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HERBICIDES WASH OFF FROM CANE TRASH BY RAINFALL

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Abstract

Over the past 150 years, coral reefs around the world have been extensively modified for agricultural production and urban settlement leading to a decline in water quality. This includes the water entering the Great Barrier Reef (GBR) lagoon of Australia. A scientific consensus statement on water quality in the GBR has concluded, *'water discharged from rivers to the GBR continues to be of poor water quality', and 'land derived contaminants, including suspended sediments, nutrients and pesticides, are present at concentrations to cause environmental harm*. This led to development of the Reef Rescue and Reef Plan programs in 2009.

Rainfall runoff of herbicides routinely used in sugarcane production has potential to cause harm to rivers, lagoons, and the GBR in Northern Australia. The fate of these herbicides can be modeled within the landscape to assist in identifying efficient strategies to reduce herbicide runoff and develop better land management practices. Little data is available on the mobility and concentrations of herbicides leaving surface trash cover during rainfall events by the process of washoff.

The purpose of this laboratory study was to quantify the amount of herbicides washing off sugar cane trash during simulated rainfall, to provide insight into herbicide behavior in the field.

Simulated rainfall was used to apply 100 mm of rain at a constant intensity of 50 mm/h on plots covered in cane trash. As an initial benchmark study, trash was sprayed with a conservative tracer, potassium bromide (KBr). The KBr results show that the concentrations of bromide washing off were initially very high, and declining exponentially as a function of time. However after about 5 minutes the wash off approaches a steady rate.

A similar procedure was used for the herbicide trials. Herbicides tested were ametryn, atrazine, tebuthiuron, S-metolachlor, diuron and hexazinone. The effect of 'time after spraying' on concentration in wash off was also investigated through a series of experiments where plots were sprayed and left for varying time durations of 24 hours, 8 days and 40 days before being rained on.

The herbicide washed off showed a sharp decline in wash off concentrations for all the

tested herbicides at 5 minutes, followed by steady decline similar to KBr wash off. Each herbicide had differing coefficients of wash off due to different sorption coefficients and different decay rates. Wash off parameters used in herbicide runoff model were fitted to the data and compared.

This study will provide insight into the exact nature of the wash off from cane trash and provide wash off parameters for herbicide modeling. This will provide information on the safe application of herbicides and efficient strategies that can be employed to reduce the herbicides wash off to GBR the water bodies.

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Glossary/Acronyms

GBR	Great Barrier Reef
KBr	Potassium Bromide
FAO	Food and Agriculture Organization
BSES	Bureau of Sugar Experiment Stations
GCTB	Green Cane Trash Blanket
WHO	World Health Organization
QLD	Queensland
ACS	Analytical Consulting Services
QHSS	Queensland Health Science Services
EC	Electrical Conductivity
PH.	Potential Hydrogen Content
K_{OC}	Soil Sorption Constant
A 2.1	Label for samples collected. The letter represents the repetition name, the two represents the duration the sample was taken for and the one is the position of the sample in sequence.

Chapter 1. Introduction

1.1. Aim

The objective of this laboratory study is to characterize wash off by rainfall of different herbicides applied to sugarcane trash after different periods of time.

1.2. Objectives/Implications

Over the past 150 years, Great Barrier Reef (GBR) catchments have been extensively modified for agricultural production and urban settlement leading to a decline in water quality entering the GBR lagoon. A scientific consensus statement by *Brodie J. et al. 2008* on water quality in the GBR concluded,

> *"water discharged from rivers to the GBR continues to be of poor water quality in many locations' and 'land derived contaminants, including suspended sediments, nutrients and pesticides, are present at concentrations to cause environmental harm*

This has led to the development of the Reef Water Quality Protection Plant (Reef Plan) in 2003 and updated in 2009 through a joint Queensland and Australian Government initiative (Department of the Premier and Cabinet 2009). Reef Rescue (2008) is a key component of "Caring for our Country", the Australian Government's over $2 billion initiative to restore the health of Australia's environment and improve land management practices. Reef Rescue's objective is to improve the water quality of the GBR lagoon by increasing the adoption of land management practices that reduce the run-off of nutrients, pesticides/herbicides and sediments from agricultural land (Department of the Premier and Cabinet 2009).

The Reef Plan aims to "*halt and reverse the decline in water quality of water entering the Reef from adjacent catchment within 10 years*". In its first release, Reef Plan (2003) identified nutrients, pesticides/herbicides and sediments as priority contaminants in the GBR catchments.(Department of the Premier and Cabinet 2009) In order to assess the long-term effectiveness of the Reef Plan, there is a need to monitor the long term trends in sediment, pesticides and nutrient delivery to the reef and to identify sub-catchment hot-spots that are responsible for delivering disproportionate quantities of sediment, pesticides and nutrients.

Lewis et al. (2009) stated that 80% of the land adjacent to the GBR is farmland that supports, intensive cropping of sugarcane and extensive beef cattle grazing. This study focuses on the herbicides wash off from sugarcane trash.

The rationale behind conducting this study is that the herbicide wash off from sugarcane is one of the forms of run-off that needs to be managed. Herbicides can be detrimental to fresh and marine water environments (Lewis et al. 2009). This includes the world's largest coral reef ecosystem, the GBR that continues to be degraded from land-based pollution (Lewis et al. 2009).

Sugar cane is one of the major primary industries, with over 6300 farms growing sugar cane in Australia alone. Sugarcane is an important industrial crop of tropical and subtropical regions and is cultivated on 20 million hectares in more than 90 countries (Vettore André 2003). Sugarcane belongs to the grass family (Poaceae), an economically important seed plant family that includes maize, wheat, rice, and sorghum as well as many forage crops.

In sugarcane, weeds have been estimated to cause 12 to 72 % reduction in cane yield depending upon the severity of infestation. The weed problem that occurs in sugarcane is very different to other plants due to 3 main reasons: (i) sugarcane is planted with wider spacing, (ii) the initial growth is very slow, and (iii) it is grown under abundant nutrient and water conditions (Stevenson, Brown & Latter 1972**).**

Herbicides are used to control weeds to prevent weed competition and losses in sugarcane production. Sugarcane is most susceptible to weed competition during the first eight to 10 weeks after emergence. Unless herbicides are applied immediately after planting, weed seed present in the soil following a fallow program will germinate, producing viable seeds and/or rhizomes (Stevenson, Brown & Latter 1972**).** There is reliance by the cane industry on herbicides for a higher yield. However, the trash blanket used to control soil erosion in sugarcane crops tends to retain the herbicides and when rainfall occurs, a proportion of these herbicides wash off. Herbicides washing off from the sugarcane trash either infiltrate into the soil, or enter surface runoff and enter the nearby water bodies, and may cause environmental damage and decline the water quality of water entering the Reef (Masters et al. 2012)**.**

There are different programs currently in process that are working on management strategies for the Reef Rescue. Targets for improvements in water quality entering GBR have been set through Reef Plan 2009. Specific water quality targets include a minimum of 20% reduction in sediment load and 50% reduction in nutrients and pesticides/herbicides pollutant loads at the end of catchment by 2013 (Department of the Premier and Cabinet 2009**).** To measure the progress towards targets, a combined monitoring and modeling at paddock through to catchment and reef scales has been established; Paddock to Reef Program (Figure 1).

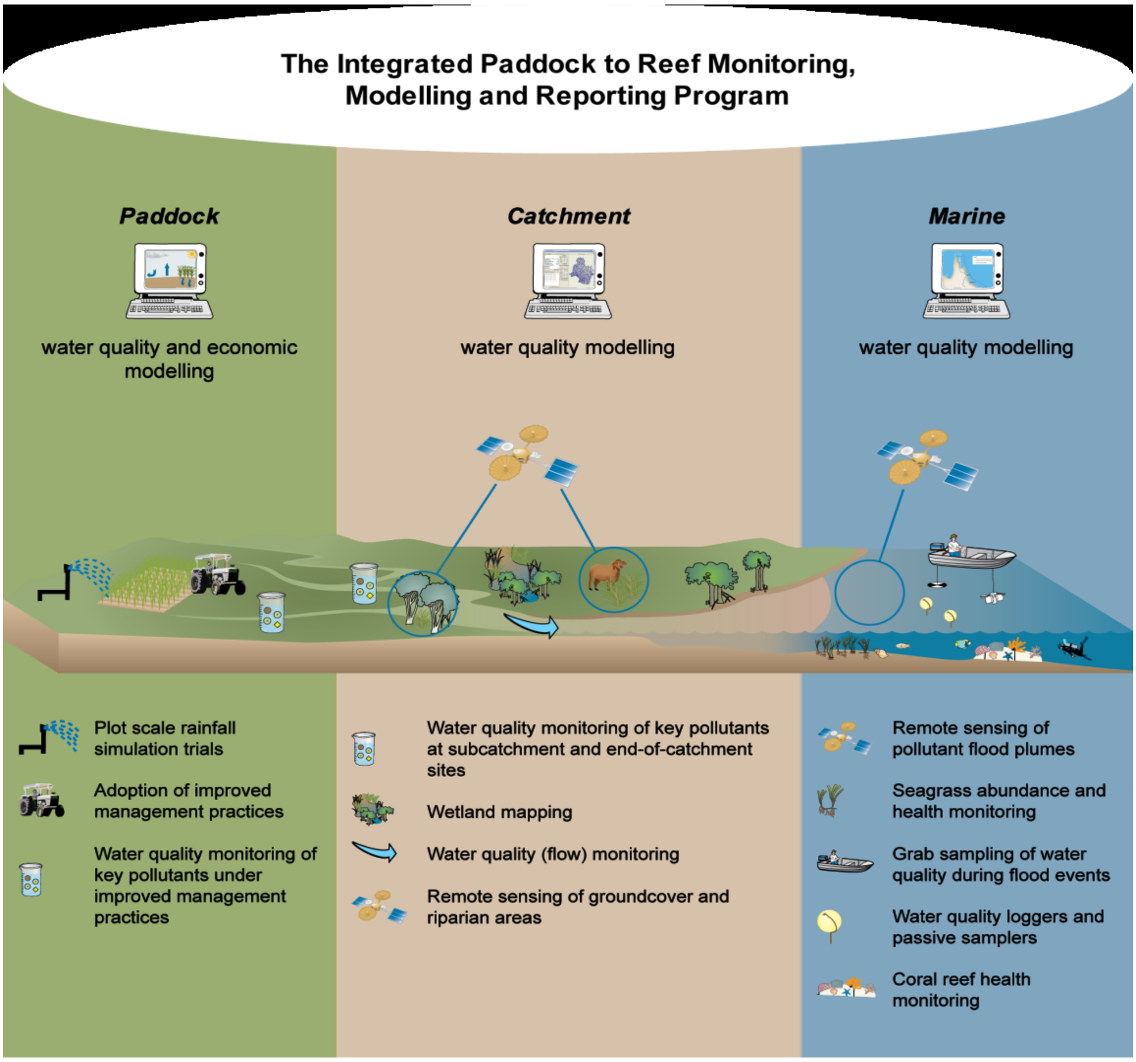


Figure 1. The conceptual framework for the Paddock to Reef Program (Department of the Premier and Cabinet 2009)

The program aims to provide evidence of links between land management activities, water quality and reef health using five lines of evidences that included: (i) the effectiveness of management practice to improve water quality, (ii) the prevalence of management practice adoption and change in catchment indicators, (iii) long-term monitoring of catchment water quality, (iv) catchment modeling, and (v) marine monitoring of GBR water quality (Carroll et al. 2012)**.** Present study is set in the first stage, to monitor the effectiveness of management practices at paddock scale to improve water quality of water entering the Reef from adjacent catchment and also to provide input data for paddock and catchment modeling to assess meeting targets.

This research aims to quantify the amount of herbicide that is being washed off from the sugarcane trash. Even though awareness of the herbicides wash off exists, herbicides concentration and changes in their properties with time are poorly understood. It is necessary to understand: (i) if retaining trash increases herbicide runoff or reduces it, (ii) if timing of rainfall affects their concentration and properties, and (iii) how are wash off herbicides concentrations and properties changed with different herbicides. The results of this study can be used to develop management strategies and provide input data for paddock and catchment modeling to provide assessment of progress towards meeting Reef Plan targets.

1.3. Outline

The objective to this dissertation is to conduct tests with different herbicides while using potassium bromide (KBr) as a standard to determine the percentage that is washed off from sugarcane trash under a rainfall simulator.

The research methodology was divided into six main parts:

- Defining the problem and the need for this study
- Reviewing the literature relevant to this topic. This will be divided into sugarcane, herbicides, wash off, and the use of bromide as tracer.
- Researching and creating a methodology suitable to test different herbicides. There will be three types of tests: (i) potassium bromide, (ii) instantaneous runoff and (iii) time after spraying.
- Conduct analysis on percentage and concentration of herbicides in samples of wash off collected.
- Research into the interpretation of the results and how to use wash off results to model at paddock scale
- Develop conclusions and recommendation to manage the problem.

Chapter 2. Literature review

2.1. Introduction

The following chapter will provide an in depth literature review into the wash off characteristics of herbicides on cane trash. This review covers several topics:

- Production of sugar cane and the crop based strategies that are currently being trialed to reduce the herbicide runoff, including wash off.
- Use of different herbicides in sugarcane and their properties.
- Amount of wash off that occurs from a wide range of plant canopies and the different variables that affect their wash off.
- Use of tracers, potassium bromide for our tracer. The main reason behind using bromide is that it is considered to be a conservative element because it does not undergo rapid microbial transformations or bind with the organic matter or clay minerals.

2.2. Sugar Cane

2.2.1. Introduction

Sugarcane (*Saccharum officinarum*), one of the world's most cultivated crops, is a tropical grass that originated in Papua New Guinea and then spread throughout the world. Sugarcane is one of the world's most significant crops. The reason it is regarded as significant is because it is a renewable, natural agricultural resource that provides sugar, besides biofuel, fibre, fertilizer and myriad of by-products/co-products with ecological sustainability (Department of Health and Aging 2004).The juice from the sugar cane's stalk is highly prized and is the source of 70 percent of the world's sugar (Department of Health and Aging 2004).

Sugarcane belongs to the grass family, an economically important seed plant family that includes maize, wheat, rice, and sorghum as well as many forage crops (Barnes 1964). Its one of the most productive and photo-synthetically efficient of all crops and has outstanding ability to synthesize and store sucrose (Barnes 1964).

In sugarcane, weeds have been estimated to cause 12 to 72 % reduction in cane yield depending upon the severity of infestation. The weed problem that occurs in sugarcane is different to other plants. This is due to four main reasons. These reasons are that sugarcane is planted with wider spacing, and the initial growth is very slow, it's grown under abundant nutrient and water conditions. (Stevenson, Brown & Latter 1972)

Weeds which occur in sugarcane include sicklepod, milkweed, guinea grass, sorghum, setaria, paspalum, nut grass and other grasses (Callow B, Fillols E & Wilcox T 2010**).** They are known to play as alternate hosts to ratoon - a disease for sugarcane that result in poor growth of cane and also affects the quality.

Herbicides are useful to prevent weed competition and losses in sugarcane product. Unless herbicides are applied immediately after planting, weed seed present in the soil following a fallow program will germinate, producing viable seeds and growing. This has an effect on the yield of sugarcane produced

The herbicides sprayed onto sugar cane are usually retained on the trash. Tillage is used because of the need to retain the trash to minimize soil erosion (Prove et al. 1995). Herbicides used in Queensland sugarcane production included 330,000 kg per year of atrazine, almost 100,000 kg per year of diuron and 76,000 kg per year of ametryn, on approximately 457,000 ha (Simpson BW, Calcino D & Haydon G 2001).

There is an associated risk of off-site movement of herbicides in runoff. Currently many sugar cane based strategies are in trial to aid in managing herbicides runoff (Carroll et al. 2012). These strategies include the use of the green cane trash blanket, controlled traffic and reduced tillage.

2.2.2. Production of Sugar Cane

Sugarcane is a crop with one of the highest production rates around the world, and is one of the most intensively farmed crops. In 2010, FAO estimates that it was cultivated on about 23.8 million hectares, in more than 90 countries, with a worldwide harvest of 1.69 billion tones. The world demand for sugar is the primary driver of sugarcane agriculture.

Brazil is the largest producer of sugar cane in the world. The next five major producers, in decreasing amounts of production, were India, China, Thailand, Pakistan and

Mexico. As shown in the graph below, over the last decade the production of sugarcane has increased worldwide. However, in Australia the amount of sugarcane production has been decreasing over the last 5 years. (Vettore André 2003)

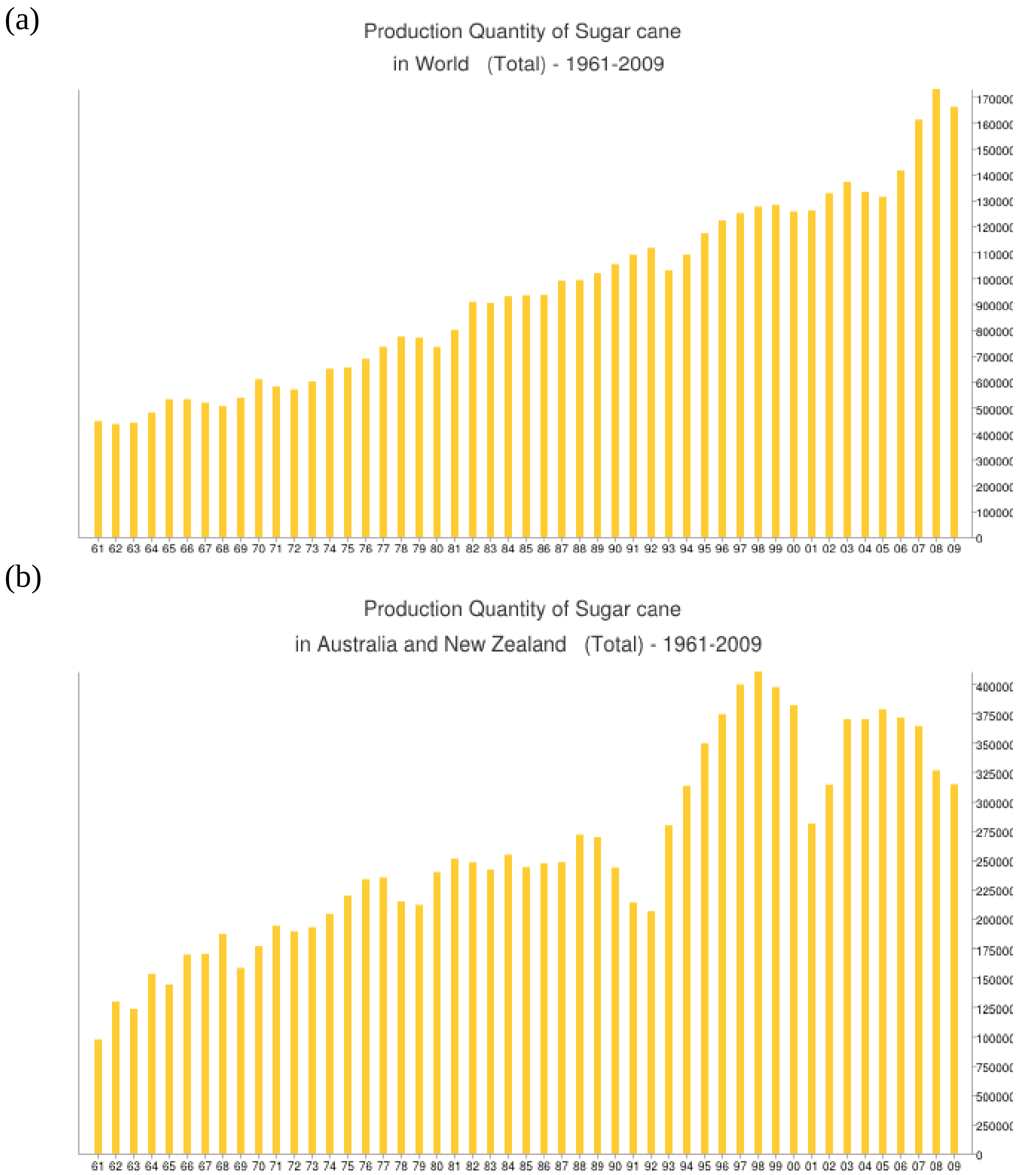


Figure 2. The amount of sugarcane in tons produced (a) worldwide compared to the (b) Australia. Over the last decade the production of sugarcane has increased worldwide. However, in Australia the amount of sugarcane production has been decreasing over the last 5

Worldwide sugarcane occupies an area of 20.42 million ha with a total production of 1333 million metric tons. Sugarcane area and productivity differ widely from country to country. Brazil has the highest area of production at 5.343 million ha, while Australia has the highest productivity at 85.1 tons/ha (Foram Sheth 2011).

Weeds are a concern for sugarcane production because they cause a 12 to 72% reduction in the amount of sugarcane produced. The percentage does depend upon the severity of infestation (Barnes 1964). Weeds can reduce sugarcane yields by competing for moisture, nutrients, and light during the growing season (Barnes 1964) According to Davis (2011), Australian sugarcane production is particularly reliant on a wide variety of herbicidal applications and a more restricted range of insecticidal controls.

2.2.3. Adoption of Green Cane Trash Blanket (GCTB)

Green cane harvesting and trash blanketing (GCTB) was introduced in Australia in the 1970's and has been widely adopted by the sugar industry, particularly in northern Queensland as an environmental protection measure (Liu D. L & Bull 1998). With green cane harvesting, the leaves and tops of the cane are left on the ground as a 'trash blanket'. Research indicates that this protects the soil from erosion (Prove BG, Doogan VJ & Truong PN 1995) leads to improvements in soil organic matter content, nutrient retention, more biodiversity, water quality and reduced costs of weed and insect control (Liu D. L & Bull 1998). The GCTB also leads to substantial improvements in profitability through labor and cost savings, reduced tillage and less crop loss under wet harvesting conditions. Also the lack of cane fires has reduced the smoke and ash nuisance for nearby communities.

Figure 3. Trash Blanket method in use at in a Bundaberg cane field. This shows how the cane may continue to grow while the soil is covered.

The trash blanket is a method used to improve yields on well-drained, sandier soils that are harvested during warmer conditions where moisture conservation is important (Eldridge 2004). The trash blanket after green harvest can restrict the growth of ratoon cane, particularly in clay soils, or after early or late season harvest. The loss of yield can be reduced by raking the trash from the cane row.

One of the main advantages to the trash blanket is that the rain doesn't belt into the soil, and the soil's firm underneath it, and the water trickles through the trash, and leaves everything very stable, enhancing infiltration and reducing soil erosion(Prove BG, Doogan VJ & Truong PN 1995). If the rain is not able to directly erode, then the effect the rain has on the amount of wash off occurring is reduced because infiltration leads to lesser amount of water available for runoff. (Eldridge 2004).

2.2.4. Conclusion

Sugarcane is one of the world’s most significant crops because it is a renewable, natural agricultural resource that provides sugar, biofuel, fibre, fertilizer and myriad of by-products/co-products with ecological sustainability.

The production of sugar cane is currently on the decrease in Australia while it is increasing on a world scale. It is currently growing in an area of more than 20.42 million ha with a total production of more than 1333 million metric tons. Herbicides are commonly used for efficient sugarcane production; however, these herbicides are running off into the water bodies.

Therefore, it is necessary to manage this problem by reducing herbicide runoff. One of the strategies currently in development is the use of the Green Cane Trash Blanket. This involves leaving the leaves and tops of the cane on the ground as a 'trash blanket'. Research indicates this protects the soil from erosion, increases soil moisture, provides weed control, nutrient and soil health advantages, and helps manage weeds.

2.3. Herbicides

2.3.1. Introduction

Nearly 70% of all pesticides used by farmers and ranchers are herbicides (World Health Organisation (WHO) 1990). Herbicides are used in sugarcane to control weeds that compete with crops for root space, nutrients and water or to remove brush or foliage so that land may be used for other purposes or to control aquatic weeds. There are two major types of herbicides used in the cane farming industry. The first type, the residual herbicides are applied pre-emergence to prevent seeds germinating and/or emerging. The other type is the knockdown herbicides. They are used to kill emerged weeds and have shorter lives (Callow B, Fillols E & Wilcox T 2010)**.** These herbicides have an important role in the economic viability and sustainability of the sugarcane industry and have contributed to the historic shift to a new farming system for sugarcane (Johnson & Ebert 2000), which promotes green cane trash blanketing (GCTB) and minimum tillage practices. This has substantially reduced rates of soil erosion, which was previously perceived as the primary threat to the GBR (Starck W 2005).

There is also a growing use of photosynthesis inhibitory (PSII) herbicides around the world today. Through there are a large number of different PSII herbicides that can be used with sugar production the most common herbicides used are diuron and atrazine (Hamilton D & Haydon G 1996). Presence of these herbicides in marine ecosystem is of particular concern as they inhibit photosynthesis and long-term chronic exposure may have adverse (Jones 2005) and sea grass communities (Haynes, Müller & Carter 2000). These are also the two herbicides currently under major examination to determine their continued usage.

2.3.2. Usage

The pesticides usage in farming is growing exponentially. In 1985, the amount of pesticides used would have been around 3 million tons. Today it is hitting the point where it nearly doubled. Herbicides are about 70% of the total pesticides used worldwide. In the period between 1972 and 1985, the sales of pesticides had doubled (World Health Organisation (WHO) 1990). This is based on the total sales of pesticides changing from US$ 3000 million to US$15900 million. Using this information it was calculated that the global consumption of pesticides in 1985 would have been about 3 million tones (World Health Organisation (WHO) 1990). However it is important to remember that the actual increase would have been slightly less due to an increase in sales of the more expensive new pesticides.

Herbicide usage rates in Australia are considered to be low by the world standards. When studying the herbicide usage in Queensland in 2001, Simpson

(Simpson BW, Calcino D & Haydon G 2001) tabulated on the basis of herbicide usage in different sugarcane growing regions. The chosen regions were based on North, Herbert, Burdekin, Central, and South. Each given amount of herbicide is for the total sugar cane crop growth area in each region. The total usage for the herbicides is quite high for sugar cane. Atrazine reached a total of 331585 kg for an area of 436000 ha.

Table 1. The amount of herbicides used on different sugarcane crops within QLD defined by area(Simpson BW, Calcino D & Haydon G 2001).

Herbicides	North (92000ha)	Herbert (56000ha)	Burdekin (71000ha)	Central (128000ha)	South (89000ha)	TOTAL (436000ha)
Atrazine	107594	33804	46480	116011	27696	331585
Diuron	34264	16718	7884	108691	29889	197446
2,4-D	50260	28237	13168	41103	8789	141557
Glyphosate	10267	4388	10052	53830	7088	85625
Ametryn	8688	2208	11768	51113	2205	75982
Paraquat	12065	3476	3752	15345	8167	42805
Trifluralin	1600	96	3768	10276	5480	21220
Asulam	1271			4659	12725	18655
MSMA	3960			5017	1359	10336
Pendimethalin	976	2760	992	539	627	5894
Hexazinone	2054	704		2758	79	5595
Ioxynil	27			3328		3355
Fluroxypur	1308	560			29	1897
2,2-DPA			296	130		426
Dicamba	191				28	219
Metolachlor	22				26	48
Diquat					17	17
Bromacil		9				9
Picloram				3		3

2.3.3. Photosystem II Herbicides

The Triazine herbicides (including atrazine) and urea derivatives (Diuron) are photosystem II (PSII) inhibitors. The use of these herbicides causes photosynthesis to be affected leading to destruction of cell membranes, more slowly than by other desiccators (Kennedy et al. 2011). Photosystem 2 inhibitors reduce the flow of electrons in the weeds from water to NADPH2+ in photosynthesis at the photochemical step (Figure 4) (Yamamoto 2001). These herbicides ensure that the electrons will only accumulate on the chlorophyll molecules. Therefore, the oxidation reactions increase to a level that is not tolerated by the plant, causing the plant to die (Kennedy et al. 2011).

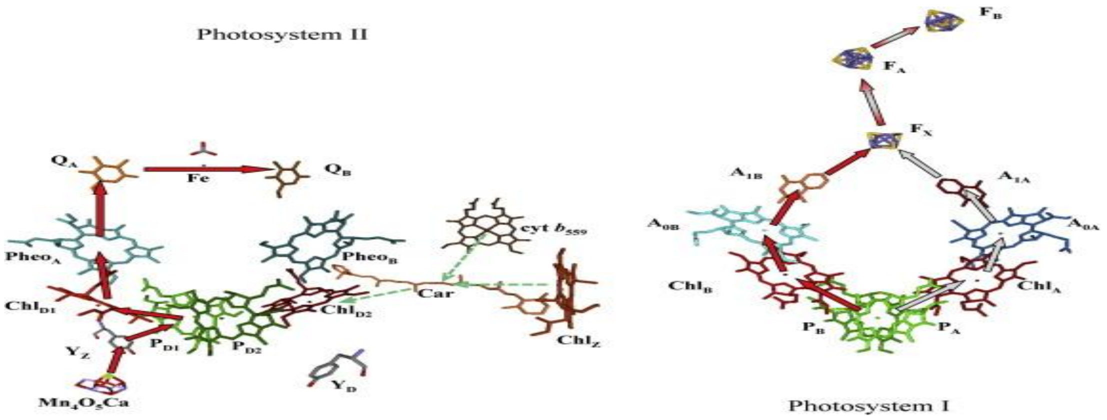


Figure 4. Biochemical diagram of the photosystem 2 process (Yamamoto 2001). Photosystem 2 inhibitors reduce the flow of electrons in the weeds from water to NADPH2+ in photosynthesis at the photochemical step. These herbicides ensure that the electrons will only accumulate on the chlorophyll molecules

Figure 5: Effect of photosystem II herbicides on plants. Leaves usually start turning yellow at the margins and progress inwards, eventually turning a red-bronze colour and desiccating from tips, edges and between veins, and then dying. In tolerant plants, the herbicides will be metabolised

Photosystem II herbicides inhibit photosynthesis and cause the leaves to become yellow and desiccate from tips, edges and between veins (Figure 5). Leaves usually start turning yellow at the margins and progress inwards, eventually turning a red-bronze colour and desiccating from tips, edges and between veins, and then dying. In tolerant plants, the herbicides will be metabolised.

