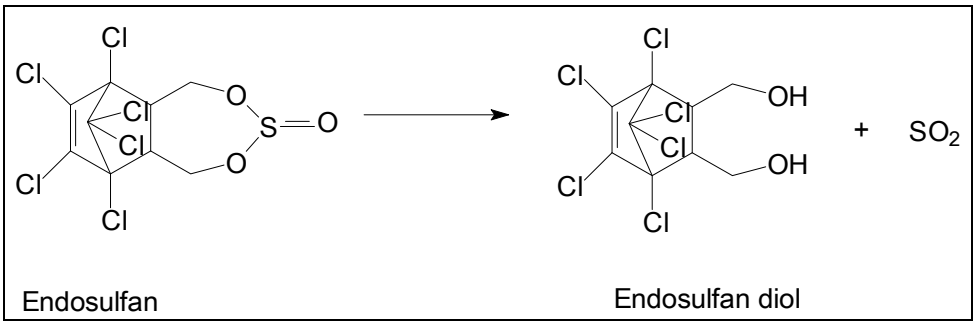
Degradation of a pesticide encapsulates the mechanisms by which the compound is chemically altered from its original state. The environmental processes that determine this outcome include photochemical, chemical and microbial degradation. It has been recognised, however, that most organic molecules do not significantly absorb solar light (Scheunert, 1993; Mazellier, Jirkovsky & Bolte, 1997). However, many publications report that diuron (Jirkovsky, Faure & Boule, 1997; Mazellier *et al.*, 1997; Lanyi & Dinya, 2005), endosulfan (Archer, Crosby & Nazer, 1972; Miles & Moy, 1979; Dureja, Walia, Tanwar & Mukerjee, 1987; Peterson & Batley, 1993) and fipronil (Bobe *et al.*, 1998; Connelly, 2001; Fenet *et al.*, 2001; Ying & Kookana, 2001; Walse, Pennington, Scott & Ferry, 2004; Zhou, Lu, Liu & Gan, 2004) do undergo photodegradation, with the consensus being that it is usually a minor pathway. Endosulfan, although photostable in solution, has been recognised to undergo photodegradation in the vapour state (NRA, 1998). Endosulfan's volatility, as will be revealed in a later section, suggests that this could be an important pathway in the atmosphere (NRA, 1998). Subsequently, however, chemical and microbial degradation pathways will be the main discussion focus for diuron, endosulfan and fipronil.

(a) Chemical Degradation

Chemical degradation reactions are mediated by reactive chemical species or molecular functions within soil, or by catalysis via non-living chemical species, such as metal oxides and organic or mineral surfaces (Scheunert, 1993). The extent by which a compound undergoes chemical degradation is commonly the outcome of its chemical nature and the conditions exhibited at a given site. The factors of most interest include pH, oxidation, reduction and hydrolysis. Diuron, fipronil and endosulfan have been reported to undergo chemical transformations with rates often reported to be much slower in the absence of microbes.

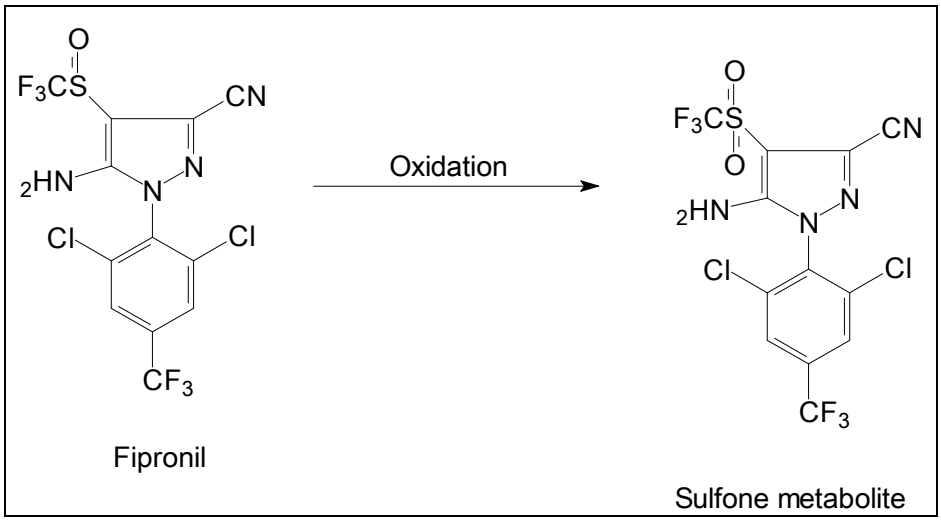
Diuron has been found to exhibit poor chemical degradation. Its higher solubility (36.4 mg L^{-1}) compared to endosulfan (0.32 mg L^{-1}) and fipronil (2.2 mg L^{-1}) has been attributed to be the result of its relatively polar nature. However, Sheng, Yang, Huang & Yang (2005) reported that diuron's electroneutrality indicates its poor ability to react with water and is further indicated by not exhibiting an acid dissociation constant (*pKa*). Chemical degradation has been reported to occur via oxidation and hydrolysis, however degradation is largely mediated by microbial action, which will be discussed in a later section.

Chemical degradation of endosulfan was reported by Kathpal, Singh, Dhankhar & Singh (1997) and Shivaramaiah *et al*. (2005) to be a minor route of dissipation at neutral pH. The only degradate yielded by chemical degradation is endosulfan diol (Kathpal *et al.*, 1997; Shivaramaiah *et al.*, 2005). This occurs through alkaline hydrolysis of the sulfite functional group (Reaction 1). Subsequently, endosulfan has been revealed to be stable in pure water at pH 5, with increasing rates of degradation observed between pH 7 and 9 (Kathpal *et al.*, 1997; Shivaramaiah *et al.*, 2005). Half-lives for α- and β-endosulfan at pH 5 are greater than 1 year, however at pH 7 and 9 the half-lives range 22 days to 7 hours and 17 days to 5.1 hours, respectively (NRA, 1998). This indicates that hydrolysis is pH dependent. Furthermore, Peterson & Batley (1993) showed that α-endosulfan consistently decayed faster than β-endosulfan at room temperature and 4^{o}C.



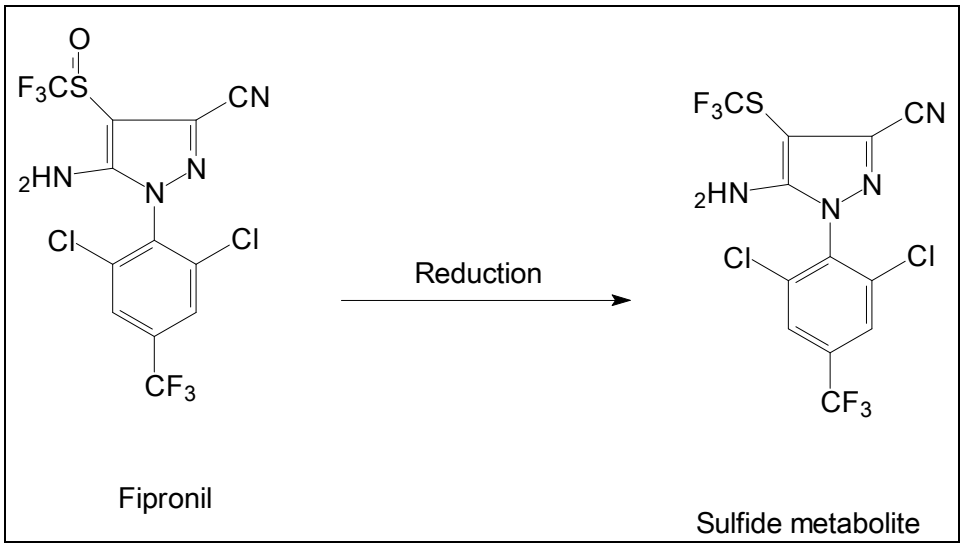
Reaction 1. Hydrolysis of endosulfan to endosulfan diol (after Shivaramaiah *et al*., 2005).

Degradation of fipronil in sterile soil has been revealed to be very slow (Fenet *et al.*, 2001; Ying & Kookana, 2002; Zhou *et al.*, 2004). The major degradates yielded include sulfone[1] and sulfide[2] products. The sulfone product is derived via oxidation of the sulfinyl group (Reaction 2) under well aerated soil conditions and with low moisture content (~15%) (Fenet *et al.*, 2001; Ying & Kookana, 2002; Zhou *et al.*, 2004). The sulfide degradate is yielded via reduction of the sulfinyl functional group. Rates of production were found to be enhanced under conditions of higher soil water content (30%), where the larger volume of water provides the required reducing conditions (Ying & Kookana, 2002). Rates of formation showed little variation with changes in temperature (Zhu, Wu, Guo & Kimaro, 2004), and fipronil is relatively stable under variable pH's (Tomlin, 1997).



Reaction 2. Oxidation of fipronil to sulfone metabolite (after Fenet *et al*., 2001).

[1] 5-amino-1-(2,6-dichloro-α,α,α-trifluoro-p-tolyl)-4- trifluoromethylsulfonylpyrazole-3-carbonitrile
[2] 5-amino-1-(2,6-dichloro-α,α,α-trifluoro-p-tolyl)-4-trifluoromethylthiopyrazole-3-carbonitrile



Reaction 3. Reduction of fipronil to sulfide metabolite (after Fenet *et al*., 2001).

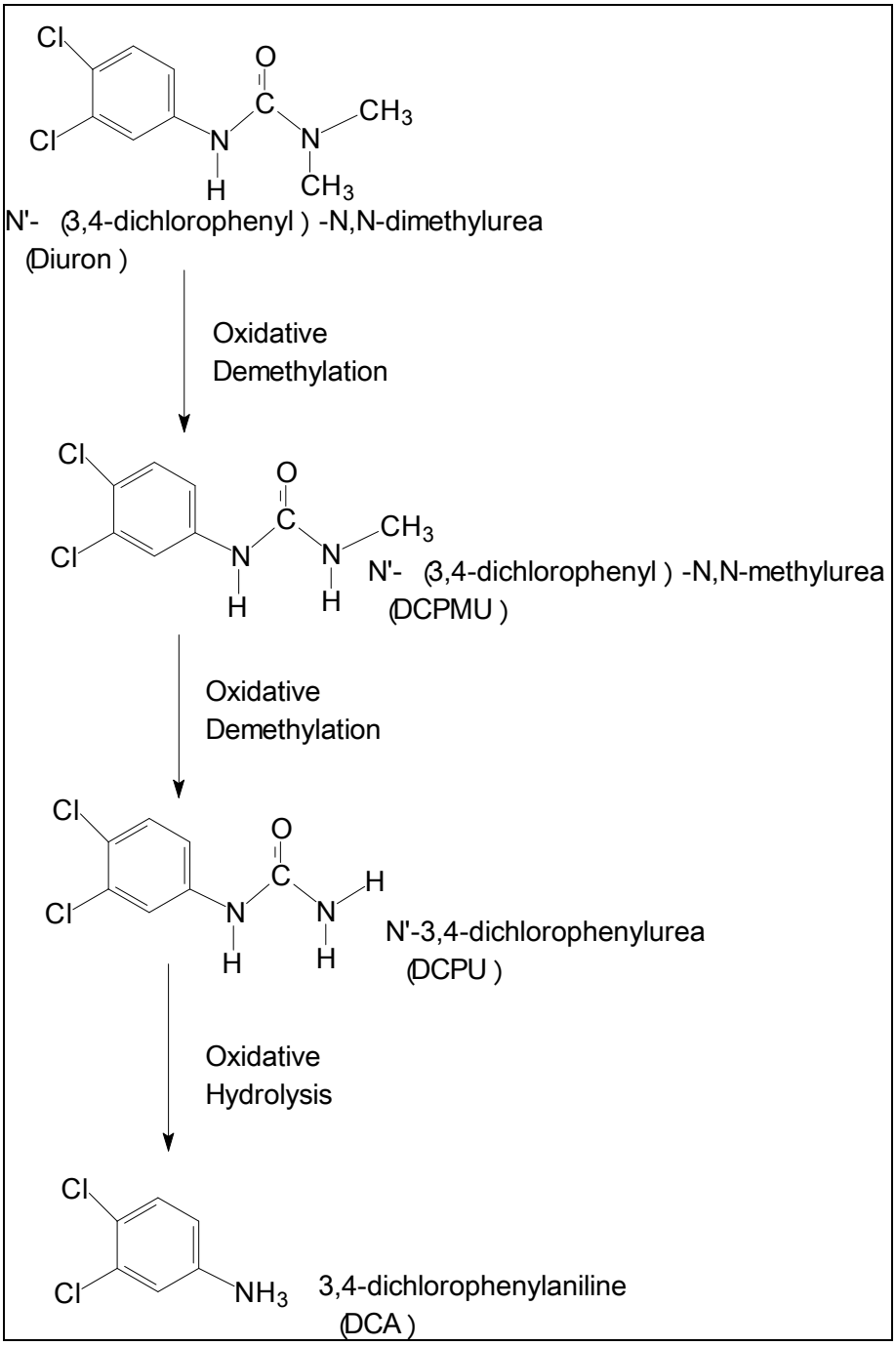
Overall, chemical degradation is a minor pathway for the dissipation of diuron, endosulfan and fipronil. Interestingly, similar results were observed for all chemicals regardless of their differing physical and chemical properties.

(b) Microbial Degradation

Biotic transformations in soil are principally those occurring in living soil organisms or catalysed by enzymes within or outside of cells (Scheunert, 1993). Enzymatic activity is often mediated by environmental conditions such as pH, water content, temperature and substrate concentration (Baer & Calvet, 1999; Knox *et al.*, 2001). Furthermore, microbial degradation of organic compounds is dictated by competition with other organic compounds exhibited in the soil, thereby limiting the overall rate of degradation (Baer & Calvet, 1999; Gooddy *et al.*, 2002). Microbial degradation in soil has been reported for diuron, endosulfan and fipronil.

Microbial degradation is considered to be the primary mechanism for diuron dissipation from soil (Gooddy *et al.*, 2002). Under well-oxygenated conditions, exhibited in a study by Gooddy *et al*. (2002), aerobic oxidative degradation resulted in successive demethylation of the urea group, followed by hydrolysis, to ultimately yield 3,4-dichlorophenylaniline (DCA) (Reaction 4). Rates of dissipation for diuron and other herbicides decreases with decreasing temperature and soil water content for a variety of soil types (Baer & Calvet, 1999). Microbial action on diuron has been revealed to be retarded by Cu toxicity, discovered after long-term application of Bordeux mixture (a blend of Calcium hydroxide and Copper (II) sulphate), in vineyards of France (Jacobson *et al.*, 2005). In practice, microbial populations are established before chemical application, and therefore

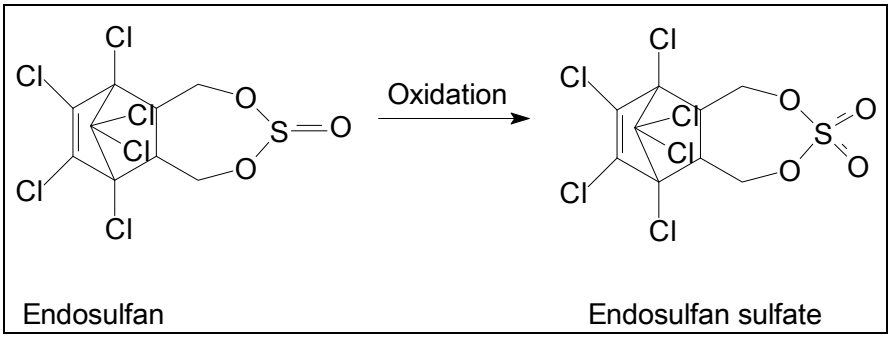
before any such degradation is considered to occur, the outcome of which is commonly a function of soil organic carbon content (Baer & Calvet, 1999; Gooddy *et al.*, 2002).



Reaction 4. Oxidative demethylation pathway of diuron (after Gooddy *et al.*, 2002).

Endosulfan breakdown by biological means occurs in soil and aqueous solution. It is widely agreed that endosulfan sulphate is the major biological degradate of endosulfan (Kennedy *et al.*, 2001), however endosulfan diol and endosulfan ether have been reported as minor metabolites (Peterson & Batley, 1993).

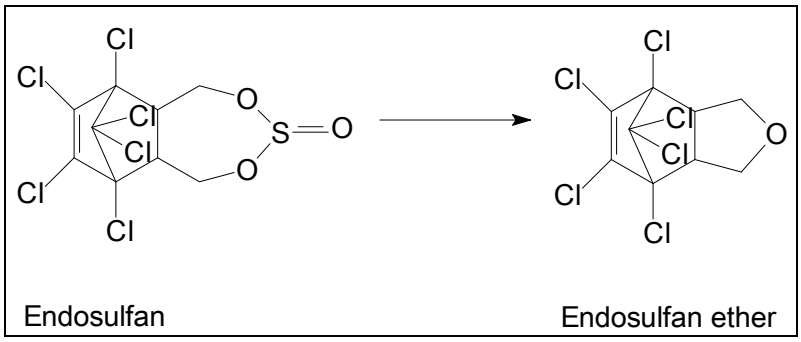
The metabolites of endosulfan sulphate and endosulfan diol are respectively yielded through oxidation and alkaline hydrolysis of the sulfite functional group (Reactions 5 & 1 respectively). Endosulfan sulphate is slightly less toxic but more persistent than α- and β-endosulfan (Peterson & Batley, 1993; Kennedy *et al.*, 2001; Leonard, Hyne, Lim, Leigh, Le & Beckett, 2001). Endosulfan sulphate is more likely to be found in sediments and soil where microbial populations are high (Peterson & Batley, 1993). Dissipation was studied by Awasthi, Ahuja, & Kumar (2000), under inoculated and uninoculated conditions of *Bacillus sp.*, and found to be dictated by pH, addition of organic carbon, moisture content, concentration of endosulfan, size of bacterial inoculum, and oxygen status of the harbouring medium. Degradation was revealed to occur five to six times faster under aerobic than anaerobic conditions (Awasthi *et al.*, 2000). Additional carbon sources were revealed to retard the rate of degradation because microbes appeared to favour them over endosulfan (Awasthi *et al.*, 2000). Variable parent isomer degradation rates has been attributed to their variable levels of toxicity and slight variation in chemical properties (Peterson & Batley, 1993). Shivaramaiah *et al*. (2005) confirmed that a declining rate of endosulfan sulphate formation was in response to endosulfan isomers being sorbed to sediment, making them unavailable for conversion.



Reaction 5. Oxidation of endosulfan to endosulfan sulphate (after Shivaramaiah *et al*., 2005).

Incubation of soil under light (2000 Lux) dramatically decreases the persistence of α-endosulfan and enhances its transformation to endosulfan sulphate, relative to dark-incubated soil samples, under both flooded and non-flooded conditions (Sethunathan, Megharaj, Chen, Williams, Lewis & Naidu, 2004). Degradation of soil-applied α-endosulfan was associated with profuse growth of indigenous phototrophic organisms such as algae in soil incubated under light (Sethunathan *et al.*, 2004). Inoculation of soil with green algae, *Chlorococcum sp.* or *Scenedesmus sp.*, further enhances the degradation of α-endosulfan. The role of algae in α-endosulfan degradation was convincingly demonstrated when degradation of α-endosulfan to

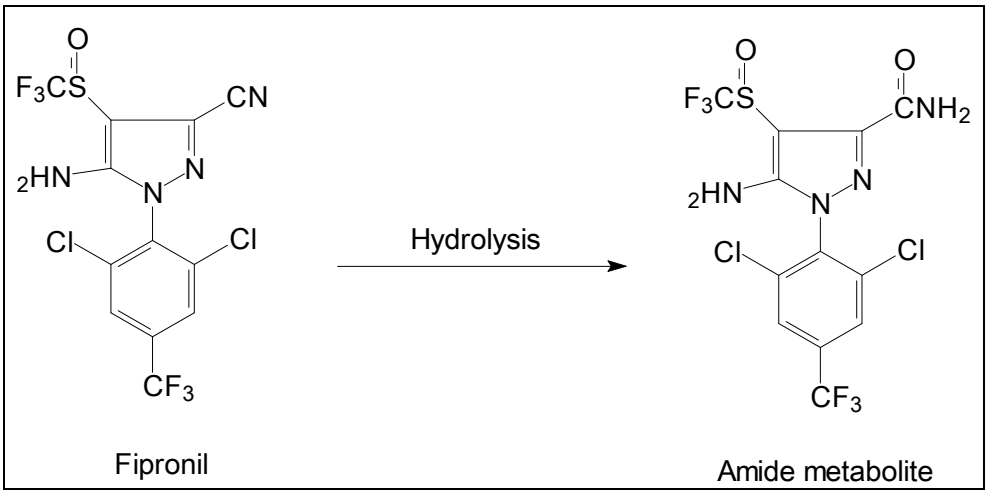
endosulfan sulphate and endosulfan ether (Reaction 6) in a defined liquid medium occurred rapidly (Sethunathan *et al.*, 2004). These phototrophic organisms, by generating oxic conditions through photosynthesis, are directly responsible for the enhanced oxidation of α-endosulfan in soil samples incubated under light (Sethunathan *et al.*, 2004).



Reaction 6. Conversion of endosulfan to endosulfan ether (after Shivaramaiah *et al*., 2005).

Biological degradation of fipronil yields three metabolites, the sulfide, sulfone and amide[3] compounds. Laboratory and field experiments produced the sulfone and sulfide derivatives via oxidation or reduction of the sulfinyl group respectively (Reactions 2 & 3 respectively) (Bobe, Coste & Cooper, 1997; Bobe *et al.*, 1998; Fenet *et al.*, 2001; Ying & Kookana, 2001). The amide metabolite results from the hydrolysis of the carbonitrile group, and is more polar than the parent compound (Reaction 7) (Bobe *et al.*, 1998). Bobe *et al*. (1998) confirmed that the production of the amide metabolite, occurring sometime after application, was attributed to slow microbial action. Wetter soils favour the formation of sulfide and amide metabolites as these conditions provide better reducing and hydrolysing environments relative to drier conditions (Ying & Kookana, 2001). Further, microbial activity is significantly reduced in low moisture conditions, however the oxidative pathway is more prominent under these conditions (Zhou *et al.*, 2004; Zhu *et al.*, 2004). Zhou *et al*. (2004) reported that the degradation of fipronil occurred at a faster rate in the vegetable pakchoi (99.6%) than soil (85.9%), where reduction, oxidation and hydrolysis pathways were revealed to be the most significant pathways. Furthermore, temperature has been indicated to have some influence on the rate of biological degradation, where slightly faster rates have been reported for higher temperatures (35^{o}C) (Zhu *et al.*, 2004).

[3] (R,S)-5-amino-1-(2,6-dichloro-α,α,α-trifluoro-p-tolyl)-4-trifluoromethylsulfinylpyrazole-3-carboxamide



Reaction 7. Hydrolysis of fipronil to amide metabolite (after Fenet *et al*., 2001).

Microbes mediate a significant degradation pathway for diuron, endosulfan and fipronil. In most cases, they catalysed reactions not observed for chemical degradation pathways, and often at significantly faster rates. Furthermore, the natural environment dictates the degradation rates and specific reaction pathways of compounds. Critical factors include water content, temperature, organic carbon, and pH. Complete understanding of these factors is limited because of the small number of studies reported in the literature.

(2) Sorption of diuron, endosulfan and fipronil to soil

Although the application target of agricultural pesticide may be foliage and/or soil, significant volatilisation and degradation of the pesticide deposit may occur. The remaining deposits are often washed off by rainfall or irrigation water into the soil, leached into the soil profile, or incorporated into the soil with crop residue (Wauchope, Yeh, Linders, Kloskowski, Tanaka, Rubin, Katayama, Kordel, Gerstl, Lane & Unsworth, 2002). Once in soil, pesticide residues partition between the aqueous and solid phases. Their distribution is described by sorption-desorption potentials (Schnoor, 1992; Ding, Novak, Herbert & Xing, 2002; Wauchope *et al.*, 2002). Sorption is the result of a complex series of equilibrium interactions between pesticide and soil components (Ding *et al.*, 2002). In essence, the extent to which a pesticide prefers one phase over the other is ultimately dictated by the physicochemical interactions exhibited between the pesticide and the harbouring medium and would overall provide an insight to the ecotoxicological potential of a pesticide in soil (Schnoor, 1992; Ding *et al.*, 2002; Wauchope *et al.*, 2002). In light of this, desorption is believed to be acting concomitant with sorption, the rate by which is often conveniently defined by the open-state equilibrium of the system. This reveals that sorption is not permanent and often hysteresis is exhibited for irreversibly bound

compounds. This section of the review will provide an insight to the factors used to estimate sorption and how certain factors operating in the soil environment have been defined to dictate sorption and desorption of diuron, endosulfan and fipronil.

(a) Characterisation of sorption

Sorption is generally characterised by a simple linear model, namely the partition coefficient K_d (Equation 1). The K_d value is simply a ratio of the sorbed phase C_s (mg kg^{-1}soil) concentration to the solution phase concentration C_e (mg L^{-1}) at equilibrium. It assumes unlimited sites (surfaces) for sorption, however other sorption models have been devised that essentially portray sorption as a site limiting process, such as the Freundlich model K_f. The rate by which sorption is attained is principally expressed by an adsorption isotherm and indicates the availability of sorption sites for a given soil (Wauchope *et al*., 2002). This entails the need to assess the change in concentration of a known solution with time, where linearity invokes sorption-desorption equilibrium. Furthermore, the capacity by which a soil may sorb pesticide is dictated by the solution concentration, which is varied to expose maximal sorption capacity. Overall, the rate by which equilibrium is attained is a function of available sorption sites, and the ease by which the compound may come into contact.

Equation 1. $$K_d = \frac{C_s}{C_e}$$

A high K_d is exhibited to be greater than 100, indicating that a pesticide is strongly sorbed and typically immobile. More problematic is that a high K_d often entails bioconcentration, hydrophobicity and insolubility (Schnoor, 1992; Ding *et al.*, 2002; Wauchope *et al.*, 2002).

Regarding K_d values, it has been further revealed by a variety of publications that the prevailing component that dictates pesticide sorption is organic carbon. This has been shown for diuron (Gaillardon, 1997; Gouy *et al.*, 1999; Roy *et al.*, 2000; Gooddy *et al.*, 2002; Yang & Sheng, 2003a; Yang & Sheng, 2003b; Sheng *et al.*, 2005; Landry *et al.*, 2006; Liyanage, Watawala, Aravinna, Smith & Kookana, 2006), endosulfan (Ghadiri & Rose, 2001; Marshall & Rutherford, 2002; Kumar & Philip, 2006) and fipronil (Bobe *et al.*, 1997; Bobe *et al.*, 1998; Ying & Kookana, 2001; Ying & Kookana, 2002; Mukherjee, 2006), and the majority of other pesticides (Kookana *et al.*, 1998; Wauchope *et al.*, 2002). Subsequently, Equation 1 has been modified to encapsulate this dominating outcome to yield the soil organic carbon (OC)

sorption coefficient K_{OC} (Equation 2). Equation 2 indicates the degree of sorption (K_d) as a result of the soil organic carbon fraction F_{OC}. Ultimately, this function regards the organic fraction as independent of soil (Ying & Kookana, 2001). A comprehensive summary of this interaction has been prepared for diuron, endosulfan and fipronil, and is given in Table 2. Notably, where the soil organic carbon fraction increases so too does K_d and K_{OC} thereby indicating the domination of the organic phase for sorption. K_{OC} is often used to characterise the mobility of pesticides in soil and is commonly reported with physical and chemical properties (Kookana *et al.*, 1998; Wauchope *et al.*, 2002).

Equation 2. $$K_{OC} = \frac{K_d}{F_{OC}}$$

Table 2 exhibits some disagreement manifested in the sorption of diuron, endosulfan and fipronil for different literature. This could be the outcome of variability in the experimental methodology; however, given the practice of sorption determination is quite uniform, (i.e. by batch or column experiments, with the former devised to assess fast sorption kinetics by way of agitation, and the latter to emulate soil profile or slow sorption kinetics) these outcomes are often described to be site specific (Vig, Singh, Agarwal, Dhawan & Dureja, 2001). In essence, sorption of diuron, endosulfan and fipronil are often defined by how the pesticide interacts with the harbouring environment; therefore, different environments result in different K_d (Scheunert, 1993; Hornsby *et al.*, 1996; Kookana *et al.*, 1998; Wauchope *et al.*, 2002; Nkedi-Kizza *et al.*, 2006).

Table 2. K_d and K_{OC} values of diuron, endosulfan and fipronil reported by publications, with reference to soil texture, location and % organic matter (as collated by the author).

Location	Soil Type	% Organic matter	K_d		K_{OC}		Reference
Diuron							
Roujan, France	Silt loam	0.60	1.94		323.00		Lennartz *et al.* (1997)
Mont Pellier, France	Silt loam	1.00	2.40		240.00		Lennartz *et al.* (1997)
Phillipines	Variable	1.05	5.5		579.00		Oliver *et al*. (2005)
Dijon, France	Dispered Clay loam	1.36	6 (K_f)		441.18		Gaillardon (1997)
Dijon, France	Undispered Clay loam	1.36	4.93 (K_f)		362.50		Gaillardon (1997)
Dijon, France	Undispered Clay loam	1.36	7.17 (K_f)		527.21		Gaillardon (1997)
La Jailliere	Sandy loam	2.00	9.60		480.00		Guoy *et al*. (1999)
Arkansas, USA	Sandy Loam	2.10	4.60		219.05		Sheng *et al*. (2005)
Arkansas, USA	Sandy Loam	2.10	3.51		166.67		Sheng *et al*. (2005)
Arkansas, USA	Sandy Loam	2.10	0.06		2.74		Sheng *et al*. (2005)
South Australia	Variable	2.23	14		618.00		Oliver *et al*. (2005)
Florida, USA	Carbonatic silt loam	2.40	2.90		121.00		Nkedi-Kizza *et al*. (2006)
Florida, USA	Carbonatic sandy loam	2.50	3.18		127.00		Nkedi-Kizza *et al*. (2006)
North East, Western Australia	Variable	2.83	14.9		536.00		Oliver *et al*. (2005)
Florida, USA	Carbonatic gravel loam	4.50	6.21		138.00		Nkedi-Kizza *et al*. (2006)
Florida, USA	Noncarbonatic fine sandy clay loam	4.60	16.84		366.00		Nkedi-Kizza *et al*. (2006)
Florida, USA	Noncarbonatic	44.00	186.56		424.00		Nkedi-Kizza *et al*. (2006)
Arkansas, USA	100% Wheat char	13	3594.00		27646		Sheng *et al*. (2005)
Arkansas, USA	Sandy Loam (1% Wheat char ammendment)	—	32.10		—		Sheng *et al*. (2005)
Endosulfan							
			α-endosulfan	β-endosulfan	α-endosulfan	β-endosulfan	
Jabiru Lagoon, Northern NSW, Australia	Sediment	0.50	21.00	36.00	3981.07	7943.28	Peterson & Batley (1993)
Psamments, Brazil	Sand	0.73	0.00	—	12600.00	—	Laabs & Amelung (2005)
Psamments, Brazil	Sand	0.73	0.00	—	7052.00	—	Laabs & Amelung (2005)

Table 2. (*cont.*)

Location	Soil Type	% Organic matter	K_d		K_{OC}		Reference
Boobora Lagoon, Northern NSW, Australia	Sediment	0.90	76.00	99.00	7943.28	10000.00	Peterson & Batley (1993)
Boobora Lagoon, Northern NSW, Australia	Sediment	0.90	85.00	143	10000.00	15848.93	Peterson & Batley (1993)
Jabiru Lagoon, Northern NSW, Australia	Sediment	1.30	133.00	137.00	10000.00	10000.00	Peterson & Batley (1993)
Jabiru Lagoon, Northern NSW, Australia	Sediment	2.20	82.00	144.00	3981.07	6309.57	Peterson & Batley (1993)
Ustox, Brazil	Medium clay	2.64	165.79	—	6280.00	—	Laabs & Amelung (2005)
Ustox, Brazil	Medium clay	2.64	231.50	—	8769.00	—	Laabs & Amelung (2005)
Boobora Lagoon, Northern NSW, Australia	Sediment	5.30	295.00	788.00	5011.87	15848.93	Peterson & Batley (1993)
Fipronil							
Ranchi, India	Sandy loam	0.07	2.05		2847.22		Mukherjee (2006)
Saguia, Niger	Sand	0.10	7.30 (K_f)		2511.89		Bobe *et al*. (1997)
Banizoumbou, Niger	Sand	0.30	4.30 (K_f)		3981.07		Bobe *et al*. (1997)
Mintaro, South Australia	Clay loam	0.51	13.84		829.00		Ying & Kookana (2001)
Roseworthy Farm, South Australia	Sandy Loam	0.68	5.34		1047.00		Ying & Kookana (2001)
Nagpur, India	medium clay	0.73	2.68		365.12		Mukherjee (2006)
Pt Wakefield, South Australia	Sandy Clay loam	0.82	6.44		678.00		Ying & Kookana (2001)
Mountadam, South Australia	Sand	0.95	8.00		1176.00		Ying & Kookana (2001)
New Dehli, India	Sandy loam	0.95	4.01		421.66		Mukherjee (2006)
O'Halloran Hill, South Australia	Heavy clay	1.31	10.08		542.00		Ying & Kookana (2001)
Nuriootpa, South Australia	Clayey sand	1.67	7.62		929.00		Ying & Kookana (2001)
Turretfield, South Australia	medium clay	1.77	13.07		738.00		Ying & Kookana (2001)
Roseworthy Campus, South Australia	Sandy loam	1.86	8.63		659.00		Ying & Kookana (2001)
Montpellier, France	Sandy clay loam	6.50	45.50 (K_f)		630.96		Bobe *et al*. (1997)

Sorption of diuron, as with most pesticides, varies with soil type and conditions. Gaillardon (1997) investigated desorption of diuron sorbed on dispersed and undispersed clay loam soil, and the influence of residence time in soil on desorption. Rapid adsorption by way of batch experiment mainly occurred over a 24 hour period, for a 0.6-3 mg kg^{-1} and 70% moisture content treatment. Column experiments revealed equilibrium attainment for 2-3 weeks. Desorption was rapid (1 hour) and only involved a small fraction of the adsorbed herbicide indicating hysteresis (Gaillardon, 1997). Long-term sorption has been postulated to be a consequence of slow diffusion into organic matter and/or small pores. Furthermore, diffusion forces into a low concentration soil solution were not sufficient to disrupt this rate limiting mechanism (Gaillardon, 1997).

Sorption of diuron is significantly correlated with soil organic matter content (Yang & Sheng, 2003b; Sheng *et al.*, 2005; Nkedi-Kizza *et al.*, 2006). This can be attributed to the abundance of polar groups exhibited in the hydrophilic regions on the surface of organic residues, which results in dipole-dipole attraction, particularly at higher moisture contents (e.g. phenolic hydroxyl groups, carboxylic acid groups, etc). This was confirmed by Roy *et al*. (2000) who found, that at low soil moisture content (< 26%) and modification of humic substances results in an increase in the number of hydrophobic surfaces (Fig. 4A) and thereby decreased the overall sorption of diuron (K_d = 8.1), but enhanced the sorption of more hydrophobic compounds, like endosulfan and fipronil. At higher moisture contents (46.6%), the hydrophilic interactions become more apparent (Fig. 4B) and sorption of diuron is more pronounced (K_d = 33.6) (Roy *et al.*, 2000).

Nkeida-Kizza *et al*. (2006) showed that for carbonate rich soils (>40% carbonate in whole soil) with similar organic carbon content (2.5-4.5%) to carbonate poor soils, exhibited lower K_{OC} for diuron. This was attributed to differences in the type of organic matter between the two soils, which Liyanage *et al*. (2006) also postulated. Sheng *et al*. (2005) publicized that sorption onto clay minerals alone was hindered by large substituents exhibited on the aromatic ring of diuron (two chlorines and N,N-dimethylurea). Gaillardon (1997) reports that adsorption of diuron was more adsorbed on a dispersed soil (K_f = 6.00) relative to undispersed soil (K_f = 4.93), where diffusion onto the surface was enhanced by the large effective surface area exhibited by the dispersed soil. Sorption of diuron in soil is not influenced by pH, due primarily to its electroneutrality (Sheng *et al.*, 2005), however Liyanage *et al*. (2006) suggests that pH has an indirect impact on sorption by way of altering the nature of organic matter, such as its state of ionisation. Overall, sorption of diuron is enhanced by soil organic matter and higher moisture content, with minor pH influence.

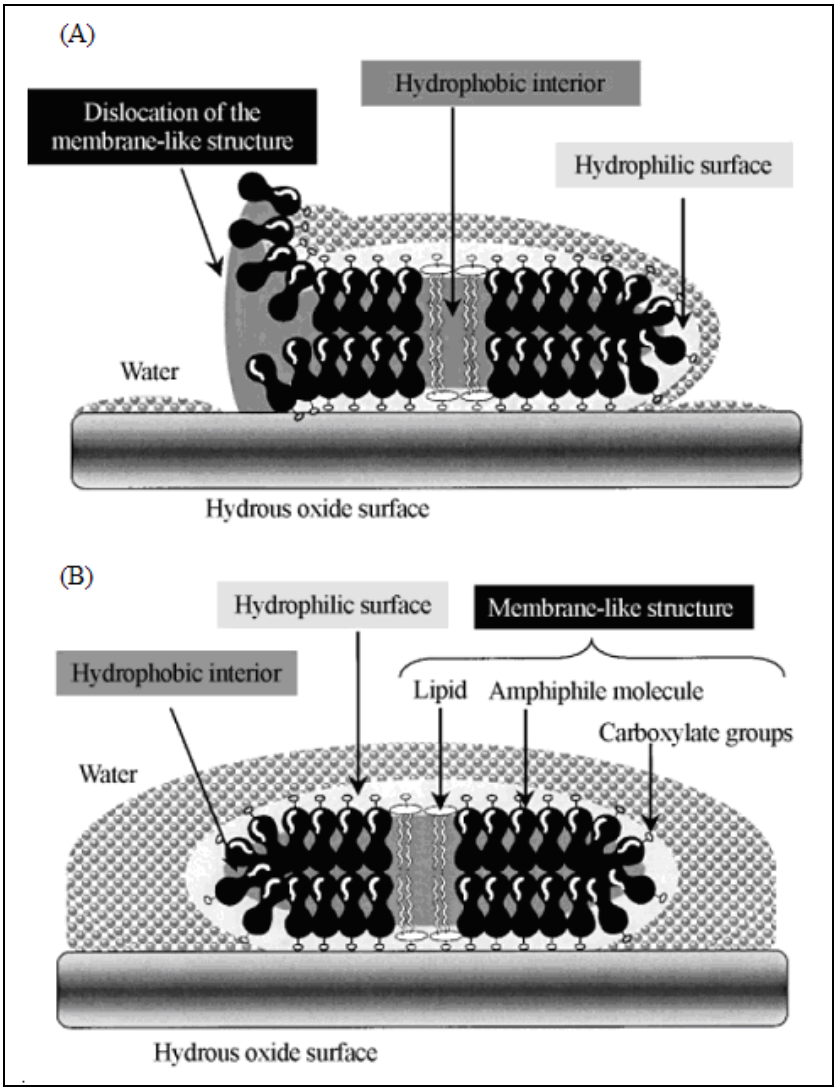


Fig. 4. Humus membrane-like structure attached to hydrous oxide surface at low (A) and high (B) soil moisture content (after Roy *et al*., 2000).

Endosulfan sorption is heavily dictated by soil organic matter. This is primarily explained by its very low solubility (0.32 mg L^{-1}) and high K_{OW} (average for α- & β-isomers = 4.76) which indicates a preference for hydrophobic media. Kumar & Philip (2006) investigated the sorption and desorption of endosulfan for a variety of soils. The sorption exhibited was rapid, with equilibrium reached in a short period of time (1.5 hours) in sandy soil, and slightly longer for clay and composted soils (4 hours) (Kumar & Philip, 2006). Decreases in organic matter content have often been reported to result in decreases in sorption potentials, with reduction in rates often more pronounced for β-endosulfan than α-endosulfan (Peterson & Batley, 1993; Leonard, Hyne, Lim & Chapman, 1999; Leonard, Hyne, Lim, Pablo & Van den Brink, 2000; Leonard *et al.*, 2001; Kumar & Philip, 2006). The partition

coefficients for β-endosulfan are consistently higher than α-endosulfan ($K_{OC\alpha}$ 3981 and $K_{OC\beta}$ 19 952) (Peterson & Batley, 1993). This has been attributed to their differences in interaction with the organic molecules, the details of which are unclear (Kumar & Philip, 2006).

Similar to adsorption, desorption of endosulfan is faster in sandy soils (0.575% organic carbon) relative to clay (2.29% organic carbon) and composted (9.51% organic carbon) soils (Kumar & Philip, 2006). The presence of organic matter decreases the desorption potential (Kumar & Philip, 2006). Given that α-endosulfan exhibits a lower K_{OC} than β-endosulfan, indicates that the former is the most susceptible to desorption than the latter. It follows that α-endosulfan is often the parent compound reported to undergo degradation to yield endosulfan sulphate because of this increased availability (Leonard *et al.*, 1999; Leonard *et al.*, 2000; Leonard *et al.*, 2001). Overall, sorption and desorption of endosulfan is strongly dictated by soil organic matter. In essence, the higher organic carbon content invokes greater persistence in a soil environment, which has ramifications for degradation processes occurring in soil.

Fipronil has been reported to have a high sorption affinity to soil organic matter. It exhibits a low solubility in water (2.2 mg L^{-1}), however, a moderate K_{OW} (4.0) and solubility in organic solvents, such as acetone (545 900 mg L^{-1}), infers its hydrophobicity. The average K_{OC} value for fipronil was revealed by Ying & Kookana (2001) to be 825 for eight varying South Australian soils. Bobe *et al*. (1997) and Mukherjee (2006) reported that fipronil has a low affinity for soil at low concentrations. This was attributed to the pesticide competing for sorption sites with the more polar water molecules. Given the lack in polarity and low solubility of fipronil, it does not have the potential to displace water molecules from the adsorption sites on soil particles thereby limiting its sorption potential. However, significant correlations with increasing soil organic matter and adsorption of fipronil have been observed (Bobe *et al.*, 1997; Ying & Kookana, 2002; Mukherjee, 2006). The outcome of this coincides with increasingly slow and irreversible sorption manifested in the strong hydrophobic forces of attraction (Mukherjee, 2006), similar to those exhibited for endosulfan. Subsequently, soil pH and clay mineral influence on adsorption is minor (Bobe *et al.*, 1997; Bobe *et al.*, 1998; Mukherjee, 2006). However, such factors were revealed to become most significant in soils low in organic matter (<2%) (Bobe *et al.*, 1997; Ying & Kookana, 2002; Mukherjee, 2006).

Adsorption of fipronil has also been revealed to increase as the soil:water ratio declined (Bobe *et al.*, 1997). This has been attributed to the increasing water content causing disaggregation of soil thereby enhancing the adsorption surface area. Furthermore, increasing

temperatures (from 22 to 35 °C) induces a significant increase in adsorption indicating that the fipronil adsorption process is endothermic (Bobe *et al.*, 1997).

It is strongly indicated that soil organic matter is a major factor for pesticide sorption by way of strong hydrophobic interactions. It was suggested by Kookana *et al*. (1998) and Baer & Calvet (1999) that it is superficial to suggest that organic matter as a whole is the main controller of sorption, regardless of its significance. They went further to suggest that underlying attributes intrinsic to the organic carbon, such as chemical nature and relative affinity for other chemicals, need to be considered (Baer & Calvet, 1999). Many publications hint at the importance of the various components that constitute organic matter, for example aromacity (Kookana *et al.*, 1998; Liyanage *et al.*, 2006); their respective roles in dictating sorption is unclear. Kookana *et al.* (1998) states that the organic factors which dictate sorption need to be characterised and quantified for their true impact on sorption so that site specific variation, such that exhibited by Liyanage *et al*. (2006) and Nkedi-Kizza *et al*. (2006), can be accounted for by region.

In conclusion, diuron, endosulfan and fipronil all exhibit a clear preference for sorption to soil, but these interactions are significantly dictated by the organic matter content of soil, the explicit details of which are ambiguous. Other factors that dictate sorption are the surface area exposure of the sorbent, concentration of the compound, and to lesser extent the pH, clay content and temperature. Further, sorption is variable across regions, and this has been attributed to the variable climate and soil conditions exhibited for a site, and the variability in the chemical nature of the organic compounds present in soil. The principal outcome to note from the process of soil sorption is an overall immobilisation of pesticide contaminants. However, sorbed material does have the potential to desorb, hence cumulative sorbed material may in fact be perceived as a contamination threat given that each sorbing entity is limited in its sorption potential.

(3) Transport

Pesticides applied to soil can move to surfacewater through runoff and erosion, to groundwater through leaching, and to the atmosphere through volatilisation drift (Schnoor, 1992; Scheunert, 1993). The focus of this review is purely hydrological processes; therefore atmospheric processes will not be discussed. However, it is important to note that many reports have revealed endosulfan volatilisation and drift to be a significant transport process (e.g. Rice, Chernyak, Hapeman & Biboulian, 1997; Kathpal *et al.*, 1997; Kennedy *et al.*, 2001; Marshall & Rutherford, 2002; Shivaramaiah *et al.*, 2005), and few reports have

suggested that diuron and fipronil move by this process. Subsequently, only runoff and subsurface (leaching) transport will be discussed in reviewing the fate of diuron, endosulfan and fipronil in the environment.

(a) Leaching

Leaching in soil encapsulates the infiltration of pesticides by way of detachment (or desorption from the soil in a liquid medium). Transport below the surface may occur purely as a solute load or bound to a sorbing media, namely colloids (Bradford, Simunek, Bettahar, Van Genuchten & Yates, 2003; Bradford, Bettahar, Simunek & van Genuchten, 2004; Kjaergaard, Moldrup, de Jonge & Jacobsen, 2004; Ranville, Chittleborough & Beckett, 2005). Since pesticides are unlikely to desorb, it has been revealed that desorption and effective transportation through a soil profile is facilitated by the dispersion of colloids from the soil surface.

Colloids or colloidal dispersions are entities that exist between the extremes of suspension and solution. That is, a dispersed (solute-like) substance (diameter <1 μm) which is distributed throughout a dispersing solvent-like substance (e.g. water) (Silberberg, 2003; Kjaergaard *et al.*, 2004; Ranville *et al.*, 2005). They may be single or an aggregation of molecules and exhibit a large surface area. In soil, they are characteristically layered silicates, sesquioxides (Fe- and Al-oxyhydroxides), organic macromolecules, and bacteria and viruses (microbes). They are derived from detachment as a consequence of raindrop impact or surface disaggregation as a result of land management (e.g. tillage), or from anthropogenic inputs (e.g. fertilisers) (Ranville *et al.*, 2005).

Colloid mobilisation is significantly dictated by the ionic strength and pH of soil solution, with direct association with isomorphous substitution and diffusion, and has limited associated with shear stress (Kjaergaard *et al.*, 2004). Additionally, physical mechanisms such as hydrodynamic shear stress generated by flowing water, flow transients manifested in temporal variability of moisture content and the movement of air-water interfaces, and colloid diffusion have been suggested to control the mobilisation of colloids (Kjaergaard *et al.*, 2004).

The diffusion potential D_p exhibited by a particle is governed by the Stokes-Einstein equation (Equation 4) which defines D_p as a function of the temperature T, viscosity μ_w, and particle diameter d_p. The extent by which colloids remain entrained in solution is governed by incessant and random motion occurring within the dispersing medium, known as Brownian motion (Silberberg, 2003; Kjaergaard *et al.*, 2004; Ranville *et al.*, 2005). From this, transport of colloidal particles through granular porous media can be described by an advection-

dispersion transport equation with terms for colloid deposition and release rates (Equation 5). It describes the evolution in time t of the colloidal mass or concentration c in suspension, and the colloidal amount deposited per unit mass of the porous matrix s_m, with an average particle velocity v_p exhibited within a porous medium being defined by porosity φ, bulk density ρ_b and length of the transporting column z, and hydrodynamic dispersion D_h as a function of c throughout the medium.

Equation 4. $$D_p = \frac{k_B T}{3\pi\mu_w d_p}$$

Equation 5. $$\frac{\partial c}{\partial t} = D_h \frac{\partial^2 c}{\partial z^2} - v_p \frac{\partial c}{\partial z} - \frac{\rho_b}{\phi}\frac{\partial s_m}{\partial t}$$

Transport of diuron, endosulfan and fipronil has been exhibited within porous media. They display variable responses to infiltrating water, the nature principally being defined by the transportation vehicle, i.e. water alone or particle facilitated.

Diuron's relatively high water solubility (36.4 mg L^{-1}) invokes a high leaching potential. Gooddy *et al*. (2002) and Landry *et al.* (2006) investigated the degradation and metabolite transport of diuron, in soil of the United Kingdom and France, respectively. Sorption of diuron was indicated to decline in effectiveness with depth in a soil profile, inline with reductions in organic carbon content (Gooddy *et al.*, 2002). It was further reported that where diuron infiltrates beyond the soil organic zone without degrading, there was little to prevent it leaching to groundwater reservoirs (Gooddy *et al.*, 2002).

Preferential flow mechanisms and coarse soil texture have been described to influence the transport of diuron down the soil profile (Gooddy *et al.*, 2002; Landry *et al.*, 2006). This is enhanced by infiltration of low ionic water, thereby promoting the dispersion and mobility of colloids and diuron through diffusion from soil (Bradford *et al.*, 2003; Bradford *et al.*, 2004; Kjaergaard *et al.*, 2004; Ranville *et al.*, 2005). The enhanced movement of diuron reduces the sorption potential to the solid phase, thereby enhancing the leaching potential (Gooddy *et al.*, 2002).

The diuron metabolites DCPU[4] and DCA[5] were reported by Gooddy *et al*. (2002) to exhibit peak concentrations arriving at depth (54 cm) before the parent compound. However,

[4] N'-3,4-dichlorophenylurea
[5] 3,4-dichlorophenylanaline

Landry *et al*. (2006) reported leachate under vegetated soil to consist primarily of the degradate DCPMU[6] (58% of 1.8 kg ha^{-1} application), for a 20 cm column. The presence of DCPMU was attributed to microbial action in the rhizosphere of plant roots (Landry *et al.*, 2006). The amount of herbicide that leached through the undisturbed 20 cm soil column within one year amounted to a small proportion (<1%) of the applied diuron. It was further indicated that grass-cover enhanced the retention and the degradation of diuron and reduced its transport potential through soil to groundwater. Therefore, the use of alternative soil management practices, such as grass cover, should be encouraged to preserve groundwater quality (Landry *et al.*, 2006). It has been concluded that diuron is a threat to and has been detected in groundwater reservoirs by Gooddy *et al*. (2002) and Landry *et al*. (2006).

The hydrophobic nature and high sorption capacity exhibited by α- and β-endosulfan generally invokes high persistence and poor ability to be translocated though a soil profile. The expectation of groundwater contamination by α- and β-endosulfan is therefore low (Marshall & Rutherford, 2002). Although, Lopez-Blanco, Cancho-Grande, Simal-Gandara, Lopez-Periago & Arias-Estevez (2005) detected endosulfan in groundwater reservoirs. Subsequently, the passage of a commercial emulsified formulation through a column of aggregated sandy loam vineyard soil of Ourense, Spain under simulated light rain was investigated (Lopez-Blanco *et al.*, 2005). Preferential flow and non-preferential flow paths in soil column were found to dictate movement of endosulfan in soil, by way of attachment to colloidal surfaces (Lopez-Blanco *et al.*, 2005). Previous studies indicated that endosulfan, as well as other pesticides, regardless of their partition coefficient, were transported to depths of up to 40 cm. Notably, retardation of the flow through these regions, higher for non-preferential flow, would dictate the residence time of solution and therefore the extent of partitioning (Lopez-Blanco *et al.*, 2005). K_d values of nonpreferential and preferential flow regions ranged from 2.06 to 9.94 L kg^{-1} and 68 to 729 L kg^{-1} respectively. It was therefore recommended that endosulfan should not be applied, or application be limited where soil wetness favours the formation and maintenance of preferential flow paths (Lopez-Blanco *et al.*, 2005) such that exhibited in cracking clay soils (e.g. Vertisol).