In a study conducted by Lewis et al. (2011) about herbicides in the GBR, it was found that hexazinone in combination with diuron and atrazine residues produced an additive mixture of photosystem II inhibitors in the Reef. The high herbicides concentrations in the GBR lagoon indicate a risk to the immediate inshore areas of the GBR lagoon; the risk may extend further offshore due to the presence of the PSII inhibitors(Lewis et al. 2011).

2.3.4. Environmental Fate

Environmental ‘fate and behavior’ refers to what happens to the herbicide after it leaves the sprayer (Ferrell 2009). Understanding fate helps us determine what position and amount of Herbicide effectively kills the weeds and how much either can contaminate the groundwater, surface water, or remains on the soil/ trash. The herbicide that falls directly upon the soil or is washed onto the soil can undergo a number of processes which may be broken down into two main groupings: degradation and transport processes. Degradation processes include biological degradation by soil organisms and abiotic chemical and photochemical transformations. Transport of herbicides within the soil compartment can occur downward into the soil profile (leaching), across the soil surface (runoff), or into the air (volatilization). There are three major types of environmental fate of herbicides that needs to be examined that have to be examined: the persistence, degradation and the mobility (Figure 6) (Ferrell 2009).

The degree of herbicide transport in the environment depends on several factors such as application rate, herbicide persistence and mobility, rainfall, topography and climate. Transport depends on how they are applied as well as physical and chemical properties. The other factor that has a major influence on the fate of an herbicide is its half-life. For example atrazine has a half-life of 60-100 days while pendimethalin only has a half-life of 44 days (Senesi & Testini 1983). The new herbicides – the knockdowns such as fluroxypyr has only a half-life of 6 days in trash.

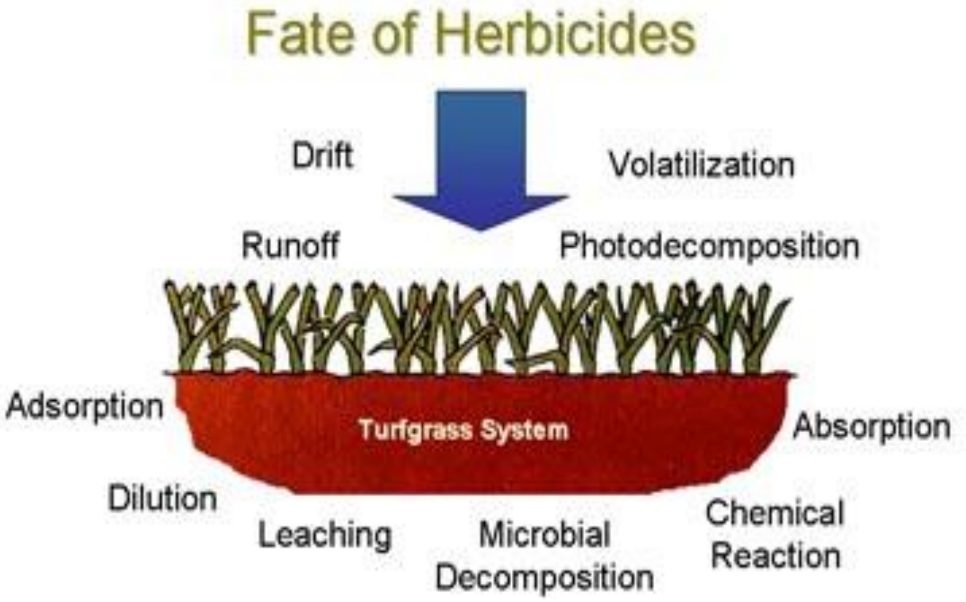


Figure 6. The possible fates of an herbicide in any natural environment (Ferrell 2009).

2.3.5. Herbicide half-life

Many of these herbicides have relatively short half-lives, which affect their wash off; if they have dissipated they are not available to wash off. Others compounds (e.g. older insecticides such as DDT) have very long half-lives and can continue in the soil for generations (Kearney P. C 1988). The "old group" of herbicide however does not behave like that. They have relatively short half-lives, particularly in tropical environments (Simpson BW, Calcino D & Haydon G 2001)**.** This leads to a lesser amount of herbicides being available for transportation via surface runoff to contaminate distant water sources.

Herbicide half-life in soil is given as a typical or average value as listed in the Footprint and USDA database (Wauchope RD et al. 1992). These values vary depending on environmental conditions and soil type.

The understanding of herbicide loss in catastrophic and critical events, or the 'risk window'(Simpson et al. 2001), and persistence in the system (half-life) provide important knowledge for herbicide management including product selection and timing of applications. Avoiding application within at least three weeks of heavy rainfall will reduce the risk of herbicide loss in runoff by an order magnitude for ametryn and atrazine, and by approximately half for diuron and hexazinone.(Kearney P. C 1988)

The use of herbicide half-lives in soil for the estimation of herbicide residues available for runoff as a function of time after application is complicated (Wauchope 1978). Various processes are not always accounted for, such as the herbicide availability and breakdown (volatilisation and photodegradation) on the surface of foliage and ground cover residues. Therefore, "half-lives" based on concentration decline in runoff over time, can give more realistic values, as they incorporate all sources of herbicide. These can be referred to as "runoff-available herbicide" half-lives. In either case (soil, foliage or runoff available), it is important to characterise herbicide behaviour for the local condition where they are used and need to be managed (Silburn & Kennedy 2007).

2.4. Herbicide properties

Table 2. Selected properties of herbicides studied. Chemical properties compiled using the 'Footprint' Pesticides Properties Database.

Herbicides	Solubility in water (mg/L)	Soil half-life, DT50 (days)	Organic carbon sorption K_{OC} (ml/g)	Chemical type
Diuron	42	90	1067	Ureas
Atrazine	33	60	100	Triazines
Ametryn	185	90	316	Triazines
Hexazinone	33,000	60	54	Triazines
S-Metolachlor	480	124	200	Aniline
Tebuthiuron	2500	400	80	Phenylureas

2.4.1.1. Atrazine

Atrazine is usually regarded as slightly soluble in water at a rate of 33 mg/L (Pesticide Properties Database (PPDB) 2009a). It is used as a selective triazine herbicide for season-long weed control in a variety of crops. It is used to control broadleaf and grassy weeds in many crops including sugarcane.

Atrazine is an herbicide with one of the high persistence rates when compare to herbicides such as hexazinone. Atrazine does not break down readily (within a few weeks) after being applied. Instead it can be carried deeper into the soil by rainfall causing the aforementioned contamination (Pesticide Properties Database (PPDB) 2009a). Chemical hydrolysis, followed by degradation by microorganisms, accounts for most of the breakdown that occurs in the environment.

Atrazine is moderately to highly mobile in soils with low clay content or low organic matter content. Because it does not adsorb strongly to soil particles and has a lengthy half-life, it has a high potential for ground water contamination despite its low solubility (Senesi & Testini 1983). The half-life of the herbicide has the greatest effect on the life of atrazine in runoff.

2.4.1.2. Diuron

Diuron is an herbicide soluble at a rate of .42mg/L, which is normally used as a pre-emergent herbicide. It’s a white crystalline solid, wettable powder.(Pesticide Properties Database (PPDB) 2009b)

Diuron has a half-life from about one month to one year for the parent, five months for the methylurea derivative (DCPMU), and one month for the urea derivative (DCPU) in soil. Locally measured field half-lives are 500 days in cane fields(Simpson BW, Calcino D & Haydon G 2001) and 30 days in a Queensland Vertosol (Silburn & Kennedy 2007)**.** Some pineapple fields contained residues three years after the last application.

Diuron is readily absorbed through the root system of plants and less readily through the leaves and stems. Diuron residues in soil are toxic to plants. Residue levels are lower in soils with low organic content.

Diuron is currently the most commonly detected herbicide in the GBR waters (Lewis et al. 2009)**.** This is due to its higher usage, persistence and mobility (Giacomazzi & Cochet 2004). Mobility in the soil is related to organic matter and to the type of the residue. The metabolites are less mobile than the parent.

2.4.1.3. Ametryn

Ametryn is another member of the Triazine chemical family. It is used to control broadleaf weeds and annual grasses in pineapple, sugarcane and bananas. Ametryn is available as an emulsifiable concentrate, flow able wettable powder and a wettable powder.

Ametryns half-life in soils, the amount of time it takes to degrade to half of the original concentration, is 70 to 250 days, depending on the soil type and weather conditions and the half-life is expected to be shorter in tropical conditions. Loss from the soil is principally by microbial degradation (Clark & Kenna 2010). Ametryn moves both vertically and laterally in soil due to its high water solubility. Because it is persistent, it may leach as a result of high rainfall, floods, and furrow irrigation.

In a study of surface and groundwater contaminants in the U.S, ametryn was found in six states in very few surface water samples and in 4% of the groundwater samples. (Clark & Kenna 2010).

2.4.1.4. Hexazinone

Hexazinone, the last major member the Triazine family, is used as a broad spectrum herbicide. It is a colorless solid (Ganapathy 1996). It exhibits some solubility in water but is highly soluble in most organic solvents except alkanes. Hexazinone is a contact and residual herbicide, readily absorbed by the leaves and roots (Ganapathy 1996).

Hexazinone has a field dissipation half-life of 139 days. The major routes of hexazinone dissipation in soil are photo degradation, biodegradation and leaching.

Hexazinone is very soluble in water and has a low average organic carbon adsorption coefficient. This suggests that hexazinone is mobile in the environment and partitions into water more than into soil (Ganapathy 1996). Hexazinone can be classified as moderately mobile in soil. It is also weakly adsorbed by soil. Compared to more basic triazines, protonation and adsorption-desorption by cation exchange would occur less readily for hexazinone due to its weak basicity. Therefore, little charged hexazinone would exist in soil and is adsorbed by soil through non-polar mechanisms (Ganapathy 1996). With the moderate to long half-life and moderate mobility, hexazinone can potentially move off-site with water in run-off and in base flow. .

2.4.1.5. S-Metolachlor

Though S-metolachlor is not a PSII herbicide it is used commonly with sugar cane and was tested in this study. S-metolachlor is widely used as an herbicide. It is a derivative of aniline and is a member of the chloroacetanilide herbicides (O'Connell, Harms & Allen 1998). Metolachlor is produced from 2-ethyl-6-methylaniline (MEA) via condensation with methoxyacetone.

Metolachlor has the potential to leach to ground water because of its relatively high water solubility. The hydrolysis half-life of metolachlor is estimated to be over 200 days. Metolachlor has a very high potential to contaminate ground water since it is relatively mobile and persistent in soil. Metolachlor has been detected under a variety of conditions in California surface water (O'Connell, Harms & Allen 1998).

Metolachlor is considered to be moderately persistent in different soil types and has an average field dissipation half-life of 124 days. Metolachlors field half-life in soil varies depending on soil type and environmental conditions, and is estimated to be between 15-132 days, 90 days (Wauchope 1978) and 30 days (Wauchope 1978), and was measured as 30 days in a Queensland Vertosol (Silburn 2003). One of the major breakdown pathways of metolachlor in the soil is by aerobic and anaerobic microorganisms (O'Connell, Harms & Allen 1998). The adsorption of the pesticide increases with increased soil organic matter and clay content, and can slow its movement in soil (O'Connell, Harms & Allen 1998).

There are also somewhat newer herbicides being used in sugar cane production, such as the knockdown fluroxypyr (Starane) and residuals such as isoxaflutole, imazapic, metribuzin and pendimethalin (Balance, Flame, Soccor and Stomp).

2.4.1.6. Tebuthiuron

Tebuthiuron is a nonselective broad spectrum herbicide of the urea class. It is used to control weeds, and woody and herbaceous plants.(Queiroz et al. 2008) It is absorbed by the roots and transported to the leaves, where it inhibits photosynthesis. Tebuthiuron is not actually registered for use with sugar cane, however it is PS2 herbicide and according to Lewis in 2009 it was detected within the GBR, due to use in grazing land for woody weed control. It is of interest to see if it has a similar wash off rate to the herbicides that are used with the sugar cane.

The US EPA considers tebuthiuron to be one of a group of pesticide compounds that have the greatest potential for leaching into, and contaminating, groundwater. The reason behind this is that tebuthiuron has all the characteristics of a material with high potential for groundwater contamination (Queiroz et al. 2008). It is highly soluble in water, adsorbs only weakly to soil particles), and is highly persistent in soils (soil half-life = 360 days). Tebuthiuron is easily moved with moisture in the soil.

In areas receiving 1000 to 1500 mm of annual rainfall, the time that it takes for half of the tebuthiuron to break down in soil is 12 to 15 months**.** It takes longer for the herbicide to break down in areas that have less rainfall. The half-life for tebuthiuron is also greater in muck and other high organic soils, regardless of rainfall (Queiroz et al. 2008).

Tebuthiuron is readily absorbed through roots. It is less likely to be absorbed by the leaves. However some tebuthiuron is broken down in the soil by 'microbes,' through the process of microbial degradation (Queiroz et al. 2008). However, tests indicate that this may not be the primary way by which tebuthiuron is degraded. Photodecomposition, or breakdown by sunlight, is negligible, as is volatilization, by which it changes from a solid to a gaseous form.

2.4.2. Management of Herbicides Runoff

There are certain practices that can be implemented to manage the amount of herbicide runoff already, though some of them may not be practical with sugar cane trash. There are three types of management practices in play: (i) management of the soil, (ii) managing the source of runoff, and (iii) management of the runoff water after it leaves the plot (Silburn, Foley & deVoil 2012). There are different practices involved with each one. The different soil management practices that reduce runoff and sediment movement include reduced tillage, retention of surface stubble or trash cover and controlled traffic farming (CTF).

The management of the source involves not only managing the type and amount of herbicide used but its placement and application method. The management of the source to reduce herbicide runoff can also include changing to an herbicide with properties that are less likely to runoff and have a less ecological impact (Silburn, Foley & deVoil 2012). If changing herbicides, it is necessary to ensure that the weed management process is not affected. Management of the runoff water after it leaves the plot involves use of practices such as silt traps, vegetative filter, and the use of storages and wetlands.

The two techniques used quite often in Australia are controlled traffic and banded applications (Silburn, Foley & deVoil 2012).Controlled Trafficking involves matching all machinery wheels to drive in ‘permanent’ wheel tracks, prevent compaction in the crop production area. Controlled traffic farming is becoming more widely utilized in extensive grain cropping in Australia and the Australian sugar cane industry but is now seen to be part of best management practices (Silburn, Foley & deVoil 2012).

Banded application is a method that involves reducing the potential movement in runoff of an herbicide by using less of the herbicide. This reduces the average concentration in the soil surface layer on a whole area basis by the ratio of the band to row width. This should result in an approximately proportional reduction in herbicide runoff when a runoff event occurs.

2.4.3. Conclusion

Herbicides are toxic materials that are used to control unwanted vegetation. Herbicides are widely used in agriculture. In the U.S.A, they account for about 70% of all agricultural pesticide use.

There are many different types of herbicides in use today; however the use of photosystem II herbicides is growing. Photosystem II herbicides refers to the herbicides like Atrazine and Diuron that reduce electron flow from water to NADPH2+ at the photochemical step in photosynthesis as their main mechanism. The photosystem II herbicides also have an additive effect that has an effect on the marine organisms in the Great Barrier Reef when washed off.

Many of the residual herbicides have moderate half-lives in soil, and dissipate over a matter of months. However, some have longer half lives in fresh and marine waters. This can lead to continued transportation of the herbicides via surface runoff while contaminating distant water sources. Unrestricted use of certain herbicides is suspected to be a major cause of pollution in rivers, streams and lakes.

There is a need to understand properties such as half-life and environmental fate of herbicides to understand their impact on wash off.

2.5. Wash off

2.5.1. Introduction

Leonard (1998) defines runoff as water and any dissolved or suspended matter it contains that leaves a plot, field, or small single cover watershed in surface drainage. He also states that specifically pesticide runoff is all dissolved, suspended particulate and adsorbed pesticide that is transported by water from a piece of land that has been treated. In contrast, washoff is the removal of pesticides from plant canopies or crop residues, such as sugar cane trash, by rainfall. Washoff water and pesticides may infiltrate or enter runoff and contribute to processes described above. Pesticides in washoff water are dominantly in the dissolved phase though some fine particulate matter may also wash off.

Excess herbicides are washed away through irrigation, rain, groundwater movement and storm water runoff. Herbicides that degrade slowly also contribute to pollution of the air and waterways. Water soluble herbicides stay in the water and are moved farther distances, because the herbicide do not settle out with sediment particles.

Runoff from areas treated with pesticides can pollute streams, ponds, lakes, and wells. Pesticide residues in surface water can harm plants and animals and contaminate groundwater (Leonard 1998). Water contamination can affect livestock and crops downstream.

The amount of herbicide runoff depends on; the slope, the texture of the soil, the soil moisture content, the amount and timing of a rain-event (irrigation or rainfall)and the type of pesticide used (Leonard 1998). Rain has the most dramatic effect on pesticide residues on plants. Rainfall can be broken down further into its properties and the way it impacts the wash off. Previous studies have found cover and canopies to have an effect on the amount of wash off and derived models based on such information.

2.5.2. Rainfall

The weather factors that are more likely to affect the rate of pesticide disappearance are relative humidity, rain, wind, temperature and sunlight. However the greatest amount of runoff occurs due to rainfall (Fleming 1994).

When looking at the effect of rainfall on the quantity of herbicides in runoff there are few factors that have to be taken into account. The major ones are rainfall intensity, rainfall amount, and most importantly timing of rainfall. Pesticide losses from runoff are greatest when it rains heavily soon after spraying.

2.5.2.1. Rainfall Intensity vs. Amount

Surface runoff occurs when rainfall rate exceeds infiltration rate. Increasing intensity increases runoff rate and energy available for extraction and transport. Increasing intensity reduces time to runoff within storm (Leonard 1998). It was surprising to find that the rainfall amount has a considerable more influence than rainfall intensity on wash off characteristics.

Rainfall amount affects total runoff volumes, the pesticide wash off from foliage relates to the total rainfall amount (Leonard 1998).

2.5.2.2. Time after spraying

Davis (2011) found that the greatest losses invariably occur in the first irrigation run-off events following herbicide application with losses in subsequent irrigation and rainfall events diminishing rapidly. Highest concentration of pesticide therefore occurs in first significant runoff event after application (Davis A.M, Thorburn P.J & Lewis S.E 2011) Pesticide concentration and availability at the soil and foliar surfaces dissipate with time thereafter.

In a study conducted by Masters et al. (2012) on reducing the amount of herbicide runoff on agricultural plots, it was found that when rainfall was experienced one day after application, a large percentage of herbicides were washed off the cane trash. However, by day 21, concentrations of herbicide residues on cane trash were lower and more resistant to wash off, resulting in lower losses in runoff (Masters et al. 2012). Consequently, ametryn and atrazine event mean concentrations in runoff were approximately 8 fold lower at day 21 compared with day 1, whilst diuron and hexazinone were only 1.6-1.9 fold lower, suggesting longer persistence of these chemicals (Masters et al. 2012).

2.5.3. Wash Off Models

Willis and McDowell (1987) showed that wash off concentration from plant canopies will be a declining exponential function of cumulative rainfall but independent of rainfall intensity. Some proportion of the compound will not wash off, that is, it is not ‘dislodgable’(Willis G.H & McDowell L.L 1987). An exponential equation is fitted to derive the parameters dislodgable fraction and exponent (rate constant of wash off), which are used to model wash off in HowLeaky.

HowLeaky is a program designed to represent a rebuilding of the PERFECT V3 model, with an enhanced interface designed to be useful to a range of non-modellers to explore the implications of alternative land-uses on water balance, runoff, erosion, and drainage (McClymont D et al. 2006). This is an experimental approach to explore whether a more user-friendly interface will enable a wider range of users to use daily simulation models as an aid to

HowLeaky uses a simple leaf area driven crop model (Leaf Area Index; LAI model) and a generic pan evaporation model (ET: Pan Model) to represent crops, pastures and trees. These models are responsive to water, temperature and radiation stress, and represent the dynamics between weather, soils and vegetation in so far as these impact on water use and water and sediment flows. (McClymont D et al. 2006). Since crop production is treated simply, these models should not be expected to simulate detailed crop management options such as soil fertility, detailed phenology or population issues.

2.5.4. Conclusion

Surface runoff is the water flow that occurs when the soil is infiltrated to full capacity and excess water from rain or other sources flows over the land. This is a major component of the water cycle and the primary agent in water erosion.

A factor that has the largest influence on runoff is precipitation. Rainfall amount, its intensity, time after spraying, and cover are different factors that need to be taken into account when studying the effect of rainfall on wash off.

Increasing intensity reduces runoff time within storm. It was surprising to find that the rainfall quantity has a considerable more influence than rainfall intensity on wash off characteristics. Time to runoff after inception of rainfall relates to how the runoff concentration increases as time to runoff decreases.

Many studies have been previously undertaken that examine the runoff from soil leading to previous development of wash models.

2.6. Effects of wash off

2.6.1. Introduction

There has been much concern about pesticides in agricultural runoff. The contaminated runoff represents not only a waste of agricultural chemicals, but also an environmental threat to downstream ecosystems.

The principal environmental issues associated with runoff are the impacts to surface water and groundwater such as Eutrophication. Ultimately these consequences translate into human health risk, ecosystem disturbance and aesthetic impact to water resources.

Contaminated surface waters risk altering the metabolic processes of the aquatic species that they host. These alterations can lead to fish kills, and alter the balance of the populations of the aquatic life present. Also aquatic species may cause a bioaccumulation of pesticides more readily than terrestrial organisms (Willis & McDowell 1982). Early on contact of pesticides with water was known to enhance phytotoxicity.

Certain model estimates indicate that 22% of the world’s coral reefs are threatened by land-based pollution (Puglise K.A & R. Kelty 2007). A great example of this damage caused by herbicide wash off is the GBR. Herbicides applied on crops in the GBR catchment in QLD have become a major threat to the GBR (Lewis S.E et al. 2009).

2.6.2. Aquatic Life

Excess herbicides are washed away through irrigation, rain, groundwater movement and storm water runoff. Herbicides that degrade slowly also contribute to pollution of the air and waterways (ller et al. 2004). Water soluble herbicides stay in the water and are moved farther distances, because the herbicide does not settle with sediment particles.

Figure 7. The damage that's caused to some of the aquatic life and their food is depicted in the picture.

Polluted stormwater runoff can adversely affect plants, fish, and animals and people (Figure 7). Excess nutrients cause algae blooms in lakes which removes oxygen from the water. Fish cannot exist in water with low dissolved oxygen levels. Bacteria and other pathogens can wash into swimming areas and necessitate beach closures (Newbold 1975). Trash washed into water bodies can choke, suffocate or disable aquatic life. Hazardous wastes can poison fish and shellfish. Sedimentation caused by erosion clouds the water and makes it impossible for aquatic plants to grow

2.6.3. Great Barrier Reef

The Great Barrier Reef is the world's largest coral reef system composed of over 2,900 individual reefs and 900 islands stretching for over 2,600 kilometers over an area of approximately 344,400 square kilometers (Duffy 2012). The reef is located in the Coral Sea, off the coast of Queensland in north-east Australia **(**Figure 8 **)**.

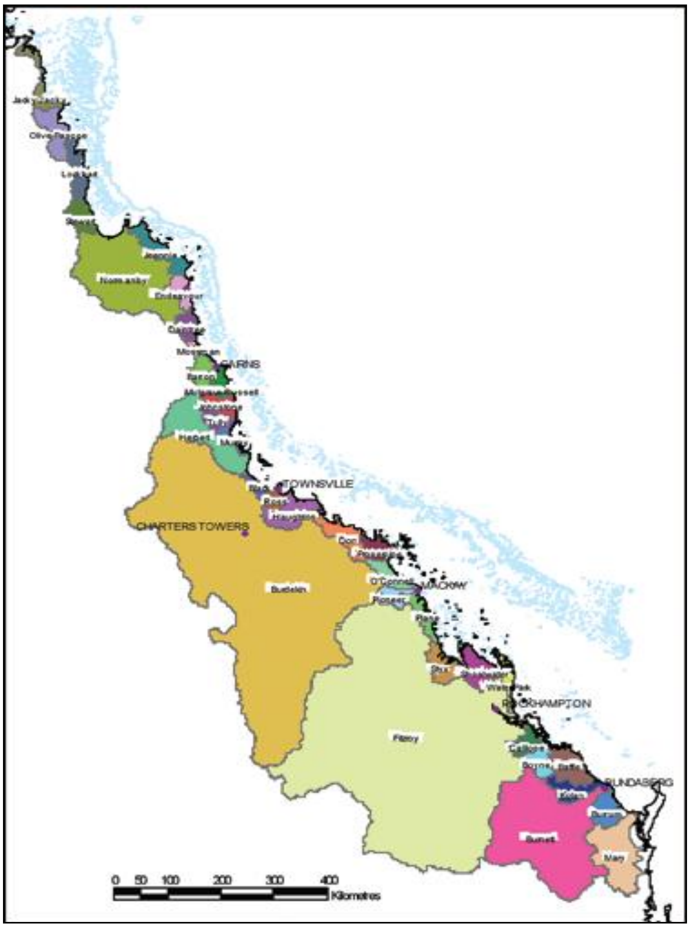


Figure 8. Map of the Great Barrier Reef World Heritage Area and surrounding catchments. The Great Barrier Reef is in the Coral Sea, on Australia's north-eastern coast. It stretches more than 2,300km along the state of Queensland's coastline

However in the coastal areas of Queensland is where the majority of sugarcane if produced. 60% of Australia crop production occurs in coast Queensland areas (Davis A.M, Thorburn P.J & Lewis S.E 2011).

The proximity of the GBR to intensive agricultural land uses places the reef and its ecosystem of great ecological and economic importance under threat. This is due to both exposure to many of the pesticides widely used in modern agricultural practices (Packett et al. 2009). It is also now well accepted that poor water quality can comprise corals and other reef organisms and impede the recovery of reef systems from bleaching events (Figure 9)

Figure 9. The Great Barrier Reef, One of the Seven Wonders of the World. The Great Barrier Reef is the world's largest living organism and is a place of remarkable natural beauty and biodiversity.

Sugar cane cultivation constitutes one of the dominant land-uses in the GBR catchment area (Packett et al. 2009). A large number of PS II herbicides that are sprayed onto the land have a tendency to wash off after a certain period of rainfall. When the herbicides do wash off they enter the nearby water bodies and water quality can be influenced by runoff and subsequent discharge from its adjacent catchments(Brodie & Waterhouse 2012).

This off-site movement of organic contaminants is a major threat to freshwater and the ecosystem. Therefore the runoff has been identified to be a major concern for the *Great Barrier Reef guidelines.* Herbicide residues have been measured in the GBR lagoon at concentrations that have the potential to harm most of the marine life (Shaw et al. 2010). Monitoring has shown that 80% of the time more than one herbicide was present. For example, during his initial tests, Lewis (2009) found that diuron (65% of samples) and atrazine (52%) were the most commonly detected herbicide residues in the GBR lagoon and were found together in most of the regions (Lewis S.E et al. 2009).

Due to this problem, in 2010 the Queensland Government introduced restrictions on using certain pesticides in GBR catchment areas in order to address pollution of the GBR region Reef. This was enforced through the Chemical Usage (Agricultural and Veterinary) Control Regulation 1999 (Qld). The restrictions apply to using, preparing, storing or possessing a prescribed product for carrying out an agricultural ERA (Environmental Defender Office 2011**).**

An "agricultural ERA" is defined as commercial sugar cane growing, or cattle grazing on more than 2000ha, in the Wet Tropics, the Mackay-Whitsunday and the Burdekin dry tropics catchment areas (Environmental Defender Office 2011**)**.

Herbicides applied on crops in the GBR catchment in QLD have become a threat to most water bodies in the area (Lewis S.E et al. 2009). Certain model estimates indicate that 22% of the world's coral reefs are threatened by land-based pollution (Puglise K.A & R. Kelty 2007)**.**

2.6.4. Conclusion

Despite this concern, presently there is little relevant information for use in making accurate predictions of the impact of specific pesticide amounts in agricultural runoff on water quality at some point downstream. There is a compelling need for fundamental research on the physical, chemical, biological and hydrological processes that regulate pesticide behavior not only in agricultural and aquatic habitats, but also during transit between the two. One of the areas with a lack of knowledge is sugar cane and the wash off that occurs from its fields.

2.7. Tracer Method

2.7.1. Introduction

In the tracer method, instead of measuring fluxes directly, tracers can be used to make accurate estimates of different recharge rates (Walker 1998). There are many types of tracers, however, for this study we require an artificial tracer for recharge estimation, which is applied below the soil surface to infer the recharge rate. The reason an artificial tracer is beneficial to this study is because it can be applied in high concentrations so that there is no ambiguity.

The tracer method is used because the movement of tracer is governed usually by long-term mean water fluxes, and does not require frequent visits to the field, and much smaller fluxes can be estimated.

However, to be able to use the trace method, the ideal tracer for each situation needs to be picked. The tracer should be able to follow the water movement. It needs to be mobile and soluble (Levy & Chambers 1987; Walker 1998). It cannot be strongly retarded by the soil or aquifer matrix. It also cannot be reactive or easily transform during transportation. This study also requires that it have low natural levels and low toxicity (Levy & Chambers 1987; Walker 1998). Based on this reasoning, bromide, an anion was chosen as the artificial tracer for this experiment.

2.7.2. Bromide as a tracer

Bromide is a chemical element with the symbol Br, an atomic number of 35, and an atomic mass of 79.904g/mol. It is in the halogen element group. Potassium has an atomic mass of 39g/mol. Combined Potassium bromide (KBr) has an atomic mass of 119.0g/mol. Potassium bromide is a typical ionic salt which is fully dissociated and near pH 7 in aqueous solution. It serves as a source of bromide ions- this reaction is important for the manufacture of silver bromide for photographic film. Under standard conditions, potassium bromide is a white crystalline powder. It is freely soluble in water.

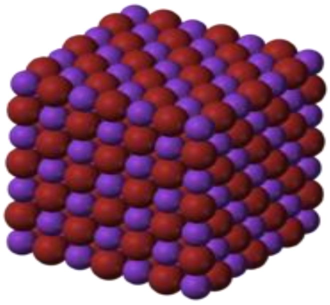


Figure 10. Atomic structure for Potassium Bromide. It shows how potassium and bromide are proportioned to create the solution. There are 39g/mol of Potassium to every 79g/mol of bromide.

Bromide is often used in the form of potassium bromide as a tracer for many experimentation (Levy & Chambers 1987). It is convenient and handy in studying the movement of both chemicals and water in solid. It is considered to be conservative because it does not undergo rapid microbial transformations or quickly bind with the organic matter of clay minerals. The other benefit of using Br is that it is not an agricultural chemical; therefore its background levels in the soil are generally very low.

Walton 2012 found when he conducted his study that a concentration of 10g/m2 of bromide are a minimum for detection in cane trash. Bromide is 67% of the total mass of the Potassium bromide.

Table 3: The proportions of potassium and bromide in different KBr solutions calculated (Bruce Cowie personal communication)

KBr			
5,7.5,15 g/m2 in 6 L		g/m2	g/m2
KBr		Br	K
5		3.4	1.6
7.5		5.0	2.5
10		6.7	3.3
15		10.1	4.9

2.7.3. Conclusion

In Australia, not all water-balance methods for estimating recharge are practical. Soil tracer techniques have been shown to be useful for Australian situations. There are many advantages of the soil trace method. These include less-frequent visits to sites, estimations of long-term mean water fluxes, and usefulness at low water flues. There are many different important tracer techniques such as a surface-applied tracer (bromide), historically applied tracers, and finally environmental tracers such as chlorine ions. An ideal tracer needs to be mobile, conservative, and low in the environment. Due to this anions and the less common isotopes are used as tracers.

There are many reasons as to why bromide is an ideal tracer. It has been used in a number of studies previously to investigate some of the mechanisms of recharge. Bromide is relatively cheap, easily measurable, has naturally low levels and is relatively mobile.

2.8. Thesis Rationale

The large use of photosystem II herbicides in the sugarcane industry, including diuron, atrazine, ametryn and hexazinone, to manage weeds and consistent detection of their residues in creeks and rivers in catchments within sugarcane industry poses a threat to World Heritage listed GBR lagoon. The adoption of farm management practices that minimize herbicide transport in rainfall-runoff is a priority for the Australian sugarcane industry.

There is an urgent need to get a thorough understanding of the herbicide wash off from sugarcane trash to develop strategies to minimise herbicide runoff from sugarcane area to GBR.

The highest risk period for herbicide loss in surface runoff and leaching is within a few weeks following application when concentrations are highest, with variations due to the herbicide type, soil type and weather conditions. Therefore, the time of herbicide application in relation to rainfall amount and intensity are important consideration in herbicide management and use.

The primary objective of this study is to quantify the concentrations of different herbicides in wash off from sugarcane trash as influenced by time after spray in relation to rainfall amount and intensity. The results of this study can be used to develop management strategies and provide input data for paddock and catchment modeling to provide assessment of progress towards meeting Reef Plan targets.

Chapter 3. Methodology

3.1. Introduction

The methodology of the experiment can be divided into a two parts. The first major part is the experimental outline. The second part of the methodology is based on a resource analysis. The resources required for this experiment are analyzed to see how much, what mode and what type of resources is needed. Therefore, the methodology covers the trash, the KBr, the rainfall simulator, and the herbicide mixtures. The final part of the methodology focuses on the different methods of analysis.

3.2. Experimental outline

There were three main sets of tests that needed to be conducted. The potassium bromide wash off, instantaneous herbicide wash off and the effect of time after spraying.

The KBr wash off tests were repeated three times to ensure consistency in results. In each test, trays were filled to the point of 100% cover with 500g of cane trash. The trash was then sprayed with 100 ml of the KBr solution. Each test was run for 2 hours to get full understanding of how the concentration of the compound in the runoff changes as the amount of cumulative rainfall increases.

Over the time period, it was necessary to collect an appropriate number of samples to be able to accurately determine the way the concentration of the substance changes. It was decided that 5 samples would be collected in the first five minutes, five samples for the next ten minutes at a two minutes interval, five samples for the next 20 minutes at 4 minutes intervals, one sample after ten minutes and then four samples at 15 minute interval.

Each sample was tested for electrical conductivity (EC) and pH to get a basic understanding of how EC changes over the time period and then a few chosen ones were sent to the lab for analysis to quantify the concentration of bromide in each of runoff solutions.

The major part of this experiment is the herbicide wash off tests. For this part of the experiment 6 stainless steel trays of 0.75m x 0.75m dimensions were used. Each of the trays was sprayed with the herbicides in a cabinet sprayer. The amounts of herbicides were calculated using their active ingredients. Due to the size of the trays for the herbicide spraying being only 0.75m x 0.75m to achieve 100% cover only 280 grams of cane trash was used. The herbicide wash off tests were run for two hours as well to ensure consistency. However, each herbicide test was only conducted twice. This gave us information on how much herbicide is washed off if rain hits the trash instantaneously after spraying.

The second part of this study is to examine how the amount of herbicide washed off is affected by time after spraying. The periods chosen for this test were: 1 day, 3 weeks, and 1 month. After each of these time periods, two runs of herbicide runoff were conducted.

To ensure the process was easy to follow be next researcher, each replication was identified by a letter in the alphabet. For example, the first run we undertook was Test A. All of the samples collected were labeled on this basis and their timing. If a sample was collected in a 2 minute duration period in example run A, it was given the name A 2.1. The one in the label identified the samples position in the succession of samples.

The runoff water samples were sent to the Queensland Health labs for analysis. The trash samples were sent to the ACS labs to determine if the herbicides were actually degrading as time went on and therefore, affecting the herbicides wash off.

3.3. Materials

The necessary resources included natural trash collected from a field site, a mixture of KBr made at a concentration substantial enough to be easily detected by the lab and an EC meter, a mixture of herbicide that features atrazine and diuron and other commonly used sugarcane herbicide and finally a rainfall simulator calibrated and designed to replicate rainfall.

3.3.1. Trash

To get a natural sample of cane trash it was collected from the Bundaberg sugarcane fields. This would ensure that the results we obtained would be similar to the results obtained from a site in the field. The sugarcane trash (variety KQ 228) was collected in September 2011 harvest, which was planted the previous year in the same month. About 15kg of trash was collected to ensure uniformity of trash throughout the study so that there would not be any change in the quality of results. The sugarcane trash was gently air dried before use to ensure that there was no previously stored moisture that could affect the runoff occurring.

The amount of cane trash used for each test was based on how much trash would collect in the field in a site of about 1 hectare. An average field usually has about 4000kg/ha – 5000 kg/ha of trash. The area of the trays used for the KBr tests were 1m^2. Therefore using a weight/volume ratio, it was calculated that each KBr run will require about 500 g/m^2 of cane trash. This would provide 100% cover on one of the 1m^2 mesh trays.

When designing the experiment for the herbicide test runs, the trays used for each of these runs was 0.75m by 0.75m. This was due to the sizing of the herbicide sprayer. Therefore, using an average field with 4000 kg/ha 5000 kg/ha of trash accumulation and a weight/ volume ratio, it was calculated that an area of 0.5625 m^2 would require only 280 grams of trash to obtain 100% cover.

3.3.2. Potassium Bromide

There is a need for a chemical to be used as a tracer to which the herbicides can be compared. Potassium bromide was chosen because according to B.S Levy and R. Chambers (1987) it is suitable for most soil-water studies. Based on their research, bromide is used in the form of Potassium bromide as a tracer for the test because it is considered to be conservative and stable. It does not undergo microbial transformations or bind with the organic matter and clay minerals.

It has a molecular weight of 119.0 g and has a pH that ranges from 5.5-8. Since bromide is 67% of the total molecular weight, it was necessary to ensure that there was a sufficient concentration of bromide in the solution. Based on R. Walton’s communications it was decided that a concentration greater than 10 gBR/m^2 would be suitable for the testing. Therefore, a total amount of 14.9 g/m^2 of potassium bromide was required, which equated to 149 g/L if 100 mL was applied to the plot area. The potassium bromide mixture was prepared in a beaker using 149 grams of KBr in 1 Liter of water.

The KBr mixture was applied onto the cane trash at a rate of 0.1L/m^2 because a usual field would have about 100L/ha applied which converts to 100ml for an m^2.

The bromide was sprayed onto the cane trash at 100ml/m^2 with a garden sprayer to ensure uniformity. Once sprayed, the tray was placed into the simulator at a slope of 1.5 radians. The slope was created with the use of bricks and bottles.

3.3.3. Herbicide Mixture

The herbicide testing required a mixture of herbicides that included the desired Photosystem 2 herbicides and the other herbicide occurring in the GBR. The exact amount of each herbicides was calculated using standard recommended rates of herbicides application in sugarcane (Callow B, Fillols E & Wilcox T 2010) (Table 4). Each herbicide was dissolved separately in 5 L water to obtain the desired rate of herbicide application on to the trash (Table 4). Each herbicide was sprayed separately on to each of the trays in spray cabinet at the Leslie Research Centre (Figure 11).

Figure 11. Leslies Research Centre's Spray cabinet that was used to uniformly spray the herbicides on the trash trays. This sprayer ensures that each tray received the same amount of each herbicide at the same rate.

Each product has specific product application rate that determine the amount of herbicide required. The spray cabinet uses a volume of 105L/ha in a cylinder of 5L size. Therefore, based on the calculation on how much herbicide amount would be required in the mix (Table 4), each herbicide was then sprayed on the 8 trays.

Table 4. Spray calibrations of the different herbicides used in the present study. The calculated amounts are based on the product application rates and the parameters of the cabinet sprayer.

Active Ingredient	Product	Product application rate L/ha	Water volume (L/ha)	Cylinder size (L)	Herbicide amount (L/kg)	Herbicide amount (mL or g)
Diuron	Barage 468 gai/kg	3	105	5	0.14	
Hexazinone	Barage 132 gai/kg	3	105	5	0.14	143
Atrazine	Gesapax Combi 500	6	105	5	0.29	143
Ametryn	Gesapax Combi 500	6	105	5	0.29	286
Tebuthiuron	Spike 80DF	2.24	105	5	0.11	286
S-metolachlor	Dual Gold	1.1	105	5	0.05	107

3.3.4. Rainfall Simulator

Rainfall simulation is a technique which aids the understanding of runoff under controlled conditions. Simulation requires that the relevant characteristics of natural rainfall be closely reproduced (Hudson 1993). Physical limitations and conflicting conditions obstruct the realization of a correct reproduction of all characteristics belonging to different kinds of natural storms.

The type of rainfall simulator used was an oscillating boom rainfall simulator. This design of rainfall simulator produces multiple drop size rainfall through the use of 2 flat fans Veejet 80100 nozzles set 1m apart (Foley J.L 2002). They were positioned to be 2m above the soil. Through previously conducted research by Loch and Foley in 1994, it is known that the mean drop diameter from the rain is 2.1mm. This simulator produces intermittent rainfall where the intensity chosen is synchronized by the number of times every minute a spray passes over the plot (Foley J.L 2002).

Figure 12. The oscillating boom rainfall simulator used for the testing. The pictures shows the two nozzles as they oscillate from one side to another

The rainfall simulator itself needed to be calibrated to rainfall intensity suitable and similar to rainfall in sugar cane production areas. Rain intensity of 50mm/hr was chosen. This intensity was determined to be most suitable, by examining the recurrence interval of different rainfalls in Mackay and Tully – two of Australia's major sugarcane farm locations. A rainfall of 50mm/hr for one hour duration tends to occur at least once a year in Mackay and a rainfall of duration of two hours tends to occur once every two years. In Tully, a rainfall of 50 mm/hr of one hour duration occurs about once a year too but a storm of the same intensity for two hours occurs once every 1.5 years.

To calibrate the simulator an empty tray was used. The simulator was run for 10 minutes and the amount of water that collected in the tray was measured for Tully and Mackay (Figure 13**).** This was then compared to the calculated value for the rainfall at intensity of 50mm/hr.

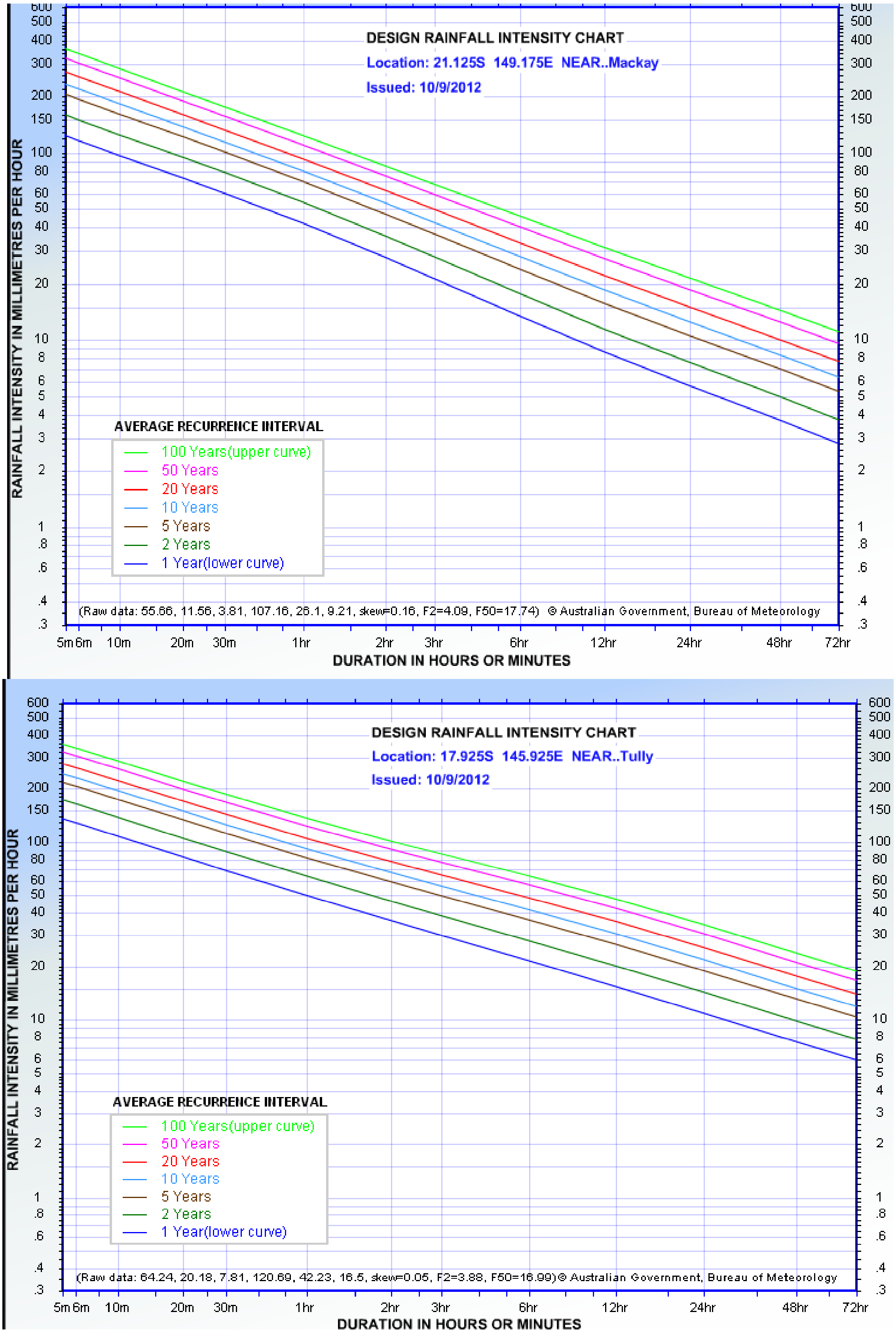


Figure 13. Intensity Frequency Duration graphs obtained from Bureau of Meteorology for Mackay and Tully

3.3.4.1. Splash

When considering the experimental procedure for this research, a factor that has to be taken into account is splash(Loch & Foley 1992). Splash refers to the scattering of fluid in flying masses; wet, stain, or soil with flying fluid. When small samples are wetted by simulated rain, a significant proportion of the sample may be lost over the plot boundary as splash, and the relative importance of this edge effect will increase as plot size is reduced.

In a case of high amount of splash, the concentration of the runoff will be affected unlike when in the field. In the field the effect of splash is contracted due to the application of herbicides all around the test site. In the lab when splash occurs, it does not hit another set of applied herbicide rather just the simulator. After testing a few strategies, it was decided to fix this problem by creating a mesh for the cane trash to sit on (Fig. 13). Therefore, when the splash occurs, there is large enough area present for the splash to hit another herbicide applied area and not reduce the concentration of the runoff.

Figure 14. One of the metal trays of area 1m² designed to reduce the effect of splash. When the cane is placed in these trays, when the herbicides splash around they hit another concentrated area rather than just the base

Each of these trays had a piece of “bird mesh” placed on top of the tray to prevent any of the cane trash falling through. This piece of bird mesh was 0.9m by 0.9 m wide. However, the bird mesh was allowing too much of the organic matter to fall through, therefore pieces of aluminum fly mesh was placed on top of the bird mesh to prevent the loss of organic matter and still allow water to fall through freely. The tray had to center to ensure that the rain sprayed evenly over the plot. Using bricks the tray was placed in flat, on top of the collection tray. These trays were used for all the bromide wash off tests (Figure 14).

Figure 15. Rainfall Simulator with a tray of trash placed underneath ready for rain.

However, when the trays were to be used for the herbicide wash off, it was not possible to use the 1m^2 trays for two reasons. Firstly, the trays were too large to fit into the Leslie Research Centre Spray cabinet **(**Figure 11**)** and secondly to achieve the most accurate results possible, it was necessary that the herbicides were not in contact with any plastics based material or any material that may be coated. Coated materials can cause the herbicides to stick and change the wash off amounts. It was found that, to avoid any loss, the type of material in direct contact with the herbicides running off should be stainless steel. However, to avoid the problem of the size of the rainfall simulator being bigger than the trays, it was decided that each of the new little trays would be placed inside one of the previously created 1 m^2 trays.

Stainless Steel is a very expensive material, therefore it was decided that only the part of the tray in contact with the herbicides washing off directly into the beakers/ bottles would be covered in stainless steel mesh while the outside of the little would be right with aluminum mesh to prevent loss of organic matter (Fig. 14).

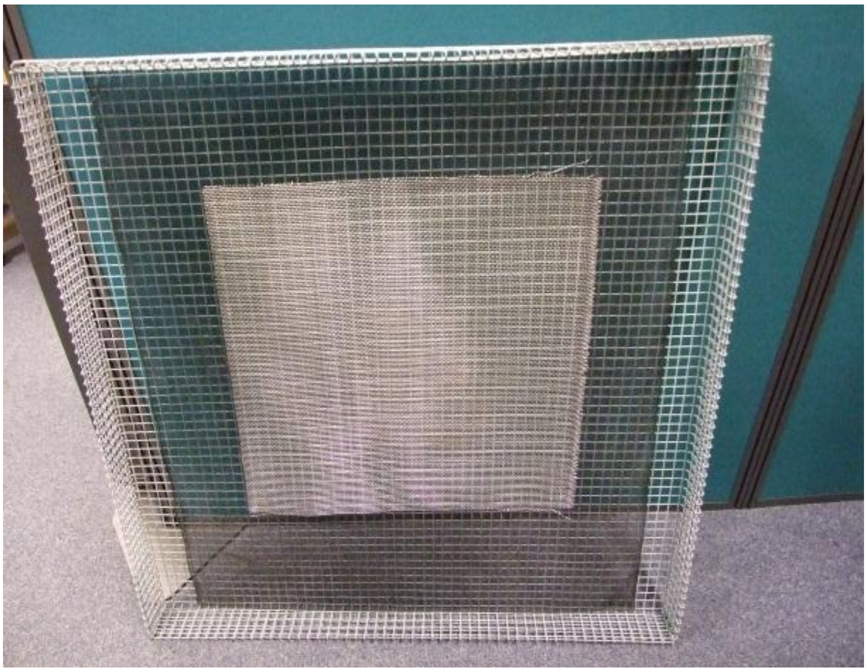


Figure 16: Picture of the trays that were designed for the herbicide testing. The outside trays coming in direct contact with herbicides wash off covered with stainless steel while trays were lined with coated aluminum material.

The other factor altered for the herbicide testing was the use of the rubber pipe for the transport of the runoff. Herbicides tend to stick to plastics and can cause losses to occur while the herbicides are being transported to the beakers or bottles. This could have a major effect on our concentration values. Therefore, the pipe used for transport of the herbicides wash off was changed to Teflon. Teflon is inert to practically all commercial chemicals, acids, alcohols, coolants, elastomers, hydrocarbons, solvents, synthetic compounds and hydraulic fluids (Speight J 2002) **.**

3.4. Measurements

To get a thorough understanding of wash off throughout the experimentation, exact amount of bromide and/or herbicides present in the samples collected needed to be known. Certain samples were selected and sent off to the lab for this analysis. EC and pH readings were also taken for all the samples.

3.4.1. EC and pH measurements

To be able to get a simple understanding of the amount of bromide that is appearing in the runoff, it was decided that the EC and pH of the sample would be measured before sending the samples off to the lab for analysis. Both conductivity and pH meters were calibrated using standard solutions.

An EC meter measures how much electricity moves through a solution—the saltier the solution, the more electricity moves through it. Electrical conductivity can be expressed in different units—for soil; EC is measured in dS/m (deci- Siemens/metre), while in water; it is measured in µS/cm (micro-Siemens/centimetre). It is important to always calibrate the EC meter before use.

PH is a measure of the activity of the (solvated) hydrogen ion. Pure water has a pH very close to 7 at 25°C. Solutions with a pH less than 7 are said to be acidic and solutions with a pH greater than 7 are basic or alkaline. PH testing was undertaken to get an idea of other chemicals that may be present other than the KBr and the effect on pH due to runoff.

3.4.2. Bromide Runoff measurement

The analysis for bromide and other substances in the first series of tests was conducted at the Soil and Water laboratory, DNRM, Toowoomba. The two tests requested were an anion analysis to determine the bromide concentration and a cation analysis to determine the potassium concentration. The anion analysis was carried out by high performance Ion chromatography as per method 4110 B (American Public Health Association/ American Water Works Association 1995b) The cation analysis was done by method ICP, method 3120 B (American Public Health Association/ American Water Works Association 1995b)

Out of all the methods available, ion chromatography was chosen because it is the only one that provides a single instrumental technique that may be used for rapid, sequential measurements (American Public Health Association/ American Water Works Association 1995b). It also eliminates the need for hazardous reagents and effectively distinguishes among the halides and the ox-ions. In Ion Chromatography, sample is injected into a stream of carbonate-bicarbonate eleuent and passed through a series of ion exchangers. The anions of interest are separated on the basis of their relative affinities for a low capacity, strongly basic anion exchanger. These anions are then directed through a hollow fibre cation exchanger membrane or membrane suppresser bathed in an acid solution. The separated anions are then turned into acids and measured by their conductivity. They are identified on the basis of retention time as compared to the standards.

Cations on the other hand are measured by Inductively Coupled Plasma (ICP) method 3120B. Inductively coupled plasma can be generated by directing the energy of a radio frequency generator into a suitable gas, usually (American Public Health Association/ American Water works Association 1995a). Other plasma gases used are helium and nitrogen. It is important that the plasma gas is pure since contaminants in the gas might quench the torch (Figure 17)

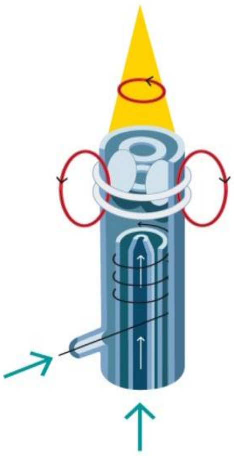


Figure 17. A diagram showing the process of inductively coupled plasma.

In ICP, coupling is achieved by generating a magnetic field by passing a high frequency electric current through a cooled induction coil. This inductor generates a rapidly oscillating magnetic field oriented in the vertical plane of the Tesla coil. The resulting ions and their associated electrons from the coil then interact with the fluctuating magnetic field (American Public Health Association/ American Water works Association 1995a). The electrons generated in the magnetic field are accelerated perpendicularly to the torch. At high speeds, cations and electrons, known as eddy current, will collide with argon atoms to produce further ionization which causes a significant temperature raise. This torch is the spectroscopic source. It contains all the analyte atoms and ions that have been excited by the heat of the plasma.

The success of ICP leans on its capability to analyze a large amount of samples in a short period with very good detection limits for most elements.

3.4.3. Herbicide runoff measurement

To determine the concentration of the herbicides, all the water samples collected were sent to Queensland Health laboratory for analysis. Queensland Health uses solid phase extraction and liquid chromatography–mass spectrometry for preparation and analysis of herbicides and pesticides in water.

The preparation of the herbicide samples was done using Solid Phase Extraction (SPE). SPE is a separation process by which compounds that are dissolved or suspended in a liquid mixture are separated from other compounds in the mixture according to their physical and chemical properties. Analytical laboratories use solid phase extraction to concentrate and purify samples for analysis. SPE uses the affinity of solutes dissolved or suspended in a liquid for a solid through which the sample is passed to separate a mixture into desired and undesired components.

The samples are actually analyzed after separation using liquid chromatography–mass spectrometry (LC-MS, or HPLC-MS) is an analytical chemistry technique that combines the physical separation capabilities of liquid chromatography with the mass analysis capabilities of mass spectrometry (Leandro et al. 2006). LC-MS is a powerful technique used for many applications which has very high sensitivity and selectivity (Fig 16). Generally its application is oriented towards the general detection and potential identification of chemicals in the presence of other chemicals (in a complex mixture). Liquid chromatography (LC)-MS is highly applicable to the analysis of a wide range of semi-polar compounds including many secondary metabolites of interest to plant researchers and nutritionists (Leandro et al. 2006).

LC-MS is an HPLC system with a mass spectrometer**.** The HPLC separates chemicals by conventional chromatography on a column. As the metabolites appear from the end of the column they enter the mass detector, where the solvent is removed and the metabolites are ionized. The metabolites must be ionized because the detector can only work with ions and not the neutral molecules. And ions only fly through a very good vacuum, so removal of the solvent is a vital first step. The mass detector then scans the molecules it sees by mass and produces a full high-resolution spectrum, separating all ions that have different masses (Leandro et al. 2006).

Figure 18. The combination of a mass spectrometer and a high performance liquid chromatographer.

3.4.4. Herbicide concentration on trash measurement

The trash sample was sent to the Analytical Consulting Services (ACS) Laboratory in Melbourne to be analysed for the exact amounts of herbicides on the trash before and after simulation. The trash was also sent to determine if the herbicides are actually degrading. If herbicides are not degrading with time after spraying, it would not have much of an effect on the concentration of herbicides that is running off. If the herbicides are actually degrading with time after spraying, that would effect on the concentration of herbicides. The concentration of herbicides on the cane trash was analysed on ultra-high pressure liquid chromatography, also known as ultra HPLC (UPLC).

UPLC is a form of column chromatography used to separate, identify, and quantify compounds. It allows for separation and analysis of small particles both quickly and effectively (Yu, Li & Zhang 2012). Liquid chromatography is the process of passing a mixture of particles to be separated through a column. The columns are filled with a packing material, known as the stationary phase. This allows the analyte, which was separated from the mixture, to be measured from other molecules. In UPLC a pump pushes the mixture, known as the mobile phase, through the columns (Yu, Li & Zhang 2012). As the mobile phase is passing through the stationary phase, a detector shows the retention times of the different molecules.

3.5. Health and safety

When potassium bromide is sprayed onto the cane trash, it is atomized and is known to cause heart failure for those not properly protected. Before spraying KBr on to the cane trash, it is necessary to ensure that bromide is not inhaled as it could cause harm. For full prevention, the sprayer has to wear a respirators, lab coat and gloves. It was also necessary to ensure that all the windows were open and the fan was on.

When the herbicides are being used it is necessary to wear full protective clothing which includes respirators, lab coat, gloves, and closed shoes. It was important to not spray herbicides with a hand sprayer. Therefore, each of the eight trays was taken to the Leslie Research Centre to be sprayed in the new spray cabinet (Figure 11). This machine allows the desired amount of herbicide to be sprayed evenly onto the trash, while preventing the harmful effect on human bodies.

3.6. Conclusion

To be able to define the methodology for this paper, it needs to be broken into three different parts.

- The experimental outline: This part explains the process undertaken to conduct this experiment.
- Resource Analysis: It explains why each piece of material was chosen, the properties that affect the procedure of the experiment and the way the resources are used. In the resource analysis the different materials covered are the potassium bromide, the herbicide mixture, the rainfall simulator, and the trash.
- The analysis of the data: This section focuses on the each of the procedures used by the lab or the tester to determine the concentration of the herbicides in the wash off.