The leaching potential for fipronil has been characterised to be low. Minor leaching was observed by Bobe *et al*. (1998) for tropical soils of Niger, with no residues detected in soil layers deeper than 10 cm, with the exception of the amide degradate. Notably, the amide degradate is more polar and therefore more soluble than the parent compound (Bobe *et al.*,

[6] N'-(3,4-dichlorophenyl)-N,N-methylurea

1998). This was further substantiated by Fenet *et al*. (2001) who did not detect fipronil or associated metabolites below 5 cm of a soil surface. This indicates that fipronil has a high affinity for sorption to soil. Bobe *et al*. (1997) and Mukherjee (2006) reported that fipronil has a low soil affinity at low initial concentrations which was attributed to the pesticide competing for sorption sites with the soil solution. This indicates that to some extent fipronil can be mobilised. However, Mukherjee (2006) found strong hysteresis for fipronil on a variety of soil types, indicating desorption is unlikely and mobility is also very low. On average, most fipronil residues were contained within the top 10-12 cm of soil profiles. The potential for residues to be translocated down a soil profile and contaminate groundwater is therefore very low (Mukherjee, 2006). Potential colloid transport of fipronil has not been well characterised to date. Given the preferential flow transport exhibited by endosulfan, and subsequent contamination of groundwater, suggests that colloidal transport of fipronil, especially associated with dissolved organic matter, would be possible, the extent of such contamination would likely be minimal.

Overall, colloid-facilitated transport of pesticides, by way of leaching, is a significant process occurring in soil. The extent of leaching is dictated by preferential flow paths and the chemical and physical properties exhibited by the soil. However, diuron, endosulfan and fipronil are likely to be highly mobile in soils that lack sufficient organic matter, given that sorption is heavily reliant on this attribute. In light of this, mobile organic colloids are the best form of colloids to facilitate the leaching process.

(b) Runoff

Runoff is attained where intensity of water application, whether it be from precipitation or irrigation, exceeds the infiltration capacity of the soil (Fetter, 2001; Nett & Hendley, 2002). Irrigated cotton regimes employ this mechanism as a means of translocating water over a large area through irrigation channels, otherwise known as flood or furrow irrigation. The rate of overland flow is a function of the water application intensity and longevity, and landscape gradient and roughness (Bloom, 1998; Silburn, Simpson & Hargreaves, 2002; Robert, 2003; Silburn, 2003; Hillel, 2004).

Pesticides have the potential to be entrained in runoff. They may be transported in the solute or in sediment fractions of the flowing water. Fawcett *et al*. (1994) distinguished between three classes of agrochemicals according to their values of K_d. It was postulated that molecules with, K_d greater than 100 were mainly transported in run-off by sorption onto eroded particles. The extent of solution transport is dependent on the ionic nature of the

transporting medium, the solubility of the pesticide, time between application and runoff events, method of application and formulation (Kookana *et al.*, 1998). In essence, where pesticides are sorbed on the soil surface, desorption occurs where the diffusive force into solution exceeds that of the sorbing force. However, colloid detachment was recognised by Kookana *et al*. (1998) and Nett & Hendley (2002) to be a major pathway for pesticide transport. This was derived under the preconception that Australian soils have a high dispersion potential and that pesticides in general are unlikely to desorb into solution due to their largely hydrophobic nature. The extent of overall entrainment is governed by advection, dispersion, and molecular and turbulent diffusion (Schnoor, 1992; Logan, 1999).

Despite their different solubilities and K_d's, diuron and endosulfan have both been exhibited to have a high runoff transport potential. However, few publications indicate the entrainment potential of fipronil. There have been widespread reports of irrigation channel (Muller, Duquesne, Ng, Shaw, Krrishnamohan, Manonmanii, Hodge & Eaglesham, 2000; Kennedy *et al.*, 2001) and other forms of surface waterbodies contaminated by pesticides (Lennartz *et al.*, 1997; Leonard *et al.*, 1999; Leonard *et al.*, 2000; Leonard *et al.*, 2001). Endosulfan and diuron were the most frequent insecticide and herbicide detected in irrigation channels of Queensland respectively (Muller *et al.*, 2000). The highest concentrations were reported to be found in irrigation drains, as opposed to irrigation channels, which suggests that much of the pesticide movement occurs through post-application runoff (Muller *et al.*, 2000).

Kennedy *et al*. (2001) found that endosulfan losses through runoff during a cotton growing season, accounted for less than 2% of the total applied pesticides (750 g ha^{-1} application rate). Furthermore, a significant correlation between endosulfan residues and sediment loads in runoff water, both at on-field flumes ($R^2 = 0.78$) and outlets ($R^2 = 0.85$) of field drains, was reported. Much of the residues, however, were found in water as opposed to sediment. Given that endosulfan has a low solubility (0.32 mg L^{-1}), and high partition coefficient it was also inferred, by Kennedy *et al*. (2001), that residues were likely to be associated with suspended colloids. However, the amount of residue detected in runoff corresponded to on-field soil residues, which had some correlation with temporal variability for on-field concentrations (Kennedy *et al.*, 2001). Conversely, concentrations in runoff induced from a storm event were described to increase with time, as a result of increasing intensity of sheet erosion as the event progressed. Kennedy *et al.* (2001) further reported that a significant proportion of endosulfan entrained in runoff was found in the aqueous fraction, and only a small fraction associated with sediment, which Nett & Hendly (2002) attributes to

colloid entrainment in direct response to disaggregation induced by raindrop impact. Notably, the largest residues are often found at the soil surface, therefore attributing to the large concentrations detected in runoff to be associated with entrained sediment and colloids, which Silburn *et al*. (2002), Silburn (2003) and Hillel (2004) attributes to the sloping nature of the irrigation field, where Queensland characteristically has higher sloping irrigated cotton fields compared to New South Wales, and therefore exhibit greater sediment loss (Silburn, 2003).

Lennartz *et al*. (1997) revealed that uncovered surfaces contribute largely to runoff and erosion risk, and generally exhibits intensive weed control. The amount of diuron transported in runoff was revealed to be significantly enhanced for a non-tilled site relative to a tilled one in vineyards of France (Lennartz *et al.*, 1997). Furthermore, tillage was revealed to enhance infiltration and reduce herbicide use thereby limiting overland flow potential and reducing overall contamination risk (Lennartz *et al.*, 1997). No-tillage regimes on fine textured soils subject to intense rainfall and long, dry periods lead to crusting of the soil surface and therefore enhanced runoff and pesticide losses (Lennartz *et al.*, 1997). Muller *et al*. (2000) suggested movement of diuron to be in the colloid and solute fractions of runoff, due largely to its relatively low hydrophobicity manifested in its polar nature. This has provided the explanation to its detection in marine sediments of coastal sugar cane cropping regions of Queensland.

Muller *et al*. (2000) reports that irrigation drains are infrequently flushed. Endosulfan and diuron contamination of surface waterbodies was therefore attributed by intense storm events that have the potential to induce flooding. Furthermore, Leonard *et al*. (2001) attributed the detection of endosulfan sulphate in the Namoi River, several weeks after application had ceased, to field runoff generated by an intense storm event. A correlation for residence times made by Kennedy *et al.* (2001) showed that a 181 mm storm event, resulting in a runoff discharge of 130 ML, resulted in the removal of 1.2 kg of endosulfan. By extrapolation, if such an event were to occur immediately following application, the same percentage would have resulted in 2.5 kg of residues loss for a 750 g ha^{-1} application rate (Kennedy *et al.*, 2001). Gaillardon (1997) indicated an increase in the overall desorption of diuron where heavier rainfall events occur. It is therefore derived that storm events are the main attributers to surface water contaminations, and that losses are a function of time between storm events.

Significant amounts of pesticide can be transported by runoff to open waterbodies, the extent of which is a function of the time after application and time between runoff events. Furthermore, it appears that significant runoff events contribute to the largest off-site removal

of pesticides. This indicates that timing of pesticide application is critical, and weather forecasts should be monitored to effectively time applications in order to limit the off-site contamination potential through runoff due to pest management schemes. In addition, technologies exist, and continue to be developed, to retard and treat irrigation tailwater. The remainder of this review will focus on such technologies suitable for use on cotton and various other agricultural farms.

V. CURRENT REMEDIATION METHODS

Successful remediation of irrigation tailwater should effectively remove or constrain pollutants mobility in irrigation or storm runoff. There are a variety of commercial and on-farm methods currently available to cotton farmers by which pesticides can be constrained from transport off-site. Such technologies range in cost, and capacity and efficiency to remove or limit the transport potential of pesticides. This section of the review provides an insight to the current remediation techniques available to cotton farmers.

(1) Commercial remediation technologies

In remediation of contaminated tailwater, pesticides may be prevented from entering water by direct management of the soil. To provide scope, there are a variety of commercial technologies available to remove organic contaminants from soil. These technologies include soil washing, air stripping, soil disposal and thermal treatment. Notably, such techniques can be utilised for on- or off-site treatment, with the latter requiring physical removal, appropriate containment and transport to a treatment facility which attracts cost (Norris, Al-Dhahir, Birnstingl, Plant, Cui & Mayell, 1999).

Soil washing involves the use of alkali agents, hydrophilic cosolvents, viscofiers, and surfactants to enhance the removal of irreversibly bound contaminants to soil through liquid displacement upon flushing of the soil (Sikdar, Grosse & Rogut, 1998; Norris *et al.*, 1999; Khaitan, Kalainesan, Erickson, Kulakow, Martin, Karthikeyan, Hutchinson, Davis, Illangasekare & Ng'oma, 2006). On-site treatment poses greater risk to groundwater reservoirs, where leaching of contaminated solvents is an uncontrollable process (Khaitan *et al.*, 2006). Further, development costs to introduce this to a site has been shown to make this method unattractive (Norris *et al.*, 1999)

Air stripping is a method used to enhance oxygen pressure and air movement at depth. The outcomes being enhanced aerobic microbial degradation and/or promotion of volatile compounds to enter gaseous phase (Khaitan *et al.*, 2006). This practice attracts higher costs because of the higher air pressures required to induce a response over large areas (Khaitan *et al.*, 2006).

Soil disposal involves the physical removal of contaminated soil off-site and disposal at designated land-fill sites. This method is often employed for soils that exhibit extensive contamination, with other remediation technologies deemed ineffective for treatment (QldEPA, 2003).

Thermal treatment entails the application of heat to soil in order to desorb organic material through volatilisation. *In situ* methods include steam injection, hot water injection and electrical heating (Khaitan *et al.*, 2006). Off-site thermal treatment involves the removal of contaminated soil and transport to a facility, where incineration of the soil at high temperatures (>850 ^{o}C) takes place for highly contaminated soils (Norris *et al.*, 1999). The disadvantage of *in situ* methods is that the contaminant has the potential to be displaced to different regions of the soil or to the atmosphere (Khaitan *et al.*, 2006). Further, off-site methods utilise temperatures that are high enough to promote effective oxidation of the contaminant (Sikdar *et al.*, 1998). In most cases, all volatile material is captured in the process, inline with environmental regulations (Sikdar *et al.*, 1998; Norris *et al.*, 1999). This method is competent at achieving decontamination; however is very expensive (Sikdar *et al.*, 1998).

These technologies show profound complexity, which is reflected in their high cost for application particularly at the large-scale. It is important to note that many of these technologies, although highly effective in their cause, are utilised for once-off remediation of contaminated soil in small areas. Such techniques would therefore be unwarranted for large-scale cotton farming where crop production and use of pesticides is continuous in practice. Further, it has been shown that the most effective treatments, inline with all environmental protocols, were those carried out off-site. For a cotton farmer, however, this cites the removal of the growth medium for cotton plants, thereby profoundly crippling production. This has invited the need to develop more proficient on-site remediation techniques for cost-effectiveness and simplicity. Such technologies have been developed and will be discussed in the proceeding section.

(2) Viable cotton farm remediation technologies

Given the diversity of commercial remediation technologies available, more proficient means of tailwater treatment have been developed. Current remedies exploit a variety of mechanisms incessantly operating in soil. The remedies aim to control transport in runoff and limit the time by which the contaminants persist in water. The principal goal being to protect or buffer surfacewater exposed to various forms of biota. Most exploit microbial degradation pathways as a means of achieving remediation (Rose *et al.*, 2005a; Rose *et al.*, 2005b), while others physically contain contaminated water on-site (Kennedy *et al.*, 2001) or limit the transport potential from the soil (Bras, Santos & Alves, 1999; Yang & Sheng, 2003a; Yang & Sheng, 2003b; Sheng *et al.*, 2005). Some of these are typical of cotton irrigation farm of northern New South Wales, because they are cost-effective and easy to maintain, while others are still in the development stage (Bras *et al.*, 1999). This section of the review provides an insight to current technologies available through the assessment of physical containment, and binding media.

(a) Physical containment

Physical containment involves the utilisation or development of a reservoir designed to hold or capture contaminated water. Initially, such a technology was utilised on irrigated cotton farms to store extracted water for subsequent use in irrigation. Its use has been extended to capture irrigation runoff for reuse in irrigation, however this has allowed for the prevention of off-site transport of pesticide contaminated water.

Kennedy *et al*. (2001) described the benefits of physically containing irrigation and storm water runoff on-farm using holding dams. It was reported that endosulfan concentrations exhibited in irrigation tailwater, of irrigated cotton farms of northern NSW, is high enough for concern to wildlife. Capture of irrigation tailwater and storm runoff was reported to protect the greater environment. It has been revealed by Cotton Australia (2006) that on-farm holding dams are currently being employed as compulsory practice to protect vulnerable waterbodies, also observed in best management practice (Williams & Willams, 2000).

Kennedy *et al*. (2001) provided a diagram highlighting the mechanisms employed by modern irrigated cotton farms in Australia. It is important to note that cotton farms are setup with many channels designed to facilitate the movement of large water volumes (Fig. 5). Furthermore, Fig. 5 insights the reuse of irrigation tailwater, where water is initially pumped to a head-ditch, run over the field via incised furrows, and remaining runoff collected at the

taildrain. The runoff is then transferred through an outlet, pumped to a return drain and back to storage. Subsequently, no runoff leaves the irrigation site thereby limiting contamination of susceptible waterbodies, such as rivers, beyond the boundaries of the farm.

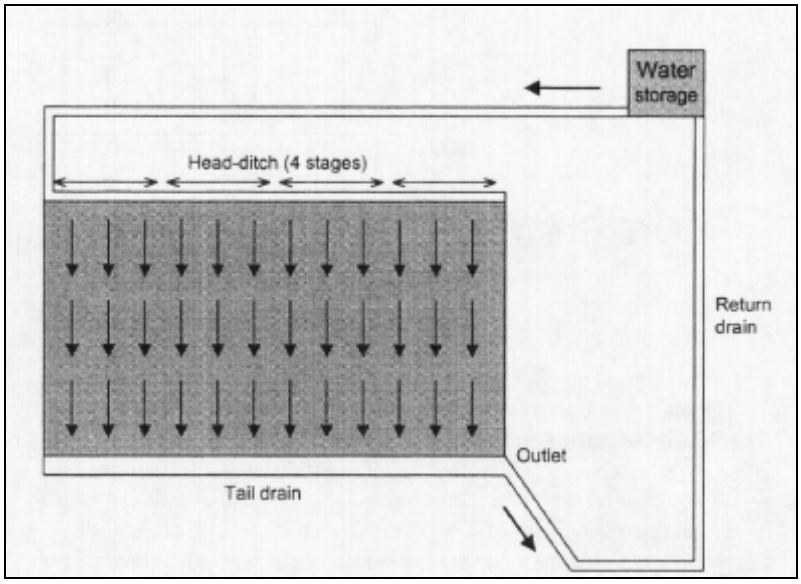


Fig. 5. Diagram of a typical cotton irrigation regime showing four irrigation stages and direction of water flow in the Namoi Catchment cotton growing area of northern New South Wales (from Kennedy *et al*., 2001).

(b) Binding media

Given that holding dams are being viewed as a means of physically preventing the off-site movement of contaminated tailwater, as highlighted by Kennedy *et al*. (2001), the exposure of contaminated water to wildlife is still prominent. This has invited the need to develop means by which pesticides remain on the farm and/or limit the exposure of contaminated water to wildlife while in the holding dams. This has been seen through the investigation of various binding media. Binding includes soil sorption and plant translocation as a means of limiting exposure, which also exhibit enhanced microbial degradation. Technologies include, soil organic amendments, subsurface filtration and phytoremediation through constructed wetlands.

Isabel *et al*. (1999) tested the capability of pine bark to remove organochlorine insecticides from water solutions. This was quantified by studying the best operating conditions for pine bark fixed bed mini-columns, the extent of removal from spiked water solutions, and assessment of saturation capacity. The extent of removal from spiked organochlorine water solutions, ranging from 1 to 10 g L^{-1}, was 97% on average for

heptachlor, aldrin, endrin, dieldrin, DDD, DDT, and DDE. Lindane was not as efficiently adsorbed (38%). Pine bark was revealed to display analogous response to that of activated carbon, which is one of the most efficient, but expensive sorbers of hydrophobic pesticides on the market. This suggests that for compounds with similar physicochemical characteristics pine bark will play a significant role, with direct reference to its cost-effective nature.

Yang & Sheng (2003a; 2003b) and Sheng *et al*. (2005) found that wheat char, derived from the burning of wheat stubble, was an effective sorbent of the herbicides diuron, bromoxynil, and ametryne. Competitive adsorption of dissolved soil organic matter and atrazine on the surface of a wheat char aged in a soil under environmentally relevant conditions slightly reduced the adsorptivity of the char. However, the adsorptivity remained high because of its initially high capacity indicating biogeochemical stability in the environment (Sheng *et al.*, 2005). Adsorption of diuron by the carbon fraction of chars from the burning of crop residues and grass was found to reduce the phytotoxicity of the pesticide, however enhanced sorption induced persistency in soil (Sheng *et al.*, 2005). Compared to soil, wheat char was 500-10 000 times more effective at sorbing diuron over the experimental concentration range (Sheng *et al.*, 2005). Yang & Sheng (2003a) report that wheat char was 400-2500 times more effective in sorbing diuron from water. A soil amendment of 1% wheat char contributed an 86% increase in the overall sorption potential of the soil (Sheng *et al.*, 2005). Wheat char was characterised to be on par with activated carbon, which is attributed to the extent of degradation induced by the burning of wheat stubble.

Rose *et al*. (2005a) investigated constructed wetlands on a cotton farm of northern New South Wales, Australia as a means of removing pesticides from contaminated tailwater. This highlighted the significance of aquatic plants in phytoremediation. Residue reductions ranging 22–53% and 32–90% were respectively observed over two growing seasons. Most significant reductions were observed in a vegetated pond, as opposed to an unvegetated pond, and also following an algal bloom. Notably, endosulfan and aldicarb residues were not able to be quantified following the algal bloom. Partitioning onto sediment was found to be a considerable sink for the insecticide endosulfan. These results demonstrated that macrophytes and algae can reduce the persistence of pesticides in on-farm tailwater.

Rose *et al.* (2005b) investigated the outcomes for enhancing natural removal processes by way of subsurface filtration and employing aquatic plants to enhance sedimentation of loaded irrigation tailwater into a holding dam. Gravel was employed as the harbouring medium for microbes which have the potential to degrade pesticides by way of enzymatic catalysis when contaminated tailwater was passed through the media. Subsequently, aquatic

plants were shown to increase sedimentation and significantly reduce the first-order total endosulfan half-life from 1.35 days to 0.77 days. Basalt gravel filter beds were shown to remove up to 41% of fluometuron (a herbicide) and 26% of total endosulfan over a 20 m distance during peak mass loading periods. Sub-surface filtration had greater benefits in that contaminated water remained inaccessible to fauna during treatment. Overall, the outcome was efficient removal of pesticides from contaminated water thereby limiting harm to exposed biota. The efficiency, however, was low and a more efficient binding organic medium was recommended.

Overall, Kennedy *et al*. (2001) reported the significance of physically containing irrigation tailwater onsite. However, given the results reported by Bras *et al*. (1999), Yang & Sheng (2003a), Sheng *et al*. (2005), Rose *et al*. (2005a) and Rose *et al*. (2005b) it can be derived that on farm sorption, particularly that associated with organic carbon amendments, may be a viable mechanism by which pesticides may be constrained from entrainment in runoff. More specifically, Rose *et al*. (2005b) highlighted the inefficiency of using a relatively inert gravel medium as a pesticide sorber. Given the majority of pesticides are hydrophobic and exhibit a preference for soil organic phase, exploitation of this was revealed to undoubtedly enhance sorption efficiency. More specifically, gin trash may offer a viable substitute for pesticide remediation of irrigation tailwater on cotton farms.

VI. THE POTENTIAL TO USE COTTON GIN TRASH TO REMEDIATE PESTICIDE CONTAMINATED TAILWATER

Gin trash is organic material produced during the cleaning and ginning of seed cotton, bolls or snapped cotton that principally has no economic value to the stakeholder (Smith, 2006). Rose *et al*. (2005b) suggested the implementation of gin trash as a pesticide sorption medium in subsurface filtration. Yang & Sheng (2003a), and Sheng *et al*. (2005) have also demonstrated the potential to retain pesticides in soil by way of adding organic amendments. The concept of utilising gin trash as an organic amendment and effective pesticide remediator has not been reported. Kennedy *et al*. (2001) reported endosulfan retention in cotton plant material, similar to gin trash, to have a half-life of 65 days, as opposed to 7.6-13 days for soil, suggesting significant retention capacity and lowered bioavailability. In essence, its sorption potential appears large but this requires substantiation.

Gin trash is recognised as a largely underutilised resource (Smith, 2006). Many publications have assessed its potential as a resource in other industries which Table 3 provides a summary. The extensive implementation of gin trash for these technologies is largely unknown.

Currently, the Australian cotton industry promotes active composting of gin trash and some work has assessed the potential for use as a fuel in electricity production for rural areas. In the 2003 Australian Cotton Industry Environmental audit, commissioned by the Cotton Research and Development Corporation, reported that gin trash is invariably utilised. However, it is not utilised as a stock feed because of the risk posed by pesticide residues exhibited within the trash (GHD, 2003). Further, gin trash was found to be stockpiled and composted on site, stockpiled at another site or transported to local farms for composting and utilisation as organic matter. It was also stated that gin trash was being used for landscaping purposes (GHD, 2003). Furthermore, the recognition that cotton farms utilise a lot of energy in production spawned the investigation into gin trash use as a biofuel in cogeneration of electricity through decomposition (GHD, 2003). Previously, gin trash was burned after harvest. However, NSW legislation has been devised to prohibit the burning of gin trash because of potential adverse environmental impacts (GHD, 2003).

Table 3. Current research on gin trash potential uses.

Gin trash use	Description	Reference
Compost	Comparison of windrow and Lipsey® composting systems	Gordon *et al*. (2001)
	Gin trash compost as a growing medium for ornamental plants	Papafotiou *et al*. (2001a; 2001b)
Biofuel	Methane production through anaerobic digestion	Funk *et al*. (2005)
	Gin trash economic feasibility as a fuel pellet	Holt *et al*. (2004)
	Developed oil and densified solid fuels from gin trash using extruder-feeder liquefaction process	White *et al*. (1996)
Stockfeed	Lamb growth in response to gin trash as a silage additive	Miron *et al*. (1995)
	Gin trash as a feed for cattle to minimise production cost	Rogers *et al*. (2002)
Contamination lagoon sealant	Shredded and compacted gin trash acting as an effective waste lagoon sealant relative to clay	Smith & Tollner (1999)

Overall, gin trash, contrary to Smith (2006), is a viable resource yet to be utilised (or recognised in its ability) in irrigated cotton farming as a means of removing contaminants from tailwater or inhibition of pesticide transport in runoff. However, research has revealed its possible beneficial utilisation in other forms of infrastructure, the extent of which is largely unknown.

VII. CONCLUSION

Although the introduction of GM cotton has reduced their application, pesticides are still widely used in irrigated cotton production, as this review shows. Their extensive use has brought many environmental impacts, the extent of which is dictated by the pesticides chemical and physical properties. However, pesticide impacts are not entirely eternal, as studies on the dissipation and fate of diuron, endosulfan and fipronil have shown to be dictated by many environmental attributes exhibited within the soil environment. The mechanisms of dissipation include photochemical, chemical and biological degradation, while sorption and transport processes dictate the fate of the pesticides in the environment. In some cases, the dissipation processes yielded more potent compounds, and their subsequent off-site migration become problematic to many forms of non-target biota.

Sorption to organic matter has been identified as the most significant process controlling the fate and dissipation of pesticides in the cotton growing environment. However, the shortfall of this connotation in the literature that organic matter is the principal sorbing medium in soil is its lack of chemical characterisation. This has been detailed through the identification of discrepancies in sorption data for diuron, endosulfan and fipronil.

Identification of toxicity from pesticides toward non-target biota, and under international pressure, prompted the development of best management practices and remediation techniques to limit environmental harm. Managing the off-site movement of pesticides has principally focussed on runoff. Subsequently, remediation techniques have been devised to exploit degradation and sorption mechanisms. Some of these technologies may be limited in their capacity, but their effectiveness could be sublime for the environmental cause. Considering this, gin trash has been identified as a large and underutilised resource on cotton farms with the potential to act as a sorption medium and principal goal of preventing or removing pesticides from entrainment. Such information or

characterisation of gin trash is not readily available, nor has it been identified in the literature suggesting the need for further research.