Chapter 4. Results and discussion

4.1. Control Tests

The trash that was used for obtaining bromide tracer and herbicides washoff was collected from a field in Bundaberg. Rainfall and washoff water were analyzed for major cations and anions that could potentially affect herbicides wash off concentrations (Table 5).

The chemicals found in washoff from trash samples without bromide and herbicides sprayed on it included chloride, bromide, calcium and sulfate (Table 5).The concentration of bromide in washoff from the cane trash was only about 5.5 mg/l, which would have little effect on wash off amounts especially in the initial wash off when concentration in the 1000's of mg/L are obtained.

The rain water that was used by the rainfall simulator contained micro amount of ions including chloride, calcium, chloride and sulfate, which could slightly affect the EC (Table 5). The concentration of bromide was below the detection limit.

Table 5: The chemicals found when raining on trash with nothing sprayed onto it. The trash has residual bromide, calcium and sulfate washing off. This indicates that there is a presence of other chemicals on the trash before spray. The rain is a sample of the collected rain water collected from the simulator. A RAIN was rain water collected in test A.

	A RAIN	Control rain	Initial Washoff Control	Final Washoff Control 2.5
Calcium (mg/l)	2.2	1.5	8.5	2.3
Magnesium (mg/l)	<0.5	<0.5	6.3	1.7
Sodium (mg/l)	<2	<2	16	5
Potassium (mg/l)	<2	<2	70	26
Sulphate as SO_4 (mg/l)	1.08	<1.00	7.35	2.23
Sulphate (mg/l)	1.19	<0.83	9.44	3.2
Chloride (mg/l)	1.98	1.55	63.3	13.5
Fluoride (mg/l)	<0.05	<0.05	<0.05	<0.05
Phosphate P (mg/l)	<0.05	<0.05	1.65	1.55
Nitrate-N (mg/l)	<0.50	<0.50	<0.50	<0.50
Nitrite-N (mg/l)	<0.05	<0.05	<0.05	<0.05
Bromide (Br) (mg/l)	<0.05	<0.05	5.54	1.1

4.2. Potassium Bromide

The first set of tests was to determine the pattern of potassium bromide wash off during rainfall events. It was also necessary to determine the relationship between Bromide and EC and the relationship between cumulative runoff and cumulative bromide wash off

When the trash was sprayed with the herbicides, it was also sprayed with the potassium bromide at the same rate as the potassium bromide tests. It was anticipated that by spraying KBr with herbicide would find a similar relationship to the first tests to confirm the bromide as a tracer.

4.2.1. Instantaneous Wash off rate of Bromide

The wash off rate can be determined through the use of the bromide concentrations and time. The test was replicated 4 times to ensure that they all produced a similar relationship. In all four runs (A, B, C and D), bromide concentration in the wash off was substantially higher in the initial 5 minutes of sampling then dropped very fast in the next 10 minutes (Figure 19). At the end of the 2 hours, all replicates had a very low concentration of bromide ranging from 0-5 mg/L. Therefore, it can be said that though there was a high concentration of bromide running off in the first 15-20 minutes, as time increases, the concentration of bromide washing off decreases. It was anticipated that herbicide wash off from trash would follow a similar pattern, although it might vary for compounds that bonded more to trash than the Br.

To determine the relationship between wash off bromide concentration and time, various forms of equations were trailed to find the best fit. It was expected there would be an exponential relationship between bromide concentrations in wash off and time (Wauchope et al. 2000); however the exponential trend line gave a poor fit. The decrease in the bromide concentration followed the pattern of a power function (Figure 20). The relationship between bromide concentrations in wash off and time was a negative power of about -1.5 with a constant determined on the basis on the initial wash off concentration.

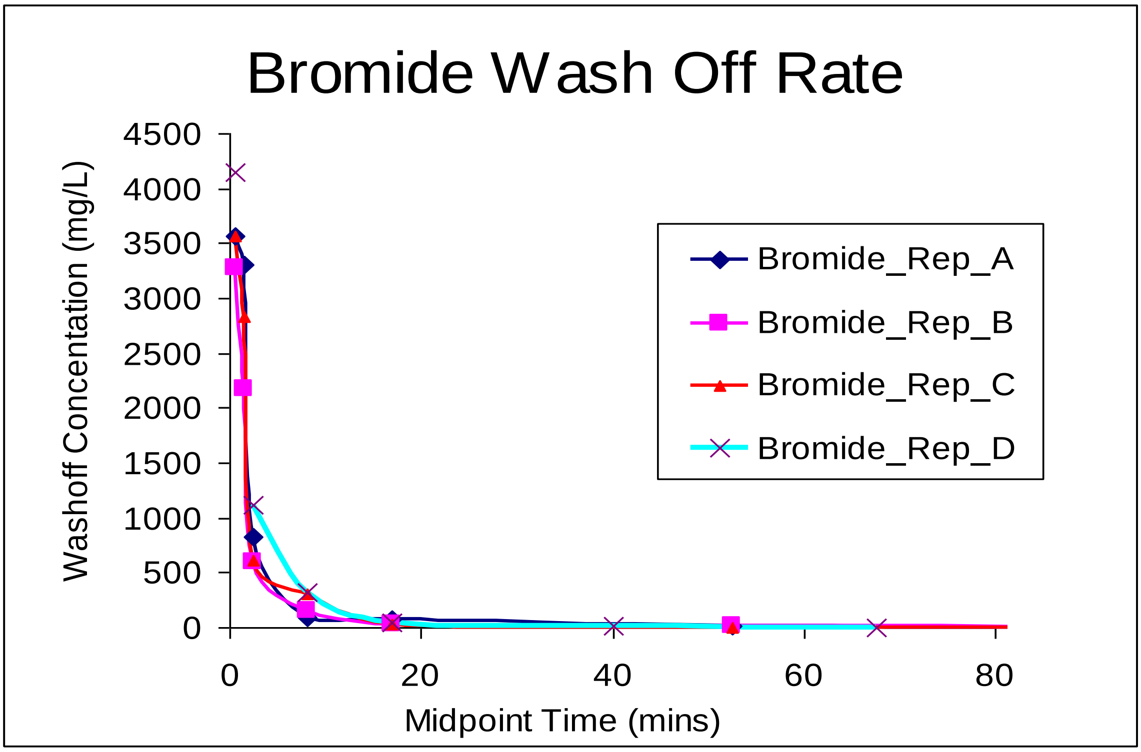


Figure 19: The decreasing power relationship between bromide wash off concentration and time. It is noticeable that there is a very high concentration initially and then the rate of wash off slows down to a steady state.

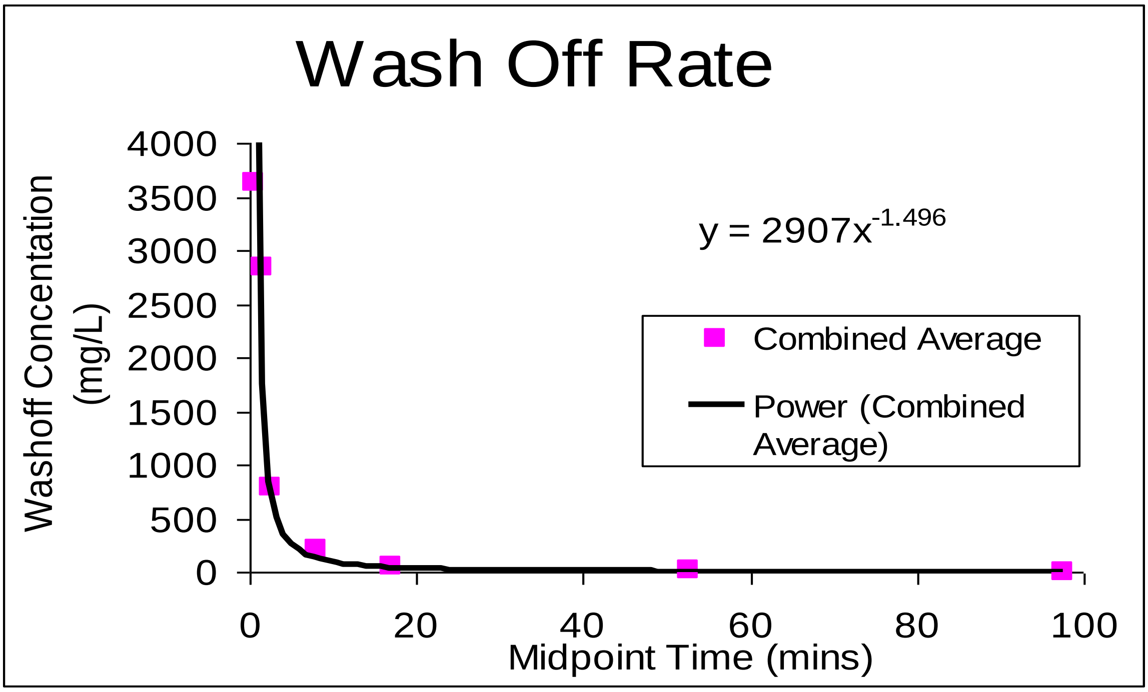


Figure 20. Average bromide wash off rate fitted with a power function. The relationship was negative power of about -1.5 with a constant determined on the basis on the initial wash off concentration.

4.2.2. Relationship between cumulative wash off and cumulative runoff

To get a full understanding of the wash off of the bromide that was sprayed on to the trash, we need to understand how the cumulative runoff and cumulative bromide were related. This relationship tells us how the concentration of the bromide is affected as the amount of rainfall that washes off from the trash increases. Cumulative bromide washoff increases rapidly as cumulative runoff reaches 5 mm in all 4 runs followed by a steady increase at a constant rate. It's interesting to note that about 80% of Bromide had washed off in the first 6 minutes (Figure 21)

Although all 4 runs follow a similar pattern, the cumulative bromide concentration in repetition B was higher as compared to run C and run D. During run B, the amount of water running of the trash was much greater than expected with the calibrated intensity. This increased the amount of cumulative runoff. We are currently unsure on the reasoning behind the simulators behavior for this run.

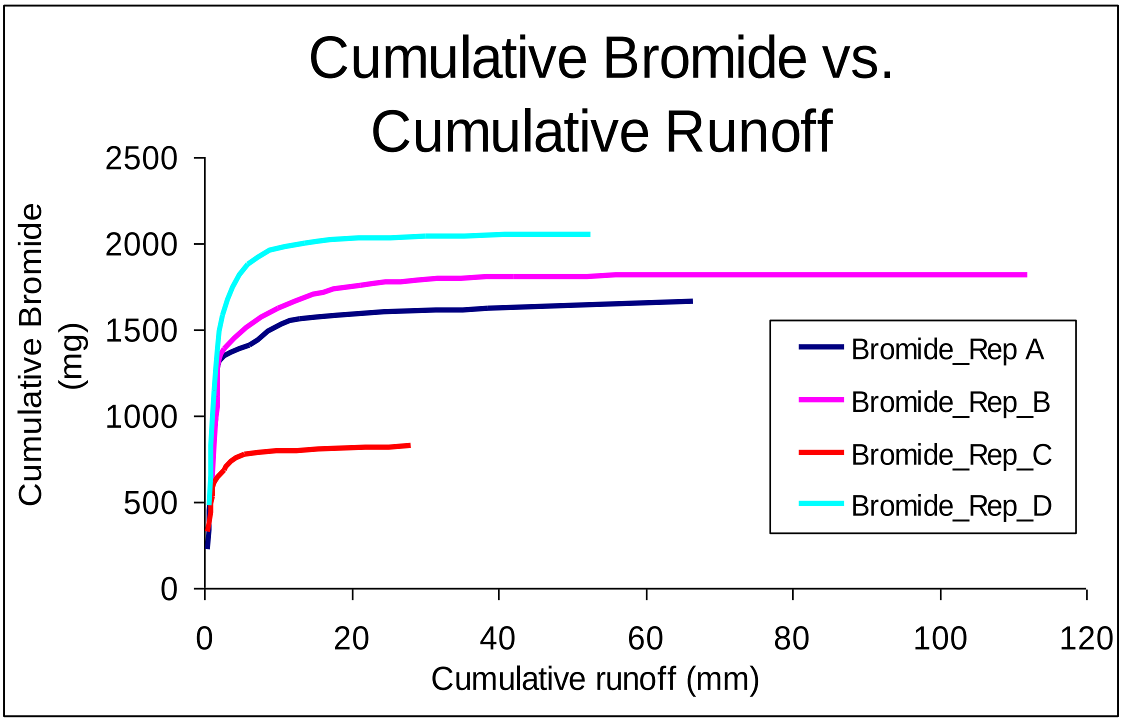


Figure 21: The relationship between cumulative bromide and cumulative runoff derived in each of the repetitions. Each of the graphs follows a similar pattern but due to the changing nature in the cumulative runoff they are not the same. There is a very quick rise in the washoff of bromide initially; however after the amount of runoff hits a certain point the cumulative bromide starts to settle down.

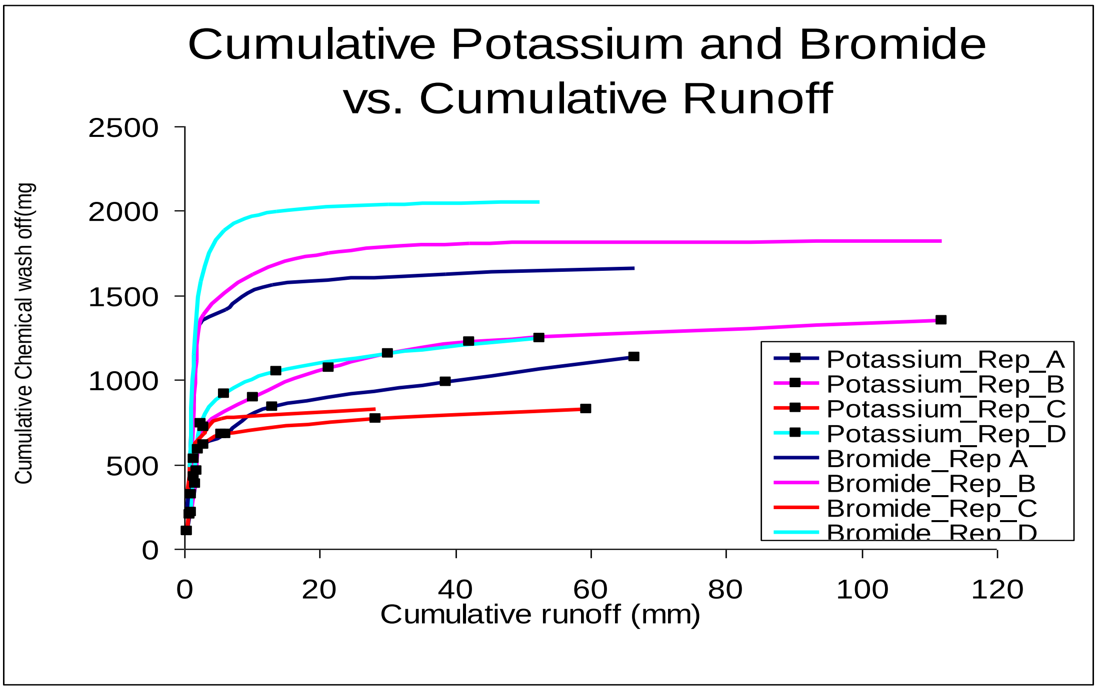


Figure 22. Comparison between cumulative wash off of Bromide and cumulative wash off of Bromide against cumulative runoff. The potassium tends stick to the trash for longer than the Bromide.

Potassium washoff was also examined to check if it had a more similar relationship to the herbicides, due to greater bonding on the trash. Potassium takes more time to wash off and also doesn't washoff at the same rate as bromide. Potassium tends to stick to the trash for a longer time than bromide and as the cumulative runoff increases the potassium slowly starts to wash off. However, once it starts to wash off it actually does so faster than the bromide **(**Figure 22**).** It took 20 min of rainfall to wash off 80% of the K, compared with 5 minutes for the Br.

4.2.3. Can Electrical conductivity be used to predict Bromide concentration

It was assumed that there would be a close to linear relationship between the electrical conductivity and the concentration of bromide in wash off. However, in the first 4 repetitions, it was found that as time of wash off increased, the increase in EC was proportionately higher than the increase in bromide concentration (Figure 23). This could be due to the presence dissolved organic compounds & the variation between plots. If measured accurately EC should follow a pattern similar to bromide concentration which can be seen in (Figure 24).

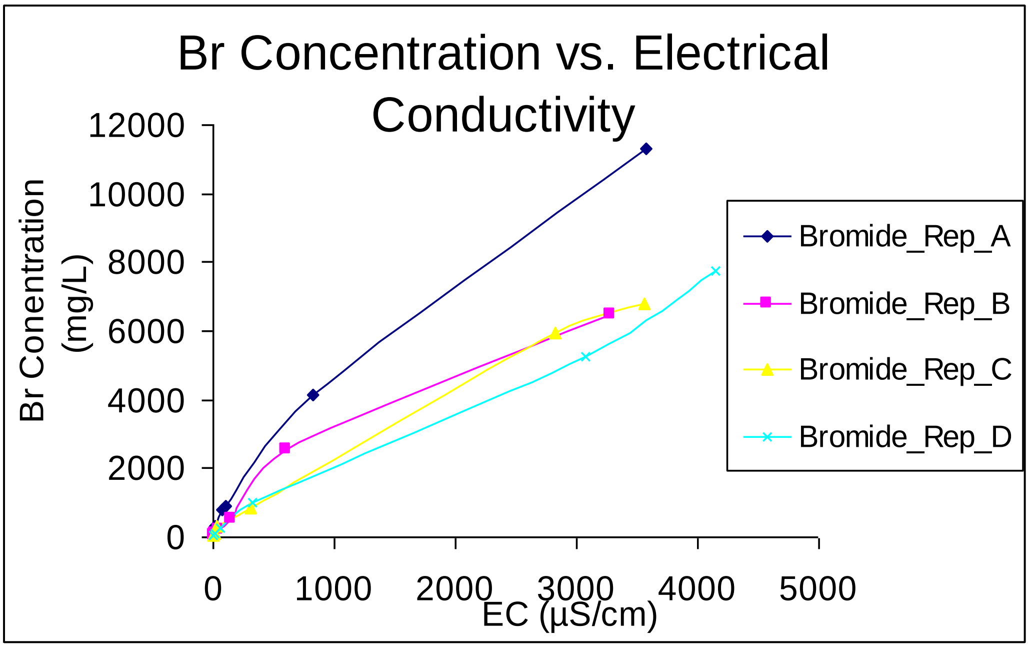


Figure 23: The relationship between bromide concentration and electrical conductivity.

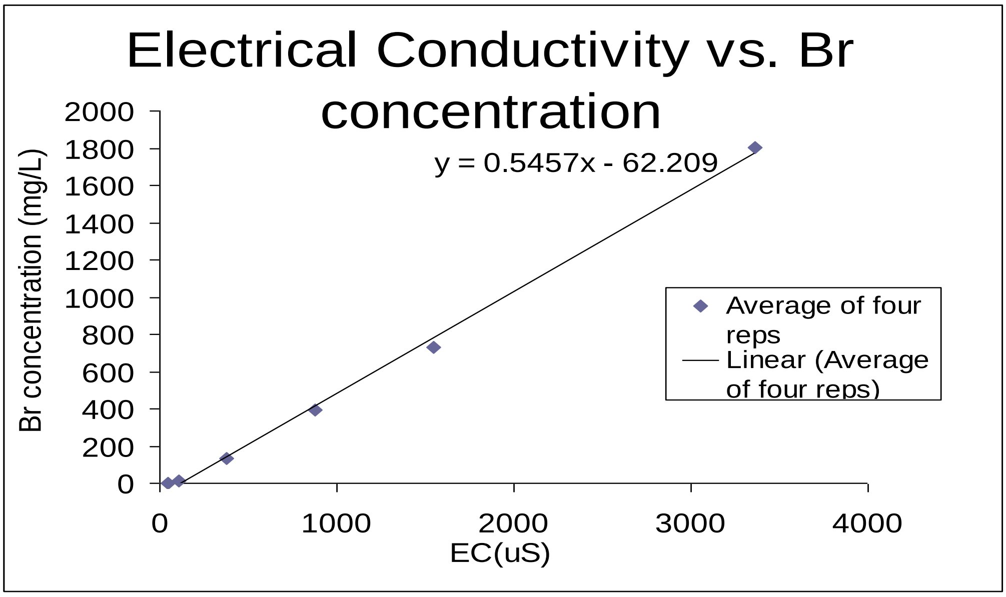


Figure 24. The relationship between Electrical Conductivity (EC) and Bromide (BR) amount washed off. These were the values obtained from the herbicide wash off tests (E-H) that had bromide sprayed on. These tests display each of the graphs having a close to linear relationship with a slope of about 0.5 and an intercept determined from the wash off rate.

When the bromide samples from the second group of testing were plotted against the electrical conductivity they were found to have linear relationship that the literature portrayed (Figure 24). The relationship was of the form $BR = 0.5 \times EC + C$, which tells that the pervious test may have contained some errors with the reading of EC or the samples may have contained other material that may have affected the values for EC. Slope value of 0.5-0.6 for the line and the value of the intercept C varies based on the test. However, the value does range around -50 to -80 and is based on the rate of wash off.

4.3. Herbicides

4.3.1. Wash off Rate

4.3.1.1. 24 Hours after spraying

For each time of herbicide wash off obtained after herbicides spray, two runs were conducted to ensure constancy of the results and to determine if concentration of different herbicides changes in 2 hours between the runs. The first run for herbicide wash off was conducted 24 hours after spraying herbicides. It was expected that the concentration of herbicides in wash off water would be greatest at 24 h after spraying. The two factors that affect wash off of herbicides are the sorption coefficients and their half-lives.

Figure 25 shows herbicides concentrations in wash off water as a function of time in the first 24 hour run. All the herbicides used in the present study had very high concentration in wash off water initially to 10 min sampling followed by slowing down to a steady rate.

Different herbicides had different concentration in washoff water (Figure 24 A) because they were applied at different rates. Tebuthiuron had highest concentration in wash off water up to the 40 min sampling as compared to all other herbicides but then decreased to a constant rate. Atrazine, diuron, hexazinone and S-metolachlor all follow a very similar pattern however; the difference is evident due to different sorption coefficients. Metolachlor and diuron essentially followed similar pattern with time. This is due to the fact that both have very similar chemical and physical properties and their adsorption factors are very similar.

The second run was conducted at 26 h after herbicides spray. It was expected that there would not be major difference between the concentration of herbicides in wash off water for 24 hrs and 26 hrs.

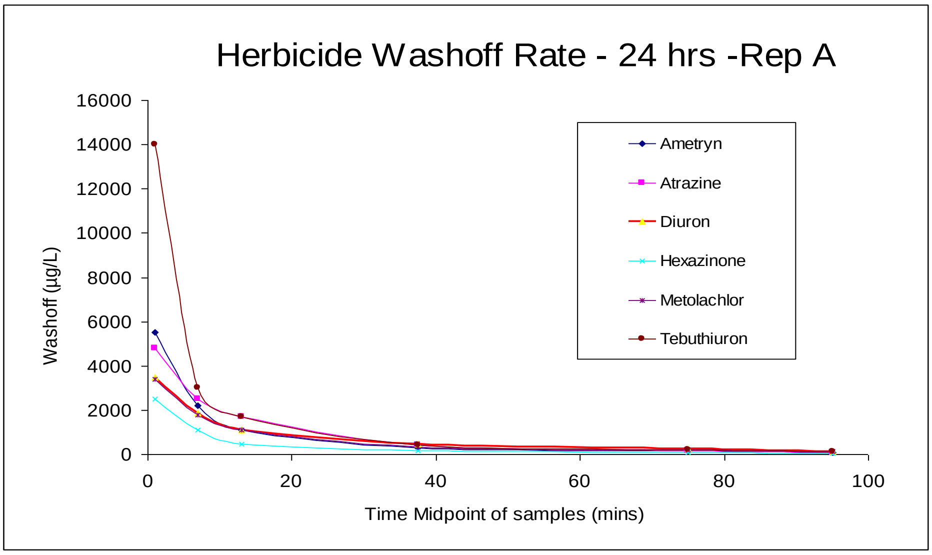


Figure 25. The First test for herbicide wash off was conducting 24 hours after spraying. These graphs show the relationship between times and wash off. Each of the herbicides has different wash off rates which is evident in the graph. The graph shows the herbicide running of at a very high rate initially and then slowing down to a constant wash off rate.

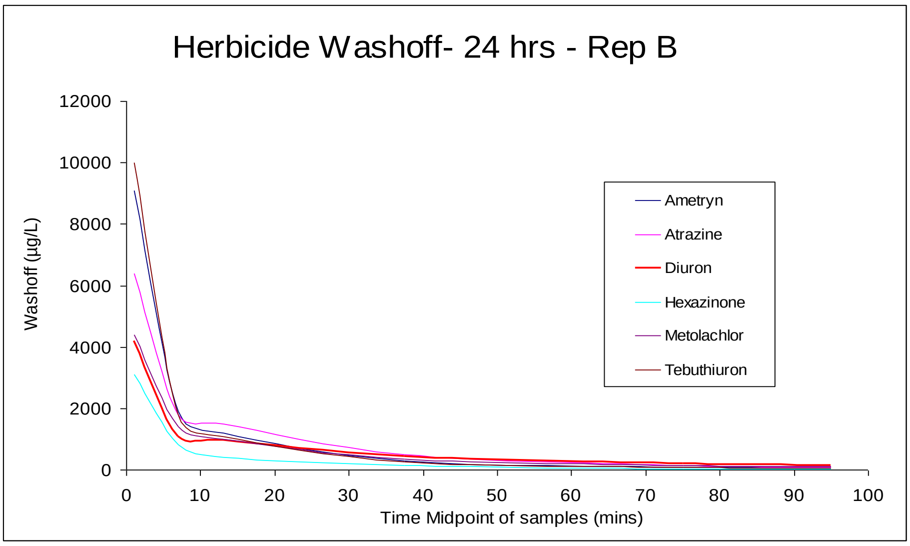


Figure 26. The second repetition for the 24 hour period experiment. The graph is showing the relationship between the wash off rate and time has stayed the same. The washes off rates still vary between the herbicides but the base relationship is still the same.

Figure 26 shows the concentration of different herbicides in wash off water at 26 h after herbicides application as a function of time. The noticeable difference was observed in tebuthiuron wash off in water. At 24-hour wash off (Figure 25), the wash off of tebuthiuron was at an extreme concentration initially as compared to the other herbicides; however at 26 hours, tebuthiuron concentration in wash off water was more similar to the other herbicides. The other noticeable differences occurred to ametryn‘s washoff. Concentration of ametryn was almost half of tebuthiuron at 24 hours whereas at 26 hour washoff, it was similar to tebuthiuron.

4.3.1.2. 8 days after spraying

To be able to examine the effects of time after spraying on the concentration of herbicide wash off in water, the rainfall simulator was run 8 days after the herbicides were sprayed onto the tray of trash (Figure 27 B). This test was to see if the amount of herbicide washing off changes based on how long the herbicdes have been on the trash.

Tebuthiuron had highest concentration in wash off initially but then decreased to a constant rate. Atrazine, diuron, hexazinone and metolachlor all followed a very similar pattern with time however; the differences were evident due to different sorption coefficients. Metolachlor and diuron had the same pattern between their wash off and time because of their similar chemical and physical properties and sorption coefficients.

4.3.1.3. 40 Days after spraying

The concentration of the wash off water changed dramatically at 40 days after herbicides spray (Figure 27 C) compared to the concentration of herbicides in wash off water from 8 days after herbicides spray (Figure 27). After 8 days, tebuthiuron had highest concentration in washoff water, however after 40 days; the concentrations in washoff water were lower than ametryn and metolachlor. Initial concentration of tebuthiuron in wash off water decreased from the 14,000 to about 3,300 mg/l, between 24 hrs and 40 days after herbicides application.

All herbicides had high washoff concentrations initially and then decreased to a constant rate. Atrazine, diuron, hexazinone and S-metolachlor all followed a very similar decrease with time, however some differences were evident due to differences in their sorption coefficient, solubility and half-lives. Metolachlor and diuron had similar concentrations in wash off water at all three time periods.

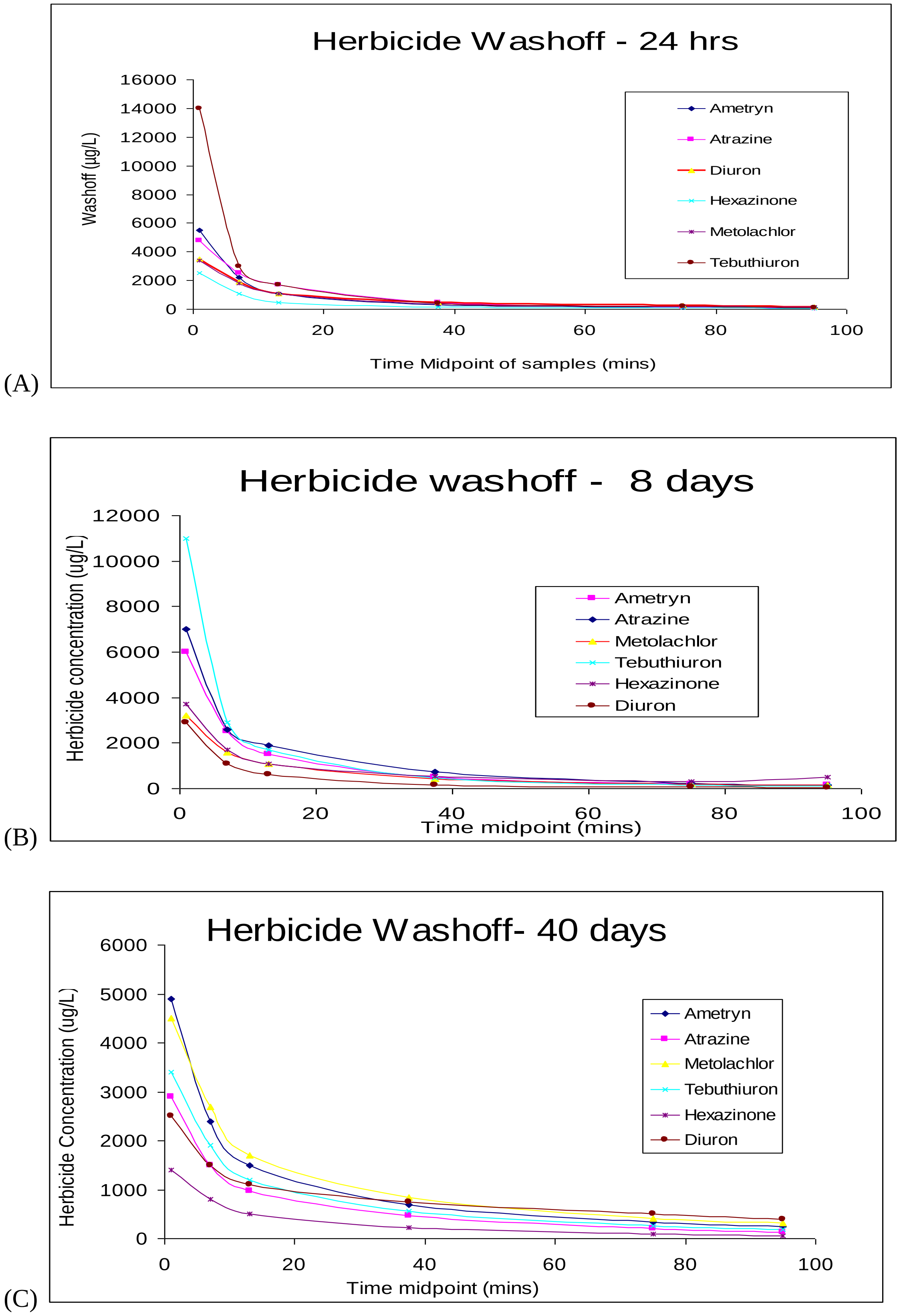


Figure 27. Comparison of the wash off rate of the herbicides (A) 24 hours, (B) 8 days after spraying and (C) 24 hours after spraying. There appears to be not much of a difference within the relationships. However there are slight differences in the initial levels of wash off.

4.3.2. Herbicide Concentration as a function of the initial wash off concentration

4.3.2.1. 24 hours

To be able to understand the differences between each herbicide, it was decided that the washoff amounts would be graphed as a function of the initial wash off. The amount of herbicide at each wash off was divided by the initial wash off. Initially the ratio for all the herbicides is 1.0, however, with increasing time of herbicides application, the concentration of herbicides in washoff decreased and resistant to wash off. The rate of washoff varied with different herbicides between 5 minutes to 30 minutes (Figure 28). After 40 minutes, the wash off ratio for each of the herbicides began to hit similar points again and steady.

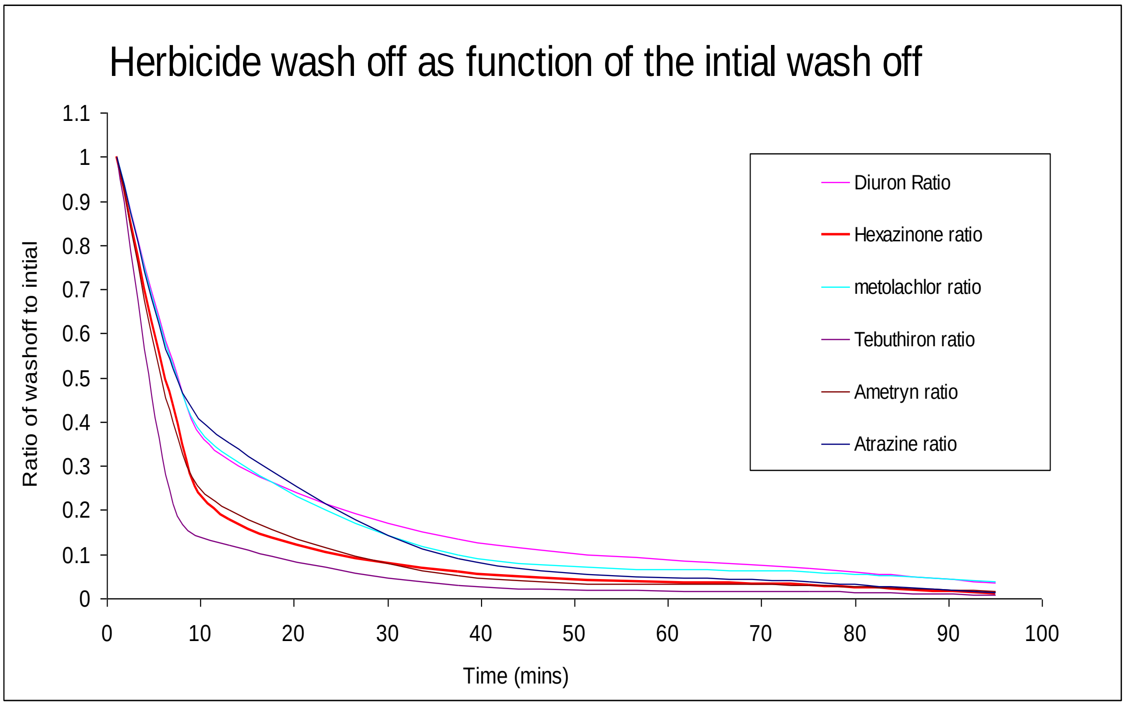


Figure 28: The ratio of herbicides in wash off water as a function of the initial herbicide washoff concentration, 24 hours after spraying. This method makes it much easier to differentiate between the herbicides, their adherence properties and the timings at which they differ greatest.

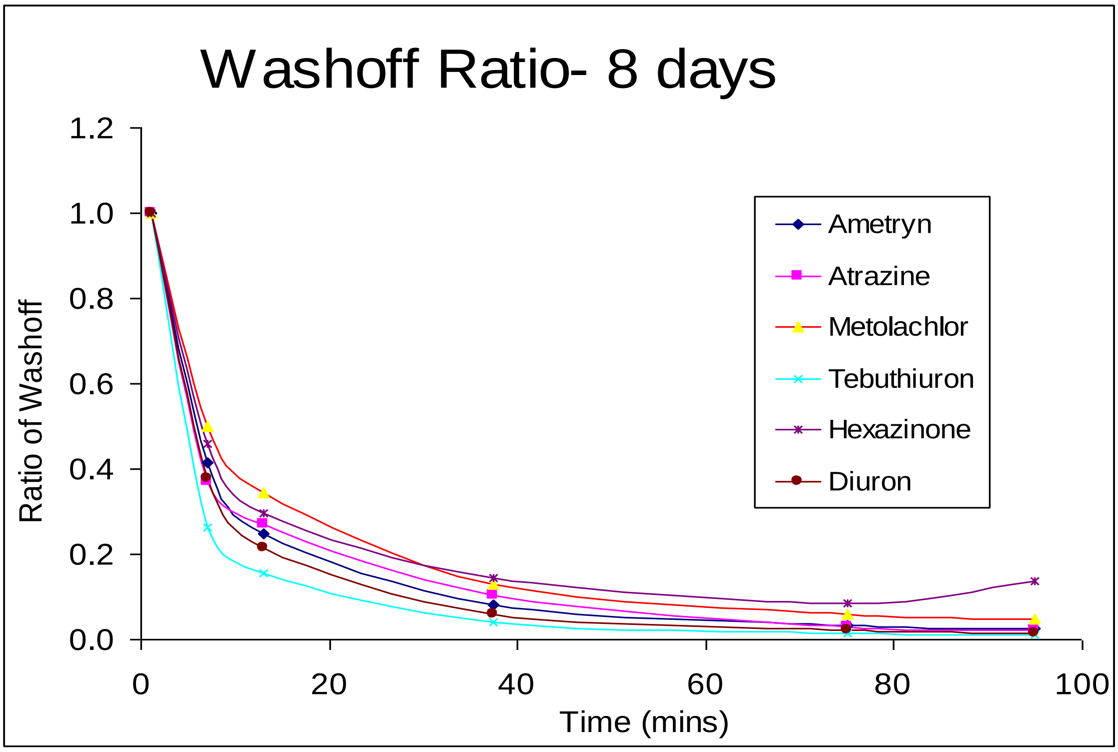
This method also makes it easier to work out which herbicide is actually washing off at fastest rate due to its properties rather than the amount applied. For example, in Figure 25 it was found that tebuthiuron had the greatest washoff rate and highest initial wash off. However, it was perceived that this may be due to a greater amount of it being applied through the mixture. Figure 28 shows that 24 hours after herbicide spray, tebuthiuron does had the greatest washoff rate. Diuron, atrazine and metolachlor had the same wash off rate initially however, after 20 minutes diuron was slowest herbicide to wash off.

4.3.2.2. What effect does time after spraying have on these ratios?

The graph of the herbicide concentration as a function of the initial wash off after 24 h spray showed that from 5 minutes to 40 minutes there was noticeable difference in the concentrations of herbicides in wash off water. However, these differences were negligible after 8 days (Figure 29 A) and 40 days after spraying (Figure 29 B).

Forty days after spraying, diuron was much slower to wash off than the other herbicides. While it was slightly slower than the other herbicides at 24 h after spraying, however, 8 days after spraying it was actually the second fastest to wash off.

The other difference that started to occur with increasing time after spraying was the timing at which the herbicides start to hit steady state. 24 hours after spraying the wash off starts to hit a steady state at about 30-35 minutes, while 8 days after spray it did not reach a steady state until about 45 minutes. 40 days after spraying, the wash off rate did not reach steady state until about 80 minutes.



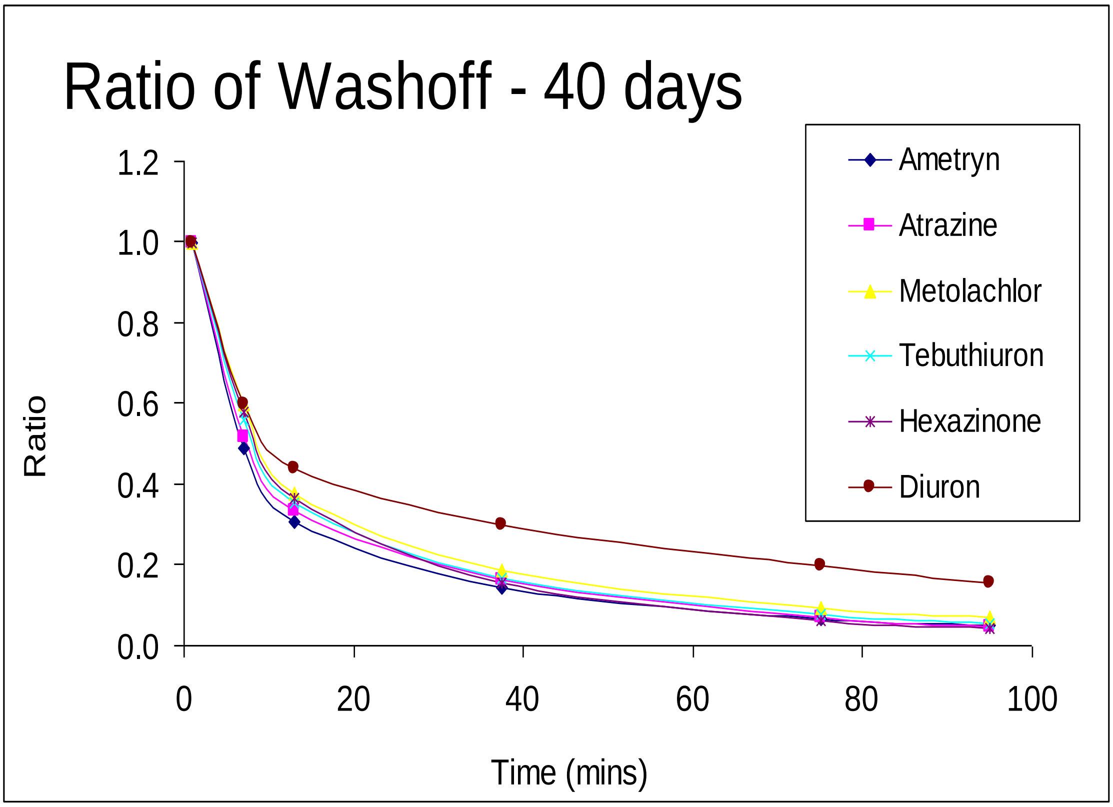


Figure 29: Comparison of the wash off concentration ratios after different time periods. They all have an initial point of 1 and as time continues the herbicides begin to differ from each other.

4.3.3. Relationship between cumulative wash off and cumulative runoff

4.3.3.1. Instantaneous Cumulative Relationships

In Figure 30 each of the colours represents a different herbicide. Dark blue is ametryn, fuschia is atrazine, turquoise is S-metolachlor, purple is tebuthiuron, Brown is hexazinone and finally yellow is diuron.

The cumulative amount for each herbicide rises almost proportionally with cumulative runoff initially (Figure 30 A). However, as the cumulative runoff continues to increase, the amount of cumulative herbicides continues to increase but at a much slower rate. At the end of the cumulative runoff period, herbicides such as tebuthiuron, atrazine and ametryn have washed off at cumulative amount greater than 10000 µg.

In all the graphs (Figure 30), S-metolachlor and diuron had very similar wash off properties. Both have low wash off rates and have similar Koc properties. These graphs also showed that hexazinone was least likely to wash off at very high amounts while tebuthiuron, followed by ametryn, tends to wash off fastest and at highest rate.

Figure 30(A) showed that ametryn and atrazine have very similar wash off properties. However, in Figure 30(B) the wash off properties of ametryn were more similar to those of tebuthiuron. Ametryn and Atrazine are both from the Triazine family and it was expected that they would have very similar properties.

4.3.3.2. What happens after 8 days?

To be able to understand if the time after spray had major effect of amount of wash off, it was necessary to compare the cumulative as well as the runoff rate.

Tebuthiuron still had the highest cumulative wash off. The major difference in the values for the cumulative runoff occurred with tebuthiuron. The other herbicides all tended to stay in the same degree of magnitude and not much change occurred (Figure 30 B).

4.3.3.3. Comparing all three time periods to see time after spraying effects

The final test involved comparing how the relationship between cumulative wash off and cumulative runoff changed when rain was applied 40 days after spraying instead of 24 hours after spraying.

The cumulative amount for each herbicide rose almost proportionally with cumulative runoff at the beginning. However, as the cumulative runoff continued to increase the amount of cumulative herbicides continued to increase but at a much steady rate.

The major difference that occurred in the cumulative wash off was the slope that was evident at the beginning of the runoff in Figure 30. During the 24 hours after rain spray the cumulative wash off began with a sharp increase which continued till about 5 mm of cumulative runoff and then slowed down to a steady rate. When the rain occurs 8 days after spray, the sharp increase in wash off continued until about 3-4 mm of runoff accumulates. This seemed very similar to the 24 hours concentrations. However, when the rain occurred 40 days after spraying, it was not till about 20 mm of cumulative runoff had occurred that the sharp increase in cumulative wash off stopped.

The total amount of cumulative wash off changed as time went on. In the initial test, tebuthiuron had the greatest cumulative wash off at 14000 µg while in the 40 days after spraying repetitions, the highest cumulative wash off was for metolachlor and ametryn at 1300 µg. However, it was necessary to remember that at the 40 days stage the trash trays had double S-metolachlor sprayed onto them, therefore indicating that when rain occurred 40 days after spray, ametryn had the greatest cumulative wash off. This indicated that time after spraying had substantial effect on cumulative wash off.

When a trend line is put through the cumulative wash off vs. cumulative run off, a logarithmic tend provides the best fit as indicated by highest R^2 values (R^2 values varied between 0.84-0.99). This was because the rate of change in the herbicides concentrations increases or decreases quickly and then levels out. Therefore, the equation follows the pattern of $y=A \ln(x) +B$ where A is the rate of change and B is based on the initial wash off concentration. As time increases the value for A should decrease. This is noticeable in the data in Appendix 8.8.

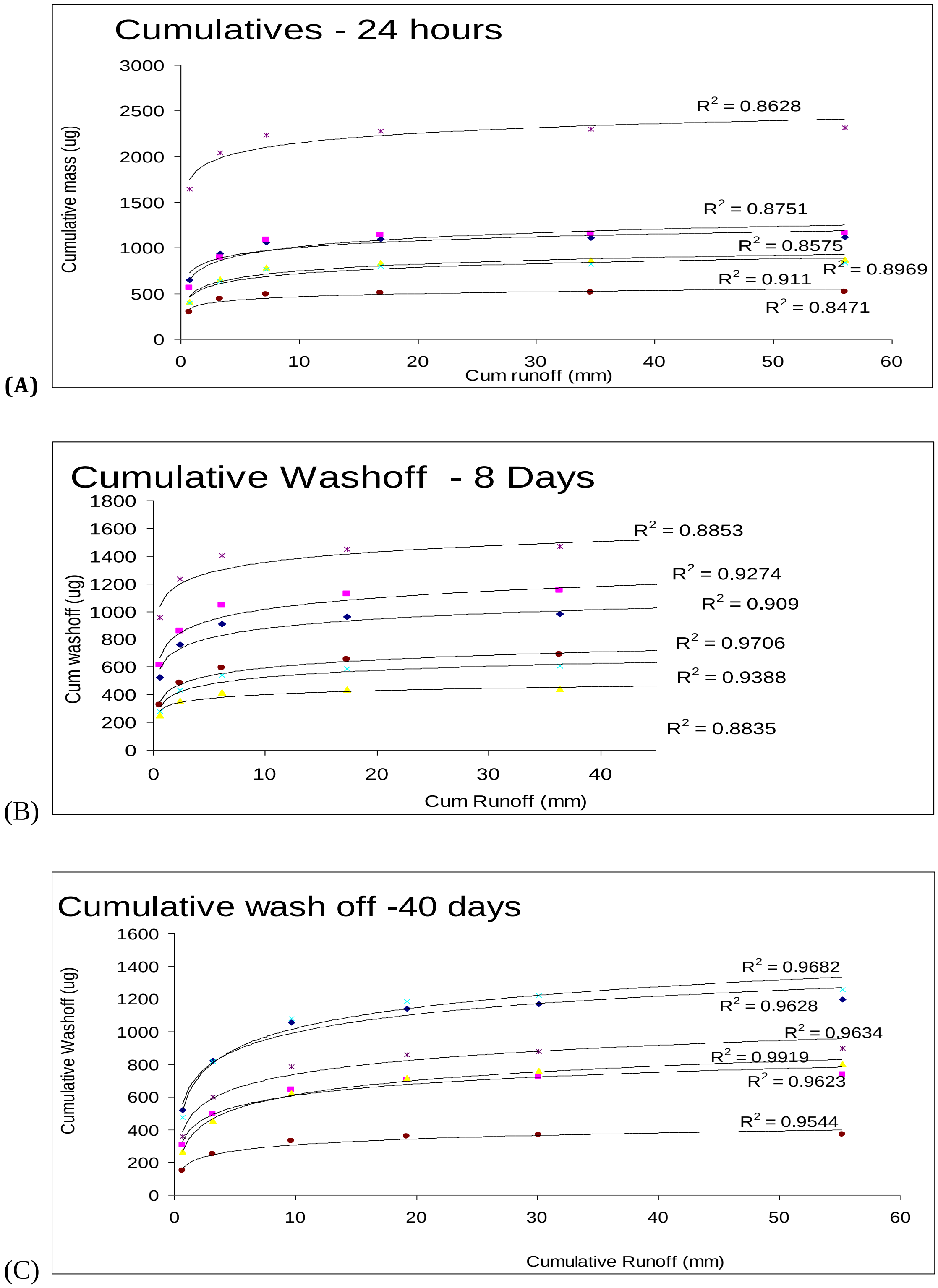


Figure 30. The relationship between cumulative runoff and cumulative wash off of each herbicide. The cumulative amount for each herbicide rises almost proportionally with cumulative runoff at the beginning. However as the cumulative runoff continues to increase the amount of cumulative herbicides continues to increase but at a steady rate. Each of the graphs has a logarithmic trend line through them.

4.3.4. Using a log scale to define the relationship between washoff rate and time

To understand the relationship between herbicide concentrations and time, the herbicides concentrations were converted to log. Figure 31 showed the relationship between wash off concentration and time when plotted on a log axis was essentially linear. It can even be said that it is close to 1/x. This indicates that as time increases on a log scale the wash off concentration decreases proportionally.

In the 24 hours graph, the concentration of the herbicides experiences the greatest initial value (Figure 31). This has a different effect of determining the relationship. During this period, the concentration is always changing even without rainfall as it was noticeable when comparing Figure 25 and Figure 26. Those two graphs showed that in the earlier stages, even two hours had a major effect on the initial concentration. In the graph for rainfall 24 hours after spray, the relationship did not fit an exact trend line for any of the herbicides other than Tebuthiuron, due to the readily changing concentration of the wash off

4.3.5. What sort of relationship is evident for herbicide wash off and time?

As time after herbicide application increases, the initial concentration begins to stabilize, the power relationship between time and herbicide concentration becomes more evident as it noticeable in Figure 32. The differences in the herbicides are not as strong except with diuron and hexazinone (Figure 32) In the 8 days period it was diuron that had the slowest wash off rate while after 40 day its wash off actually increased rapidly. Hexazinone relationship had become more stable and after 40 days it had the slowest wash off rate.

When the herbicides were all graphed on a log-log scale and best fit line was placed as shown in Figure 32, the exponent for the herbicides varied around 0.8-0.9. Bromide was chosen as a tracer for the herbicides. However, when the relationship between Bromide wash off concentration and time was graphed, it gave a relationship of y=2906x^ (1.5). This exponent of 1.5 was the important part. It determines the exact relationship between wash off and time as the 2906 varied based on the initial wash off point. This indicates that bromide might not be the best tracer for these herbicides.

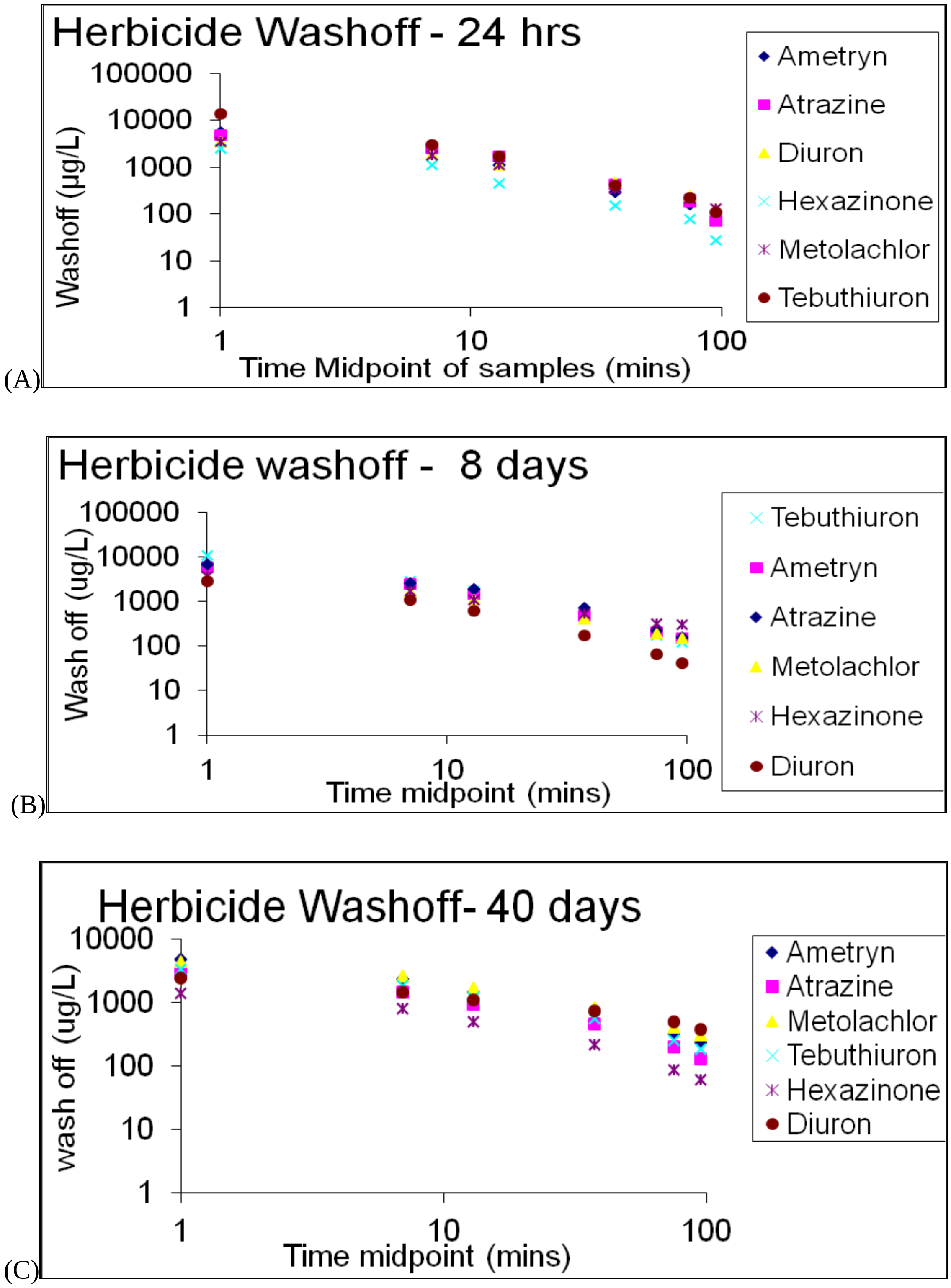


Figure 31. The decreasing power relationship between concentration and time with both axes set to a log axis. A log axis was chosen because we are aware that as time increases, concentration should be decreasing proportionally. Graph represents the relationship after 24 hours, Graph B shows the relationship when rained upon after 8 days and Graph C shows the relationship when rained upon after 40 days.

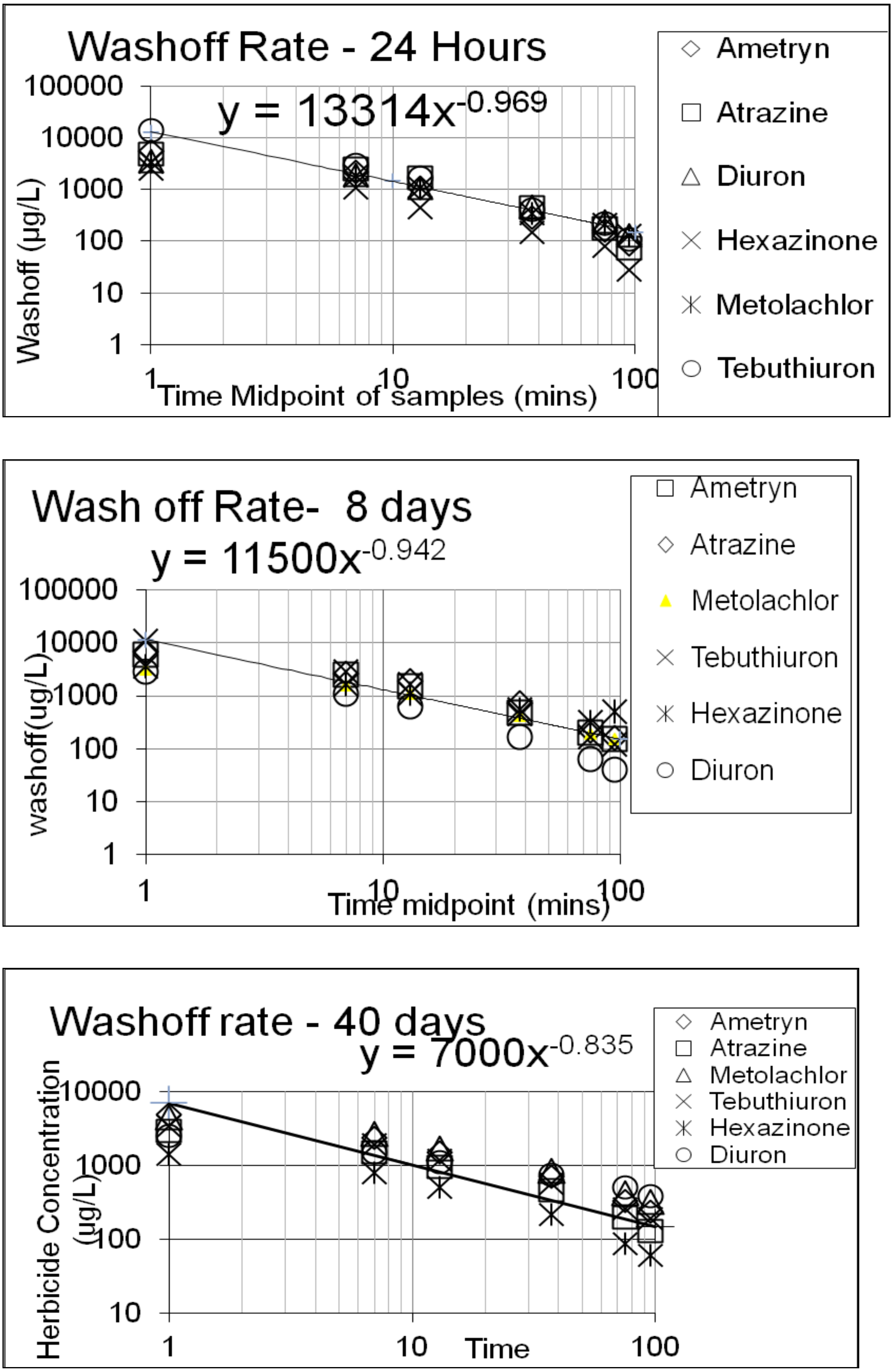


Figure 32. Log graphs showing the relationship between time and herbicide concentration. The power relationship is shown as linear line with a log graph. This can be used to find an estimate of the model that is present.