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PAPER II: THESIS

Pesticide Remediation of Irrigation Tailwater on Australian Cotton Farms: Composted Gin Trash as a Pesticide Sorption Medium

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Abstract. Pesticide concentrations currently detected in irrigation tailwater of Australian cotton farms are sometimes high enough for exposure concern. This paper investigates the potential use of composted cotton gin trash as a pesticide sorption medium in remediation of contaminated tailwater. Sorption and desorption of environmentally relevant concentrations of endosulfan sulphate and diuron to composted cotton gin trash was investigated using batch-equilibrium methods. A more dynamic sorption assessment was attempted by running break-through columns. Composted gin trash was found to contain a large organic matter fraction (25.22%), the majority of which expected to consist mainly of humic and fulvic compounds. Rapid sorption of endosulfan sulphate resulted in equilibrium (4 h). Similarly, diuron sorption was rapid but failed to reach equilibrium, even after two days. The partition coefficients K_d and the organic carbon partition coefficient K_{OC} showed diuron (K_d = 70.03; K_{OC} = 472.11) and endosulfan sulphate (K_d = 877.55; K_{OC} = 3480.22) to have a strong preference for the solid phase, particularly the organic carbon fraction. Sorption isotherms exhibited no limitation of diuron and endosulfan sulphate sorption for the range of applied concentrations. Desorption kinetics showed endosulfan sulphate to not desorb, however rapid attainment of desorption equilibrium (4 h) was observed for diuron, with limited desorption (30.7%). Desorption isotherms showed limited desorption (4.8-6.3%) for higher range applied concentrations (50-100 μg L^{-1}) of endosulfan sulphate, however all applied concentrations of diuron (1-500 μg L^{-1}) were shown to partially desorb (33.8-44.1%). The mechanisms of sorption and limited desorption was ultimately attributed to a combination of hydrophobic and hydrophilic interactions with the humic components of compost. An attempt to employ break-through columns to measure sorption-desorption yielded no measurable results due to poor column hydraulic conductivity and an organic leachate produced continuous 100% absorbance on the spectrophotometer. Overall, composted cotton gin trash was found to exhibit a profound sorption capacity for both diuron and endosulfan sulphate, to an extent that was superior to many sorbents reported in the literature. It is considered to have potential for remediation of tail waters.

Additional keywords: sub-surface filtration, humic micelle, herbicide, insecticide, sorbent.

Introduction

Pesticides in surface waterbodies can pose a significant hazard to various forms of biota if there is exposure. In 1985 the NSW State Pollution Control Commission (SPCC) recognised the threat of pesticide pollution of inland rivers from irrigated cotton farms (Muschal and Warne 2003). It was further found that inland rivers are a vital environmental resource, with a number of productive purposes, therefore warranting protection. Consequently, from 1990 the Australian cotton industry set out to devise a number of environmentally sound strategies aimed at off-setting adverse environmental impacts from cotton production. For example, recycling of irrigation tailwater was recommended.

More recent strategies are managed and detailed in the best management practices program (BMP) (Williams and Willams 2000). Pesticide management has been constrained to realistically manageable attributes of a cotton farm that involves care with irrigation tailwater and preventing farm runoff. As a more recent proposal, this paper focuses on pesticide remediation of irrigation tailwater, specifically through the assessment of composted gin trash as a potential sorption medium for three pesticides, diuron, endosulfan sulphate and fipronil.

Pesticide concentrations currently detected in irrigation tailwater of Australian cotton farms are sometimes high enough for exposure concern (Rose *et al.* 2005a). It is common practice that irrigation tailwater be retained in on-farm holding dams to protect vulnerable surface waterbodies, such as lakes and rivers (Kennedy *et al.* 2001). Exposure of biota from contaminated water, however, is still possible. This has justified the need for the irrigated cotton industry to investigate a number of mechanisms that may filter or remove pesticides from runoff or retain the pesticides on-farm as a means of buffering exposed waterbodies from contaminants.

Current methods of contaminated tailwater remediation involve exploiting a number of degradation and fate mechanisms commonly observed in the environment. Most exploit

microbial and phytobiological degradation pathways (Rose *et al.* 2005a; Rose *et al.* 2005b), while others aim to limit the transport potential of pesticides from the soil through the utilisation of sorption mechanisms (Bras *et al.* 1999; Yang and Sheng 2003a; 2003b; Sheng *et al.* 2005).

The most effective filter of organic pollutants is activated carbon, but its high cost makes it an unattractive means of filtering large volumes of water on cotton farms. It has been widely demonstrated, however, that soil organic matter and other organic amendments offer enhanced pesticide sorption capacity (Bollag *et al.* 1992; Cox *et al.* 2004). Taking advantage of such a mechanism for filtration of pesticides from tailwater is common in the literature, and uses of various composts have been demonstrated to be proficient at removing potentially hazardous concentrations of pesticides (Bras *et al.* 1999; Yang and Sheng 2003a; 2003b; Sheng *et al.* 2005). For example, Yang and Sheng (2003a; 2003b); and Sheng *et al*. (2005) found that wheat char, derived from the burning of wheat stubble, was an effective sorbent of the herbicides diuron, bromoxynil, and ametryne. A soil amendment of wheat char (1%), was revealed to contribute an 86% increase in the overall sorption potential of soil (Sheng *et al.* 2005). Isabel *et al*. (1999) found that pine bark was able to remove, on average, 97% of 1 to 10 g L^{-1} concentrations of the organochlorine insecticides heptachlor, aldrin, endrin, dieldrin, DDD, DDT, and DDE from water solutions. Both pine bark and wheat char were described to display analogous response to that of activated carbon. Rose *et al*. (2005a) highlighted the inefficiency of using basalt gravel, and to some extent woodchip, as a sacrificial sorption medium for a variety of pesticide contaminants in subsurface filtration because of insufficient biofilm colony formation. Subsequently, composted cotton gin trash has been identified to potentially fulfil such a role as both a soil amendment and/or use in other filtration mechanisms, such as sub-surface filtration (Rose *et al.* 2005a), in treatment or filtration of contaminated tailwater.

Composted cotton gin trash

The material derived from the cleaning and ginning of harvested cotton, known as gin trash, is composted to produce a product that is likely to be rich in humic-type organic compounds. Humification of organic substrates is the process that produces these polyphenolic compounds (Bollag *et al.* 1992; Cox *et al.* 2004). Such negatively charged polyphenolic compounds also have a high binding affinity for hydrophobic organic pesticides (Bollag *et al.* 1992; Cox *et al.* 2004). Cotton gin trash currently provides no economic value (Smith 2006), and there is no available data to indicate its pesticide binding ability. It has been utilised in a number of unrelated industries, however its current use as a soil amendment has been constrained due to quarantine issues with *Fusarium* sp. since gin trash may harbour the pathogen.

Sorption of pesticides

The usual method of assessing the binding capacity of a substrate is through sorption-desorption studies. Sorption is a mechanism that encapsulates both adsorption and absorption processes of attraction and is the result of a complex series of equilibrium interactions that exist between a pesticide and various soil components (Ding *et al.* 2002). The extent to which a pesticide prefers one phase over the other is a manifestation of the physicochemical interactions that exist between the pesticide and the harbouring medium. Understanding this provides insights into the likelihood of mobility of a pesticide in the environment (Schnoor 1992; Ding *et al.* 2002; Wauchope *et al.* 2002). The process of desorption is believed to act concomitantly with sorption, the rate often being conveniently defined by the equilibrium of the system. This reveals that sorption is not permanent and hysteresis is often exhibited for irreversibly bound compounds.

The soil sorption coefficient K_d and the soil organic carbon sorption coefficient K_{OC} are basic parameters used by environmental scientists and regulatory agencies to quantify

pesticide sorption interactions (Wauchope *et al.* 2002). A standard procedure, recognised worldwide, has been adopted by the Organisation for Economic Co-operation and Development (OECD) (2000) and is presently the common method used to investigate sorption of various chemicals. Another method increasingly used to assess sorption to various binding media, is running break-through columns. Such columns aim to assess sorption under conditions that simulate dynamic attributes of the natural environment (Burgisser *et al.* 1993).

Characteristics of three pesticides

Diuron, endosulfan and fipronil are three pesticides widely used in the irrigated cotton industry. Diuron is a soil applied pre-emergent herbicide used to control a number of broad-leaf weeds (Gooddy *et al.* 2002), as well as the defoliation of cotton. Diuron functions as a photosynthesis inhibitor, binding at the secondary quinone binding site of reaction centre II (RCII) exhibited in the photosystem II (PSII) apparatus of chloroplasts in plants (Zer and Ohad 1995; Gooddy *et al.* 2002). There it disrupts a series of reactions that normally aid the formation of glucose, the principal carbohydrate used by plants as a source of chemical energy. Such an interaction results in slow starvation and desiccation of the target plant. Diuron is characterised by having a highly polar urea functional group, attributing to its solubility in water (36.4 mg L^{-1}; Tomlin 1997); and non-polar, highly stable chlorinated aromatic ring, that results in its hydrophobic nature ($\log K_{OW}$[7] = 2.85; Tomlin 1997) (Fig. 1a). Crossan (2002) detected, on average, 25 μg L^{-1} of diuron in irrigation tailwater, and because of its solubility high concentrations are commonly detected.

Endosulfan is a broad spectrum insecticide that exists as two isomers, α- and β-endosulfan. The compound acts as a nerve agent, targeting the gamma-aminobutyric acid (GABA)-regulated chloride channels of nerve cells (Bloomquist 1993; 2003). The outcome of

[7] Octanol:water partition coefficient

its action being disruption of the nerve cell functions, resulting in the death of the target insect. It is characterised by an extensively chlorinated cyclohexane component and sulphite (SO_3) functional group (Fig. 1b). The compound is deemed insoluble in water (α-endosulfan = 0.32 mg L^{-1} and β-endosulfan = 0.33 mg L^{-1}; Tomlin 1997) and hydrophobic ($logK_{OW}$ = 4.74 and 4.79 for α- and β-endosulfan, respectively; Tomlin 1997). Its principal breakdown product is endosulfan sulphate that is yielded through microbiological oxidation of the sulphite functional group (Fig. 2) (Peterson and Batley 1993; Awasthi *et al.* 2000; Kennedy *et al.* 2001; Leonard *et al.* 2001; Shivaramaiah *et al.* 2005). It is the major degradate of endosulfan detected in irrigation tailwater and is more toxic to fish than its parent isomers (Leonard *et al.* 2001). They further suggested that high aqueous concentrations and persistence of endosulfan sulfate detected in water indicates it contributes to most observed toxicity to non-target aquatic biota in natural water bodies, compared to its parent isomers that are generally detected at much lower concentrations (Leonard *et al.* 2001). Kennedy *et al*. (2001) reported endosulfan residues in irrigation tailwater to range from 2.5-50 μg L^{-1}.

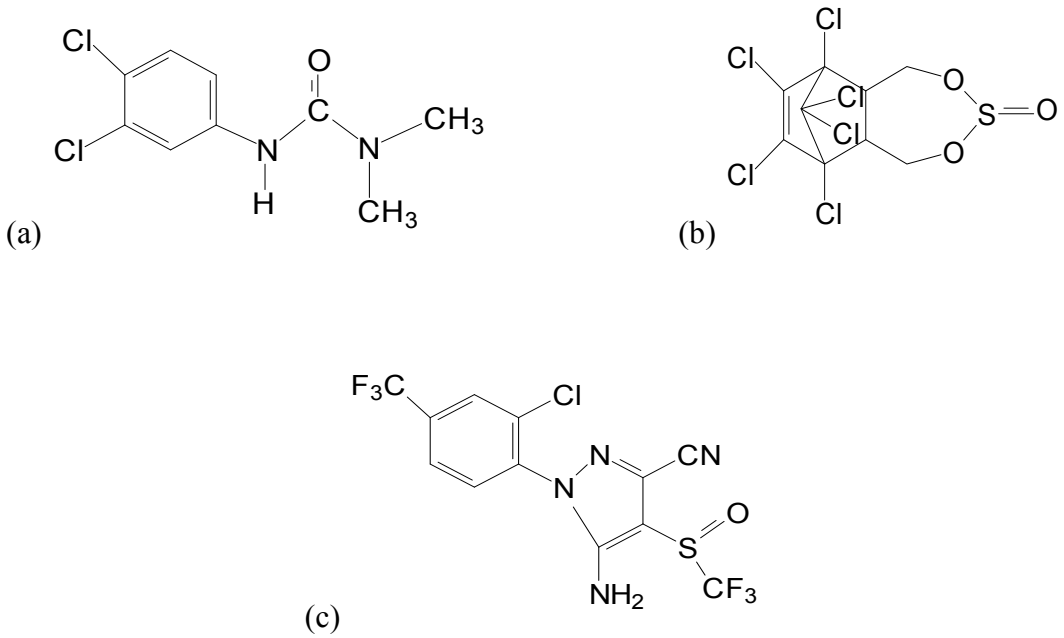

Fig. 1. Chemical structures of (a) diuron, (b) endosulfan and (c) fipronil (from Tomlin, 1997).

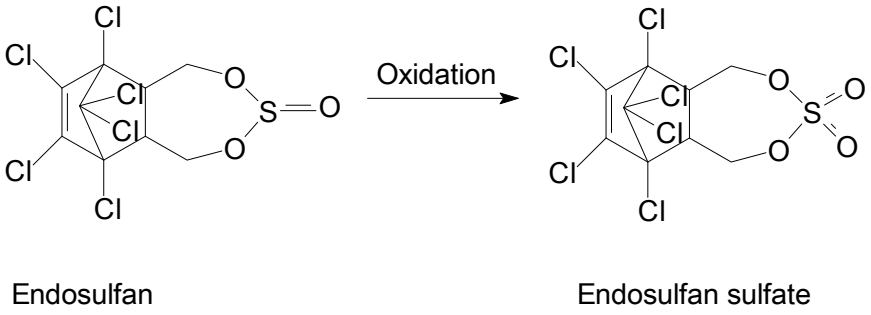

Fig. 2. Oxidation of endosulfan to endosulfan sulphate (after Shivaramaiah *et al*., 2005).

Fipronil is a broad spectrum insecticide that also acts as a nerve agent, targeting the gamma-aminobutyric acid (GABA)-regulated chloride channels of nerve cells (Bloomquist 1993; 2003). Fipronil is characterised by having a slightly polar trifluoromethyl and sulfinyl functional groups that attribute to its solubility in water (2.2 mg L^{-1}; Tomlin 1997); and very stable and non-polar phenylpyrazole functional group, that attributes to its hydrophobicity ($\log K_{OW}$ = 4.0; Tomlin 1997) (Fig. 1c). Fipronil is increasingly becoming the insecticide of choice in irrigated cotton production. There is little data available to indicate its presence in irrigation tailwater. However, because of its potential toxicity to non-target organisms as well as exhibiting properties that are comparable to both diuron and endosulfan sulphate makes this compound worthy of investigation.

Aims of this project

This paper investigates the sorption ability of composted gin trash for environmentally relevant concentrations of diuron and endosulfan sulphate. The project aimed to assess sorption through batch equilibrium studies, and potential sorption reversibility through batch equilibrium desorption. Furthermore, a dynamic assessment of sorption was assessed using break-through column studies. Time constraints to complete this project meant that fipronil was unable to be investigated for both sorption and desorption.

Methods

Sorbent

Composted cotton gin trash was collected indiscriminately from a large stockpile located at Auscott Ltd, Narrabri, north-western NSW, Australia (Fig. 3). Except for organic matter determination, the material was air-dried and sieved to a particle size of less than 2 mm and then oven dried at 105^{o}C for 24 h to homogenise the media (OECD 2000). Once oven dried, the material was stored in a sealed glass jar and kept at room temperature.

Fig. 3. Photographs of composted cotton gin trash stockpile (left) and collection of composted (right).

Organic carbon content

The organic matter and mineral content of the composted gin trash was determined using the weight loss-on-ignition (WLOI) method (Zhang *et al.* 2005). Four replicates of 10 g (± 0.1 mg) of fresh composted gin trash were weighed out into clean dry 20 mL crucibles (of known weight). The samples were oven dried at 105^{o}C for 24 h to remove moisture. The dried samples were then cooled in a desiccator containing $CaCl_2$ pellets at room temperature, weighed ($Weight_{105}$), and placed in a Gallenkamp muffle furnace. The muffle furnace heated the samples to 550^{o}C for 24 h and the samples were allowed to cool in a desiccator at room temperature and weighed ($Weight_{550}$) (Zhang *et al.* 2005). The material that did not combust

at 550^{o}C was assumed to be mineral matter, and all organic matter lost as CO_2 and H_2O (Zhang *et al.* 2005). The organic matter content was determined by Equation 1:

$$LOI(\%) = OM\% = \frac{Weight_{105} - Weight_{550}}{Weight_{105}} \times 100\% \quad (1)$$

Batch experiments

Two types of batch experiments, sorption and desorption, were performed on the composted gin trash. Both experiments involved the measurement of kinetic reactions, subsequently measured through time-series equilibration; and isothermic reactions between the sorbent (composted gin trash) and different concentrations of the sorbate (pesticide). The methodology used was optimised from the standard procedure endorsed by OECD (2000).

Chemicals and stock solution

Solid technical grade diuron (98.6% w/w) standard was donated by Nufarm, Australia and analytical grade endosulfan sulphate (>99% w/w) was purchased from Hoescht, Germany. Other chemical reagents and solvents were of pesticide residue analysis grade purchased from Crown Scientific, Australia.

Stock pesticide solutions of 1000 mg L^{-1} were prepared by dissolving 100 mg (±0.1 mg) of solid pesticide in 100 mL (±0.1 mL) of acetone. Intermediate stocks of 100 and 10 mg L^{-1} were also prepared by serial dilution of concentrated 1000 mg L^{-1} stock in acetone. Stock solutions were stored in 200 mL amber glass bottles and kept in a freezer (-20^{o}C).

Solutions of 0.01 M $CaCl_2$ and 2 mM $NaHCO_3$ were respectively prepared by weighing 2.2197 g (±0.0001 g) and 336 mg (± 0.1 mg) and dissolving in 2 L of nanopure water obtained from a Millipore NP instrument following deionization or distillation. All solutions were kept in sealed amber glass bottles at room temperature.

Sorption kinetics

Following K_d estimation techniques, outlined in OECD (2000), using the respective octanol:water partition coefficient (K_{OW}) for diuron and endosulfan sulphate, an adequate sorbent:sorbate ratio of 1:50 was devised.

Following the parallel method for sorption kinetics, 2 g (± 0.001 g) of oven dried composted cotton gin trash was accurately weighed and 100 mL of 0.01 M calcium chloride solution was decanted into a series of 250 mL conical flasks. The flasks were stoppered with aluminium foil lined rubber stoppers and allowed to equilibrate for about 12 h through gentle agitation at 120 rpm on a B Braun CERTOMAT® R orbital shaker. Using relevant volumes of 100 mg L^{-1} intermediate pesticide stock, final concentrations of 50 µg L^{-1} of diuron and 10 µg L^{-1} of endosulfan sulphate, variably found in irrigation tailwater (Kennedy *et al.* 2001; Crossan 2002), were spiked into designated flasks of compost/0.01 M $CaCl_2$ slurry, ensuring that no more than 100 µL (or 0.1%) of acetone was added (OECD 2000). All flasks were gently agitated at 120 rpm on a CERTOMAT® R orbital shaker and 50 mL aliquots were extracted from duplicate flasks for each pesticide at times 1 h, 3 h, 6 h, 9 h, 12 h, 24 h, 32 h and 48 h from spiking. Single blank flasks, without sorbate (pesticide), and duplicate controls without sorbent (compost) were extracted at 6 h and 48 h.

The respective conical flasks were removed from the orbital shaker and coarser suspended sorbent allowed to settle for approximately 5 min. The supernatant was decanted into 200 mL amber glass bottles, ensuring minimal agitation of the sorbent in solution. The amber bottles were capped with foil-lined lids and placed in a freezer (-20^{o}C) for later extraction.

In a subsequent experiment, sorption was measured over a 2 h period to assess kinetics at earlier time intervals, to that of the 48 h experiment. The same procedure as above was

followed, except duplicate flask aliquots were taken after 10 min, 20 min, 40 min, 1.5 h and 2 h from spiking.

Sorption isotherm

Using the same compost:solution ratio, a total of 14 flasks for each pesticide were prepared. Following 12 h slurry equilibration, duplicate flasks were spiked with relevant volumes of 1000 mg L^{-1} (diuron) and 100 mg L^{-1} (endosulfan sulphate) stock solutions to make final concentrations of 500, 250, 100, 50, 25, 10 and 5 μg L^{-1} of diuron, and 100, 75, 50, 10, 5, 2.5 and 1 μg L^{-1} of endosulfan sulphate (total of 14 flasks for each pesticide). Duplicate control flasks containing 250 and 25 μg L^{-1} of diuron and 75 and 5 μg L^{-1} of endosulfan suphate in 100 mL of 0.01 M $CaCl_2$ (without sorbent) were also prepared. All flasks were gently shaken and allowed to equilibrate at 120 rpm on a B Braun CERTOMAT® R orbital shaker for a time indicated by the time taken to attain equilibrium in the sorption kinetics experiment, for diuron and endosulfan sulphate (OECD 2000).

After equilibration, the flasks were allowed to stand for approximately 5 mins to allow for coarse compost material to fall from suspension. Slightly more than 50 mL of the supernatant, for diuron and endosulfan sulphate flasks, was decanted into 200 mL amber glass bottles and refrigerated for later extraction and analysis.

Desorption kinetics

Oven-dried composted gin trash (2 g ± 0.001 g) was added to 0.01 M $CaCl_2$ solution (100 mL) in a series of 200 mL Pyrex® centrifuge bottles. The bottles were capped with foil-lined lids and allowed to equilibrate for 12 h via gentle agitation at 60% speed on an end-over-end rotary shaker (400 mm diameter) driven by a 2318P Baldor Industrial motor and controlled by a Penta KB Power™ Vari-Drive® DC motor speed control. Individual centrifuge bottles were

spiked with relevant volumes of 100 mg L^{-1} diuron and endosulfan sulphate pesticide stocks, to make final concentrations of 50 μg L^{-1} and 10 μg L^{-1}, respectively. The centrifuge bottles were than allowed to equilibrate with the slurry for a time indicated by the sorption kinetics experiment. All bottles were centrifuged at 1500 rpm on a Dupont RC-5 Superspeed Refrigerated centrifuge for 10 min and the supernatant discarded. The discarded supernatant was replaced with 100 mL of 0.01 M $CaCl_2$ solution. The bottles were then mixed on a rotary shaker, and replicate bottles were centrifuged for 10 min at 1500 rpm after 1 h, 3 h, 6 h, 12 h, 24 h, 32 h, and 48 h from supernatant replacement. Slightly more than 50 mL of the supernatant was decanted into 200 mL amber glass bottles and refrigerated before extraction and analysis.

Desorption isotherm

A desorption isotherm experiment was run for the same pesticide concentrations used in the sorption isotherm experiment. The same compost:0.01 M $CaCl_2$ ratios were prepared in 200 mL Pyrex centrifuge bottles and allowed to equilibrate on a rotary shaker (60% speed) for 12 h. Individual duplicate bottles (total of 14 for each pesticide) were spiked with relevant volumes of 1000 mg L^{-1} of diuron or 100 mg L^{-1} endosulfan sulphate stock solutions. The bottles were allowed to equilibrate on a rotary shaker (60% power), centrifuged at 1500 rpm for 10 min on a Dupont RC-5 Superspeed Refrigerated centrifuge and the supernatant was discarded. The compost was resuspended in 100 mL of fresh 0.01 M $CaCl_2$ and gently shaken on a rotary shaker. Due to time constraints, the desorption equilibrium time was not estimated from the desorption kinetics, as suggested by OECD (2001). Instead, a 24 h equilibration time for endosulfan sulphate was devised from a 6 h desorption equilibrium time of α- and β-endosulfan observed by Kumar and Philip (2006) for a composted soil. The increased length of time was devised to encapsulate any desorption lag given the different type of sorbents

used. Given its dynamic nature, diuron desorption was allowed to equilibrate for the maximum allowable time (48 h) outlined in OECD (2000). Following equilibration, the centrifuge bottles were centrifuged at 1500 rpm for 10 min and slightly more than 50 mL of the supernatant was decanted into 200 mL amber glass bottles for later extraction and analysis.

Extraction and analysis of pesticides

Diuron

Diuron samples that were frozen were allowed to defrost at room temperature. A small portion (about 2 mL) of analyte was extracted and filtered through a 0.22 μm sartorius Minisart RC 15 single-use RC-membrane syringe filter into analysis vials. The samples were analysed using an Applied Biosystems 3200 Q Trap LC/MS/MS, equipped with a Shimadzu SIL-20A Prominence autosampler, Shimadzu LC-20AD Prominence liquid chromatograph, and Shimadzu DGU-20A_3 Prominence degasser, located at Agrisearch Analytical, Sydney (Fig. 4). Concentrations were devised by preparing a standard curve with stock standards redissolved in 50:50 acetonitrile:water after evaporation of acetone. An example of instrumental response is given in Appendix 1.1, together with a generated standard curve used to ascertain concentrations of unknowns.

The method used to prepare diuron for analysis was substantiated by preparing triplicate 50 μg L^{-1} diuron standards in 0.01 M $CaCl_2$ (100 mL) solution. Subsequent analysis yielded 95% (± 1%) recoveries.

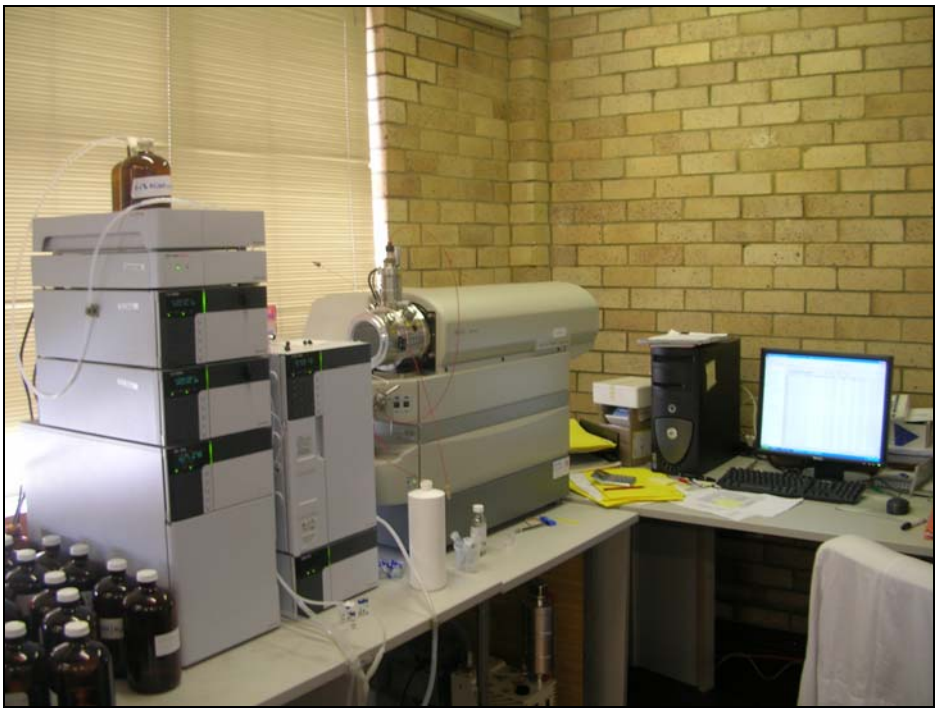

Fig. 4. Photograph of LC/MS/MS used to analyse samples for diuron.