4.3.6. Herbicide washoff comparison after different time periods

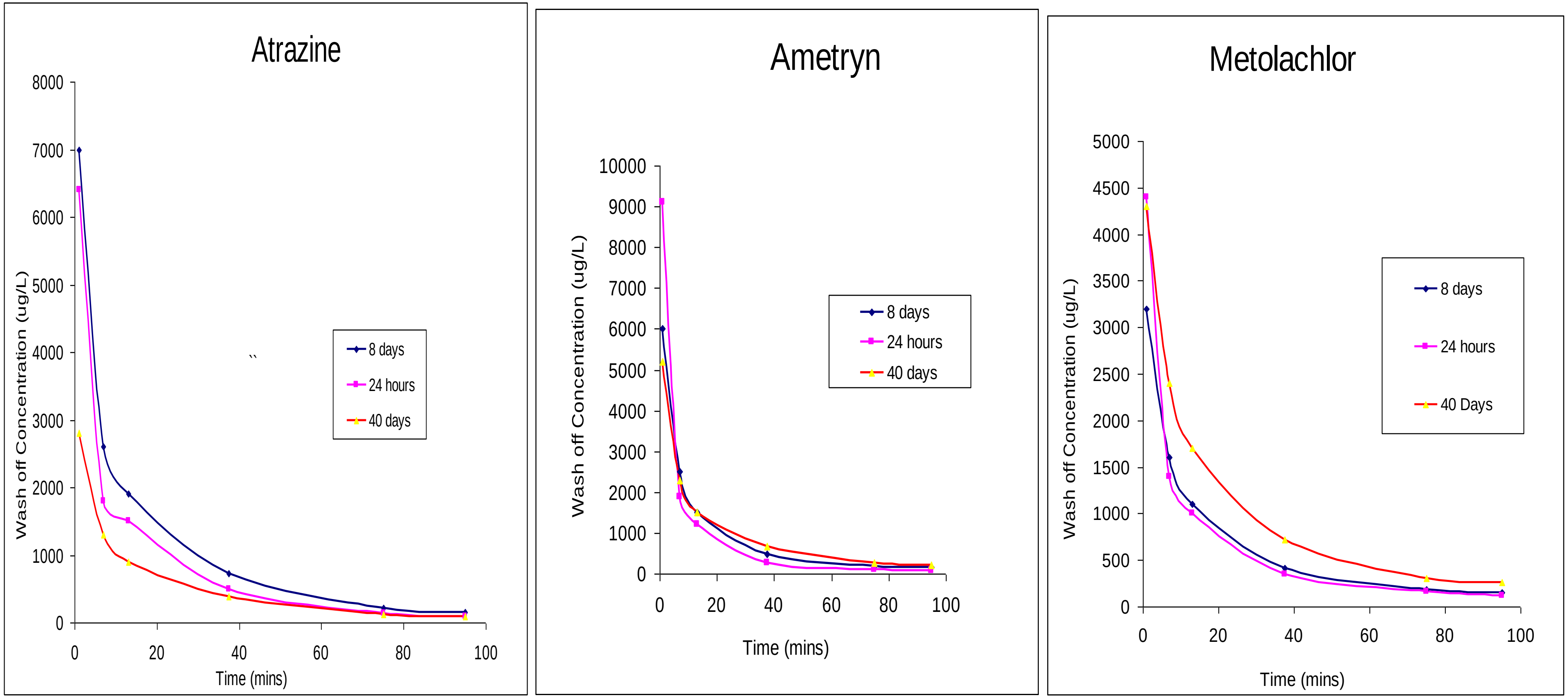


Figure 33. The graphs for atrazine, ametryn and S- metolachlor showing the effect of time after spraying. Each graph shows the washoff concentration 24hours, 8 days and 40 days after spraying. Note: at 40 days, metolachlor had been applied twice.

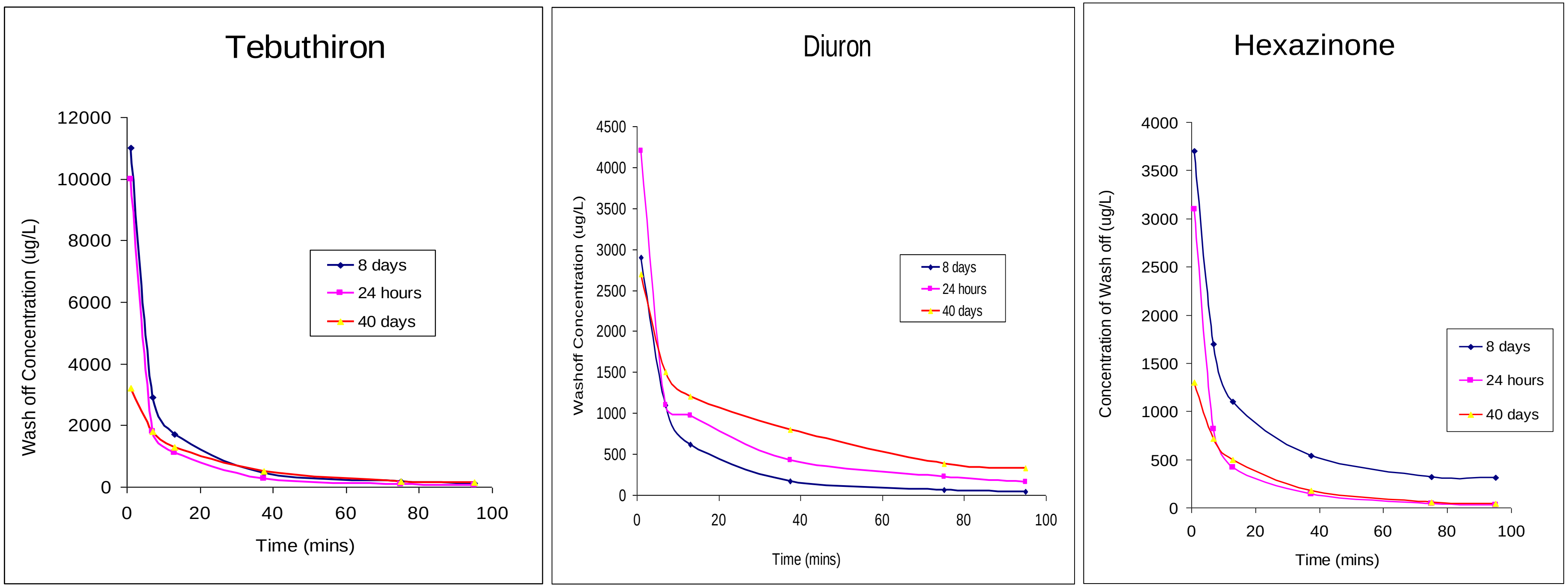


Figure 34. The graphs for Diuron, Tebuthiuron and Hexazinone showing the effect of time after spraying. Each graph shows the runoff rate at, 8 days 24hour and 40 days after spraying.

The graphs above display the effect of time of spraying has on the amount of wash off for each herbicide. Each herbicide has different Koc properties which affects its wash off properties and its degradation properties. This will change how much of each herbicide washes off nitially and how much of it washes off after the herbicides have been on the trash for 8 days and then 40 days. Certain herbicide behave as expected such as ametryn where the rate of wash off stays very similar but the initial wash off amount differs greatly.

4.4. Herbicides on Trash

The effect of time after spraying on the rate of wash off was based on two major factors, the soil sorption constant, and the half-life of the herbicide. To take into account the degradation of the herbicide when comparing the effects of time after spraying, it was chosen to take samples of the sprayed trash just before and after the rainfall.

Table 6 shows that each of the herbicides were applied at different amounts, therefore to be able to examine the herbicides amounts, analysis of the proportionalities rather than the actual values were chosen.

Table 6. The amount of herbicides in mg/kg on the trash before and after rainfall. These values were recorded at 24 hours, 8 days and 40 days after spraying. The table also shows the percentage of the herbicide left on the trash after rainfall.

time		Diuron	Atrazine	Ametryn	Hexazinone	Metolachlor	Tebuthiuron
24 hrs	E Before	200	130	130	65	140	160
24 hrs	E After	6.7	1.9	4.3	1.3	12	3.8
% Left after rain		**3.4**	**1.5**	**3.3**	**2**	**8.6**	**2.4**
8 days	G Before	110	85	95	21	57	73
8 days	G After	9	4	7.8	2.1	14	6.5
% Left after rain		**8.2**	**4.7**	**8.2**	**10**	**24.6**	**8.9**
40 days	**I Before**	82	78	180	10	92	56
40 days	**I After**	30	12	30	4.6	30	17
% Left after rain		**36. 6**	**15.4**	**16.7**	**46.**	**32.6**	**30.4**

The first factor that was analyzed was the difference between the concentration of herbicides before rainfall and after rainfall. The best way to analyze this was to work out how much of the initial herbicide concentration was left on the trash. During the first wash off test after 24 hours, most of the herbicides had less than 5% left while S-metolachlor had less than 10% left (Table 6). As time went on the percentage of the herbicide left, started to differ as each herbicide began to stick more or degrade.

Table 7. The concentration of herbicides in before rain samples compared to the percentage of the initial herbicide concentration.

	24 hrs	8 days	40 days	
Diuron	200	110	82	
Atrazine	130	85	78	
Ametryn	130	95	180	
Hexazinone	65	21	10	
Metolachlor	140	57	92	
Tebuthiuron	160	73	56	
	Percentage of initial concentration			Fixed Metolachlor
Diuron	100	55.0	41.0	41.0
Atrazine	100	65.4	60.0	60.0
Ametryn	100	73.1	138.5	138.5
Hexazinone	100	32.3	15.4	15.4
Metolachlor	100	40.7	65.7	32.9
Tebuthiuron	100	45.6	35.0	35.0

Table 7 shows what percentage of the initial herbicide concentration was left on the trash after 8 days and 40 days, before rain. After 8 days there was still more than 50% of diuron, atrazine and ametryn left on the trash. However more than 50% of hexazinone, metolachlor, and tebuthiuron had degraded indicating that these three herbicides have half-lives shorter than one week on trash (Table 7).

When examining the proportionalities after 40 days, the value for ametryn was to be disregarded because there was more ametryn on the trash after 40 days than the initial concentration. Though metolachlor concentration was also greater than the 8 days value, there was an awareness that it was due to an intentional double spray. Therefore, when analyzing the proportionalities of concentration for metolachlor it was halved. The interesting thing about atrazine was that after 40 days there was only 15% left on trash after rain but very little of the herbicide degrades. Since there was more than 60% left after 40 days, it was the only herbicide that did not reach its half-life point.

Between the 8 day and 40 day tests the only herbicide that gave a major degradation in that period was hexazinone. However while saying that we also need to realize that by 40 days hexazinone tends to stick to trash a lot more (Table 7). When raining 24 hours sentence after spray only 2% of herbicide was left after rain, however when raining 40 days after spray over 45% of the herbicide stayed on the trash after 2 hours of rain.

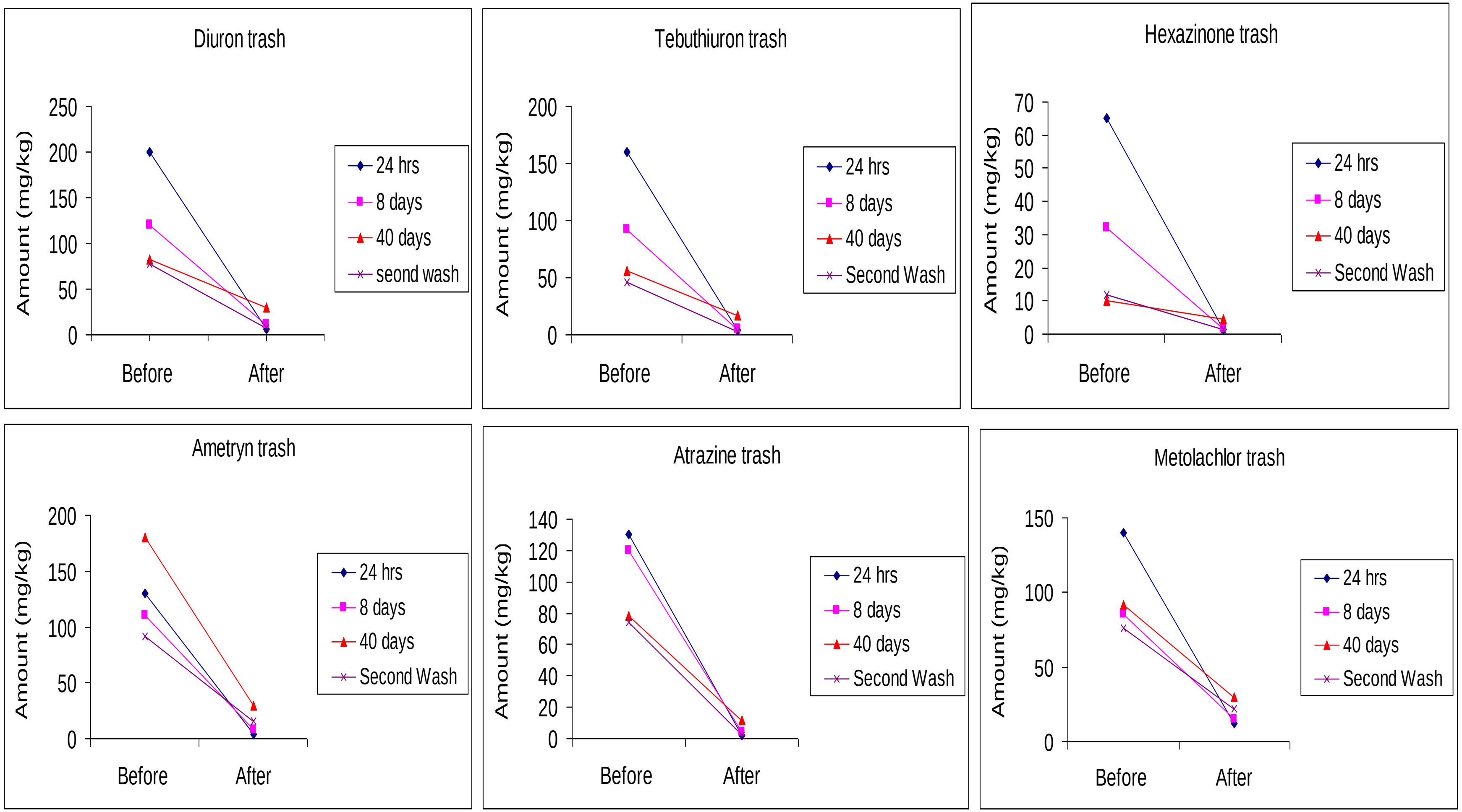


Figure 35. Comparison of the before and after rainfall herbicide concentrations at each time period.

Chapter 5. General Discussion

The off-site transport of agricultural chemicals, such as herbicides, into freshwater and marine ecosystems is a worldwide concern (Van Dam et al. 2011). The detection of agricultural chemicals, including herbicides and nutrients in freshwater and marine ecosystems in GBR (Rayment G.E 2003) continue to be of increasing concern to public, researchers and policy makers (Carroll et al. 2012). Recent estimates suggest that at least 30,000 kg/yr of herbicides are exported to the GBR (Kroon et al. 2012). This estimate comprises of photosystem- II (PSII) inhibiting herbicides only (atrazine, ametryn, hexazinone, diuron, simazine and tebuthiuron). Agricultural related industries including the Australian sugar industry are under pressure to adopt farm management practices that minimise herbicide transport in rainfall-runoff, particularly in coastal catchments that are draining into the World Heritage listed GBR lagoon (Department of the Premier and Cabinet 2009).

Sugarcane in Australia is grown along the eastern coast of Queensland, where 587,500 ha of farm land drained into the GBR (QLUMP (1996-2006)). Australian sugarcane industry is particularly reliant on a wide variety of herbicides that are necessary to prevent weed competition. During high intensity rainfall events, the residual herbicides such as diuron, atrazine, ametryn, hexazinone and metolachlor have been consistently detected in creeks and rivers around the catchments with sugarcane (Bainbridge et al. 2009; (Lewis et al. 2009) as well as in coastal waters of the GBR (Lewis et al. 2009; Shaw et al. 2010). The presence of these herbicides in marine ecosystems is of particular concern as they inhibit photosynthesis and long term chronic exposure may have adverse eco-toxicological effects on coral (Jones 2005) and sea grass communities (Haynes, Müller & Carter 2000).

Currently many sugarcane based management strategies are under trial to see if they will reduce the risk of off-site movement of agrochemicals (Carroll et al. 2012). In particular, the primary management strategies are green cane harvesting and trash blanketing (GCTB), controlled traffic, and reducing use of PSII herbicides.

Quantification of herbicides transport in surface runoff is one of the weakest areas of understanding of environmental fate and behaviour of pesticides, especially with GCTB. Better understanding of herbicides runoff would allow comparisons of the behaviour of different herbicides to improve quality of water entering GBR. There are a number of factors that affect fate of herbicides in surface runoff that include hydrology, herbicide properties, application method, presence of trash in sugarcane, timing of herbicide application in relation to timing of rainfall (Silburn & Kennedy 2007).

In the present study, consistent with the bromide concentrations, the highest concentrations were detected in the first runoff samples for all herbicides which was consistent with what was expected from previous studies (Muller et al. 2004); (Masters et al. 2012) suggesting that the highest risk of herbicide loss in runoff was within the first rain after its application. The concentrations of all herbicides in wash off water declined rapidly after 10 min of rainfall then slowing down to a steady low rate.

In the present study, for all herbicides, there was rapid initial decline)Table 6) in herbicide concentration on cane trash, which might have been a result of volatilisation and photodecomposition, and could be major pathways of loss of herbicides intercepted by crop residues (Locke & Bryson 1997). High initial losses (up to 70%) had also been found for residual herbicides on corn residues within 24 h of spraying, and were presumed to be a result of volatilisation (Baker J.L & Shiers L.E 1989).

When the rainfall was experienced 1 day after application, a large percentage of all herbicides were washed off the cane trash. These losses were considered large (Wauchope 1978), which could be due to the large portion of ‘dislodgable’ herbicides washed off the cane trash (McDowell. L.L et al. 1984**).** A similar substantially high loss of banded herbicides on cane trash was obtained by Masters et al (2012). In the present study, by day 8 herbicides residues on cane trash were substantially lower than day 1 and were more resistant to wash off, thereby resulting in lower runoff losses. At day 40, herbicides residues on cane trash further reduced, suggesting that herbicides were more resistant to wash off or had a less ‘dislodgable’ component. This suggests that the highest risk to herbicide loss in runoff was within 1 week after application. Willis et al (1992) found that insecticide residues on cotton foliage became increasingly resistant to wash off with increased time between insecticide application and rainfall.

For all herbicides at different timing after application, the highest concentration of all herbicides were measured at 2 min of rainfall and decline steadily subsequently. In most cases, 80% of the wash off from cane trash was in the first ~40 min of rainfall simulation., suggesting it is possible that further losses in runoff would occur with consecutive rainfall events (Ghadiri, Shea & Wicks 1984). Willis et al 1992 also reported that most of the wash off of insecticides from cotton foliage occurred early in each rainfall event. A number of studies have demonstrated that highest risk of rainfall wash off from the cane trash was shortly after application (Selim & Zhu 2005);(Wauchope, Johnson & Sumner 2004);(Masters et al. 2012)**)**. Wauchope et al (2004) found that a majority of foliar applied pesticides occurred within a few days after application. However, in contrast to results from this study, the wash off was completed within a few minutes of rainfall commencement.

The concentration of diuron, atrazine, ametryn, hexazinone, metolachlor and tebuthiuron displayed logarithm decline between the cumulative herbicide washoff and cumulative water washoff (Figure 30). Coefficients of correlation for the non-linear relationships ranged from 40 to 100 as can be seen in Appendix 8.8. Contrary to these results, Silburn et al. (1996) reported an exponential decline in endosulfan concentrations when washing off cotton canopies.

A power relationship was established between the logarithm of herbicide concentration and the logarithm of the runoff rate for all the herbicides at different timing of their applications. This suggests that runoff rate plays an important role in the dynamics of the herbicide transport processes. A similar linear relationship between the logarithm of herbicide concentration and the logarithm of the runoff rate was reported by Muller (2004) for hexazinone and atrazine.

All of the herbicide became less prone to washoff with time after application. Although concentrations of all herbicides in the present study followed similar rapid decline initially followed by a steady decline, pattern of this decline varied with different herbicides. The percentage of herbicide on trash after rain 1 day after application of herbicide ranged between 1.5 to 8.5% which increased to 4 to 25% 8 days after application and 15-46% 40 days after application. In general, differences between concentrations of herbicides on trash after rain at day 1 were negligible (1.5-3.3%) except for metolachlor (8%). For different herbicides, the concentration on trash after rain was in the decreasing order of atrazine> hexazinone> tebuthiuron> ametryn> diuron> metolachlor. These differences between concentrations of herbicides on trash were prominent (15-46%) for rain on 40 days after application and were in the decreasing order of atrazine> ametryn> tebuthiuron> metolachlor> diuron> hexazinone.

In general, concentration of atrazine in wash off water were highest and hexazinone the lowest. These differences in concentration of different herbicides are expected due to differences in their application rate, solubility, half-life and K_{OC} (Table 6) (Table 2) Atrazine, diuron and ametryn, because of their low solubility and higher K_{OC}, had the tendency to wash off more compared to hexazinone. Their use could be restricted during the wet season that would greatly reduce likelihood of their off-site transport. However, this may be different in furrow irrigated systems, as the highest losses were measured during dry season (Davis 2012)

The length of time between herbicide application and rainfall was a dominant factor affecting herbicides loss in runoff in this and other studies (Masters et al. 2012; Silburn, Foley & deVoil 2012; Wauchope 1978). Therefore, timing of commercial herbicide applications need to be managed to reduce the likelihood of their off-site transport. In this study, diuron, atrazine, ametryn and hexazinone were still detected in runoff 40 days after application. It may be necessary to restrict the use of these herbicides to the months of May to September as it would reduce the likelihood of their off-site transport (Masters et al. 2012). This is necessary because the herbicides persistence and timing are leading to consistent detection of PSII herbicides in event runoff in rivers and flood plumes throughout GBR (Lewis et al. 2011).

Throughout this experiment we chose to use bromide as a tracer for the herbicide wash off. Bromide is a good tracer because it is convenient and handy in studying the movement of both chemicals and water in solid. It is considered to be conservative because it does not undergo rapid microbial transformations or quickly bind with the organic matter of clay minerals. The other benefits of using Br is that it is not an agricultural chemical; therefore its background levels in the soil are generally very low; and it is cheaper to have analyzed.

However, when the relationship between bromide wash off concentration and time was graphed, it gave a relationship of about y=2906x^(1.5). This exponent of 1.5 is the important part. It determines the exact relationship between wash off and time as the 2906 varies based on the initial wash off point. When the herbicides were all graphed on a log-log scale and a power trend line was placed through them as shown in (Figure 32) the exponent for the herbicides was around 0.8-0.9 and not 1.5. This indicates that bromide might not be the best tracer for these herbicides. This difference indicates that the herbicides might have greater bonding or sorption to cane trash than the bromide.

Chapter 6. Future study

The Reef Plan aims to "*halt and reverse the decline in water quality enter in the Reef within 10 years*". In its first release, Reef Plan (2003) identified nutrients and sediments as priority contaminants in the Great Barrier Reef (GBR) catchments. In order to assess the long-term effectiveness of the Reef Plan, there is a need to monitor the long term trends in sediment, pesticides and nutrient load to the reef and to identify (sub) catchment hot-spots that are responsible for delivering disproportionate quantities of sediment and nutrients.

This study is set in the first stage: the paddock stage. This research aims to quantify the amount of herbicide that is being washed off from the sugar cane trash. The issue is that even though there is an awareness that the wash off occurs, it properties with different herbicides and times is poorly understood. It is necessary to understand, if retaining trash increases herbicide runoff or reduces it, if the timing of rainfall affects it and how the wash off changes with different herbicides.

The next stage for this project is to examine the other factors that can affect the herbicide wash off from sugar cane trash due to rainfall. The first thing that we will need to test is what the effect of varying the rainfall intensity is on the rate of wash off. There should not be a major change as shown by Willis and McDowell for crop canopies, however we do need to test it.

Similarly, the effect of mulch thickness needs to be determined. Currently this research has been done on the basis of the amount of trash needed for a 100% cover. Now it is necessary to examine if the amount of wash off changes when the amount of trash present is double or in a much thicker layer. It is expected that there will be a difference in the amount of cumulative wash off, as the herbicides will have to pass through a lot more trash before being able to be washed off.

The final thing that needs to be tested is the effect of emerging residual herbicides. The herbicides that we have tested in this study are the older (established) residual herbicides and they are the ones that have been detected by Lewis (2009) in the GBR lagoon. However there is a new group of herbicides currently being used in the sugar cane industry – the emerging herbicides. These herbicides are imazapic, isoxaflutole, metolachlor, pendimethalin, metribuzin and trifloxysulfuron. Some of these residual herbicides have a broader range of properties than the older residuals, and my react with trash and washoff differently. We need to understand if the wash off of these herbicides is very different to the older residual herbicides.

Once all the factors affecting wash off of herbicides from sugar cane trash due to rainfall have been examined it is necessary to model the results. A runoff model simulates the rainfall - runoff response of a rainfall catchment area. It produces a time series of runoff rates based on input meteorological time series. “HowLeaky” model will be used for trash results. A model is necessary to understand how sensitive the parameters are and how thing can vary over time.

There is a strong need for the adoption of farm management practices that minimize herbicide transport in rainfall-runoff as a priority for the Australian sugarcane industry, particularly in the coastal catchments draining into the World Heritage listed Great Barrier Reef (GBR) lagoon. All the factors affecting wash off will have to be examined because there is a need to use this information to determine and test different strategies to combat or prevent runoff. This will include developing new strategies and examining the strategies outlined by Mark Silburn in the paper “Managing runoff of herbicides under rainfall and furrow irrigation with wheel traffic and banded spraying” and more broadly in the Paddock to Reef Program (Carroll et al. 2012) These strategies are currently under consideration to manage the amount of herbicide runoff. . It needs to be examined if these will be successful for herbicide wash off, or do we need to develop more strategies

Once improved washoff parameters have been determined they can be used in the paddock modelling in the GBR catchments. The results of this paddock modelling are then used in the catchment modeling. This focuses on the water quality of the key pollutants of sub catchments and end-of catchments sites.

Chapter 7. Conclusion

This research aimed to quantify the amount of different herbicides washing off sugarcane trash due to rainfall instantaneously and after certain time periods. .

There are number of factors that affect fate of herbicides in surface runoff that include the herbicide properties, application method, presence of residues or trash in sugarcane, and timing of herbicide application in relation to timing of rainfall.

The highest concentrations were detected in the first runoff samples for all herbicides, suggesting that the highest risk of herbicide loss in runoff is in the first rain after its application. For all herbicides at different timings after application, the highest concentration of all herbicides were measured at 2 min of rainfall simulation and decline steadily subsequently

All of the herbicides were less prone to wash off with increasing time after application. In general, differences between concentrations of herbicides on trash after rain at day 1 were negligible. Concentration of atrazine in wash off water was highest and hexazinone lowest. The results indicate that in first rain after spraying the amount of herbicides with potential to contribute to runoff is quite high, even if there is no more than 10 mm of rain.

The herbicides dissipated on the cane trash (without rain) with time after application, some halving within eight days and all but atrazine and ametryn halving within 40 days. This has consequences for weed management and for the risk of herbicide runoff. Herbicides that are less stable on trash than on soil will have a higher risk of runoff losses when used in trash retained systems.

Further work is recommended to determine other factors that affect the amount of herbicides washing off sugar cane trash and to determine the washoff behaviour of the emergent herbicides. The final thing that needs to be done to ensure full understanding of “herbicide wash off from sugar cane trash” is modelling of the data through programs such as HowLeaky. There is a large amount of herbicides washing off from sugar cane trash; is it infiltrating into soil or contributing to runoff?

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Appendix

8.1. Project Specification

University of Southern Queensland

Faculty of Engineering and Surveying

ENG4111/Eng4112 Research Project

Project Specification

For: Aaditi Dang

Topic: Herbicides wash off from cane trash due to rainfall

Supervisors: Dr. Ian Craig

Dr**.** Mark Silburn Principle Scientist, Department of Natural Resource and Mines

Enrolment: ENG4111 – S1, D, 2012, ENG4112 – S2, D, 2012

Project Aim: The objective of this study is the determine the exact amount of wash off that occurs from different herbicides due to rainfall when sprayed on cane trash

Sponsorship: Department of Environment & Resource Management

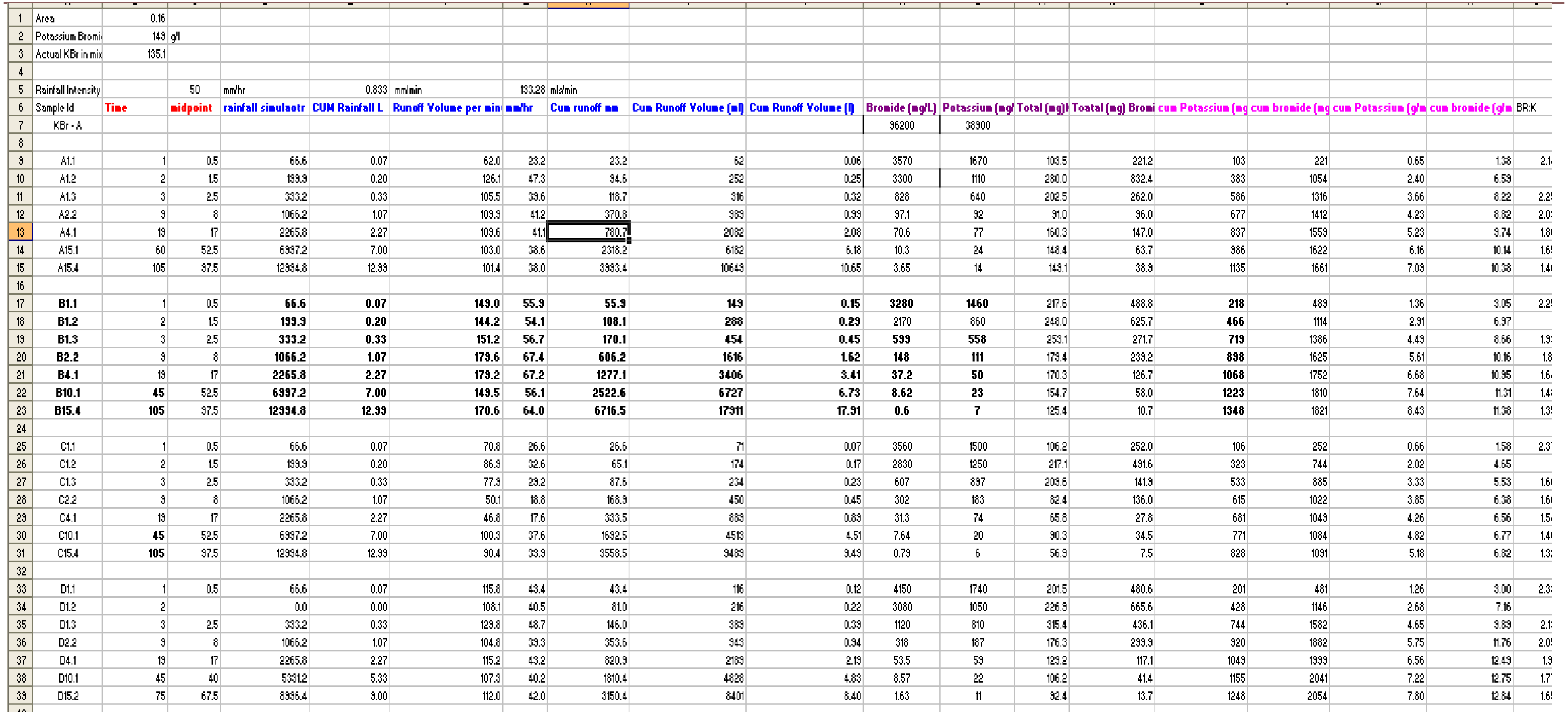
Program:

- Research the importance of sugar cane and its necessity for herbicides. Research the properties and historical usage of the herbicides usually associated with the production of sugar cane and their environmental fate.
- Prepare rainfall simulator and the equipment necessary for the simulation
- Using bromide run as a standardized test of rainfall simulator to determine the intensity, splash and application rates.
- Get all the herbicides trays sprayed ready for testing, remember to take into account time after testing.
- Run the rainfall simulator for 2 hours for each herbicide with at least 2 tries. Collect periodic samples.
- Send all the samples for testing to the lab.
- Analyze and graph all the results with a thorough discussion
- Write up report

If time permits

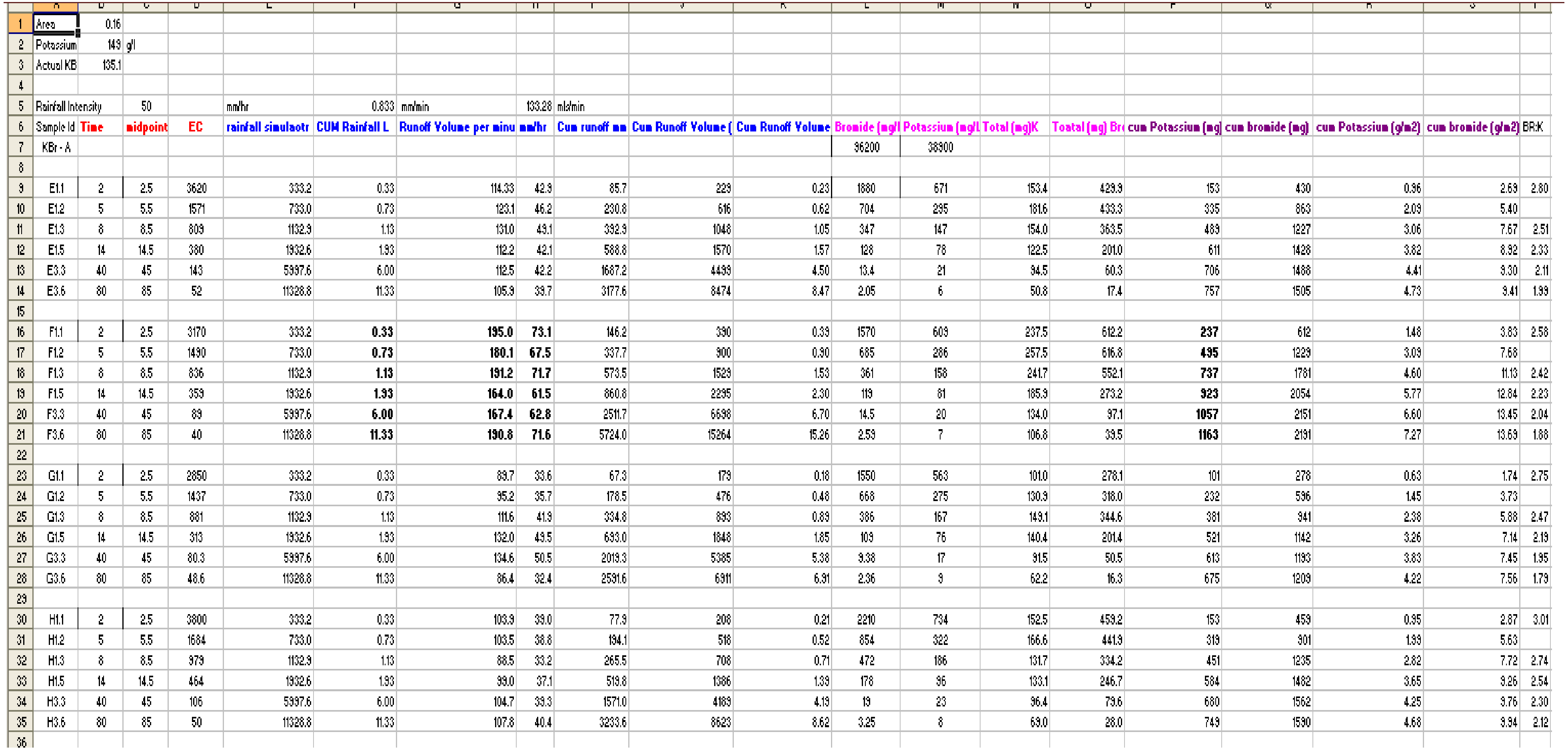
- ○ Research the best ways to manage this problem

8.2. Bromide Data Sheet



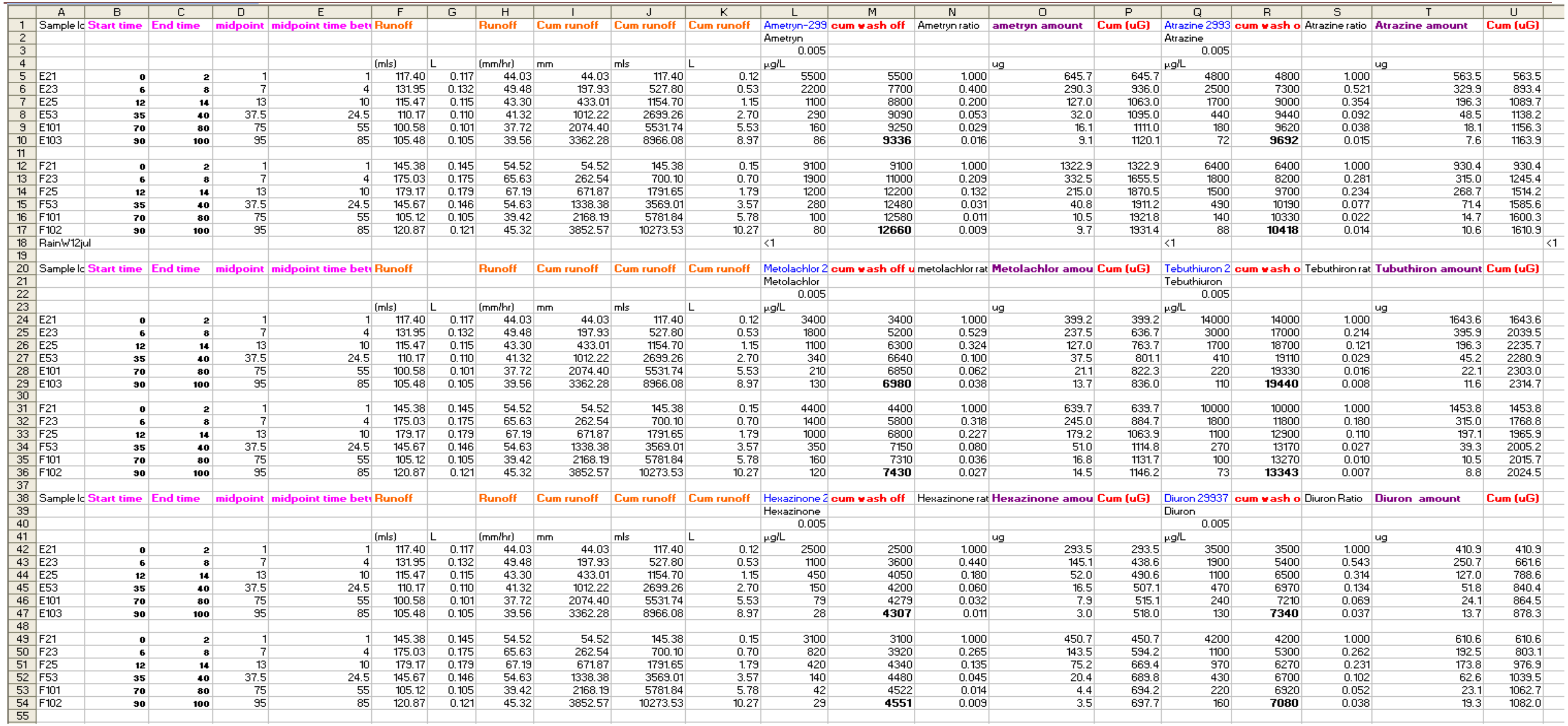
1	Area	0.16																
2	Potassium Bromi	149	g/l															
3	Actual KBr in mix	135.1																
4																		
5	Rainfall Intensity		50	mm/hr	0.833	mm/min	133.28	ml/min										
6	Sample Id	Time	midpoint	rainfall simulaotr	CUM Rainfall L	Runoff Volume per min	mm/hr	Cum runoff mm	Cum Runoff Volume (ml)	Cum Runoff Volume (l)	Bromide (mg/L)	Potassium (mg	Total (mg) I	Toatal (mg) Bromi	cum Potassium (mg	cum bromide (mg	cum Potassium (g/m	cum bromide (g/m	BR:K
7	KBr - A										36200	38300							
8																			
9	A1.1	1	0.5	66.6	0.07	62.0	23.2	23.2	62	0.06	3570	1670	103.5	221.2	103	221	0.65	1.38	2.1
10	A1.2	2	1.5	199.9	0.20	126.1	47.3	94.6	252	0.25	3300	1110	280.0	832.4	383	1054	2.40	6.59	
11	A1.3	3	2.5	333.2	0.33	105.5	39.6	116.7	316	0.32	828	640	202.5	262.0	586	1316	3.66	8.22	2.2
12	A2.2	9	8	1066.2	1.07	109.9	41.2	370.8	989	0.99	97.1	92	91.0	96.0	677	1412	4.23	8.82	2.0
13	A4.1	19	17	2265.8	2.27	109.6	41.1	780.7	2082	2.08	70.6	77	160.3	147.0	837	1559	5.23	9.74	1.8
14	A15.1	60	52.5	6997.2	7.00	103.0	38.6	2318.2	6182	6.18	10.3	24	148.4	63.7	986	1622	6.16	10.14	1.6
15	A15.4	105	97.5	12994.8	12.99	101.4	38.0	3993.4	10649	10.65	3.65	14	149.1	38.9	1135	1661	7.09	10.38	1.4
16																			
17	**B1.1**	1	0.5	**66.6**	**0.07**	**149.0**	**55.9**	**55.9**	**149**	**0.15**	**3280**	**1460**	217.6	488.8	**218**	489	1.36	3.05	2.2
18	**B1.2**	2	1.5	**199.9**	**0.20**	**144.2**	**54.1**	**108.1**	**288**	**0.29**	2170	860	248.0	625.7	**466**	1114	2.91	6.97	
19	**B1.3**	3	2.5	**333.2**	**0.33**	**151.2**	**56.7**	**170.1**	**454**	**0.45**	**599**	**558**	253.1	271.7	**719**	1386	4.49	8.66	1.9
20	**B2.2**	9	8	**1066.2**	**1.07**	**179.6**	**67.4**	**606.2**	**1616**	**1.62**	**148**	**111**	179.4	239.2	**898**	1625	5.61	10.16	1.8
21	**B4.1**	19	17	**2265.8**	**2.27**	**179.2**	**67.2**	**1277.1**	**3406**	**3.41**	**37.2**	**50**	170.3	126.7	**1068**	1752	6.68	10.95	1.6
22	**B10.1**	**45**	52.5	**6997.2**	**7.00**	**149.5**	**56.1**	**2522.6**	**6727**	**6.73**	**8.62**	**23**	154.7	58.0	**1223**	1810	7.64	11.31	1.4
23	**B15.4**	**105**	97.5	**12994.8**	**12.99**	**170.6**	**64.0**	**6716.5**	**17911**	**17.91**	**0.6**	**7**	125.4	10.7	**1348**	1821	8.43	11.38	1.3
24																			
25	C1.1	1	0.5	66.6	0.07	70.8	26.6	26.6	71	0.07	3560	1500	106.2	252.0	106	252	0.66	1.58	2.3
26	C1.2	2	1.5	199.9	0.20	86.9	32.6	65.1	174	0.17	2830	1250	217.1	491.6	323	744	2.02	4.65	
27	C1.3	3	2.5	333.2	0.33	77.9	29.2	87.6	234	0.23	607	897	209.6	141.9	533	885	3.33	5.53	1.6
28	C2.2	9	8	1066.2	1.07	50.1	18.8	168.9	450	0.45	302	183	82.4	136.0	615	1022	3.85	6.38	1.6
29	C4.1	19	17	2265.8	2.27	46.8	17.6	333.5	889	0.89	31.3	74	65.8	27.8	681	1049	4.26	6.56	1.5
30	C10.1	**45**	52.5	6997.2	7.00	100.3	37.6	1692.5	4513	4.51	7.64	20	90.3	34.5	771	1084	4.82	6.77	1.4
31	C15.4	**105**	97.5	12994.8	12.99	90.4	33.9	3558.5	9489	9.49	0.79	6	56.9	7.5	828	1091	5.18	6.82	1.3
32																			
33	D1.1	1	0.5	66.6	0.07	115.8	43.4	43.4	116	0.12	4150	1740	201.5	480.6	201	481	1.26	3.00	2.3
34	D1.2	2		0.0	0.00	108.1	40.5	81.0	216	0.22	3080	1050	226.9	665.6	428	1146	2.68	7.16	
35	D1.3	3	2.5	333.2	0.33	129.8	48.7	146.0	389	0.39	1120	810	315.4	436.1	744	1582	4.65	9.89	2.1
36	D2.2	9	8	1066.2	1.07	104.8	39.3	353.6	943	0.94	318	187	176.3	299.9	920	1882	5.75	11.76	2.0
37	D4.1	19	17	2265.8	2.27	115.2	43.2	820.9	2189	2.19	53.5	59	129.2	117.1	1049	1999	6.56	12.49	1.9
38	D10.1	45	40	5331.2	5.33	107.3	40.2	1810.4	4828	4.83	8.57	22	106.2	41.4	1155	2041	7.22	12.75	1.7
39	D15.2	75	67.5	8996.4	9.00	112.0	42.0	3150.4	8401	8.40	1.63	11	92.4	13.7	1248	2054	7.80	12.84	1.6

8.3. Second group of Bromide data sheet



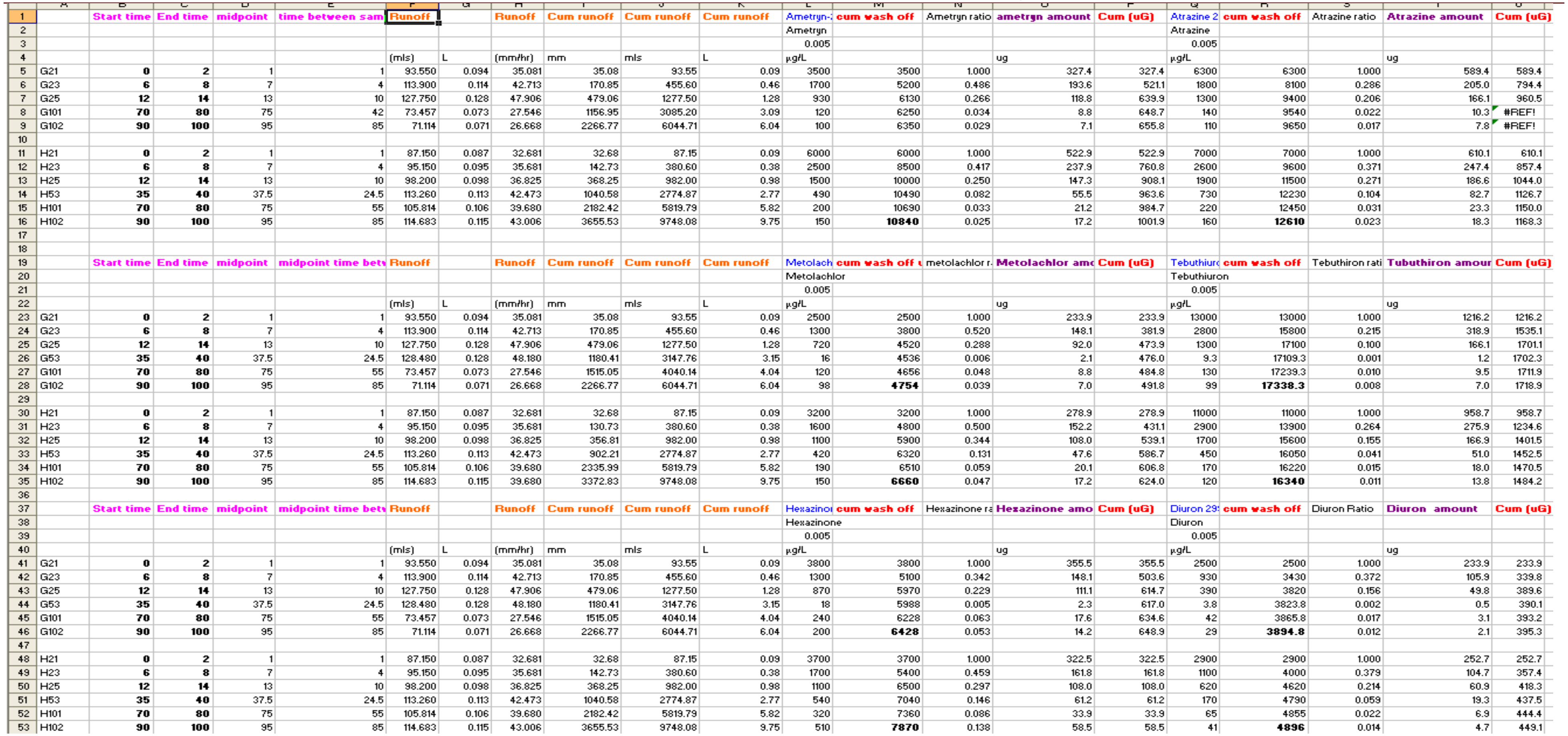
1	Area	0.16																		
2	Potassium	149	g/l																	
3	Actual KB	135.1																		
4																				
5	Rainfall Intensity		50		mm/hr	0.833	mm/min	133.28	ml/min											
6	Sample Id	Time	midpoint	EC	rainfall simulaotr	CUM Rainfall L	Runoff Volume per minu	mm/hr	Cum runoff mm	Cum Runoff Volume (	Cum Runoff Volume	Bromide (mg/l	Potassium (mg/l	Total (mg)K	Toatal (mg) Br	cum Potassium (mg)	cum bromide (mg)	cum Potassium (g/m2)	cum bromide (g/m2)	BR:K
7	KBr - A											36200	38300							
8																				
9	E1.1	2	2.5	3620	333.2	0.33	114.33	42.9	85.7	229	0.23	1880	671	153.4	429.9	153	430	0.96	2.69	2.80
10	E1.2	5	5.5	1571	733.0	0.73	123.1	46.2	230.8	616	0.62	704	295	181.6	433.3	335	863	2.09	5.40	
11	E1.3	8	8.5	809	1132.9	1.13	131.0	49.1	392.9	1048	1.05	347	147	154.0	363.5	489	1227	3.06	7.67	2.51
12	E1.5	14	14.5	380	1932.6	1.93	112.2	42.1	588.8	1570	1.57	128	78	122.5	201.0	611	1428	3.82	8.92	2.33
13	E3.3	40	45	143	5997.6	6.00	112.5	42.2	1687.2	4499	4.50	13.4	21	94.5	60.3	706	1488	4.41	9.30	2.11
14	E3.6	80	85	52	11328.8	11.33	105.9	39.7	3177.6	8474	8.47	2.05	6	50.8	17.4	757	1505	4.73	9.41	1.99
15																				
16	F1.1	2	2.5	3170	333.2	**0.33**	**195.0**	**73.1**	146.2	390	0.39	1570	609	237.5	612.2	**237**	612	1.48	3.83	2.58
17	F1.2	5	5.5	1490	733.0	**0.73**	**180.1**	**67.5**	337.7	900	0.90	685	286	257.5	616.8	**495**	1229	3.09	7.68	
18	F1.3	8	8.5	836	1132.9	**1.13**	**191.2**	**71.7**	573.5	1529	1.53	361	158	241.7	552.1	**737**	1781	4.60	11.13	2.42
19	F1.5	14	14.5	359	1932.6	**1.93**	**164.0**	**61.5**	860.8	2295	2.30	119	81	185.9	273.2	**923**	2054	5.77	12.84	2.23
20	F3.3	40	45	89	5997.6	**6.00**	**167.4**	**62.8**	2511.7	6698	6.70	14.5	20	134.0	97.1	**1057**	2151	6.60	13.45	2.04
21	F3.6	80	85	40	11328.8	**11.33**	**190.8**	**71.6**	5724.0	15264	15.26	2.59	7	106.8	39.5	**1163**	2191	7.27	13.69	1.88
22																				
23	G1.1	2	2.5	2850	333.2	0.33	89.7	33.6	67.3	179	0.18	1550	563	101.0	278.1	101	278	0.63	1.74	2.75
24	G1.2	5	5.5	1437	733.0	0.73	95.2	35.7	178.5	476	0.48	668	275	130.9	318.0	232	596	1.45	3.73	
25	G1.3	8	8.5	881	1132.9	1.13	111.6	41.9	334.8	893	0.89	386	167	149.1	344.6	381	941	2.38	5.88	2.47
26	G1.5	14	14.5	313	1932.6	1.93	132.0	49.5	693.0	1848	1.85	109	76	140.4	201.4	521	1142	3.26	7.14	2.19
27	G3.3	40	45	80.3	5997.6	6.00	134.6	50.5	2019.3	5385	5.38	9.38	17	91.5	50.5	613	1193	3.83	7.45	1.95
28	G3.6	80	85	48.6	11328.8	11.33	86.4	32.4	2591.6	6911	6.91	2.36	9	62.2	16.3	675	1209	4.22	7.56	1.79
29																				
30	H1.1	2	2.5	3800	333.2	0.33	103.9	39.0	77.9	208	0.21	2210	734	152.5	459.2	153	459	0.95	2.87	3.01
31	H1.2	5	5.5	1684	733.0	0.73	103.5	38.8	194.1	518	0.52	854	322	166.6	441.9	319	901	1.99	5.63	
32	H1.3	8	8.5	979	1132.9	1.13	88.5	33.2	265.5	708	0.71	472	186	131.7	334.2	451	1235	2.82	7.72	2.74
33	H1.5	14	14.5	464	1932.6	1.93	99.0	37.1	519.8	1386	1.39	178	96	133.1	246.7	584	1482	3.65	9.26	2.54
34	H3.3	40	45	106	5997.6	6.00	104.7	39.3	1571.0	4189	4.19	19	23	96.4	79.6	680	1562	4.25	9.76	2.30
35	H3.6	80	85	50	11328.8	11.33	107.8	40.4	3233.6	8623	8.62	3.25	8	69.0	28.0	749	1590	4.68	9.94	2.12
36																				