Endosulfan sulphate

Frozen endosulfan sulphate aliquots (inclusive of blanks and controls) were allowed to defrost at room temperature (20-25^{o}C). The aliquots were shaken for one minute with 5 mL of dichloromethane in a Teflon® separating funnel three times. The dichloromethane solvent was passed through anhydrous sodium sulphate (about 3 g) suspended by non-adsorbent cotton wool in a glass filter funnel. The combined extracts were collected into a 100 mL pear-shaped flask, evaporated to near dryness on a Buchi Rotavapor R-114 rotary evaporator with a Buchi B-480 water bath (60^{o}C) and an LKB 2219 Multitemp II thermostatic circulator (4^{o}C) used for the cooling of vapour; and exchanged three times with 5 mL of hexane. After the final evaporation, the volume was made up to 0.5 mL with hexane. The volume was recovered for gas chromatographic (GC) analysis, after filtering through 0.45 µm sartorius Minisart SRP 15 single-use PTFE syringe filter.

The extracts were analysed using a gas chromatograph-mass spectrometer (GC-MS). The set-up consisted of an Agilent 6890 Series gas chromatograph system, equipped with an

Agilent 7683 series injector, an Agilent 5973 Network Mass Selective Detector and Phenomenex L-32-GGC capillary column, located at Agrisearch Analytical, Sydney (Fig. 5). Concentrations were devised by developing a standard curve and applying a 100-fold concentration factor. An example of instrumental response for a blank, spiked standard and sample, and a constructed standard curve used to devise concentrations is shown in Appendix 1.2.

The method used to extract endosulfan sulphate was substantiated by preparing triplicate 10 μg L^{-1} endosulfan sulphate standards in 0.01 M $CaCl_2$ (100 mL). Subsequent extraction and analysis yielded 100% (± 11%) recoveries.

Fig. 5. Photograph of GC-MS used to analyse for endosulfan sulphate.

Break-through column study

A glass column of 25 mm internal diameter and 300 mm length was packed with oven dry composted gin trash under saturated conditions of 5 mM $NaHCO_3$ mobile-phase solution. The mobile phase concentration was devised to emulate typical concentrations of HCO_3^- found in

surface water of the Namoi catchment (DNR 2005; as cited by Rose 2006). A 6-600 rpm peristaltic pump (Cole-Parmer) with a Masterflex speed controller was used to pump mobile phase through the packed column. Pesticide in eluate was to be detected by a 100-20 UV-vis spectrophotometer (Hitachi) with 1 mm quartz flow cell attached to a chart recorder set at 1 mV deflection (Omni-scribe) (Fig. 6). Individual stock solutions of 10 mg L^{-1} diuron and 0.1 mg L^{-1} endosulfan sulphate were prepared, as well as 250 mg L^{-1} KBr tracer solution.

The saturated column was allowed to drain freely under gravity to equilibrate the matrix with mobile phase. The conductivity of the column under gravity was measured and forcing mobile phase through the column using the peristaltic pump was attempted. However, because of poor conductivity and continuous 100% absorbance, this experiment was abandoned given time constraints.

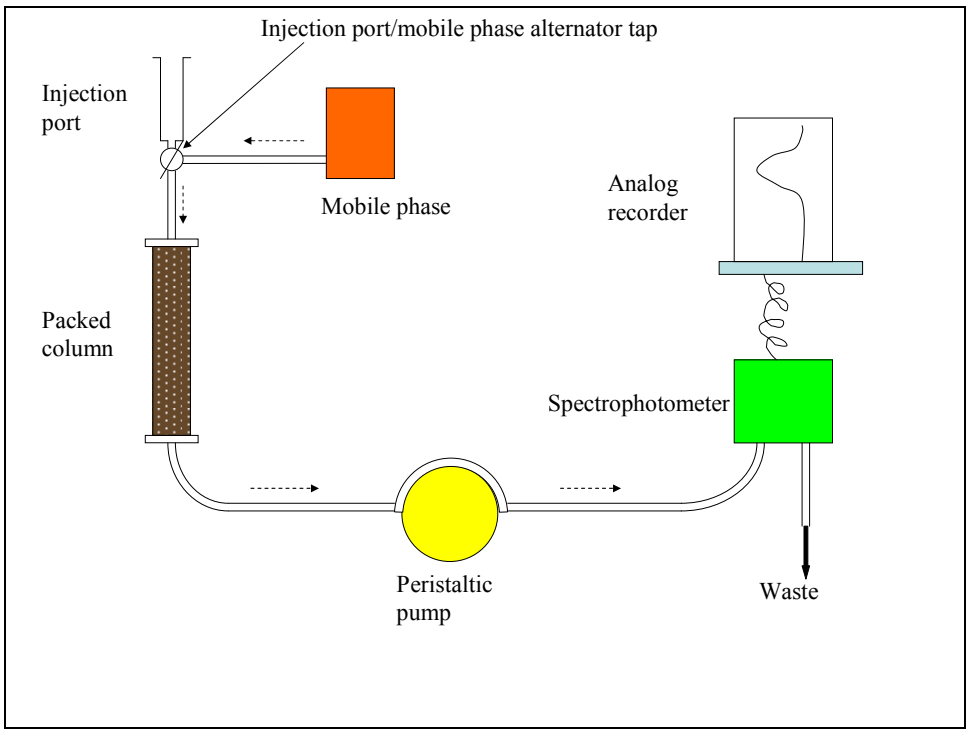

Fig. 6. Apparatus setup of break-through column study (Adapted from Rose 2006).

Batch equilibrium data analysis

Batch sorption-desorption data analysis was carried out following the method provided by OECD (2000). Where indicated, regression analyses were carried out using GenStat statistical software package, after manipulation of the raw data through various calculation steps given in the proceeding section.

Batch sorption kinetics

The batch kinetics sorption data were fit to an exponential model (Equation 2) using Genstat statistical software package, where C_s is the mass of sorbed pesticide (μg g^{-1}), x is time (min) and a and b are empirical constants. All data, however, were returned in units of μg L^{-1} and C_s was determined via Equation 3, where $C_{aq}(t_0)$ is the initial pesticide concentration (μg L^{-1}), $C_{aq}(t_i)$ is the concentration in solution at time step t_i (μg L^{-1}), m_{gt} is the mass of composted cotton gin trash (g), V is the solution volume (L) and 1000 is the conversion factor for L to mL.

$$C_s = a(1 - e^{-x/b}) \tag{2}$$

$$C_s = \frac{(C_{aq}(t_0) - C_{aq}(t_i))}{m_{gt}} \frac{V}{1000} \tag{3}$$

Sorption S_{ti} is defined as the percentage of substance sorbed as a result of the quantity present at the beginning of the test (OECD 2000). The extent of endosulfan sulphate and diuron sorption was calculated using Equation 4 for the time step *ti* when sorption equilibrium of the kinetics experiments was attained, where m_s^{eq} is the mass of sorbed pesticide at equilibrium (μg) and m_0 is the initial mass of pesticide in the flask (μg).

$$S_{t_i} = \frac{m_s^{eq}.100\%}{m_0} \quad (4)$$

The partition coefficient K_d (mL g^{-1}) was calculated for both diuron and endosulfan sulphate kinetic experiments. It is defined as the ratio between the mass of pesticide sorbed to composted gin trash C_s^{eq} (µg g^{-1}) and concentration of the pesticide remaining in solution C_{aq}^{eq} (µg mL^{-1}) at equilibrium (Equation 5) (OECD 2000). A K_d greater than 1 indicates that the pesticide has a preference for the solid phase, over that of the aqueous.

$$K_d = \frac{C_s^{eq}}{C_{aq}^{eq}} \quad (5)$$

The organic carbon partition coefficient K_{OC} relates K_d to the organic carbon content of the sorbent (Equation 6). The coefficient is ultimately dependent on the assumption that non-polar organic chemicals have a preference for carbon fractions of sorbents (OECD 2000). Such a relationship was determined for both diuron and endosulfan sulphate. The organic matter content of the sorbent was used in place of organic carbon, however the coefficient was raised by a factor of 1.70, where VanLoon and Duffy (2005) indicated that the percentage of organic matter is on average constituted by 60% organic carbon, that ultimately raises K_{OC}'s by a factor of 1.7.

$$K_{OC} = \frac{K_d}{\%OC} = \frac{K_d}{\%OM} \times 1.70 \quad (6)$$

Batch sorption isotherms

The sorption isotherms of diuron and endosulfan sulphate were fit to the Freundlich (1926) sorption model. The Freundlich (1926) sorption isotherm K_f ($\mu g^{1-1/n}(cm^3)^{1/n}g^{-1}$) model (Equation 6) relates the amount of pesticide sorbed C_s^{eq} ($\mu g\ g^{-1}$) to the concentration of test substance in solution C_{aq}^{eq} ($\mu g\ mL^{-1}$) at equilibrium, where n is a regression constant (OECD 2000). The coefficient was calculated using the linear form of the Freundlich model (Equation 7) (OECD 2000) that was then fit using linear regression analysis in Genstat statistical software package, with the gradient of the line returning $1/n$ and the y-intercept returning $\log K_f$, and subsequent back-transformation yielding K_f. Where K_f is greater then 1 indicates pesticide preference for the solid phase.

$$C_s^{eq} = K_f C_{aq}^{eq\,1/n} \tag{6}$$

$$\log C_s^{eq} = \log K_f + 1/n.\log C_{aq}^{eq} \tag{7}$$

Batch desorption kinetics

The desorption kinetics results were plotted for sorbed mass of pesticide to composted gin trash ($\mu g\ g^{-1}$) against time (min) and an exponential model fit to the data using Genstat statistical software. The desorption coefficient K_{des} ($mL\ g^{-1}$) describes the ratio between the content of the pesticide remaining on the composted cotton gin trash and the mass concentration of the desorbed pesticide in solution, where desorption equilibrium is reached (OECD 2000). This relationship is given by Equation 8 (OECD 2000):

$$K_{des} = \frac{m_s^{ads} - m_{aq}^{des}}{m_{aq}^{des}} \frac{V_T}{m_{gt}} \tag{8}$$

where m_s^{ads} is the mass of pesticide adsorbed on the composted gin trash at sorption equilibrium (µg) (as indicated by the sorption kinetics experiment), m_{aq}^{des} is the total mass of pesticide desorbed from the compost at desorption equilibrium (µg), V_T is the total volume of the aqueous phase in contact with the compost during desorption kinetics (mL), and m_{gt} is the mass of composted gin trash (g).

Batch desorption isotherms

The extent of partitioning at desorption equilibrium under the applied conditions of desorption isotherm experiments was assessed using the Freundlich desorption isotherm equation (Equation 9). The model relates the content of the test substance remaining sorbed on the composted gin trash C_s^{deq} (µg g^{-1}) to the concentration of the pesticides in solution C_{aq}^{deq} (µg mL^{-1}) at desorption equilibrium (OECD 2000). For each applied concentration, C_s^{deq} was calculated using Equation 10, where m_s^{ads} is the mass of substance in the aqueous phase at sorption equilibrium (µg) (obtained from sorption isotherm sorbed masses), and m_{aq}^{deq} is the mass of substance in solution at desorption equilibrium (µg).

$$C_s^{deq} = K_f^{des}.C_{aq}^{deq\ 1/n} \tag{9}$$

$$C_s^{deq} = \frac{m_s^{ads} - m_{aq}^{deq}}{m_{soil}} \tag{10}$$

The Freundlich desorption coefficient K_f^{des} however, was calculated using the linear form of the Freundlich desorption isotherm, given in Equation 12. This involved plotting the

log-transformation of C_s^{deq} against C_{aq}^{deq} and applying regression analysis to obtain the regression constant n and K_f^{des}, respectively given by the slope and intercept of the fit.

$$\log C_s^{deq} = \log K_f^{des} + 1/n.\log C_{aq}^{deq} \quad (12)$$

Results

Organic and mineral matter content

The results from the weight loss-on-ignition determination of organic matter are shown in Table 1. It can be concluded that one-quarter of the composted gin trash is constituted by organic matter, lost as carbon dioxide, with the remaining three-quarters assumed to be mineral matter.

Table 1. Summary of organic matter and mineral matter fractions (%) of composted gin trash.

Attribute	*Fraction (%)*
Organic matter	25.22 (± 2.92)
Mineral matter	74.79 (± 2.92)

Sorption kinetics

The results for the sorption kinetics of both endosulfan sulphate and diuron were plotted against time (mins) and exponential model fit (Fig. 7 and 8 respectively), with raw data and output respectively given in Appendix 2.2 and 2.3. In both cases, fast initial sorption was observed. Endosulfan sulphate attained sorption equilibrium after 240 min (or 4 h) (Fig. 7). Diuron, however, did not reach sorption equilibrium and continued to sorb up to the maximum allowed reaction time of 2880 min (2 days) (Fig. 8).

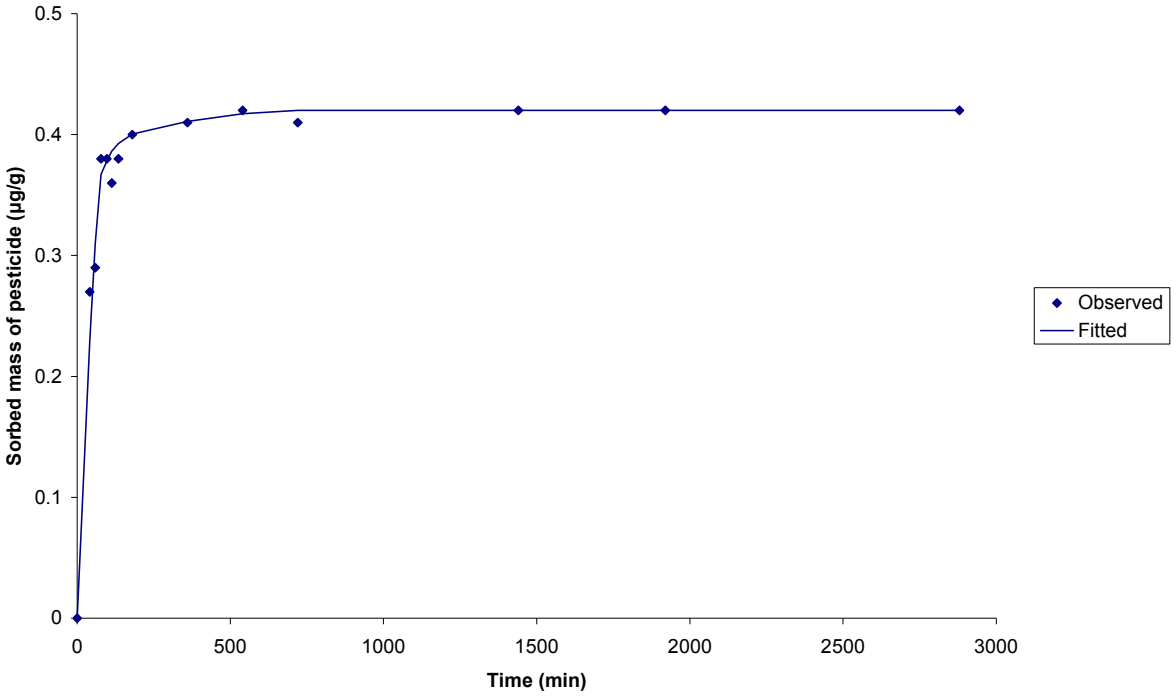

Fig. 7. Graph of endosulfan sulphate sorption kinetics showing observed and fitted results for sorbed mass of pesticide (µg g^{-1}) against time (min) ($r^2 = 0.96$).

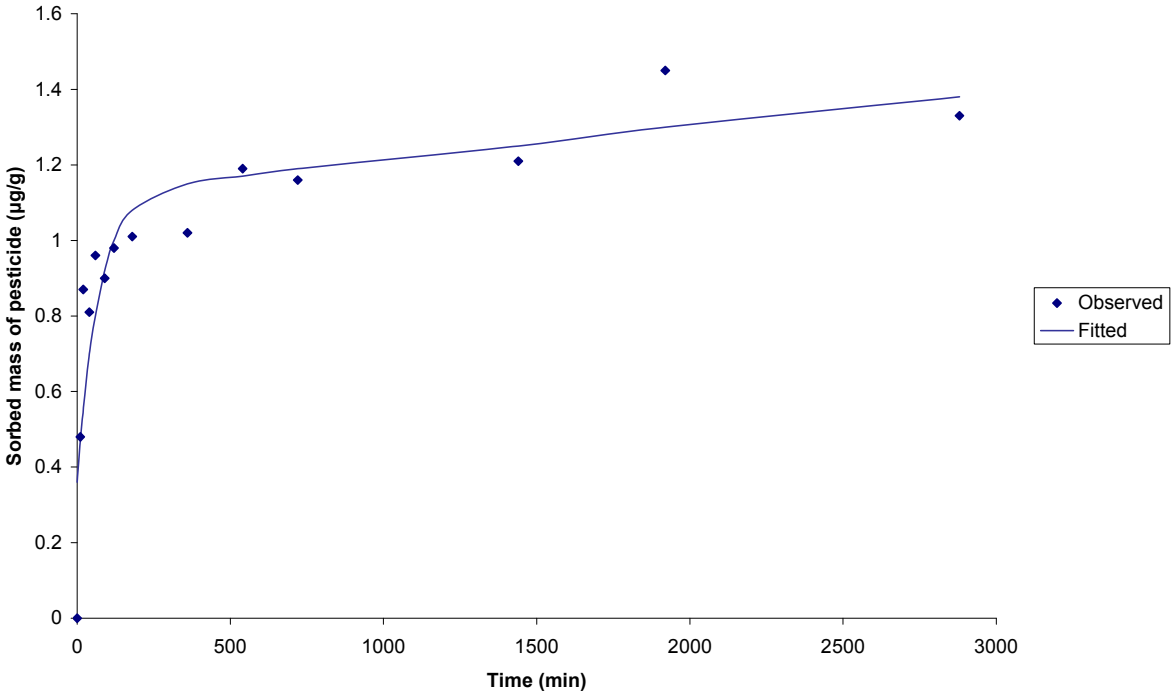

Fig. 8. Graph of diuron sorption kinetics showing observed and fitted results for sorbed mass of pesticide (µg g^{-1}) against time (min) ($r^2 = 0.77$).

The various partition coefficients (K_d and K_{OC}), for both endosulfan sulphate and diuron, are given in Table 2. In the case of diuron, equilibrium sorbed mass of pesticide was taken at the maximum allowable reaction time (2 days). Endosulfan sulphate was taken at equilibrium (4 h). In both cases, the partition coefficients K_d and K_{OC} exceeded 1 and more than 50% applied pesticide was sorbed (Table 2).

Table 2. Summary of partition coefficient (K_d), organic carbon partition coefficient (K_{OC}) and proportion sorbed at equilibrium (%) for diuron and endosulfan sulphate sorption kinetics.

Pesticide	K_d *(mL g^{-1})*	K_{OC} *(mL g^{-1})*	*Proportion sorbed at equilibrium (%)*
Endosulfan sulphate	877.55	3480.22	95.70
Diuron	70.25	472.11	58.42

Sorption isotherms

The sorption isotherms for endosulfan sulphate and diuron are respectively shown in Figures 9 and 10. A strong linear association between sorbed mass of pesticide and dissolved concentration was observed for both pesticides, as the linear regressions indicate (Fig. 9 and 10; Appendix 2.4 and 2.5 respectively). The linear form of the Freundlich (1926) model fit both the endosulfan sulphate and diuron isotherm relationships well, with coefficients of variation (r^2) being greater than 0.90 (Table 3). The calculated regression coefficient $1/n$ was greater than 1 for endosulfan sulphate, and less than 1 for diuron (Table 3). Both diuron and endosulfan sulphate yielded Freundlich partition coefficients K_f much greater than 1 (Table 3).

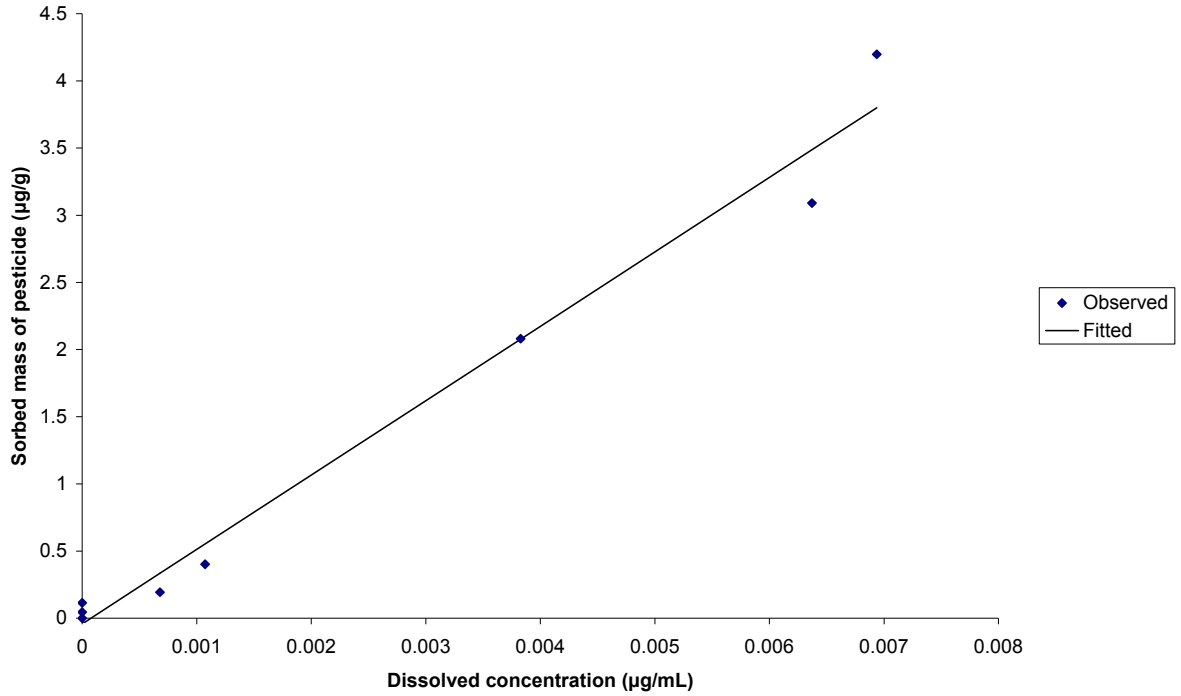

Fig. 9. Graph of endosulfan sulphate sorption isotherm depicting observed and fitted results of sorbed mass of pesticide (µg g^{-1}) against dissolved concentration of pesticide (µg mL^{-1}) ($r^2 = 0.98$).

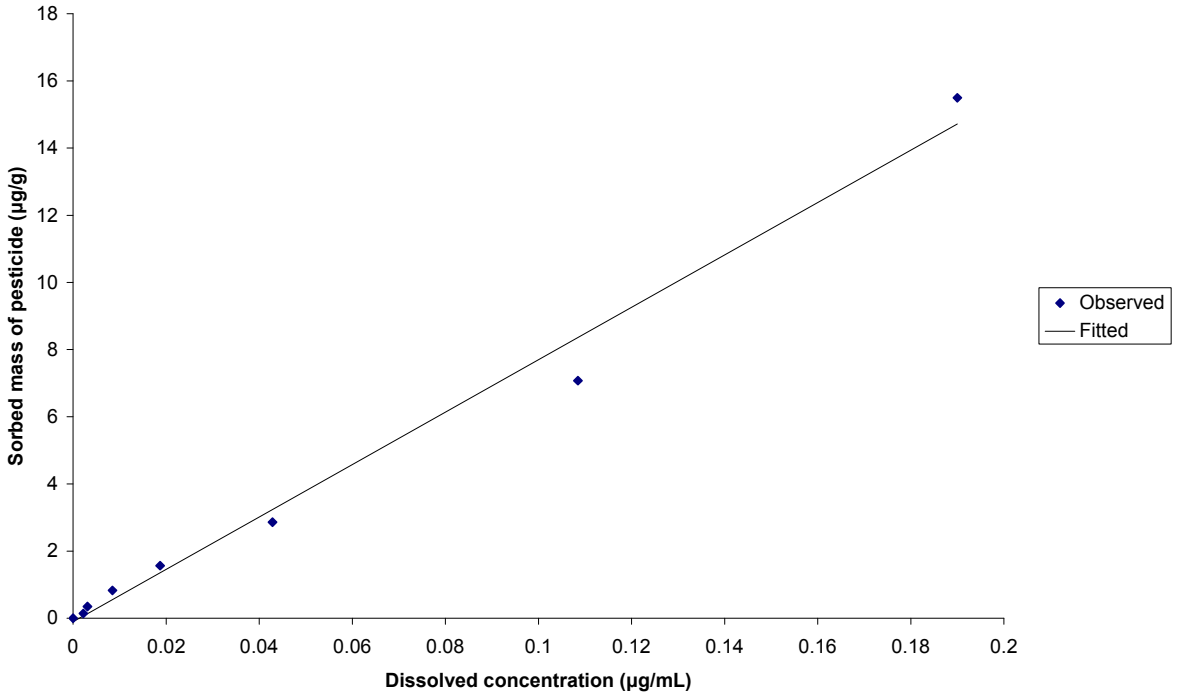

Fig. 10. Graph of diuron sorption isotherm depicting observed and fitted results of sorbed mass of pesticide (µg g^{-1}) against dissolved concentration of pesticide (µg mL^{-1}) ($r^2 = 0.98$).

Table 3. Summary of Freundlich isotherm model partition (K_f) and regression (1/*n*) coefficients and coefficients of determination (r^2).

Pesticide	K_f $(\mu g^{1-1/n}.mL^{1/n}.g^{-1})$	*1/n*	r^2
Endosulfan sulphate	2197.86	1.26	0.99
Diuron	67.87	0.96	0.98

The extent of both diuron and endosulfan sulphate sorption for the range of applied concentrations are reported in Table 4. It was found that composted gin trash sorbed between 88.2-100% of the applied endosulfan sulphate, and 55.9-68.95% of applied diuron (Table 4).

Table 4. Summary of sorption isotherm sorbed (%) endosulfan sulphate and diuron for the applied concentrations (µg L^{-1}) onto composted cotton gin trash.

Applied concentration $(\mu g\ L^{-1})$		*% sorbed at equilibrium*	
Endosulfan sulphate	Diuron	Endosulfan sulphate	Diuron
1	5	100	55.9
2.5	10	100	69.0
5	25	85.1	66.2
10	50	88.2	62.6
50	100	91.6	57.2
75	250	90.7	56.6
100	500	92.4	62.0

Desorption kinetics

The results for diuron desorption kinetics is shown in Figure 11 (Appendix 2.7). All endosulfan sulphate time steps yielded results that were below the limit of detection of the GC-MS (Appendix 2.6), and therefore the amount desorbed over a period of 48 h assumed to be zero and the sorbed mass constant, and K_{des} was indeterminable (Table 5). Diuron, on the other hand, exhibited rapid initial rates of desorption, followed by equilibrium after 240 min

(4 h) (Fig. 11). The desorption coefficient K_{des} for diuron was calculated to be much greater than 1 and less than 50% of the sorbed diuron was found to have desorbed at equilibrium (Table 5).

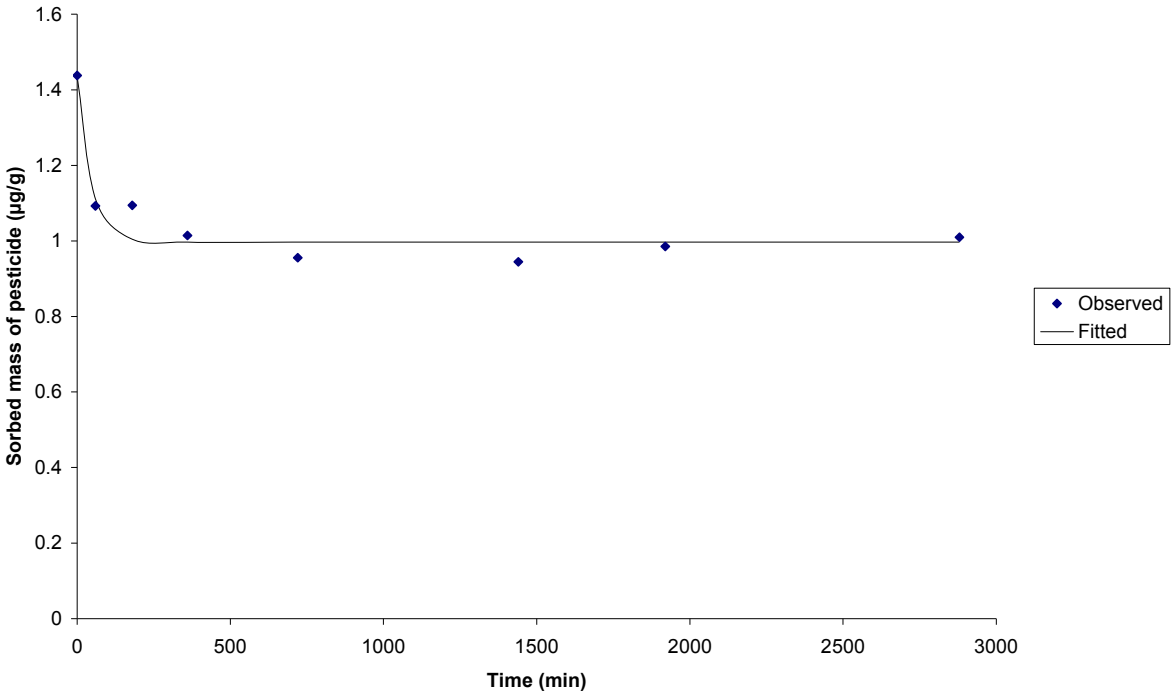

Fig. 11. Graph of diuron desorption kinetics showing observed and fitted results for sorbed mass of pesticide (µg g^{-1}) against time (min) ($r^2 = 0.77$).

Table 5. Summary of desorption coefficient (K_{des}) and proportion desorbed at equilibrium (%) for diuron and endosulfan sulphate desorption kinetics.

Pesticide	K_{des} *(mL g^{-1})*	*Proportion desorbed at equilibrium (%)*
Endosulfan sulphate	N/D	0
Diuron	117.86	30.7

N/D: Not determinable

Desorption isotherms

Desorption isotherm plots of endosulfan sulphate and diuron, show a strong linear association between sorbed mass and dissolved concentration (Fig. 12 and 13; and Appendix 2.8 and 2.9 respectively). The results show for the applied concentration range of 1-10 µg L^{-1}, no sorbed endosulfan sulphate desorbed, and that no more than 6.3% desorbed for higher applied concentrations (Fig. 12; Table 6). Diuron, however, exhibited desorption in the range of 31-43.4% over the applied pesticide concentrations (Fig. 13; Table 6).

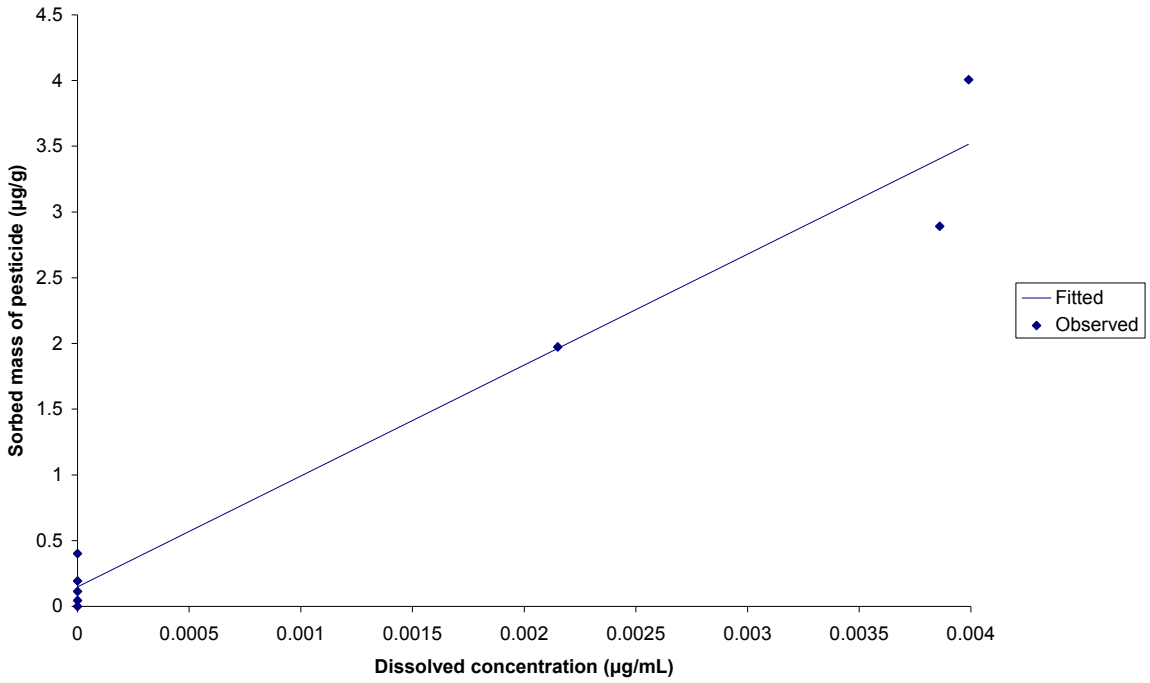

Fig. 12. Graph of endosulfan sulphate desorption isotherm depicting observed and fitted results of sorbed mass of pesticide (µg g^{-1}) against dissolved concentration of pesticide (µg mL^{-1}) ($r^2 = 0.96$).

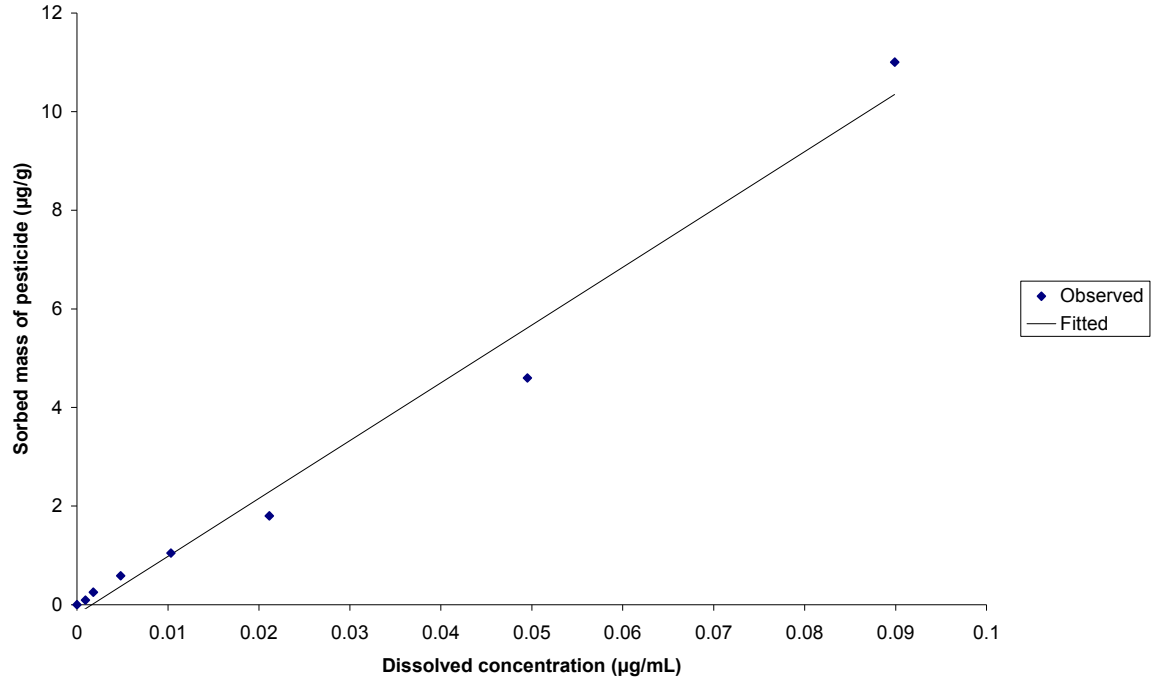

Fig. 13. Graph of diuron desorption isotherm depicting observed and fitted results of sorbed mass of pesticide (µg g^{-1}) against dissolved concentration of pesticide (µg mL^{-1}) (r^2 = 0.98).

Table 6. Summary of desorption isotherm desorbed (%) endosulfan sulphate and diuron for the applied concentrations (µg L^{-1}) onto composted cotton gin trash after sorption equilibrium.

Applied concentration (µg L^{-1})		*% desorbed at equilibrium*	
Endosulfan sulphate	Diuron	Endosulfan sulphate	Diuron
1	5	0	44.1
2.5	10	0	31.1
5	25	0	33.8
10	50	0	37.4
50	100	5.2	42.9
75	250	4.8	43.4
100	500	6.3	38.0

The linear form of the Freundlich (1926) desorption model fit the diuron desorption isotherm relationship well (r^2 = 0.98), and the endosulfan sulphate isotherm marginally well (r^2 = 0.65) (Table 7). The calculated regression coefficients 1/*n* were less than 1, and the Freundlich partition coefficients K_f^{des} were much greater than 1 for both pesticides (Table 7).

Table 7. Summary of desorption isotherm Freundlich desorption coefficients K_f^{des}, regression constant 1/*n* and coefficient of determination r^2 for endosulfan sulphate and diuron.

Pesticide	K_f^{des} $(\mu g^{1-1/n}.mL^{1/n}.g^{-1})$	*1/n*	r^2
Endosulfan sulphate	575.44	0.93	0.65
Diuron	71.52	0.92	0.98

Break-through column

Dynamic sorption assessment of diuron and endosulfan sulphate, via column sorption studies, did not progress beyond conditioning of the column matrix with a mobile phase of 2 mM $NaHCO_3$. The column discharge (Fig. 14) constantly measured 100% absorbance on the spectrophotometer. Furthermore, the hydraulic conductivity of the packed column did not exceed 1 mL min^{-1} under gravity. Therefore, break-through detection was not possible with composted gin trash.

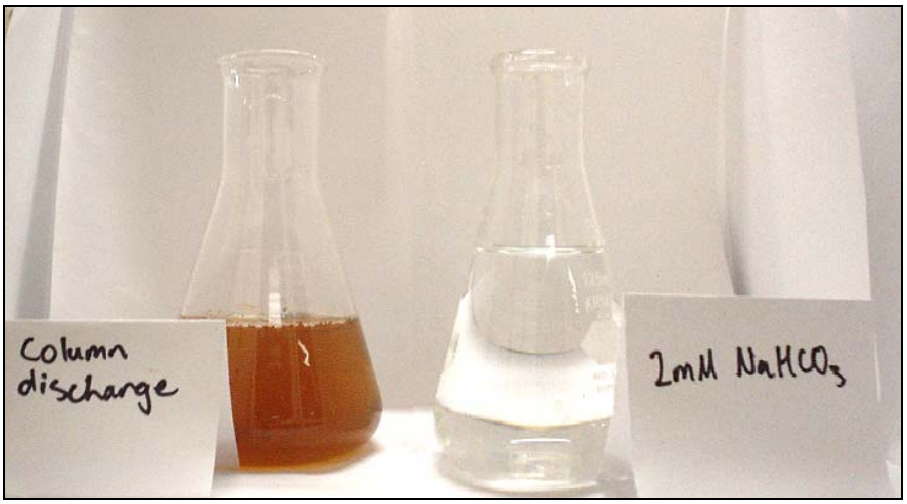

Fig. 14. Photographs of break-through column discharge (left) and 2 mM $NaHCO_3$ mobile phase solution (Right).

Discussion

This paper aimed to investigate the sorption potential of composted gin trash for environmentally relevant concentrations of endosulfan sulphate and diuron found in irrigation tailwater. Results from these studies may validate the use of composted gin trash as a pesticide sorption medium in irrigation tailwater management.

All batch sorption-desorption studies showed that both diuron and endosulfan sulphate have a strong preference for the solid phase, particularly the organic carbon fraction. This is indicated by high partition coefficients K_d, K_{oc}, K_f, K_{des}, and K_f^{des}. The outcome of sorption and desorption, however, is manifested in the chemical and physical properties of the interacting mediums, i.e. compost and pesticide (Scheunert 1993; Hornsby *et al.* 1996; Kookana *et al.* 1998; Wauchope *et al.* 2002; Nkedi-Kizza *et al.* 2006). This section of the report discusses the observed characteristics of the composted gin trash and the implications they pose to various mechanisms that influence sorption and desorption of the two pesticides. In quantifying the benefits, a comparison with literature sorption data for various types of sorbents is also provided. Further, various complications observed in the break-through column experiment and a need to make it functional is also explored, as well as areas warranting further research.

Characteristics of composted gin trash

The composted gin trash was found to consist of a large proportion of combustible organic matter (25.22%). Composting of plant material is a process of humification (Bollag *et al.* 1992). The compounds that are produced from this process include humic and fulvic acids (Bollag *et al.* 1992). Such polymeric compounds consist of an aromatic core containing mono-, di- and polyphenolic subunits (Bollag *et al.* 1992). These humic and fulvic acid

compounds have been widely demonstrated to act as strong sorbing sites for a wide number of pesticides (Bollag *et al.* 1992; Kookana *et al.* 1998; Roy *et al.* 2000).

The structural arrangement commonly observed when humic acids are placed in water is that of a micelle (Roy *et al.* 2000). The micelle of humic acid is characterised by having a membrane-like structure consisting of a hydrophobic interior and hydrophilic exterior, where the latter displays polar organic functional groups, such as carboxylic acid and alcohol groups (Bollag *et al.* 1992; Roy *et al.* 2000). The most persistent complexes have been described to result from direct covalent bonding with pesticides that resemble similar chemical functionalities to humus (Bollag *et al.* 1992). This suggests that for composted gin trash, the strong presence of humic compounds attributes binding affinity for diuron and endosulfan sulphate. With organic carbon generally considered to be the principal pesticide sorbing component of soil (Kookana *et al.* 1998), the complexity of humic compounds suggests that sorption to humus may not be uniform in nature. Based on these results, it appears that unique sorption mechanisms are operating for diuron and endosulfan sulphate, the outcome being a combination of both hydrophobic and hydrophilic interactions with different parts of these molecules.

Sorption of two pesticides

Fast initial rates of sorption were observed for both endosulfan sulphate and diuron sorption kinetics (Fig. 7 and 8 respectively). This was as expected, for the maximum number of binding sites on the composted gin trash was available for sorption (Kumar and Philip 2006) and strong diffusion into organic matter was operating (Gaillardon 1997). As time progressed, endosulfan sulphate attained equilibrium, and diuron continued to sorb to the composted gin trash immediately after fast initial sorption rates. In both cases, a number of sorption mechanisms were likely to be operating to influence the observed rates.

Sorption of endosulfan sulphate

The endosulfan sulphate kinetics experiment exhibited a fast rate of sorption, the outcome being equilibrium after 4 h (Fig. 7). Strong hydrophobic interaction with humic compounds in the compost material, on account of its poor solubility (0.117-0.22 mg L^{-1}) and strong preference for hydrophobic phases (high logK_{OW} = 3.66), was concluded to be the mechanism driving the rapid rate of sorption (Kumar and Philip 2006). The high partition (K_d = 877.55) and organic carbon partition coefficients (K_{OC} = 3480.22), derived from the sorption kinetics equilibrium, substantiates a clear preference for endosulfan sulphate to the solid phase, particularly the organic carbon fraction.

The linearity of the sorption isotherm (Fig. 9), where the regression constant 1/*n* was greater than 1 (1.26), signified that sorption was not limited for the range of applied concentrations, but continued to increase for increasing solution concentrations. Importantly, the Freundlich model accounts for any variability in sorption ability, where it assumes that all sites on the surface of a sorbent are not equal in nature and that sorption becomes increasingly difficult as the number of binding sites become deficient (VanLoon and Duffy 2005). In essence, the model indicates ease of sorption under the applied conditions. A high Freundlich partition coefficient (K_f = 2197.86) and linearity of the isotherm suggests that saturation of binding sites on 2 g of composted gin trash with endosulfan sulphate was not reached. This is further clarified by Table 4 that exhibited little deviation from 90% sorption for the range of applied concentrations in the sorption isotherm experiment. Hence composted gin trash has an even greater binding affinity for endosulfan sulphate to the applied concentrations in this study.

Sorption performance of composted gin trash for endosulfan sulphate

Quantification of the benefits in using composted gin trash as a pesticide sorption medium for endosulfan sulphate, relative to soil, has been made through comparison of sorption characteristics observed in the literature. Little comparative data is available for endosulfan sulphate sorption; however assessments for its parent isomers, α- and β-endosulfan, have been made on the basis that they exhibit similar chemical and physical properties (Tomlin 1997; ATSDR 2000).

When compared to composted gin trash Kumar and Philip (2006) observed similar rapid rates of endosulfan sorption, with equilibrium reached in a short period of time in sandy soils (1.5 h), and slightly longer for clay and composted soils (4 h). The extent of partition between such soils was most pronounced for the clay and composted soils that respectively contained 2.29% and 9.51% organic matter, compared to 0.58% for the sand (Table 8). Therefore, it is no surprise that the time taken to achieve equilibrium with composted gin trash, containing 25.22% organic matter, was slightly longer to that of the clay and composted soil used by Kumar and Philip (2006), as the extent of partition was far greater (Table 8).

Contrary to Kumar and Philip's (2006) observations, Rose (2006) observed slower rates of α-, β- endosulfan and endosulfan sulphate sorption onto basalt gravel, when compared to eucalyptus woodchip (6 h), with the former not attaining sorption equilibrium after 36 h and yielding the lowest partition coefficients (Table 8). In both cases, partition between gravel and wood chip was much lower than that of composted gin trash (Table 8). Similarly, Laabs and Amelung (2005) reported limited partition of α-endosulfan on sand and medium clay soils (Table 8).

A similar outcome for endosulfan sulphate partition was made by Peterson and Batley (1993), who observed strong partition of α- and β-endosulfan ($K_{d\alpha\text{-endo}}$ = 295 and $K_{d\beta\text{-endo}}$ = 788; Table 8) in river sediments containing 5.30% organic matter, at Boobora Lagoon,

Northern NSW, Australia. Furthermore, Peterson and Batley (1993) were able to demonstrate variable partitions on lagoon sediments of the same area that had different organic matter fractions (Table 8). The outcome was almost a positive correlation, with the largest partition observed for lagoon sediments that had the greatest organic matter content. However, the reported partition coefficients were much lower than for composted gin trash (Table 8).

Given that similar properties are exhibited between endosulfan sulphate and its parent isomers, α- and β-endosulfan, composted gin trash has been found to effectively sorb environmentally relevant concentrations that are outstanding to various sorbent types observed in the literature. Specifically, the presence of a large organic matter fraction has influenced this outcome.

Table 8. Comparative assessment of α-, β- endosulfan and endosulfan sulphate Partition coefficients for coefficients reported in the literature to partition coefficients derived for composted gin trash and endosulfan sulphate sorption

Location	*Soil Type*	*% Organic matter*	K_d *(mL g^{-1})*		K_{OC} *(mL g^{-1})*		*Reference*
Endosulfan sulphate							
	Composted cotton gin trash	**25.22**	**877.55**		**3480.22**		
—	Eucalyptus woodchip	—	211.5		—		Rose (2006)
—	Basalt gravel	—	29.9		—		Rose (2006)
Endosulfan							
			α-endosulfan	β-endosulfan	α-endosulfan	β-endosulfan	
Jabiru Lagoon, Northern NSW, Australia	Sediment	0.50	21.00	36.00	3981.07	7943.28	Peterson & Batley (1993)
India	Sandy soil	0.575	8.09	8.62	2391.30	2548.73	Kumar and Philip (2006)
Psamments, Brazil	Sand	0.73	91.98	—	12600.00	—	Laabs & Amelung (2005)
Boobora Lagoon, Northern NSW, Australia	Sediment	0.90	76.00	99.00	7943.28	10000.00	Peterson & Batley (1993)
Boobora Lagoon, Northern NSW, Australia	Sediment	0.90	85.00	143	10000.00	15848.93	Peterson & Batley (1993)
Jabiru Lagoon, Northern NSW, Australia	Sediment	1.30	133.00	137.00	10000.00	10000.00	Peterson & Batley (1993)
Jabiru Lagoon, Northern NSW, Australia	Sediment	2.20	82.00	144.00	3981.07	6309.57	Peterson & Batley (1993)
India	Clay	2.29	43.10	75	3199.82	5567.69	Kumar and Philip (2006)
Ustox, Brazil	Medium clay	2.64	165.79	—	6280.00	—	Laabs & Amelung (2005)
Boobora Lagoon, Northern NSW, Australia	Sediment	5.30	295.00	788.00	5011.87	15848.93	Peterson & Batley (1993)
India	Compost	9.51	24.06	49.58	430.14	886.35	Kumar and Philip (2006)
—	Basalt gravel	—	36.5	31.0	—	—	Rose (2006)
—	Wood chip	—	228.5	236.9	—	—	Rose (2006)

Text in **bold** indicate results from this study; '—' indicates not reported.

Sorption of diuron

The initial fast then slower rates of diuron sorption to composted gin trash (Fig. 8) suggested that a number of rate-determining mechanisms were operating. It is widely known that sorption of diuron is significantly correlated with soil organic matter (Yang and Sheng 2003b; Sheng *et al.* 2005; Nkedi-Kizza *et al.* 2006). This can be illustrated by its hydrophobic nature, as demonstrated by its high octanol:water partition coefficient (K_{OW} 2.85) (Tomlin 1997). However, being slightly polar, also makes it attracted to the solution phase, as signified by its solubility in water (36.4 mg L^{-1}) (Tomlin 1997). Competing dipole-dipole attraction into solution, attraction to the surface polar functional groups of humic micelles and hydrophobic attraction into the interior of humic micelles, were expected to be operating forces influencing sorption rate of diuron.

Attraction into solution appeared to be limited in its entirety, as the partition of diuron after 2 days was shown to exhibit a clear preference for the solid phase (K_d = 70.03), in particular the organic carbon fraction (K_{OC} = 472.11). Roy *et al*. (2000) found, that higher moisture conditions (46.6%) enhanced the sorption of diuron to humic micelles compared to low moisture conditions (<26%; K_d = 8.1), for a loam soil containing 2.4% organic matter. This was attributed to enhanced available organic hydrophilic sites at the surface of humic micelles, whereas drier conditions improved the exposure of hydrophobic surfaces thereby limiting diuron sorption. A vast number of binding sites available at initial contact with solution has attributed to the observed fast rates of diuron sorption. However, competition for surface functional groups with other polar molecules and ions in solution (such as Ca^{2+} and Cl^- in 0.01 M $CaCl_2$ solution) as the number of available binding sites becomes deficient would appear to be a mechanism that is limiting the overall sorption of diuron.

Brusseau *et al.* (1991) attributes sorption-related non-equilibrium to intraorganic matter diffusion. This involves diffusive mass transfer of pesticide within the matrix of

organic matter (Brusseau *et al.* 1991; Fortin *et al.* 1997). The outcome of such a mechanism has been described to affect the sorption of polar organic compounds (Brusseau *et al.* 1991; Fortin *et al.* 1997), such as diuron. Similarly, Gaillardon (1997) attributed slower rates of diuron sorption to diffusion into organic matter and/or small pores in a clay loam soil (1.36% organic carbon).

The linearity of the sorption isotherm (Fig. 10), where the regression constant $1/n$ was less than 1 (0.96), signified that sorption of diuron was becoming increasingly difficult for the range of applied concentrations. This is confirmed by the Freundlich partition coefficient (K_f = 67.87) being similar to the partition coefficient K_d (70.25). However, the extent of sorption over all the applied concentrations was not found to be limiting, as a narrow range of sorption percentages was observed (55.9-69.0%; Table 4). This indicates that diffusion is a mechanism acting to constrain total sorption of diuron, as a result of its polarity. Hence, composted gin trash has a sorption capacity for diuron that is ultimately dependent on the aqueous phase concentration; however preference for the solid phase was shown to be the outcome regardless of applied concentration.

Competition for polar binding sites at the humus micelle surface with water and slow diffusion into the hydrophobic interior of the humic micelles were the rate limiting sorption mechanisms operating to constrain diuron from reaching sorption equilibrium. The outcome of such interactions has resulted in diuron having a K_d and K_f that describes it as having a preference for the solid phase (K_d and K_f being much greater than 1), but has also constrained it from reaching sorption equilibrium (Brusseau *et al.* 1991; Fortin *et al.* 1997). Partition is much lower than that of the more hydrophobic endosulfan sulphate, but is a common outcome for more soluble organic pesticides that have to contend with competing forces (Ahmad *et al.* 2005).