8.4. Herbicides wash off data sheet – 24 hrs.



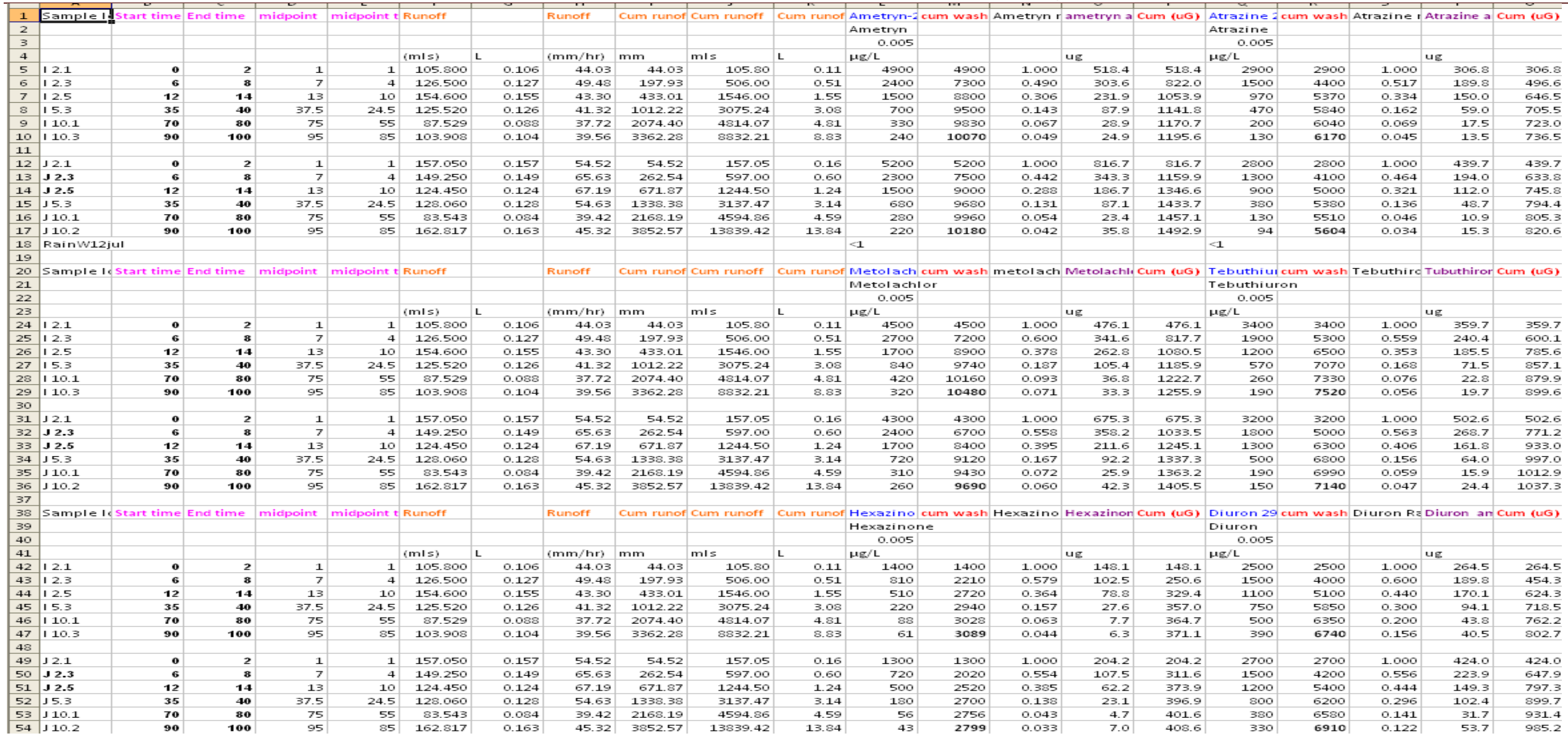
	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	
1	Sample lc	Start time	End time	midpoint	midpoint time bet	Runoff		Runoff	Cum runoff	Cum runoff	Cum runoff	Ametryn-299	cum wash off	Ametryn ratio	ametryn amount	Cum (uG)	Atrazine 2993	cum wash o	Atrazine ratio	Atrazine amount	Cum (uG)	
2												Ametryn					Atrazine					
3												0.005					0.005					
4						(mls)	L	(mm/hr)	mm	mls	L	µg/L			ug		µg/L			ug		
5	E21	0	2	1	1	117.40	0.117	44.03	44.03	117.40	0.12	5500	5500	1.000	645.7	645.7	4800	4800	1.000	563.5	563.5	
6	E23	6	8	7	4	131.95	0.132	49.48	197.93	527.80	0.53	2200	7700	0.400	290.3	936.0	2500	7300	0.521	329.9	893.4	
7	E25	12	14	13	10	115.47	0.115	43.30	433.01	1154.70	1.15	1100	8800	0.200	127.0	1063.0	1700	9000	0.354	196.3	1089.7	
8	E53	35	40	37.5	24.5	110.17	0.110	41.32	1012.22	2699.26	2.70	290	9090	0.053	32.0	1095.0	440	9440	0.092	48.5	1138.2	
9	E101	70	80	75	55	100.58	0.101	37.72	2074.40	5531.74	5.53	160	9250	0.029	16.1	1111.0	180	9620	0.038	18.1	1156.3	
10	E103	90	100	95	85	105.48	0.105	39.56	3362.28	8966.08	8.97	86	**9336**	0.016	9.1	1120.1	72	**9692**	0.015	7.6	1163.9	
11																						
12	F21	0	2	1	1	145.38	0.145	54.52	54.52	145.38	0.15	9100	9100	1.000	1322.9	1322.9	6400	6400	1.000	930.4	930.4	
13	F23	6	8	7	4	175.03	0.175	65.63	262.54	700.10	0.70	1900	11000	0.209	332.5	1655.5	1800	8200	0.281	315.0	1245.4	
14	F25	12	14	13	10	179.17	0.179	67.19	671.87	1791.65	1.79	1200	12200	0.132	215.0	1870.5	1500	9700	0.234	268.7	1514.2	
15	F53	35	40	37.5	24.5	145.67	0.146	54.63	1338.38	3569.01	3.57	280	12480	0.031	40.8	1911.2	490	10190	0.077	71.4	1585.6	
16	F101	70	80	75	55	105.12	0.105	39.42	2168.19	5781.84	5.78	100	12580	0.011	10.5	1921.8	140	10330	0.022	14.7	1600.3	
17	F102	90	100	95	85	120.87	0.121	45.32	3852.57	10273.53	10.27	80	**12660**	0.009	9.7	1931.4	88	**10418**	0.014	10.6	1610.9	
18	RainW12jul											<1					<1					<1
19																						
20	Sample lc	Start time	End time	midpoint	midpoint time bet	Runoff		Runoff	Cum runoff	Cum runoff	Cum runoff	Metolachlor 2	cum wash off u	metolachlor rat	Metolachlor amou	Cum (uG)	Tebuthiuron 2	cum wash o	Tebuthiron rat	Tubuthiron amount	Cum (uG)	
21												Metolachlor					Tebuthiuron					
22												0.005					0.005					
23						(mls)	L	(mm/hr)	mm	mls	L	µg/L			ug		µg/L			ug		
24	E21	0	2	1	1	117.40	0.117	44.03	44.03	117.40	0.12	3400	3400	1.000	399.2	399.2	14000	14000	1.000	1643.6	1643.6	
25	E23	6	8	7	4	131.95	0.132	49.48	197.93	527.80	0.53	1800	5200	0.529	237.5	636.7	3000	17000	0.214	395.9	2039.5	
26	E25	12	14	13	10	115.47	0.115	43.30	433.01	1154.70	1.15	1100	6300	0.324	127.0	763.7	1700	18700	0.121	196.3	2235.7	
27	E53	35	40	37.5	24.5	110.17	0.110	41.32	1012.22	2699.26	2.70	340	6640	0.100	37.5	801.1	410	19110	0.029	45.2	2280.9	
28	E101	70	80	75	55	100.58	0.101	37.72	2074.40	5531.74	5.53	210	6850	0.062	21.1	822.3	220	19330	0.016	22.1	2303.0	
29	E103	90	100	95	85	105.48	0.105	39.56	3362.28	8966.08	8.97	130	**6980**	0.038	13.7	836.0	110	**19440**	0.008	11.6	2314.7	
30																						
31	F21	0	2	1	1	145.38	0.145	54.52	54.52	145.38	0.15	4400	4400	1.000	639.7	639.7	10000	10000	1.000	1453.8	1453.8	
32	F23	6	8	7	4	175.03	0.175	65.63	262.54	700.10	0.70	1400	5800	0.318	245.0	884.7	1800	11800	0.180	315.0	1768.8	
33	F25	12	14	13	10	179.17	0.179	67.19	671.87	1791.65	1.79	1000	6800	0.227	179.2	1063.9	1100	12900	0.110	197.1	1965.9	
34	F53	35	40	37.5	24.5	145.67	0.146	54.63	1338.38	3569.01	3.57	350	7150	0.080	51.0	1114.8	270	13170	0.027	39.3	2005.2	
35	F101	70	80	75	55	105.12	0.105	39.42	2168.19	5781.84	5.78	160	7310	0.036	16.8	1131.7	100	13270	0.010	10.5	2015.7	
36	F102	90	100	95	85	120.87	0.121	45.32	3852.57	10273.53	10.27	120	**7430**	0.027	14.5	1146.2	73	**13343**	0.007	8.8	2024.5	
37																						
38	Sample lc	Start time	End time	midpoint	midpoint time bet	Runoff		Runoff	Cum runoff	Cum runoff	Cum runoff	Hexazinone 2	cum wash off	Hexazinone rat	Hexazinone amou	Cum (uG)	Diuron 29937	cum wash o	Diuron Ratio	Diuron amount	Cum (uG)	
39												Hexazinone					Diuron					
40												0.005					0.005					
41						(mls)	L	(mm/hr)	mm	mls	L	µg/L			ug		µg/L			ug		
42	E21	0	2	1	1	117.40	0.117	44.03	44.03	117.40	0.12	2500	2500	1.000	293.5	293.5	3500	3500	1.000	410.9	410.9	
43	E23	6	8	7	4	131.95	0.132	49.48	197.93	527.80	0.53	1100	3600	0.440	145.1	438.6	1900	5400	0.543	250.7	661.6	
44	E25	12	14	13	10	115.47	0.115	43.30	433.01	1154.70	1.15	450	4050	0.180	52.0	490.6	1100	6500	0.314	127.0	788.6	
45	E53	35	40	37.5	24.5	110.17	0.110	41.32	1012.22	2699.26	2.70	150	4200	0.060	16.5	507.1	470	6970	0.134	51.8	840.4	
46	E101	70	80	75	55	100.58	0.101	37.72	2074.40	5531.74	5.53	79	4279	0.032	7.9	515.1	240	7210	0.069	24.1	864.5	
47	E103	90	100	95	85	105.48	0.105	39.56	3362.28	8966.08	8.97	28	**4307**	0.011	3.0	518.0	130	**7340**	0.037	13.7	878.3	
48																						
49	F21	0	2	1	1	145.38	0.145	54.52	54.52	145.38	0.15	3100	3100	1.000	450.7	450.7	4200	4200	1.000	610.6	610.6	
50	F23	6	8	7	4	175.03	0.175	65.63	262.54	700.10	0.70	820	3920	0.265	143.5	594.2	1100	5300	0.262	192.5	803.1	
51	F25	12	14	13	10	179.17	0.179	67.19	671.87	1791.65	1.79	420	4340	0.135	75.2	669.4	970	6270	0.231	173.8	976.9	
52	F53	35	40	37.5	24.5	145.67	0.146	54.63	1338.38	3569.01	3.57	140	4480	0.045	20.4	689.8	430	6700	0.102	62.6	1039.5	
53	F101	70	80	75	55	105.12	0.105	39.42	2168.19	5781.84	5.78	42	4522	0.014	4.4	694.2	220	6920	0.052	23.1	1062.7	
54	F102	90	100	95	85	120.87	0.121	45.32	3852.57	10273.53	10.27	29	**4551**	0.009	3.5	697.7	160	**7080**	0.038	19.3	1082.0	
55																						

8.5. Herbicide wash off data sheet – 8 days



	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U
1		Start time	End time	midpoint	time between sam	Runoff		Runoff	Cum runoff	Cum runoff	Cum runoff	Ametryn-	cum wash off	Ametryn ratio	ametryn amount	Cum (uG)	Atrazine 2	cum wash off	Atrazine ratio	Atrazine amount	Cum (uG)
2												Ametryn					Atrazine				
3												0.005					0.005				
4						(mls)	L	(mm/hr)	mm	mls	L	µg/L			ug		µg/L			ug	
5	G21	**0**	**2**	1	1	93.550	0.094	35.081	35.08	93.55	0.09	3500	3500	1.000	327.4	327.4	6300	6300	1.000	589.4	589.4
6	G23	**6**	**8**	7	4	113.900	0.114	42.713	170.85	455.60	0.46	1700	5200	0.486	193.6	521.1	1800	8100	0.286	205.0	794.4
7	G25	**12**	**14**	13	10	127.750	0.128	47.906	479.06	1277.50	1.28	930	6130	0.266	118.8	639.9	1300	9400	0.206	166.1	960.5
8	G101	**70**	**80**	75	42	73.457	0.073	27.546	1156.95	3085.20	3.09	120	6250	0.034	8.8	648.7	140	9540	0.022	10.3	#REF!
9	G102	**90**	**100**	95	85	71.114	0.071	26.668	2266.77	6044.71	6.04	100	6350	0.029	7.1	655.8	110	9650	0.017	7.8	#REF!
10																					
11	H21	**0**	**2**	1	1	87.150	0.087	32.681	32.68	87.15	0.09	6000	6000	1.000	522.9	522.9	7000	7000	1.000	610.1	610.1
12	H23	**6**	**8**	7	4	95.150	0.095	35.681	142.73	380.60	0.38	2500	8500	0.417	237.9	760.8	2600	9600	0.371	247.4	857.4
13	H25	**12**	**14**	13	10	98.200	0.098	36.825	368.25	982.00	0.98	1500	10000	0.250	147.3	908.1	1900	11500	0.271	186.6	1044.0
14	H53	**35**	**40**	37.5	24.5	113.260	0.113	42.473	1040.58	2774.87	2.77	490	10490	0.082	55.5	963.6	730	12230	0.104	82.7	1126.7
15	H101	**70**	**80**	75	55	105.814	0.106	39.680	2182.42	5819.79	5.82	200	10690	0.033	21.2	984.7	220	12450	0.031	23.3	1150.0
16	H102	**90**	**100**	95	85	114.683	0.115	43.006	3655.53	9748.08	9.75	150	**10840**	0.025	17.2	1001.9	160	**12610**	0.023	18.3	1168.3
17																					
18																					
19		Start time	End time	midpoint	midpoint time bet	Runoff		Runoff	Cum runoff	Cum runoff	Cum runoff	Metolach	cum wash off u	metolachlor r	Metolachlor amo	Cum (uG)	Tebuthiur	cum wash off	Tebuthiron rati	Tubuthiron amour	Cum (uG)
20												Metolachlor					Tebuthiuron				
21												0.005					0.005				
22						(mls)	L	(mm/hr)	mm	mls	L	µg/L			ug		µg/L			ug	
23	G21	**0**	**2**	1	1	93.550	0.094	35.081	35.08	93.55	0.09	2500	2500	1.000	233.9	233.9	13000	13000	1.000	1216.2	1216.2
24	G23	**6**	**8**	7	4	113.900	0.114	42.713	170.85	455.60	0.46	1300	3800	0.520	148.1	381.9	2800	15800	0.215	318.9	1535.1
25	G25	**12**	**14**	13	10	127.750	0.128	47.906	479.06	1277.50	1.28	720	4520	0.288	92.0	473.9	1300	17100	0.100	166.1	1701.1
26	G53	**35**	**40**	37.5	24.5	128.480	0.128	48.180	1180.41	3147.76	3.15	16	4536	0.006	2.1	476.0	9.3	17109.3	0.001	1.2	1702.3
27	G101	**70**	**80**	75	55	73.457	0.073	27.546	1515.05	4040.14	4.04	120	4656	0.048	8.8	484.8	130	17239.3	0.010	9.5	1711.9
28	G102	**90**	**100**	95	85	71.114	0.071	26.668	2266.77	6044.71	6.04	98	**4754**	0.039	7.0	491.8	99	**17338.3**	0.008	7.0	1718.9
29																					
30	H21	**0**	**2**	1	1	87.150	0.087	32.681	32.68	87.15	0.09	3200	3200	1.000	278.9	278.9	11000	11000	1.000	958.7	958.7
31	H23	**6**	**8**	7	4	95.150	0.095	35.681	130.73	380.60	0.38	1600	4800	0.500	152.2	431.1	2900	13900	0.264	275.9	1234.6
32	H25	**12**	**14**	13	10	98.200	0.098	36.825	356.81	982.00	0.98	1100	5900	0.344	108.0	539.1	1700	15600	0.155	166.9	1401.5
33	H53	**35**	**40**	37.5	24.5	113.260	0.113	42.473	902.21	2774.87	2.77	420	6320	0.131	47.6	586.7	450	16050	0.041	51.0	1452.5
34	H101	**70**	**80**	75	55	105.814	0.106	39.680	2335.99	5819.79	5.82	190	6510	0.059	20.1	606.8	170	16220	0.015	18.0	1470.5
35	H102	**90**	**100**	95	85	114.683	0.115	39.680	3372.83	9748.08	9.75	150	**6660**	0.047	17.2	624.0	120	**16340**	0.011	13.8	1484.2
36																					
37		Start time	End time	midpoint	midpoint time bet	Runoff		Runoff	Cum runoff	Cum runoff	Cum runoff	Hexazino	cum wash off	Hexazinone ra	Hexazinone amo	Cum (uG)	Diuron 29	cum wash off	Diuron Ratio	Diuron amount	Cum (uG)
38												Hexazinone					Diuron				
39												0.005					0.005				
40						(mls)	L	(mm/hr)	mm	mls	L	µg/L			ug		µg/L			ug	
41	G21	**0**	**2**	1	1	93.550	0.094	35.081	35.08	93.55	0.09	3800	3800	1.000	355.5	355.5	2500	2500	1.000	233.9	233.9
42	G23	**6**	**8**	7	4	113.900	0.114	42.713	170.85	455.60	0.46	1300	5100	0.342	148.1	503.6	930	3430	0.372	105.9	339.8
43	G25	**12**	**14**	13	10	127.750	0.128	47.906	479.06	1277.50	1.28	870	5970	0.229	111.1	614.7	390	3820	0.156	49.8	389.6
44	G53	**35**	**40**	37.5	24.5	128.480	0.128	48.180	1180.41	3147.76	3.15	18	5988	0.005	2.3	617.0	3.8	3823.8	0.002	0.5	390.1
45	G101	**70**	**80**	75	55	73.457	0.073	27.546	1515.05	4040.14	4.04	240	6228	0.063	17.6	634.6	42	3865.8	0.017	3.1	393.2
46	G102	**90**	**100**	95	85	71.114	0.071	26.668	2266.77	6044.71	6.04	200	**6428**	0.053	14.2	648.9	29	**3894.8**	0.012	2.1	395.3
47																					
48	H21	**0**	**2**	1	1	87.150	0.087	32.681	32.68	87.15	0.09	3700	3700	1.000	322.5	322.5	2900	2900	1.000	252.7	252.7
49	H23	**6**	**8**	7	4	95.150	0.095	35.681	142.73	380.60	0.38	1700	5400	0.459	161.8	161.8	1100	4000	0.379	104.7	357.4
50	H25	**12**	**14**	13	10	98.200	0.098	36.825	368.25	982.00	0.98	1100	6500	0.297	108.0	108.0	620	4620	0.214	60.9	418.3
51	H53	**35**	**40**	37.5	24.5	113.260	0.113	42.473	1040.58	2774.87	2.77	540	7040	0.146	61.2	61.2	170	4790	0.059	19.3	437.5
52	H101	**70**	**80**	75	55	105.814	0.106	39.680	2182.42	5819.79	5.82	320	7360	0.086	33.9	33.9	65	4855	0.022	6.9	444.4
53	H102	**90**	**100**	95	85	114.683	0.115	43.006	3655.53	9748.08	9.75	510	**7870**	0.138	58.5	58.5	41	**4896**	0.014	4.7	449.1

8.6. Herbicide wash off data sheet – 40 days



1	Sample I	Start time	End time	midpoint	midpoint t	Runoff		Runoff	Cum runof	Cum runoff	Cum runof	Ametryn-2	cum wash	Ametryn r	ametryn a	Cum (uG)	Atrazine 2	cum wash	Atrazine r	Atrazine a	Cum (uG)
2												Ametryn					Atrazine				
3												0.005					0.005				
4						(mls)	L	(mm/hr)	mm	mls	L	µg/L			ug		µg/L			ug	
5	I 2.1	0	2	1	1	105.800	0.106	44.03	44.03	105.80	0.11	4900	4900	1.000	518.4	518.4	2900	2900	1.000	306.8	306.8
6	I 2.3	6	8	7	4	126.500	0.127	49.48	197.93	506.00	0.51	2400	7300	0.490	303.6	822.0	1500	4400	0.517	189.8	496.6
7	I 2.5	12	14	13	10	154.600	0.155	43.30	433.01	1546.00	1.55	1500	8800	0.306	231.9	1053.9	970	5370	0.334	150.0	646.5
8	I 5.3	35	40	37.5	24.5	125.520	0.126	41.32	1012.22	3075.24	3.08	700	9500	0.143	87.9	1141.8	470	5840	0.162	59.0	705.5
9	I 10.1	70	80	75	55	87.529	0.088	37.72	2074.40	4814.07	4.81	330	9830	0.067	28.9	1170.7	200	6040	0.069	17.5	723.0
10	I 10.3	90	100	95	85	103.908	0.104	39.56	3362.28	8832.21	8.83	240	10070	0.049	24.9	1195.6	130	6170	0.045	13.5	736.5
11																					
12	J 2.1	0	2	1	1	157.050	0.157	54.52	54.52	157.05	0.16	5200	5200	1.000	816.7	816.7	2800	2800	1.000	439.7	439.7
13	J 2.3	6	8	7	4	149.250	0.149	65.63	262.54	597.00	0.60	2300	7500	0.442	343.3	1159.9	1300	4100	0.464	194.0	633.8
14	J 2.5	12	14	13	10	124.450	0.124	67.19	671.87	1244.50	1.24	1500	9000	0.288	186.7	1346.6	900	5000	0.321	112.0	745.8
15	J 5.3	35	40	37.5	24.5	128.060	0.128	54.63	1338.38	3137.47	3.14	680	9680	0.131	87.1	1433.7	380	5380	0.136	48.7	794.4
16	J 10.1	70	80	75	55	83.543	0.084	39.42	2168.19	4594.86	4.59	280	9960	0.054	23.4	1457.1	130	5510	0.046	10.9	805.3
17	J 10.2	90	100	95	85	162.817	0.163	45.32	3852.57	13839.42	13.84	220	10180	0.042	35.8	1492.9	94	5604	0.034	15.3	820.6
18	RainW12jul											<1					<1				
19																					
20	Sample I	Start time	End time	midpoint	midpoint t	Runoff		Runoff	Cum runof	Cum runoff	Cum runof	Metolach	cum wash	metolach	Metolachl	Cum (uG)	Tebuthiu	cum wash	Tebuthirc	Tubuthiror	Cum (uG)
21												Metolachlor					Tebuthiuron				
22												0.005					0.005				
23						(mls)	L	(mm/hr)	mm	mls	L	µg/L			ug		µg/L			ug	
24	I 2.1	0	2	1	1	105.800	0.106	44.03	44.03	105.80	0.11	4500	4500	1.000	476.1	476.1	3400	3400	1.000	359.7	359.7
25	I 2.3	6	8	7	4	126.500	0.127	49.48	197.93	506.00	0.51	2700	7200	0.600	341.6	817.7	1900	5300	0.559	240.4	600.1
26	I 2.5	12	14	13	10	154.600	0.155	43.30	433.01	1546.00	1.55	1700	8900	0.378	262.8	1080.5	1200	6500	0.353	185.5	785.6
27	I 5.3	35	40	37.5	24.5	125.520	0.126	41.32	1012.22	3075.24	3.08	840	9740	0.187	105.4	1185.9	570	7070	0.168	71.5	857.1
28	I 10.1	70	80	75	55	87.529	0.088	37.72	2074.40	4814.07	4.81	420	10160	0.093	36.8	1222.7	260	7330	0.076	22.8	879.9
29	I 10.3	90	100	95	85	103.908	0.104	39.56	3362.28	8832.21	8.83	320	10480	0.071	33.3	1255.9	190	7520	0.056	19.7	899.6
30																					
31	J 2.1	0	2	1	1	157.050	0.157	54.52	54.52	157.05	0.16	4300	4300	1.000	675.3	675.3	3200	3200	1.000	502.6	502.6
32	J 2.3	6	8	7	4	149.250	0.149	65.63	262.54	597.00	0.60	2400	6700	0.558	358.2	1033.5	1800	5000	0.563	268.7	771.2
33	J 2.5	12	14	13	10	124.450	0.124	67.19	671.87	1244.50	1.24	1700	8400	0.395	211.6	1245.1	1300	6300	0.406	161.8	933.0
34	J 5.3	35	40	37.5	24.5	128.060	0.128	54.63	1338.38	3137.47	3.14	720	9120	0.167	92.2	1337.3	500	6800	0.156	64.0	997.0
35	J 10.1	70	80	75	55	83.543	0.084	39.42	2168.19	4594.86	4.59	310	9430	0.072	25.9	1363.2	190	6990	0.059	15.9	1012.9
36	J 10.2	90	100	95	85	162.817	0.163	45.32	3852.57	13839.42	13.84	260	9690	0.060	42.3	1405.5	150	7140	0.047	24.4	1037.3
37																					
38	Sample I	Start time	End time	midpoint	midpoint t	Runoff		Runoff	Cum runof	Cum runoff	Cum runof	Hexazino	cum wash	Hexazino	Hexazinon	Cum (uG)	Diuron 29	cum wash	Diuron Ra	Diuron an	Cum (uG)
39												Hexazinone					Diuron				
40												0.005					0.005				
41						(mls)	L	(mm/hr)	mm	mls	L	µg/L			ug		µg/L			ug	
42	I 2.1	0	2	1	1	105.800	0.106	44.03	44.03	105.80	0.11	1400	1400	1.000	148.1	148.1	2500	2500	1.000	264.5	264.5
43	I 2.3	6	8	7	4	126.500	0.127	49.48	197.93	506.00	0.51	810	2210	0.579	102.5	250.6	1500	4000	0.600	189.8	454.3
44	I 2.5	12	14	13	10	154.600	0.155	43.30	433.01	1546.00	1.55	510	2720	0.364	78.8	329.4	1100	5100	0.440	170.1	624.3
45	I 5.3	35	40	37.5	24.5	125.520	0.126	41.32	1012.22	3075.24	3.08	220	2940	0.157	27.6	357.0	750	5850	0.300	94.1	718.5
46	I 10.1	70	80	75	55	87.529	0.088	37.72	2074.40	4814.07	4.81	88	3028	0.063	7.7	364.7	500	6350	0.200	43.8	762.2
47	I 10.3	90	100	95	85	103.908	0.104	39.56	3362.28	8832.21	8.83	61	3089	0.044	6.3	371.1	390	6740	0.156	40.5	802.7
48																					
49	J 2.1	0	2	1	1	157.050	0.157	54.52	54.52	157.05	0.16	1300	1300	1.000	204.2	204.2	2700	2700	1.000	424.0	424.0
50	J 2.3	6	8	7	4	149.250	0.149	65.63	262.54	597.00	0.60	720	2020	0.554	107.5	311.6	1500	4200	0.556	223.9	647.9
51	J 2.5	12	14	13	10	124.450	0.124	67.19	671.87	1244.50	1.24	500	2520	0.385	62.2	373.9	1200	5400	0.444	149.3	797.3
52	J 5.3	35	40	37.5	24.5	128.060	0.128	54.63	1338.38	3137.47	3.14	180	2700	0.138	23.1	396.9	800	6200	0.296	102.4	899.7
53	J 10.1	70	80	75	55	83.543	0.084	39.42	2168.19	4594.86	4.59	56	2756	0.043	4.7	401.6	380	6580	0.141	31.7	931.4
54	J 10.2	90	100	95	85	162.817	0.163	45.32	3852.57	13839.42	13.84	43	2799	0.033	7.0	408.6	330	6910	0.122	53.7	985.2

8.7. Trash Data

time	Sample name	Diuron	Atrazine	Ametryn	Hexazinone	Metolachlor	Tebuthiuron
24 hrs	Rep 1 Before	200	130	130	65	140	160
24 hrs.	Rep 1 After	6.7	1.9	4.3	1.3	12	3.8
24 hrs.	Rep 2 After	10	3.3	7.1	2.6	17	5.5
8 days	Rep 1 Before	110	85	95	21	57	73
8 days	Rep 1 After	9	4	7.8	2.1	14	6.5
8 days	Rep 2 Before	120	120	110	32	85	92
8 days	Rep 2 After	11	3.9	8.2	1.6	15	5.3
40 days	Rep 1 Before	82	78	180	10	92	56
40 days	Rep 1 After	30	12	30	4.6	30	17
40 days	Rep 2 Before	missing	missing	missing	missing	missing	missing
40 days	Rep 2 After	17	8.4	28	4.0	28	15
second rain	Rep 1 Before	78	74	92	12	76	46
second rain	Rep 1 After	7.4	2.0	16	1.3	22	3.2
second rain	Rep 2 Before	95	110	130	14	86	44
second rain	Rep 2 After	4.6	0.98	13	0.58	22	2.4

8.8. Calculated Data

Ametryn						Cumulative Logarithmic relationship		
	Time after spraying	Rain Rate (mm/hr)	Washoff Rate (mm/hr)	Cum Wash off (g/m2)	% of applied	a	b	R2
E	24 hours	50-55	**42.57**	0.00700	4.6672	106.1	760.74	0.8575
F	24 hours	50-55	**54.45**	0.01207	8.0476			
G	8 days	50-55	**35.98**	0.00410	2.7325	99.6	647.31	0.909
H	8 days	50-55	**39.53**	0.00626	4.1747			
I	40 days	50-55	**43.99**	0.00747	4.9817	160.14	626.71	0.9628
J	40 days	50-55	**50.32**	0.00933	6.2204			

Atrazine						Cumulative Logarithmic relationship		
	Time after spraying	Rain Rate (mm/hr)	Washoff Rate (mm/hr)	Cum Wash off (g/m2)	% of applied	a	b	
E	24 hours	50-55	**42.57**	0.00727	4.8495	137.95	696.07	0.88
F	24 hours	50-55	**54.45**	0.01007	6.7122			
G	8 days	50-55	**35.98**	0.00612	4.0774	119.02	742.44	0.9274
H	8 days	50-55	**39.53**	0.00730	4.8680			
I	40 days	50-55	**43.99**	0.00562	3.7485	102.23	374.58	0.9623
J	40 days	50-55	**50.32**	0.00648	4.3222			

Metolachlor								
						Cumulative Logarithmic relationship		
	Time after spraying	Rain Rate (mm/hr)	Washoff Rate (mm/hr)	Cum Wash off (g/m2)	% of applied	a	b	
E	24 hours	50-55	**42.57**	0.00522	4.9478	99.28	490.46	0.897
F	24 hours	50-55	**54.45**	0.00716	6.7836			
G	8 days	50-55	**35.98**	0.00307	2.9105	72.68	358.12	0.94
H	8 days	50-55	**39.53**	0.00390	3.6933			
I	40 days	50-55	**43.99**	0.00785	7.4332	184.18	595.81	0.9682

J	40 days	50-55	**50.32**	0.00878	8.3186			

Tebuthiuron						Cumulative Logarithmic relationship		
	Time after spraying	Rain Rate (mm/hr)	Washoff Rate (mm/hr)	Cum Wash off (g/m2)	% of applied	a	b	
E	24 hours	50-55	**42.57**	0.01447	20.6665	151.42	1801.7	0.8628
F	24 hours	50-55	**54.45**	0.01265	18.0763			
G	8 days	50-55	**35.98**	0.01074	15.3476	108.72	1104.8	0.8853
H	8 days	50-55	**39.53**	0.00928	13.2522			
I	40 days	50-55	**43.99**	0.00562	8.0325	127.85	445.3	0.9634
J	40 days	50-55	**50.32**	0.00648	9.2618			

Hexazinone						Cumulative Logarithmic relationship		
	Time after spraying	Rain Rate (mm/hr)	Washoff Rate (mm/hr)	Cum Wash off (g/m2)	% of applied	a	b	
E	24 hours	50-55	**42.57**	0.00324	8.1760	49.9	350.5	0.8471
F	24 hours	50-55	**54.45**	0.00436	11.0124			
G	8 days	50-55	**35.98**	0.00406	10.2410	83.351	401.6	0.9706
H	8 days	50-55	**39.53**	0.00466	11.7699			
I	40 days	50-55	**43.99**	0.00232	5.8568	52.9	185.55	0.9544
J	40 days	50-55	**50.32**	0.00255	6.4486			

Diuron						Cumulative Logarithmic relationship		
	Time after spraying	Rain Rate (mm/hr)	Washoff Rate (mm/hr)	Cum Wash off (g/m2)	% of applied	a	b	R2
E	24 hours	50-55	**42.57**	0.00547	3.8979	106.27	503.76	0.911
F	24 hours	50-55	**54.45**	0.00676	4.8166			
G	8 days	50-55	**35.98**	0.00247	1.7595	40.554	307.88	0.88
H	8 days	50-55	**39.53**	0.00281	1.9993			
I	40 days	50-55	**43.99**	0.00502	3.5734	127.17	320.88	0.9919
J	40 days	50-55	**50.32**	0.00616	4.3856			