Sorption performance of composted gin trash for diuron

In quantifying the benefits of composted gin trash at sorbing environmentally relevant concentrations of diuron, comparisons have been made for reported literature partition studies on a range of soil types. Table 9 shows a range of collated partition coefficients K_d and K_{OC}.

Yang & Sheng (2003a; 2003b) and Sheng *et al*. (2005) found that wheat char, derived from the burning of wheat stubble, was an effective diuron sorbent. Compared to a sandy loam soil (2.10% organic carbon; K_d = 3.51), wheat char alone (13% organic carbon) was 500-10 000 times more effective at sorbing diuron (K_d = 3594) (Sheng *et al.* 2005). A soil amendment of 1% wheat char contributed an 86% increase in the overall sorption potential of the sandy loam soil (K_d = 32.6) (Sheng *et al.* 2005). Relative to composted gin trash, the wheat char alone was 51 times more superior (Table 9).

Lennartz *et al.* (1997), Gaillardon (1997), Guoy *et al*. (1999), Oliver *et al*. (2005), and Nkedi-Kizza *et al*. (2006) reported limited partition for a range of soils that contained much less organic matter to that of composted gin trash (Table 9). Specifically, Sheng *et al*. (2005) found that sorption of diuron onto clay minerals alone was hindered by large substituents exhibited on the aromatic ring of diuron (two chlorines and N,N-dimethylurea), and the electroneutrality of diuron further enhances this outcome. Notably, all the soils exhibited organic carbon partition coefficients that were within the realms of composted gin trash. This highlights the strong influence that organic carbon has on diuron partition, as a whole, which Table 9 effectively demonstrates.

Overall, the extent of partition for diuron to composted gin trash is strongly influenced by organic matter, in particular the humic components. This has brought with it a partition coefficient that is outstanding to an array of sorbents identified in the literature, with the exception of wheat char (Sheng *et al*. 2005).

Table 9. Summary of collated literature diuron partition (K_d) and organic carbon partition (K_{OC}) coefficients for a range sorbing media

Location	*Soil Type*	*% Organic matter*	K_d *(mL g^{-1})*	K_{OC} *(mL g^{-1})*	*Reference*
Diuron					
	Composted cotton gin trash	**25.22**	**70.03**	**472.11**	
Mont Pellier, France	Silt loam	1.00	2.40	240.00	Lennartz *et al.* (1997)
North East Western Australia	Variable	1.05	5.5	579.00	Oliver *et al*. (2005)
Dijon, France	Dispered Clay loam	1.36	6 (K_f)	441.18	Gaillardon (1997)
Dijon, France	Undispered Clay loam	1.36	7.17 (K_f)	527.21	Gaillardon (1997)
La Jailliere	Sandy loam	2.00	9.60	480.00	Guoy *et al*. (1999)
Arkansas, USA	Sandy Loam	2.10	3.51	166.67	Sheng *et al*. (2005)
Philippines	Variable	2.23	14	618.00	Oliver *et al*. (2005)
Florida, USA	Carbonatic sandy loam	2.50	3.18	127.00	Nkedi-Kizza *et al*. (2006)
South Australia	Variable	2.83	14.9	536.00	Oliver *et al*. (2005)
Florida, USA	Noncarbonatic fine sandy clay loam	4.60	16.84	366.00	Nkedi-Kizza *et al*. (2006)
Florida, USA	Noncarbonatic	44.00	186.56	424.00	Nkedi-Kizza *et al*. (2006)
Arkansas, USA	100% Wheat char	13	3594.00	27646.15	Sheng *et al*. (2005)
Arkansas, USA	Sandy Loam (1% Wheat char ammendment)	—	32.10	—	Sheng *et al*. (2005)

Text in **bold** indicate results from this study; '—' indicates not reported.

Desorption

Desorption is a mechanism that characterises whether pesticide sorption is reversible. Through batch equilibrium assessment, diuron and to some extent endosulfan sulphate, were found to desorb from composted cotton gin trash, their mechanisms varying according to their interactions with the aqueous and solid phases of the defined matrix.

Desorption of endosulfan sulphate

The desorption kinetics experiments produced no measurable desorption of endosulfan sulphate from composted cotton gin trash and indicates that endosulfan sulphate is irreversibly bound. This outcome is due to the strong covalent hydrophobic interactions, between endosulfan sulphate and the hydrophobic components of humic micelles, highlighted earlier.

The linear desorption isotherm (Fig. 12), having a regression coefficient 1/*n* less than 1 (Table 7), indicates that for increasing dissolved concentrations, the amount of sorbed pesticide decreases. For higher sorbed masses of endosulfan sulphate, however, desorption occurred. This suggests that diffusion of higher sorbed masses into solution were able to overcome the strong hydrophobic interactions with the compost, resulting in desorption (Kumar and Philip 2006). However, it is important to recognise that for the lower range of applied concentrations (1-50μg L^{-1}) desorption was not observed (Fig. 12; Table 6). Specifically, such concentrations are within the range likely to be found in irrigation tailwater, as reported by Crossan (2002) and the highest concentration for α- and β- endosulfan in storm runoff of a cotton farm, observed by Kennedy *et al*. (2001), was 50 μg L^{-1}. This evidence suggests that composted gin trash effectively sorbs a range of environmentally relevant concentrations of endosulfan sulphate, to an extent that desorption was not observed, however at higher ranges desorption was limited. This is supported by the outcome of a high

Freundlich desorption partition coefficient (K_f^{des} = 575.80) that indicates endosulfan sulphate as having a strong preference for the solid phase.

There are few publications reporting desorption of endosulfan sulphate, although desorption of the parent compounds α- and β-endosulfan have been reported. Kumar and Philip (2006) found desorption of endosulfan to be faster in sandy soils (0.575% organic carbon) relative to clay (2.29% organic carbon) and composted (9.51% organic carbon) soils (Kumar & Philip, 2006). The presence of organic matter was found to decrease the desorption potential (Kumar and Philip 2006). Similarly, Ismail *et al*. (2002) attributed 39.57% and 22.78% desorption of endosulfan from a sandy loam (1.92% organic carbon) and clay soil (1.64% organic carbon), respectively, to weak binding on account of the low organic carbon fraction. Overall, composted cotton gin trash is effective at binding endosulfan sulphate, to the extent that only limited desorption was observed, when compared to a range of soil types reported in the literature.

Desorption of diuron

Rapid initial rates of diuron desorption resulted in equilibrium (Fig. 11). A limited fraction of the sorbed diuron desorbed (30.7%). This was further indicated by the desorption coefficient K_{des} (117.86) that showed diuron to have a strong preference for the solid phase under the induced conditions. The outcome of desorption, however, has been attributed to diffusion forces into solution (Gaillardon 1997; Inoue *et al.* 2006) that were sufficient to overcome the polar and hydrophobic attractions of diuron to the humic micelle components of the compost described earlier.

The linear desorption isotherm (Fig. 13), having a regression coefficient 1/*n* less than 1 (Table 7), indicates that for increasing dissolved concentration, the amount of sorbed diuron decreases. The preference for the solid phase, however, is still evident for the range of applied

concentrations, as indicated by the large K_f^{des} (71.52), which is very similar to the sorption coefficients K_d (70.25) and K_f (67.87). This suggests that the extent of partition under all the applied conditions was relatively constant, however only limited desorption was observed (31-44%; Table 6). These results indicate that diffusion forces into solution, for a range of sorbed masses, were able to overcome the range of interactions that exist between diuron and the compost. This has resulted in desorption, to the extent that a defined partition is achieved regardless of the sorbed mass, an outcome demonstrated by the linearity of the desorption isotherm. Overall, composted gin trash effectively contained the majority of applied diuron concentrations, a characteristic that has been explained by limited desorption.

A number of publications reporting desorption of diuron for a range of sorbing media have been identified, however few report the relevant desorption coefficients to enable adequate comparison to composted cotton gin trash. Gaillardon (1997) reported rapid desorption of diuron for a clay loam soil containing 1.36% organic carbon that resulted in equilibrium after 1 h. Reddy *et al*. (1992) similarly observed 32% desorption of diuron for a range of sandy soils containing 0.50-1.67% organic carbon. Inoue *et al*. (2006) attributed desorption hysteresis for a 0.48 mg L^{-1} application of diuron in heavy clay soils (1.8% organic matter; K_f^{des} = 1.15), to soil organic carbon content relative to sandy clay loam soils containing less than 1% organic matter (K_f^{des} = 1.07). It was suggested that higher organic carbon content of the heavy clay soil resulted in the formation of larger soil aggregates that enhanced the tortuosity of the internal soil porosity. The result was described to physically constrain the movement of diuron into the aqueous phase. This may further lead onto the hysteretic effect of slow diuron diffusion into organic matter that slowed the rate of sorption, reported by Brusseau *et al*. (1991), except that the reverse may be occurring in response to diffusion forces, resulting in hysteresis. Overall, it appears that the obtained diuron desorption results are within observations reported in the literature, and that desorption is operating to

limit the effective sorbed mass of diuron to composted gin trash. Furthermore, the extent of desorption appears to be much lower than that reported by Inoue *et al*. (2006), as the large partition coefficients illustrated that diuron exhibited a strong preference for the composted cotton gin trash.

Break-through column and the need for dynamic assessment

Due to a number of constraining factors, dynamic sorption assessment of endosulfan sulphate and diuron was unable to be carried out using the break-through column experiment. The experiment did, however, produce some interesting observations about the nature of the composted gin trash, in particular its complexity. A number of explanations and proposed methods to overcome such complications, as well as further implications posed by the observations, will be explored.

The discharge yielded from the column that produced 100% absorbance on the spectrophotometer, indicated the dispersive nature of the compost. The material likely to attribute to this outcome was soluble fulvic and humic fractions that had been displaced from the compost into the mobile phase through dispersion (Bollag *et al.* 1992). The concentration of the dispersed material in solution was so high that no light, in the UV-visible range, was able to penetrate the suspension, making detection of any pesticide in solution impossible. Pre-treatment of the compost through washing with water has been identified in a number of publications (e.g. Burgisser 1993; Rose 2006) as a means of devouring the sorbent of its soluble and colloidal fractions. Such methods may be employed under the assumption that soluble and colloidal components may be removed through weathering in the field. It has been recognised, however, that such material, as well as various other colloidal compounds, have the potential to transport pesticides in the solution phase (Bollag *et al.* 1992; Kennedy *et al.* 2001; Leonard *et al.* 2001; Crossan *et al.* 2002; VanLoon and Duffy 2005). This suggests a

need to investigate the mobility and quantify whether such material is capable of transporting chemical.

The dispersive nature and abundance of mobile colloidal fraction, as well as refining the particle size of the compost to less than 2 mm, were likely factors attributing to the low hydraulic conductivity (less than 1 mL min^{-1}) of the composted gin trash in the break-through column. The outcome of this has implications for the time required to achieve break-through as well as degradation of pesticides through biotic and abiotic processes, before effective and measurable pesticide elution is attained. Such a problem may be overcome by amending the composted gin trash with an inert more porous compound, such as sand, glass beads or soil. This may have further application with dilution of dispersed humic compounds. However, where dispersion may not be overcome, the evolved pesticide may be measured by taking aliquots at defined time intervals, followed by extraction and analysis in the appropriate instrument, similar to Ahmad *et al*. (2005). It is important to note that a UV-visible spectrophotometer was used in this study for simplicity and that this was not the only available means of detection.

There is a desire to overcome the complications that have arisen in this project and carry out a more dynamic sorption assessment of composted gin trash using break-through column studies. Burgisser *et al.* (1993) highlighted the inaccuracies and difficulties in using batch equilibrium methods in assessing chemical sorption to soil:

- the solution to sorbent ratio is (usually) much higher than that which would occur in the field
- the sample is shaken vigorously leading to abrasion and dispersion of the sorbent resulting in greater sorbent/solute contact than is experienced in the field
- a large number of samples are required to generate an isotherm

Column studies effectively eliminate the onset of these compounding issues associated with traditional batch equilibrium studies. Furthermore, Rose (2006) highlighted that batch studies are useful for a comparison of sorbents, the data obtained from them, however, is sometimes less reliable and more difficult to use for *in situ* modelling, as a prerequisite to field trials. Furthermore, column studies better represent the sorbent-solute interactions experienced in filter systems, and they are easy to perform once they are set-up, compared to batch equilibrium studies (Burgisser *et al.* 1993).

Based on a range of implications posed by inaccuracies revealed to persist in traditional equilibrium batch sorption studies, there is a strong desire to overcome the complications observed for the break-through column study carried out in this project in future work. Such data would be useful in environmental modelling as a means of providing substantiation for large-scale use as a pesticide binding medium, which is the desired outcome for this preliminary assessment.

Areas for further research

Although this project was specifically aimed at characterising composted cotton gin trash for its pesticide binding ability, a number of other potential uses of this material have been identified. Such uses have been found to have manifestations in the fields of pesticide science, microbiology, and soil science.

This study has undoubtedly shown that composted gin trash has the capacity to bind an array of diuron and endosulfan sulphate concentrations observed in the field. It may be necessary to investigate its sorption affinity for a range of other pesticides used in the irrigated cotton industry, such as fipronil. This would provide substantiation for its broad application as a pesticide binding medium in remediation of pesticide contaminated tailwater.

On account of its large organic matter fraction, composted cotton gin trash may be used as a nutrient source for pesticide degrading microbes in subsurface filtration of tailwater. This idea leads on from Rose (2006), who noted the inefficiency of using basalt gravel and woodchip as a pesticide sorbent that also acted as the harbouring medium for microbes in the subsurface filtration of irrigation tailwater. Insufficient biofilm development, on account of poor nutrient content of the harbouring medium, limited the removal of pesticides from tailwater, even though promising results were reported. Assessing the ability of composted gin trash to support developing biofilms may enhance the filtration mechanism outlined by Rose (2006).

Composted gin trash may also provide added benefits in the area of soil science. The high organic matter content indicates it to return a significant quantity of organic matter as soil amendment. Enhancing the organic carbon to any soil has been shown to provide enhanced soil structural stability, water holding capacity and pesticide retention for a range of soils.

Composted gin trash is a largely unutilised resource that offers no economic return to the cotton industry. However, further research into a number of these areas may uncover an array of potentially beneficial uses for composted gin trash, whether it is in cotton production or elsewhere.

Conclusion

It has been found that composted gin trash, because of its large organic matter fraction, can effectively sorb environmentally relevant concentrations of endosulfan sulphate and, to some extent, diuron. Unique sorption-desorption mechanisms were identified to be operating for diuron and endosulfan sulphate. These outcomes occurred due to a combination of hydrophobic and hydrophilic interactions with humic components of the compost medium.

The extent of sorption for a range of applied concentrations was not found to be limited for endosulfan sulphate and diuron, when compared to other sorbents reported in the literature. Furthermore, limited desorption of endosulfan sulphate and diuron for a range of environmentally relevant concentrations was observed. This suggests that composted gin trash may be an efficient medium used to buffer tailwater storages through use in sub-surface filtration, or as a soil amendment on cotton fields or tail ditches. However, results obtained using batch equilibrium studies do not provide the means of substantiating its use in the field. Such problems have been highlighted; hence the need to overcome the complications observed for the break-through column study is essential for a more dynamic assessment of sorption necessary for *in situ* environmental modelling. However, these preliminary results suggest that composted gin trash offers an effective filter medium in remediation of pesticide contaminated tailwater.

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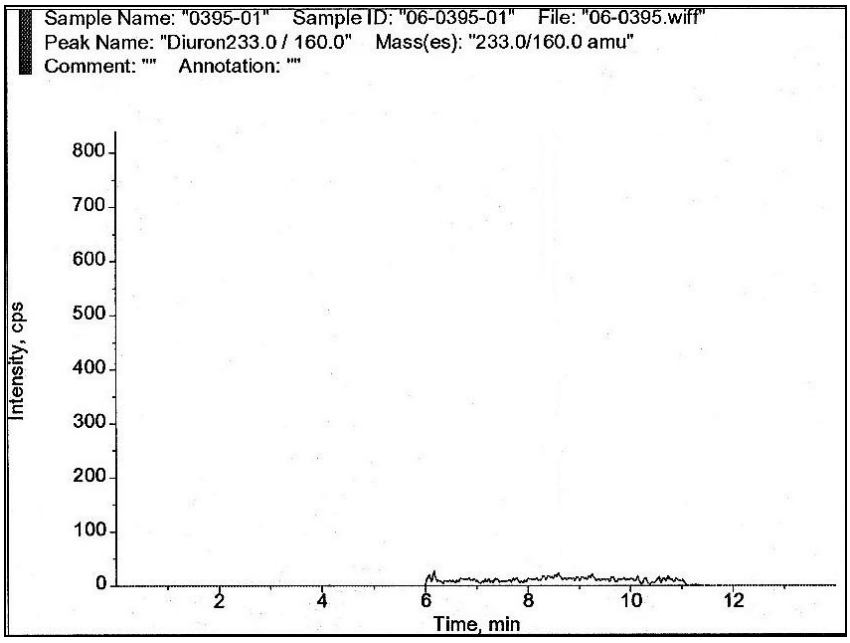
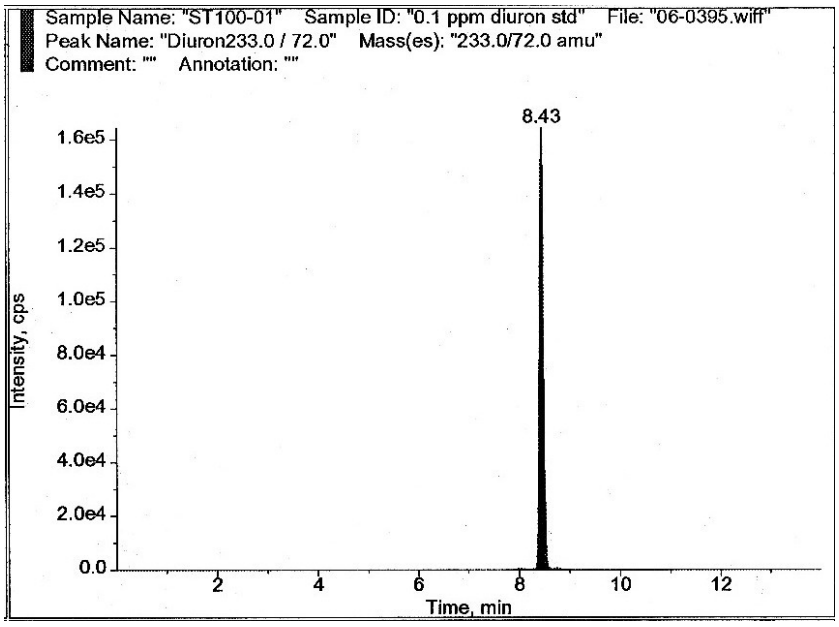
Appendix

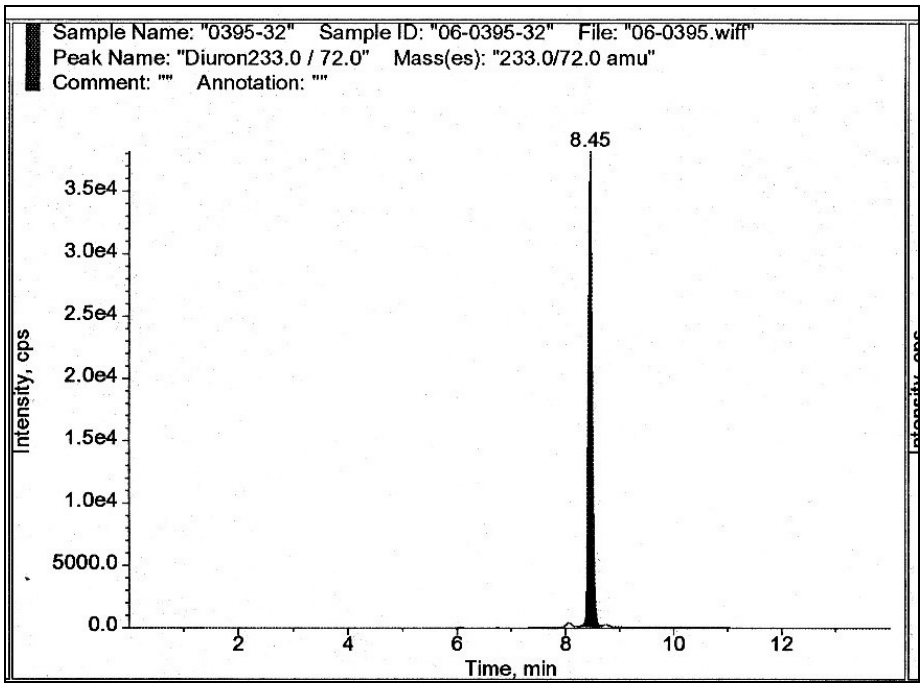
Appendix 1.1 LC/MS/MS instrument response for diuron. (a) blank; (b) 100 µg L^{-1} standard; (c) sample; and (d) standard curve



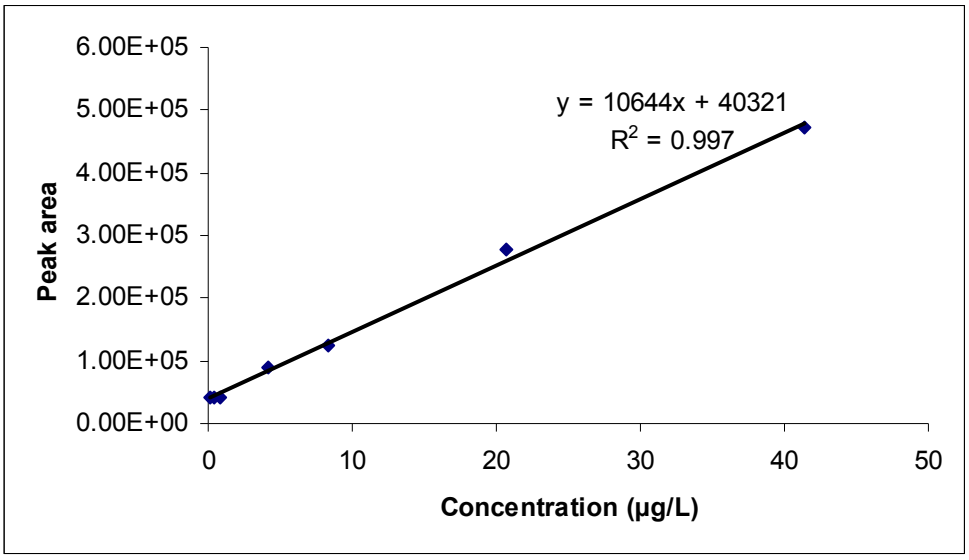
(a)



(b)

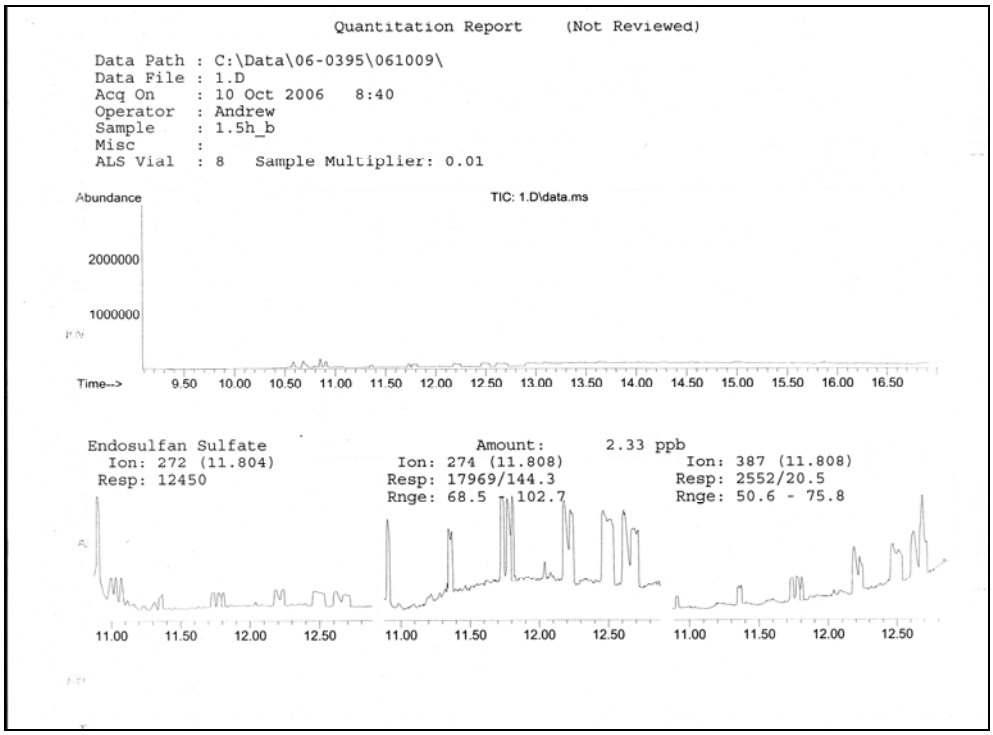

Sample Name: "0395-32" Sample ID: "06-0395-32" File: "06-0395.wiff"
Peak Name: "Diuron233.0 / 72.0" Mass(es): "233.0/72.0 amu"
Comment: "" Annotation: ""
8.45
3.5e4
3.0e4
2.5e4
2.0e4
1.5e4
1.0e4
5000.0
0.0
Intensity, cps
2
4
6
8
10
12
Time, min

(c)

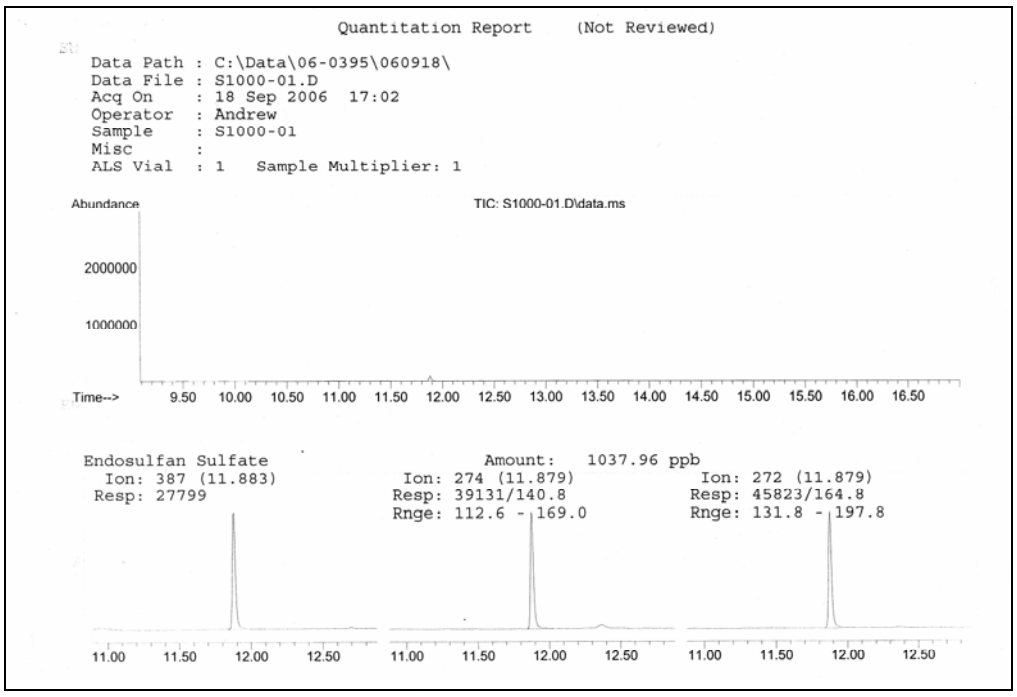

6.00E+05
5.00E+05
4.00E+05
3.00E+05
2.00E+05
1.00E+05
0.00E+00
Peak area
y = 10644x + 40321
R2 = 0.997
0
10
20
30
40
50
Concentration (µg/L)

(d)

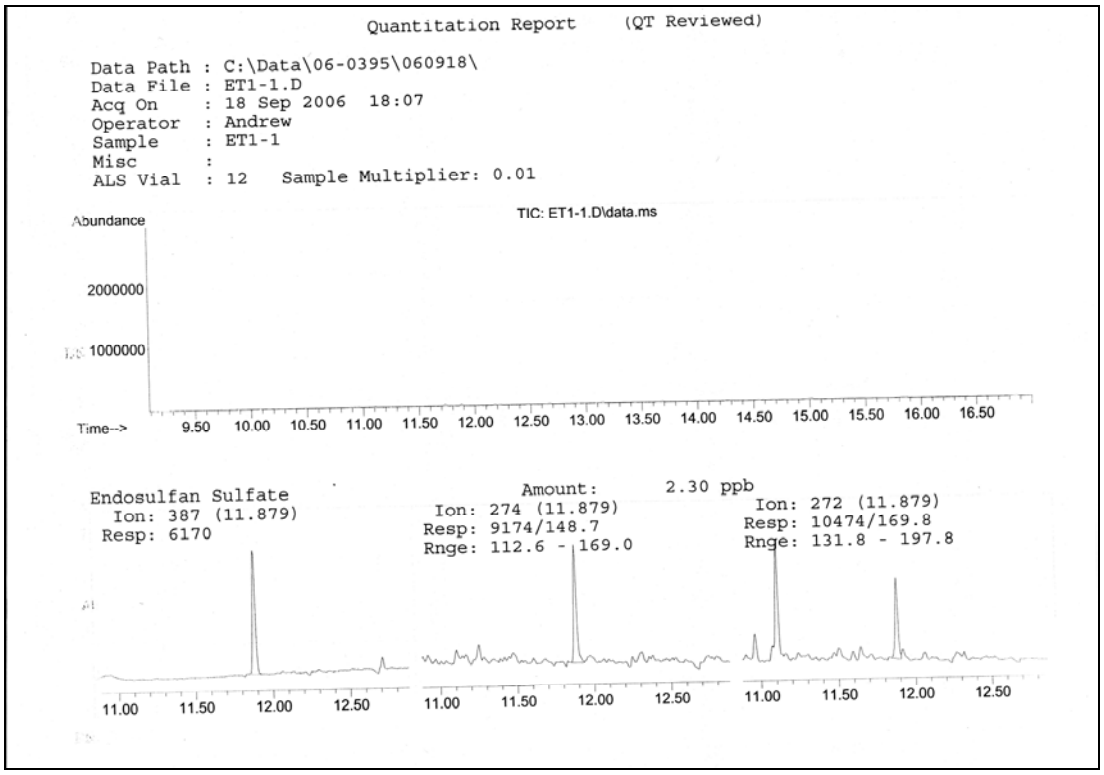
Appendix 1.2 GC-MS instrument responses for endosulfan sulphate (retention time ~11.9 minutes). (a) Blank; (b) 1000 µg L^{-1} standard; (c) sample; and (d) standard curve.



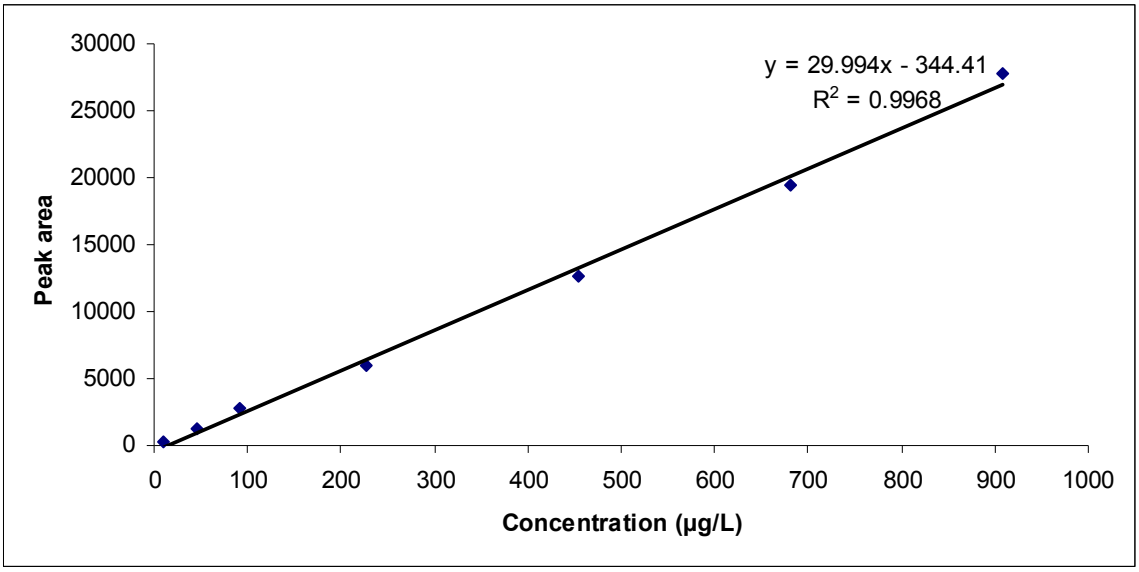
(a)



(b)


Quantitation Report (QT Reviewed)
Data Path : C:\Data\06-0395\060918\
Data File : ET1-1.D
Acq On : 18 Sep 2006 18:07
Operator : Andrew
Sample : ET1-1
Misc :
ALS Vial : 12 Sample Multiplier: 0.01
TIC: ET1-1.D\data.ms
Abundance
2000000
1000000
Time-->
9.50 10.00 10.50 11.00 11.50 12.00 12.50 13.00 13.50 14.00 14.50 15.00 15.50 16.00 16.50
Endosulfan Sulfate
Ion: 387 (11.879)
Resp: 6170
Amount: 2.30 ppb
Ion: 274 (11.879)
Resp: 9174/148.7
Rnge: 112.6 - 169.0
Ion: 272 (11.879)
Resp: 10474/169.8
Rnge: 131.8 - 197.8
11.00 11.50 12.00 12.50
11.00 11.50 12.00 12.50
11.00 11.50 12.00 12.50

(c)


y = 29.994x - 344.41
R2 = 0.9968
Peak area
Concentration (µg/L)
30000
25000
20000
15000
10000
5000
0
0 100 200 300 400 500 600 700 800 900 1000

(d)

Appendix 2.1 organic carbon determination

Sample	GT weight (g)	wt @ 105	wt @ 550	%Organic matter	% mineral fraction
1	10.067	7.021	5.270	24.939	75.061
2	10.037	6.595	5.201	21.137	78.863
3	10.012	6.759	4.938	26.942	73.058
4	10.053	6.050	4.303	28.876	71.124
5	10.02	6.513	4.938	24.182	75.818
			Avge	25.215	74.785
			St dev	2.922	2.922

Appendix 2.2 Kinetics results (a) for endosulfan sulphate and (b) Genstat non-linear regression analysis output

(a)

ID	Concentration (µg/L)
48 h endo kinetics	
UEBT1-1	0
UET1-1	1.48
UET1-2	1.39
UET2-1	1.08
UET2-2	1.01
UET3-1	0.95
UET3-2	0.85
UET4-1	0.79
UET4-2	0.67
UEBT2-1	0
UET5-1	0.74
UET5-2	1.02
UET6-1	0.64
UET6-2	0.71
UET7-1	0.58
UET7-2	0.62
UET8-1	0.52
UET8-2	0.98
C1-1	9.90
C1-2	9.38
C2-1	10.02
C2-2	9.51

ID	Concentration (µg/L)
2 h endo kinetics	
10-b	0
10_1	3.70
10_2	3.63
20_B	0
20_1	3.24
20_2	3.19
40_B	0
40_1	1.48
40_2	1.62
1h-1	1.39
1h-2	0.80
1.5h_B	0
1.5-1	2.99
1.5-2	0.87
2h-B	0
2h-1	1.13
2h-2	1.75

(b)

Nonlinear regression analysis

Response variate: endo_unfil_microg_g
Explanatory: Time_endo_unfil
Fitted Curve: A + B*(R**X) + C*(S**X)
Constraints: R < 1; S < 1

Summary of analysis

Source	d.f.	s.s.	m.s.	v.r.	F pr.
Regression	4	0.160256	0.0400640	93.60	<.001
Residual	9	0.003852	0.0004280		
Total	13	0.164108	0.0126237		

Percentage variance accounted for 96.6
Standard error of observations is estimated to be 0.0207.

Estimates of parameters

Parameter	estimate
R	0.9170
S	0.9972
B	-0.3599
C	-0.04587
A	0.4216

Fitted values and residuals

Unit	Explanatory	Response	Fitted value	Standardized residual	Leverage
1	0.0000	0.00	0.02	*	*
2	10.0000	0.27	0.23	*	*
3	20.0000	0.29	0.31	*	*
4	40.0000	0.38	0.37	*	*
5	60.0000	0.38	0.38	*	*
6	90.0000	0.36	0.39	*	*
7	120.0000	0.38	0.39	*	*
8	180.0000	0.40	0.39	*	*
9	360.0000	0.41	0.40	*	*
10	540.0000	0.42	0.41	*	*
11	720.0000	0.41	0.42	*	*
12	1440.0000	0.42	0.42	*	*
13	1920.0000	0.42	0.42	*	*
14	2880.0000	0.42	0.42	*	*
Mean	598.5714	0.35	0.35	*	*

Appendix 2.3 Sorption kinetics results (a) for diuron and (b) Genstat non-linear regression analysis output

(a)

ID	Concentration (µg/L)
Diuron 48h kinetics	
UDBT1-1	0
UDBT1-2	0
UDT1-1	27.50
UDT1-2	28.53
UDT2-1	33.60
UDT2-2	24.77
UDT3-1	29.56
UDT3-2	23.08
UDT4-1	27.50
UDT4-2	27.70
UDBT2-1	0
UDBT2-2	0
UDT5-1	29.75
UDT5-2	20.92
UDT6-1	23.18
UDT6-2	21.48
UDT7-1	21.86
UDT7-2	20.73
UDT8-1	18.48
UDT8-2	19.32
C1-1	48.96
C1-2	47.00
C2-1	50.51
C2-2	50.23

ID	
2 h diuron kinetics	Concentration (µg/L)
10_1	44.9
10_2	26.9
20_1	25.3
20_2	25
40_1	22.1
40_2	21.4
1h-1	18.8
1h-2	18.7
1.5-1	31.3
1.5-2	20.6
2h-1	16.6
2h-2	16.4

(b)

Nonlinear regression analysis

Response variate: Sorbed_mass_micro_g_g
Explanatory: Time_mins
Fitted Curve: A + B*(R**X) + C*X
Constraints: R < 1

Summary of analysis

Source	d.f.	s.s.	m.s.	v.r.	F pr.
Regression	3	1.4116	0.47052	15.47	<.001
Residual	10	0.3042	0.03042		
Total	13	1.7157	0.13198		

Percentage variance accounted for 77.0
Standard error of observations is estimated to be 0.174.

Estimates of parameters

Parameter	estimate
R	0.9860
B	-0.7390
C	0.0001053
A	1.110

Fitted values and residuals

Unit	Explanatory	Response	Fitted value	Standardized residual	Leverage
1	0.0000	0.00	0.36	*	*
2	10.0000	0.48	0.47	*	*
3	20.0000	0.87	0.55	*	*
4	40.0000	0.81	0.70	*	*
5	60.0000	0.96	0.80	*	*
6	90.0000	0.90	0.92	*	*
7	120.0000	0.98	1.00	*	*
8	180.0000	1.01	1.08	*	*
9	360.0000	1.02	1.15	*	*
10	540.0000	1.19	1.17	*	*
11	720.0000	1.16	1.19	*	*
12	1440.0000	1.21	1.25	*	*
13	1920.0000	1.45	1.30	*	*
14	2880.0000	1.33	1.38	*	*
Mean	598.5714	0.95	0.95	*	*

Appendix 2.4 Endosulfan sulphate sorption isotherm (a) raw data, (b) Genstat log-linear and (c) linear regression analyses

(a)

ID	Concentration (µg/L)
endo isotherm	
E100-1	7.288826686
E100-2	6.585431608
E75-1	7.460515453
E75-2	5.28389918
E50-1	4.320326609
E50-2	3.33456736
E10-1	1.178073887
E10-2	0.969493318
E5-1	0.655913008
E5-2	0.702866209
E2.5-1	0
E2.5.-2	0
E1-1	0
E1-2	0

(b)

Regression analysis

Response variate: log_sorbed_mass
Fitted terms: Constant, log_conc

Summary of analysis

Source	d.f.	s.s.	m.s.	v.r.	F pr.
Regression	1	1.367506	1.367506	470.21	<.001
Residual	3	0.008725	0.002908		
Total	4	1.376231	0.344058		

Percentage variance accounted for 99.2
Standard error of observations is estimated to be 0.0539.

Estimates of parameters

Parameter	estimate	s.e.	t(3)	t pr.
Constant	3.342	0.153	21.83	<.001
log_conc	1.2695	0.0585	21.68	<.001

Fitted values and residuals

Unit	Response	Fitted value	Standardized residual	Leverage
3	-0.7138	-0.6800	-1.00	0.60
4	-0.3970	-0.4276	0.72	0.38
5	0.3183	0.2731	0.96	0.23
6	0.4900	0.5542	-1.50	0.38

7	0.6231	0.6010	0.53	0.41
Mean	0.0641	0.0641	-0.06	0.40

(c)

Regression analysis

Response variate: Sorbed_mass_pesticide_g_g
Fitted terms: Constant, %_g_mL

Summary of analysis

Source	d.f.	s.s.	m.s.	v.r.	F pr.
Regression	1	18.5205	18.52046	282.91	<.001
Residual	6	0.3928	0.06546		
Total	7	18.9132	2.70189		

Percentage variance accounted for 97.6
Standard error of observations is estimated to be 0.256.

Message: the following units have large standardized residuals.

Unit	Response	Residual
8	4.199	2.15

Estimates of parameters

Parameter	estimate	s.e.	t(6)	t pr.
Constant	-0.042	0.119	-0.35	0.736
%_g_mL	553.8	32.9	16.82	<.001

Fitted values and residuals

Unit	Response	Fitted value	Standardized residual	Leverage
1	0.000	-0.042	0.19	0.22
2	0.045	-0.042	0.39	0.22
3	0.114	-0.042	0.69	0.22
4	0.193	0.334	-0.60	0.17
5	0.401	0.552	-0.64	0.15
6	2.081	2.077	0.02	0.16
7	3.090	3.487	-1.99	0.39
8	4.199	3.800	2.15	0.47
Mean	1.265	1.265	0.02	0.25

Appendix 2.5 Diuron sorption isotherm (a) raw data, (b) Genstat linear and (c) log linear regression analysis

(a)

ID	Concentration (µg/L)
D5-1	4.41
D5-2	0
D10-1	4.08
D10-2	2.13
D25-1	10.6
D25-2	6.31
D50-1	20.9
D50-2	16.5
D100-1	42.3
D100-2	43.4
D250-1	113
D250-2	104
D500-1	189
D500-2	191

(b)

Regression analysis

Response variate: Sorbed_mass
Fitted terms: Constant, concentration_g_mL

Summary of analysis

Source	d.f.	s.s.	m.s.	v.r.	F pr.
Regression	1	198.981	198.9812	461.85	<.001
Residual	6	2.585	0.4308		
Total	7	201.566	28.7952		

Percentage variance accounted for 98.5
Standard error of observations is estimated to be 0.656.

Message: the following units have large standardized residuals.

Unit	Response	Residual
7	7.075	-2.25
8	15.500	2.40

Message: the following units have high leverage.

Unit	Response	Leverage
8	15.500	0.75

Estimates of parameters

Parameter	estimate	s.e.	t(6)	t pr.
Constant	-0.108	0.287	-0.37	0.721
concentration_g_mL	78.03	3.63	21.49	<.001

Fitted values and residuals

Unit	Response	Fitted value	Standardized residual	Leverage
1	0.000	-0.108	0.18	0.19
2	0.140	0.064	0.13	0.19
3	0.345	0.135	0.35	0.18
4	0.827	0.552	0.46	0.17
5	1.565	1.352	0.35	0.15
6	2.857	3.236	-0.62	0.13
7	7.075	8.359	-2.25	0.24
8	15.500	14.719	2.40	0.75
Mean	3.539	3.539	0.13	0.25

(c)

Regression analysis

Response variate: log_sorbed_mass
Fitted terms: Constant, log_concentration

Summary of analysis

Source	d.f.	s.s.	m.s.	v.r.	F pr.
Regression	1	3.05045	3.050451	322.96	<.001
Residual	5	0.04723	0.009445		
Total	6	3.09768	0.516280		

Percentage variance accounted for 98.2
Standard error of observations is estimated to be 0.0972.

Estimates of parameters

Parameter	estimate	s.e.	t(5)	t pr.
Constant	1.8317	0.0987	18.55	<.001
log_concentration	0.9593	0.0534	17.97	<.001

Appendix 2.6 Endosulfan sulphate desorption kinetics raw data

Endo Desorption kinetics	
ID	Concentration (µg/L)
D-ET1-1	<LOD
D-ET1-2	<LOD
D-ET2-1	<LOD
D-ET2-2	<LOD
D-ET3-1	<LOD
D-ET3-2	<LOD
D-ET4-1	<LOD
D-ET4-2	<LOD
D-ET5-1	<LOD
D-ET5-2	<LOD
D-ET6-1	<LOD
D-ET6-2	<LOD
D-ET7-1	<LOD
D-ET7-2	<LOD

Appendix 2.7 Diuron desorption kinetics (a) raw data and (b) statistical output

ID	Concentration (µg/L)
init_DT1-1	16.7
init_DT1-2	15.9
init_DT2-1	17.5
init_DT6-2	16.7
des_DT1-1	8.34
des_DT1-2	5.46
des_DT2-1	6.59
des_DT2-2	7.15
des_DT3-1	8.17
des_DT3-2	8.77
des_DT4-1	9.72
des_DT4-2	9.56
des_DT5-1	9.62
des_DT5-2	10.1
des_DT6-1	8.88
des_DT6-2	9.21
des_DT7-1	8.69
des_DT7-2	8.44
des_blank_DT4	0.284
des_blank_DT5	0.355
des_blank_DT7	0.175

Nonlinear regression analysis

Response variate: sorbed_mass_g_g
Explanatory: Time_mins
Fitted Curve: A + B*(R**X)
Constraints: R < 1

Summary of analysis

Source	d.f.	s.s.	m.s.	v.r.	F pr.
Regression	2	0.16555	0.082773	30.96	0.002
Residual	5	0.01337	0.002674		
Total	7	0.17891	0.025559		

Percentage variance accounted for 89.5
Standard error of observations is estimated to be 0.0517.

Estimates of parameters

Parameter	estimate	s.e.
R	0.97790	0.00797
B	0.4377	0.0558
A	0.9968	0.0218

Fitted values and residuals

Unit	Explanatory	Response	Fitted value	Standardized residual	Leverage
1	0.0000	1.4377	1.4345	1.91	1.00
2	60.0000	1.0927	1.1113	-1.91	0.96
3	180.0000	1.0942	1.0046	1.88	0.15
4	360.0000	1.0142	0.9969	0.37	0.17
5	720.0000	0.9557	0.9968	-0.87	0.18
6	1440.0000	0.9447	0.9968	-1.11	0.18
7	1920.0000	0.9855	0.9968	-0.24	0.18
8	2880.0000	1.0095	0.9968	0.27	0.18
Mean	945.0000	1.0668	1.0668	0.04	0.38

Appendix 2.8 Endosulfan sulphate desorption isotherm (a) raw data (b) Genstat log-linear and (c) linear regression analysis output

(a)

Endo Desorption isotherm	
ID	Concentration (µg/L)
E1-1A	<LOD
E1-2A	<LOD
E2-5-1A	<LOD
E5-1A	<LOD
E5-2A	<LOD
E10-1A	<LOD
E10-2A	<LOD
E50-1A	2.32
E50-2A	1.98
E75-1A	4.44
E75-2A	3.54
E100-1A	3.12
E100-2A	4.60

(b)

Regression analysis

Response variate: log_des_sorbed_mass_endo
Fitted terms: Constant, log_des_dissolved_conc_endo

Summary of analysis

Source	d.f.	s.s.	m.s.	v.r.	F pr.
Regression	1	0.039079	0.039079	4.74	0.274
Residual	1	0.008250	0.008250		
Total	2	0.047330	0.023665		

Percentage variance accounted for 65.1
Standard error of observations is estimated to be 0.0908.

Estimates of parameters

Parameter	estimate	s.e.	t(1)	t pr.
Constant	2.76	1.06	2.60	0.234
log_des_dissolved_conc_endo	0.925	0.425	2.18	0.274

Fitted values and residuals

Unit	Response	Fitted value	Standardized residual	Leverage
1	0.6027	0.5403	1.00	0.53
2	0.4610	0.5270	-1.00	0.47
3	0.2953	0.2918	1.00	1.00
Mean	0.4530	0.4530	0.33	0.67

(c)

Regression analysis

Response variate: Mass_substance_remaining_on_comp
Fitted terms: Constant, Desorbed_concentration_g_mL_Cdes

Summary of analysis

Source	d.f.	s.s.	m.s.	v.r.	F pr.
Regression	1	16.3299	16.3299	161.97	<.001
Residual	6	0.6049	0.1008		
Total	7	16.9348	2.4193		

Percentage variance accounted for 95.8
Standard error of observations is estimated to be 0.318.

Message: the following units have large standardized residuals.

Unit	Response	Residual
1	4.006	2.09
2	2.891	-2.13

Estimates of parameters

Parameter	estimate	s.e.	t(6)	t pr.
Constant	0.148	0.140	1.06	0.329
Desorbed_concentration_g_mL_Cdes	843.7	66.3	12.73	<.001

Fitted values and residuals

Unit	Response	Fitted value	Standardized residual	Leverage
1	4.006	3.515	2.09	0.45
2	2.891	3.405	-2.13	0.42
3	1.974	1.962	0.04	0.16
4	0.401	0.148	0.89	0.19
5	0.193	0.148	0.16	0.19
6	0.114	0.148	-0.12	0.19
7	0.045	0.148	-0.36	0.19
8	0.000	0.148	-0.52	0.19
Mean	1.203	1.203	0.01	0.25

Appendix 2.9 Diuron desorption isotherm raw data (a) Genstat log-linear and (c) linear regression analysis output

(a)

ID	Concentration (µg/L)
des_D5-1	0.97
des_D5-2	0.87
des_D10-1	1.72
des_D10-2	1.86
des_D25-1	4.78
des_D25-2	4.62
des_D50-1	10.29
des_D50-2	10.37
des_D100-1	21.17
des_D100-2	21.13
des_D250-1	49.49
des_D250-2	49.57
des_D500-1	89.88
des_D500-2	89.92

(b)

Regression analysis

Response variate: Log_Cs
Fitted terms: Constant, LogCaq

Summary of analysis

Source	d.f.	s.s.	m.s.	v.r.	F pr.
Regression	1	1.80846	1.808462	357.59	<.001
Residual	4	0.02023	0.005057		
Total	5	1.82869	0.365738		

Percentage variance accounted for 98.6
Standard error of observations is estimated to be 0.0711.

Estimates of parameters

Parameter	estimate	s.e.	t(4)	t pr.
Constant	1.854	0.110	16.85	<.001
LogCaq	0.9215	0.0487	18.91	<.001

(c)

Regression analysis

Response variate: amount_remaining_g_g
Fitted terms: Constant, desorbed_conc_g_mL

Summary of analysis

Source	d.f.	s.s.	m.s.	v.r.	F pr.
Regression	1	98.155	98.1552	314.50	<.001
Residual	6	1.873	0.3121		
Total	7	100.028	14.2897		

Percentage variance accounted for 97.8
Standard error of observations is estimated to be 0.559.

Estimates of parameters

Parameter	estimate	s.e.	t(6)	t pr.
Constant	-0.192	0.247	-0.78	0.466
desorbed_conc_g_mL	117.28	6.61	17.73	<.001

Fitted values and residuals

Unit	Response	Fitted value	Standardized residual	Leverage
1	0.000	-0.192	0.38	0.19
2	0.094	-0.084	0.35	0.19
3	0.255	0.018	0.47	0.18
4	0.587	0.371	0.42	0.17
5	1.049	1.019	0.06	0.15
6	1.800	2.288	-0.93	0.13
7	4.599	5.616	-2.07	0.23
8	11.005	10.351	2.42	0.77
Mean	2.424	2.424	0.14	0.25